European Train the Trainer Programme for Responders

Lecture 8

Ignition sources and prevention of ignition

LEVEL IV

Specialist officer

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

This topic is also available at levels I & III.

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

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Clean Hydrogen Partnership

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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. The main ignition parameters such as MIE and auto-ignition temperature are treated here. The lecture details the main types of ignition sources and explains the most common hydrogen ignition mechanisms. Particular attention is paid to the phenomenon of spontaneous ignition during a sudden hydrogen release and the factors affecting it. The measures to prevent potential hydrogen ignition and control the ignition sources are also discussed in detail in this lecture.

Keywords

Minimum ignition energy (MIE), auto-ignition temperature, ignition sources, ignition mechanisms, spontaneous ignition, reverse Joule-Thompson effect, diffusion ignition

Table of contents

Summary 3
Keywords 3
1. Target audience 6
1.1 Roll description: Specialist 6
1.2 Competence level: Specialist 6
1.3 Prior learning: Specialist 6
2. Introduction and objectives 7
3. Ignition sources 8
3.1 Electrostatic discharge ignition 9
3.1.1 A spark from an isolated conductor 10
3.1.2 A brush discharge 11
3.1.3 A corona discharge 12
3.2 Mechanical ignition 13
3.3 Ignition by a hot surface 13
3.4 Adiabatic compression ignition 14
4. Hydrogen ignition mechanisms 15
4.1 Ignition and reverse Joule-Thomson effect 16
4.2 Minimum Ignition Energy (MIE) 17
4.3 Triboelectricity 18
4.4 Auto-ignition temperature 19
4.5 Diffusion ignition 19
5. Spontaneous ignition of a sudden releases 20
5.1 Diffusion ignition mechanism 20
5.2 Physical mechanism 25
5.2.1 An instantaneous opening 25
5.2.2 Effect of a valve opening rate 26
5.2.3 Transition to a sustained fire 27
5.2.4 Effect of a flame separation by vortex 29
5.3 Spontaneous ignition in a T-shaped PRD 30
5.3.1 Experimental set-up 30
5.3.2 Effect of a storage pressure 31
6. Prevention of hydrogen ignition 36
6.1 Ex-zone classification 37

6.2 Electrostatic spark ignition prevention....38
6.3 Control of thermal and mechanical sources of ignition....39
References....41

1. Target audience

The information contained in this lecture is targeted at the level of specialist officer and above. This lecture is also available at levels I: Fire fighter.

The role description, competence level and learning expectations assumed at specialist officer level are described below.

1.1 Roll description: Specialist

Specialists assist Incident Commanders with advice and by directing and supervising technical operations that involve the use of knowledge, skills or equipment related to a specific risk or response activity. Typical incidents involve hazardous materials, transportation vehicles, climatic events, structural and other built environment failures and emergency response logistics.

1.2 Competence level: Specialist

A scientific, engineering and empirical foundation in the subject area with skills, extended by experience, to apply that information, knowledge in an interpreted and useful way to enable the Incident Commander and other first responders under the specialist's direction to respond effectively and safety to the emergency situation.

1.3 Prior learning: Specialist

EQF 5 Comprehensive, specialised, factual and theoretical knowledge within a field of work or study and an awareness of the boundaries of that knowledge. A comprehensive range of cognitive and practical skills required to develop creative solutions to abstract problems. Exercise management and supervision in contexts of work or study activities where there is unpredictable change; review and develop performance of self and others.

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.

The work carried out by Astbury and Hawksworth [1] in 2007 gives an analysis of the statistics of hydrogen ignition incidents and decsribes some mechanisms, which 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 addition, the work carried out at HySAFER centre (UU) on spontaneous ignition of a sudden release is also presented in this lecture. The ignition prevention measures, and control of the ignition sources are covered as well.

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;
- Describe why the Joule-Thomson effect is unlikely the source of hydrogen ignition;
- 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;
- Explain the effect of triboelectricity on hydrogen ignition;
- Evaluate stages of spontaneous ignition of a sudden hydrogen release;
- Recognise the means to control hydrogen ignition sources;
- Classify electrical equipment depending on the Ex-zone;
- 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)

From the analysis carried out by Astbury and Hawksworth [1], it was concluded that a single mechanism is not able to explain all the recorded incidents. Two or more potential mechanisms may work together. It is known that the MIE of gases and vapours decreases as the temperature increases [2], the expanding hydrogen would increase its temperature due to the reverse Joule–Thomson effect (discussed in detail in Section 3.1), and hence its ignition energy would reduce. Similarly, if e.g. a jet were to entrain particles through e.g. abrasion of a surface in contact with the flow path, the required energy for ignition from a corona discharge would be lower, so it is likely that less corona charging current would be required to ignite the hydrogen [3].

In several incidents, there is a suggestion in the reports that electrostatic effects may have been responsible. One of the incidents involved only a fine stream of mercury, without other potential ignition sources inside the closed system. The potential for drops and bursting bubbles to generate electrostatic charges has been proposed by Blanchard [4], and the ability of such charges to ignite sensitive atmospheres has been illustrated by Pratt [5].

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.

3.1.1 A spark from an isolated conductor

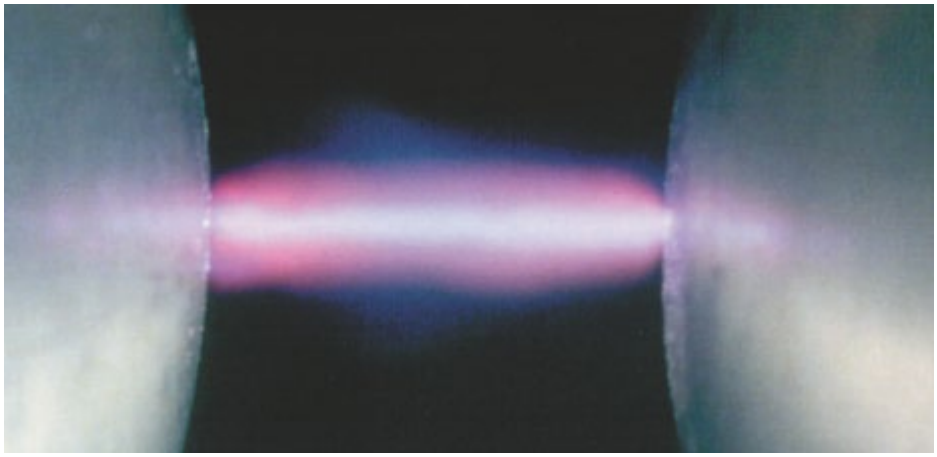

Figure 1 Spark image

The energy from a spark discharge from an isolated conductor is calculated as

$$E = CV^2/2 \tag{1}$$

where C is a capacitance of the item, and V is a potential (voltage). For example, a person has a capacitance C of about 100 pF, depending on the body size, the area of their feet, and the design and thickness of the soles of the footwear [1]. Taking the typical MIE of 0.29 mJ (E) for hydrocarbon-air mixtures, for example for propane-air, the voltage required to produce a spark of a sufficient energy to ignite the atmosphere can be calculated as:

$$V = \sqrt{\frac{2E}{C}} \tag{2}$$

Substitution gives V = 2408 V. For the air, the dielectric strength is about 30 kV/cm. So, the gap between the charged conductor and the earthed point required for breakdown to occur would be about 2400/30 = 0.08 cm (corresponding to 0.8 mm or 800 micrometres).

People typically cannot feel an electrostatic shock of less than about 1 mJ, so they would be unaware of the potential to ignite a hydrocarbon-air mixture [1]. The gap, over which the spark passes from a person to earth, is rarely of a form which has pointed electrodes. Typically, a finger has a tip radius of about 6 mm. Therefore, a fingertip approaching a flat earthed metal surface, though having a gap of 800 micrometres. It would present a large and almost flat area around the point at which the spark passes. This would tend to quench any ignition. This phenomenon of a spark not igniting a flammable mixture between two parallel plates is discussed by Metzler [6] with relation to the prediction of MIE. The quenching of flames by parallel surfaces in close proximity has also been investigated by Potter [7], who found that hydrocarbons have quenching distances of 2-3 mm.

Thus, theoretically, any ignition would not propagate from the plasma channel of the spark at such a “low” voltage of 2400 V. With breakdown strength of 30 kV/cm, and a gap of 2 mm

which would just allow the flame to propagate in hydrocarbon-air mixture, a potential of 6 kV would be required for a spark to occur [1].

If hydrogen is now considered, the corresponding voltages and gaps are much lower compared to hydrocarbons [1]. The dielectric strength of hydrogen atmospheres is only 17.5 kV/cm [8] and its quenching gap is only 0.64 mm [9]. The variation of dielectric strength with concentration of hydrogen in air mixtures is unknown, but as a simple case, it could be assumed to be linear within a specified narrow concentration range, so the theoretical dielectric strength of about stoichiometric mixture of 30 vol. % of hydrogen in air would be (0.3×17.5 + 0.7×30) = 26.25 kV. With a quenching distance of 0.64 mm and a dielectric strength of 26.25 kV/cm the breakdown potential would correspond to a voltage of 26.25×0.064 = 1.68 kV, which corresponds to a stored energy of $0.5\times[100\text{x}10^{-12}]\times[1.68\text{x}10^{3}]^2 = 1.41\text{x}10^{-4}$ J, i.e. 0.141 mJ. This is more than sufficient to ignite the stoichiometric hydrogen-air mixture that requires only 0.017 mJ [3].

Thus, whilst electrostatic charging of those who refuel their vehicles with petrol rarely gives rise to ignitions, it is significant that the voltage required for hydrogen to be ignited is below **2 kV**. This voltage can be generated easily on people, without them being aware of it, standing on an insulating surface, so there is a potential for personnel to ignite hydrogen leaks very easily, without any apparent ignition source being present [1].

3.1.2 A brush discharge

A brush discharge is characterised by many individual plasma channels, combining at the conductor.

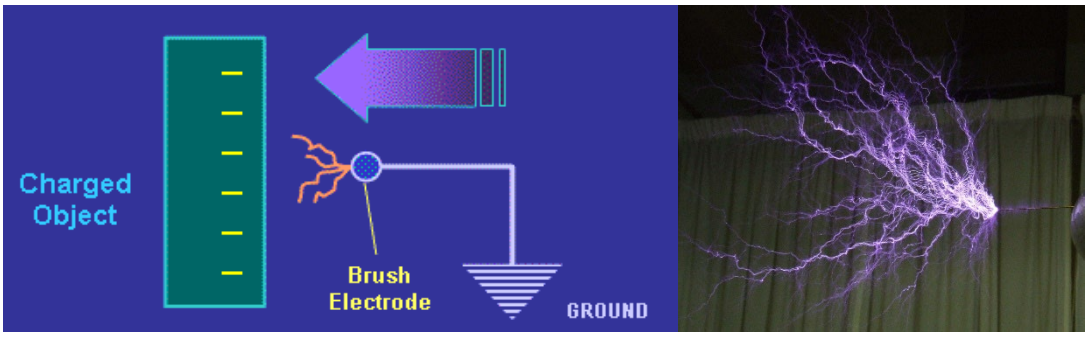

Figure 2 A diagram of brush discharge [Google images]

The brush discharge is shown in Figure 2. Because the charged surface is a non-conductor, a capacitance and, hence, the energy cannot be determined. The work published by Gibson and Harper [10] introduced the term ‘incendivity’ or equivalent energy, which is, when the brush discharge has the ability to ignite an atmosphere with the same minimum ignition energy as a spark, will just ignite the flammable atmosphere. Typical equivalent energies were found to be

about 4 mJ for brush discharges from flat polyethylene sheets. However, Ackroyd and Newton [11] found that some more modern plastics, and thin plastic coatings on earthed metal, had higher equivalent energies.

3.1.3 A corona discharge

A corona discharge is an electrical discharge caused by the ionization of a fluid such as air surrounding a conductor carrying a high voltage. It represents a local region where the air (or other fluid) has undergone electrical breakdown and become conductive, allowing charge to continuously leak off the conductor into the air. A corona occurs at locations where the strength of the electric field (potential gradient) around a conductor exceeds the dielectric strength of the air. It is often seen as a bluish glow in the air adjacent to pointed metal conductors carrying high voltages, and emits light by the same property as a gas discharge lamp. The diagram of a variety of forms of corona discharge from different metal objects are shown in Figure 3.

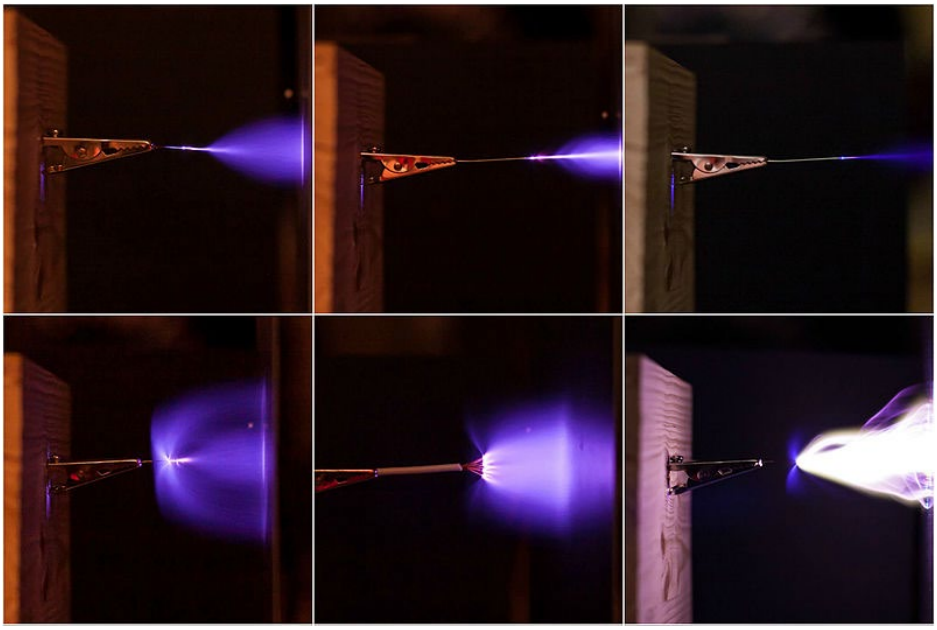

Figure 3 A variety of forms of corona discharge from various metal objects [Corona discharge - Wikipedia].

A corona discharge can ignite hydrogen-air mixture without there being a discrete spark or a single discharge event [1]. The voltage required for a corona depends on a tip-radius [12]. Cross and Jean [13] give an equation to determine the voltage required for a corona to start from a point given its tip-radius. The prevention of ignition of hydrogen deliberately vented to the atmosphere has been applied before by using a polished toroidal ring at the end of the vent to ensure that the effective tip radius is large. In practice, corrosion and dirt deposits are effectively small radius protrusions, so anything which affects the polished finish could create small radius protrusions which would still have an effect [1]. 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 [12].

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]. This is the usual method of determining the auto-ignition temperatures, and the value obtained is dependent on the apparatus used. It is known that the higher the temperature the shorter the ignition delay time. The lowest temperatures for ignition are associated with large volumes and surface areas [12]. Hot surface ignition temperature depends on the characteristic size of the hot surface. As shown in Figure 4, hydrogen is represented by the curve labelled as 'Group IIC'.

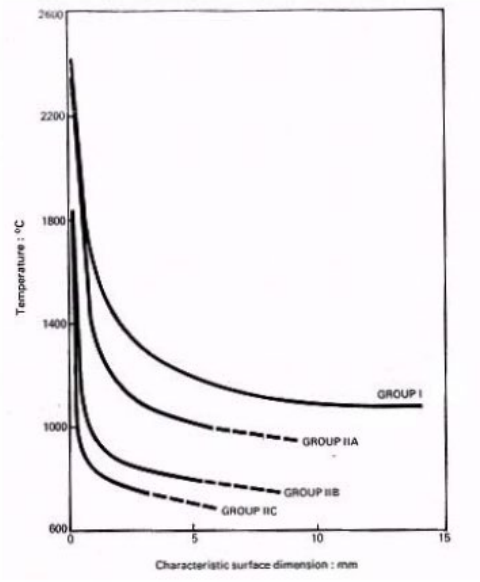

Figure 4. Hot surface ignition temperature as a function of hot surface characteristic size [12].

Bulewicz et al. [14] demonstrated that a hot plate position and the mode of heating influenced ignition. The authors have used a slow-heating method, where free-convection was important, and a time delay between an exposure and ignition was apparent, depending on the rate of temperature rise. The orientation of the heating surface also affected the delay, with a longer delay when the heated surface was pointing down as opposed to the one when the heated surface was pointing up. Ungut and James [15] also reported that surfaces located at the top of an enclosure having longer induction times. A catalytic surface (e.g. Pt-platinum) has a dramatic effect on the ignition temperature: ignitions are reported at temperatures as low as 70 ºC (please note that standard auto-ignition temperature is 510 ºC [12].

3.4 Adiabatic compression ignition

The ideal gas, when compressing it at constant entropy, would increase the pressure due to the compression in accordance with the relationship $PV^{\gamma}=const$. It can be shown with use of the equation of state for the ideal gas that the following relationship $TV^{\gamma-1}=const$ is valid as well. For example, for the compression ratio $V_1/V_2=28$ at the initial temperature of 293.15 K ($\gamma=1.39$) this theoretical relationship would increase the temperature to $T_2=T_1(V_1/V_2)^{\gamma-1}=1075.2$ K, i.e. the temperature rise of 782 K. However, in the experiments conducted by Pan et al. [16], the measured temperature realised by the compression ratio of 28 times was only 149 K. Based on this, Astbury and Hawksworth [1] concluded that isentropic compression is unlikely to occur in practice. However, the work carried out by Cain [17] indicates that the compression ignition of hydrogen-oxygen-helium mixtures occurs at a relatively constant temperature of 1050 K, at pressure rise ratios of 35-70 starting at 300 K at atmospheric pressure. The reverse calculation indicates that a temperature rise from 300 to 1050 K would require a pressure rise ratio of $P_2/P_1=(T_1/T_2)^{\gamma/(\gamma-1)} = (1050/300)^{(1.39/0.39)}=86.9$. Thus, adiabatic compression mechanism requires pressure rise ratio greater than that measured by Cain [17], suggesting that there is another ignition mechanism present [1].

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].

[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.

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 (cracked the valve open) to clear any dirt out of the connection, and when he did so, the escaping gas ignited immediately. Bond [18] 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. [19] 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) [20], Groethe et al. (2005) [21].

4.1 Ignition and reverse Joule-Thomson effect

While the sudden releases of many gases such as methane, propane and nitrogen lead to a decrease in temperature. For hydrogen, on the contrary, the temperature increases when it expands at constant enthalpy into surroundings, which is because hydrogen has a Joule-Thomson inversion temperature. When temperature is above the Joule-Thomson inversion temperature, the Joule-Thomson coefficient becomes negative and the isenthalpic gas expansion leads to warming instead of cooling. Some literature sources state that this makes hydrogen more susceptible to ignition following its sudden release from a pressurised vessel. However, Astbury and Hawksworth [1] disregarded the Joule-Thomson effect as a potential mechanism of ignition in considered experiments. They made this conclusion using data by Michels et al. [22] that the Joule-Thomson coefficient for hydrogen, estimated for expansion from pressure 250 MPa and initial temperature 150 °C down to 100 MPa, does not exceed 0.53 K. Thus, the ignition through this mechanism is highly unlikely at the pressures in most of the incidents discussed above.

4.2 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 [12]. 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 5, 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 6). Over the flammable range of hydrogen-air mixtures, the ignition energy varies by almost three orders of magnitude.

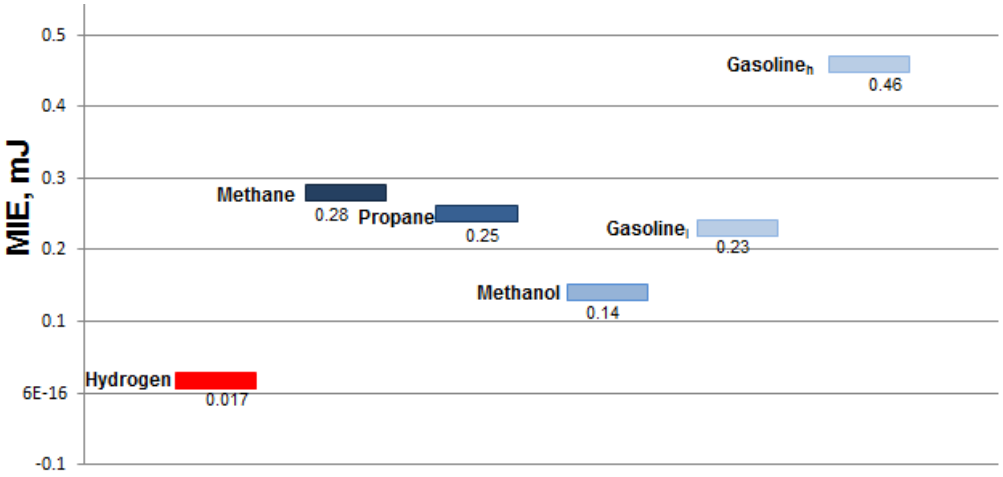

Figure 5. The values of MIE of hydrogen and other fuels.

As shown in Figure 6, 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.

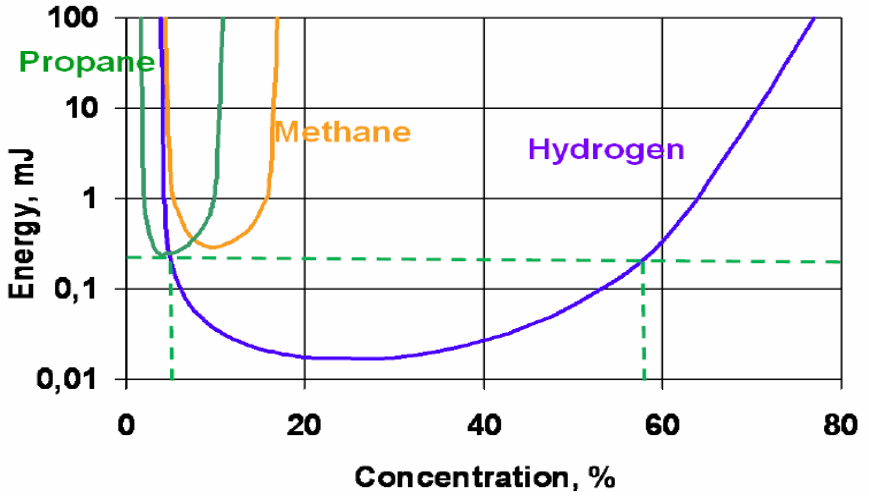

Figure 6. The dependence of the ignition energy on the concentration of a fuel (hydrogen, propane or methane) in the air [23].

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% [24].

4.3 Triboelectricity

Hydrogen is an electrical insulator in both gaseous and liquid phases. The flow or agitation of hydrogen gas or liquid may generate charges of static electricity similar to all non-conductive liquids or gases. For this reason, all hydrogen conveying equipment must be thoroughly grounded. Only above some critical “breakdown” voltage, where ionization occurs, and it does become an electrical conductor [25]. When high velocity hydrogen flow accompanies high-pressure vessel blow-down, this property can potentially be responsible for the generation of static electrical charge in piping particles by triboelectricity, which is a type of contact electrification in which certain materials become electrically charged after they come into contact with another different material and are then separated [3]. The probability of hydrogen ignition by this mechanism increases with increase of the blow-down time (i.e. time needed to empty a storage tank) with the same other conditions.

4.4 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 [25]. 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 [26]. Hot air jet ignition temperature is 670 ºC [27].

4.5 Diffusion ignition

The phenomenon of diffusion ignition has been calculated by Wolanski and Wojcicki [28], 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. Wolanski and Wojcicki also [28] calculated that the gas composed of hydrogen and nitrogen (3:1 mixture), would ignite in air if the shock wave exceeded a Mach number of 2.8 at a temperature of 575 K. A shock wave of this Mach number would be produced by an upstream pressure of 3.9 MPa. They also calculated that the ignition would occur at a lower Mach number of only 1.7, corresponding to an upstream pressure of 1.3 MPa, when the shock wave was reflected by an obstacle. There is no indication whether the auto-ignition temperature was measured at the expected final pressure in the shock tube or at atmospheric pressure in the work of Wolanski and Wojcicki [28]. Although their shock tube experiments produced ignition, the initial temperature was rather high at 575 K (302 ºC), requiring an increase of only 110 K to reach their auto-ignition temperature of hydrogen. This means that more research on this mechanism is needed. Astbury and Hawksworth [1] suggested that the diffusion ignition mechanism is only likely if the initial temperature is high. However, they continued that when the valves on cylinders were briefly opened directly into the atmosphere, presumably to clear any debris from the cylinder, the ignition had occurred. The diffusion ignition effect appears to be reproducible in shock tubes or similar closed equipment. Wolanski and Wojcicki [28] appear to have only carried out work using a hydrogen-nitrogen mixture. Since 2007, more experimental and numerical works have been performed on the diffusion mechanism. This is reported partially in the Section 4 of the lecture.

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 [28] 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.

Experimental proof of spontaneous ignition by the diffusion mechanism for the releases from high pressure equipment to the atmosphere through a tube was obtained in a "controlled laboratory environment" by Dryer et al. [29], Golub et al. [30, 31], Pinto et al. [32] and Mogi et al. [33]. In these experiments hydrogen at elevated pressures was separated from the air in a pipe at atmospheric pressure by a flat burst disk. To facilitate spontaneous ignition various extension tubes and attachments were positioned downstream of a burst disk. Figure 7 illustrates critical conditions for experimentally registered spontaneous ignition obtained by different research groups mentioned above. The data by Dryer et al. [29] are not shown in Figure 7 due to the complicated internal geometry of fittings and a rupture disk used, which lowers the minimum pressure sufficient for spontaneous ignition down to 2.04 MPa. Although the data on spontaneous ignition of releases through practical fittings is very useful for hydrogen safety engineering, internal configurations of the fittings leaves a number of uncertainties in formulation of numerical experiments and prevents direct comparison with experimental results of other groups. Experimental results agree with a general trend of the decrease of the critical (limit) pressure with the increase of a pipe length. However, the critical conditions of spontaneous ignition vary substantially due to difference in test arrangements. Sensitivity of spontaneous ignition to different not yet fully understood factors poses a number of issues to be studied.

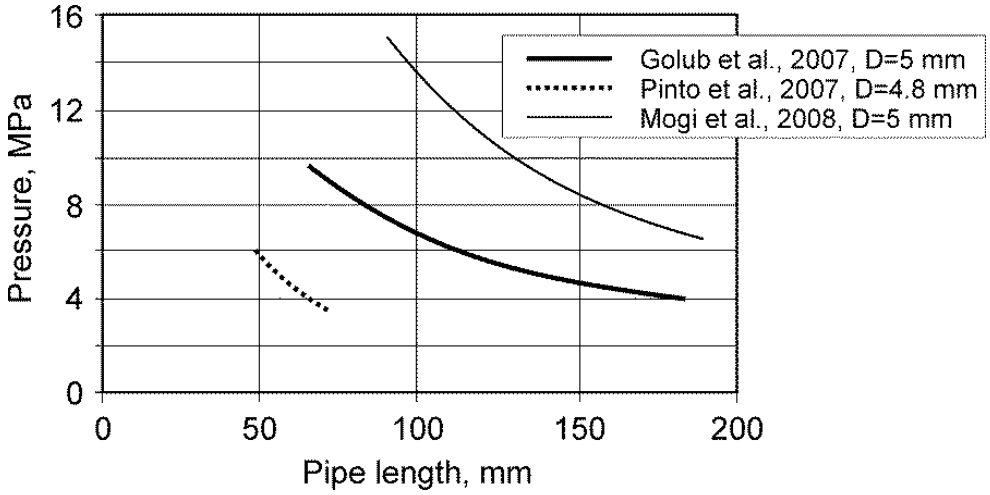

Figure 7. Hydrogen 'ignition' pressure as a function of a pipe length in series of tests with flat burst disks [3].

Figure 7 shows an essential difference in critical conditions for spontaneous ignition obtained in different studies. It can be seen, for example that for hydrogen storage pressure of 6 MPa in experiments carried out by Pinto et al. [32] the 50 mm pipe length is sufficient to provide spontaneous ignition. However, at the same storage pressure and practically with the same internal diameter the channel length sufficient to provide spontaneous ignition in the experiments performed by Golub et al. [30, 31] is 110 mm, and in the tests by Mogi et al. [33] the minimum length increases by four times to 200 mm. How can these differences can be explained?

First of all, Golub et al. [30, 31] registered the onset of spontaneous ignition by monitoring the shock propagation and location of radiation from chemical reaction inside the pipe. Hence, critical conditions for spontaneous ignition in their experiments represent the distance from the rupture disk to the location where ignition was captured by a radiation gauge. Mogi et al. [33] judged the occurrence of spontaneous ignition by optical observation of the area near the pipe exit to the atmosphere. They showed that in some experiments spontaneous ignition did occur, but combustion was blown out by the flow. Unfortunately, no critical conditions for such releases were reported. Nevertheless, this fact confirms that not all spontaneously ignited releases transit into sustained jet fires. This is one likely reason for the shift of the critical curve in Mogi et al. experiments [33] compared to those by Golub et al. [30, 31]. However, the most probable reason explaining the shift of Mogi et al. data to higher pressures for the same pipe length was suggested in [3]. Indeed, in the experiments by Mogi et al. [33], the internal surface of the pipe between the diaphragm (rupture disk) and the exit to atmosphere was washed away by the aqueous Na_2CO_3 solution (1%) in order to allow visualization of the flame through the reaction of sodium. This solution could have interfered with boundary layer flow and chemistry of hydrogen combustion and draw away some heat from the process. Thus, the process happened later along the tube for the same initial pressure.

The experimental procedure applied by Pinto et al. [32] was different as hydrogen was compressed just before the burst disk rupture using a piston combined with the shock tube.

Nitrogen gas was injected into the high-pressure section of the shock tube upstream of the piston to push it towards hydrogen gas in order to generate high pressure of hydrogen to burst the disk. This compression obviously caused heating of hydrogen in high-pressure chamber and the release was not at the ambient temperature, but somewhat higher. But since, neither the temperature measurements in high-pressure chamber, nor information of the time, during which hydrogen was compressed, are available, it is difficult to estimate accurately the initial hydrogen temperature.

The results of the experiments performed by Pinto et al. [32] are in full compliance with those by Bazhenova et al. [34], who stated that the increase of initial hydrogen temperature stimulates the spontaneous ignition to occur earlier and under lower initial pressures. The higher initial temperature of hydrogen is the most likely reason for a shorter tube required for spontaneous ignition in the experiments by Pinto et al. [32] for the chosen pressure compared to the experiments by Golub et al. [30, 31] and Mogi et al. [33].

The way how the burst disk ruptures is probably the most important factor for spontaneous ignition as this affects the hydrogen-air mixing [29]. In the experiments discussed by Golub et al. [30, 31] burst disks were incised in the form of the cross to facilitate sharp “petal” opening at predetermined pressure, whereas in the experiments by others a wider stochastic burst disk rupture pressure distribution was observed. Stochastic nature of an in-house made burst disk rupture produces variations in structure and strength of the shock wave generated, even at constant burst pressure, and obviously can affect the repeatability of experimental data. Very good repeatability of the experiments is stated by Golub et al. [30, 31] both in the measured pressure behind the generated shock wave, and the minimum initial pressure, which would provide spontaneous ignition at fixed tube length.

Pinto et al. [32] compared the results for smooth and screwed tubes. It was found that the same initial pressure, causing spontaneous ignition in a smooth tube, fails to cause an ignition in the case of a screwed tube. This observation, however, conflicts with the opinion of Dryer et al. [29], who found that the experiments with several tubes mated together produced an ignition, whilst a single tube (no mating unions) did not, for the same initial pressure, the internal diameter and the overall tube length. These observations underline that the interaction of the developing boundary layer with the roughness of the walls in the tube section, downstream of the burst disk, can either promote or delay spontaneous ignition [3].

Dryer et al. [29] reported that spontaneous ignition events are statistically distributed in a narrow pressure range between 2.04 and 2.21 MPa, with zero probability for membrane failure at pressures less than 2.04 MPa and with certain inflammation for failure at pressures above 2.21 MPa. The experimental study by Golub et al. [35] argues on a possibility of spontaneous ignition in a T-shaped channel for initial hydrogen pressure in the range of 1.2-2.9 MPa. Dryer et al. [29] speculate on the importance of the initial stage of a membrane rupture on the mixing and subsequent spontaneous ignition process. They concluded that at low pressures, the chemical ignition time becomes the limiting factor, while at high pressures the mixing time to

achieve significant flammable mixture volume limits the process. There is a need to clarify the physics of the spontaneous ignition in order to control it appropriately.

There are also a number of experiments [36-47] conducted to investigate the high-pressure hydrogen spontaneous ignition during its sudden release. Some research focused on the influencing factors, e. g. Mogi et al. [36] and Lee et al. [37] employed tubes with different lengths in their experiments and hydrogen was released at different storage pressures. They found that spontaneous ignition took place if storage pressure was sufficient high even though a shorter tube was used. The minimum storage pressure required for spontaneous ignition decreased as the tube length increased. The sufficient high storage pressure provides sufficient energy to produce high intensity shock wave which heats the air ahead to a high temperature. In addition, the tube is necessary to have a sufficient length therefore a mixing zone is generated due to multi-dimensional shock reflection and shock-shock interactions. However, if the length of tube increases over a critical length, i.e. 1.2 m, argued by Kitabayashi et al. [38], the spontaneous ignition in the mixture could be extinguished in the tube. Golovastov et al. [39] used a photomultiplier tube and light diode to register the rupture rate of the burst disk and the moment of the spontaneous ignition. It was shown that both the initial pressure of hydrogen and the rupture rate of the burst disk influenced the high-pressure hydrogen spontaneous ignition. Faster rupture rate decreases the minimum storage pressure required for spontaneous ignition. Kaneko et al. [40] used different materials (copper, aluminum and brass) burst disks with different thickness (0.2 - 0.5 mm) and scores in their investigations. They stated that the rupturing conditions of burst disk is one of the main factors affecting the high-pressure hydrogen spontaneous ignition. The studies of Sun's group in University of Science and Technology of China [41-43] investigated the geometry of downstream tubes (Omega-shaped and tubes with different bending angles) on the high-pressure hydrogen spontaneous ignition. The results showed that the varying internal geometries of downstream tubes would induce significant shock reflection in the tube. Shock overpressure is higher compared with straight tubes. Moreover, for bending tubes, shock overpressure is higher in smaller angle tubes. Thus, spontaneous ignition is more likely to take place in a smaller angle tube. Opening ratios of the burst disk has a significant effect on the occurrence of the spontaneous ignition. It is found that spontaneous ignition cannot take place when opening ratio of the burst disk is smaller than 0.5 even if burst pressure is as high as 9.0 MPa [44]. In addition, the minimum burst pressure required for spontaneous ignition decreases with increasing of the tube dimensions (L/D) [45]. Kimet al. [46] firstly employed a tube with two side windows to investigate the mechanisms of spontaneous ignition. The visualization study showed that the spontaneous ignition originally took place at the tube boundary layer behind the front center of the mixing area, after which the flame propagated upstream and downstream along the boundary layer. The spontaneous ignition was accompanied by the complex mixing induced by the multidimensional shock reflection and shock-shock interaction. And there existed a critical static pressure threshold at the boundary layer for spontaneous ignition to occur. Yamashita et al. [47] found that the first kernel appeared near the wall. Another kernel emerged from the

outer side the tube wall and gradually emerged throughout the tube. At last, these flames combined to form a large flame region inside the tube.

Numerical studies [48-57] have been conducted as well. Wen et al. [48] stated that the finite rupture process of the burst disk played a very important role in the spontaneous ignition, which induced significant mixing of hydrogen and air at contact surface via shock reflection and shock-shock interactions. Parametric studies were conducted as well to study the effects of rupture rate, storage pressure, tube length and tube diameter on the spontaneous ignition and similar conclusions were obtained. The studies of the same group [49,50] investigated the effect of internal geometries and the obstacle plate on the hydrogen spontaneous ignition numerically. The results showed that the presence of the internal geometries significantly increased the possibility of the spontaneous ignition and the presence of an obstacle plate quenched the flame following the spontaneous ignition. Bragin et al. [51,52] simulated the high-pressure hydrogen spontaneous ignition using LES model and successfully reproduced the flame separation outside the tube. The membrane rupture simulation showed that a hydrogen-air mixture layer existed along the boundary layer where spontaneous ignition took place afterwards. The only 3D CFD model and simulations conducted by Ulster University [51,52] were validated against the spontaneous ignition experiments. Terashima et al. [53] used different initial shape of the diaphragm in their simulation and found that for a greatly deformed diaphragm, three ignition events were identified inside the tube. Lee et al. [54,55] found that there was a significant relevance between the ignition features and the burst conditions. Yamada et al. [56,57] suggested that the shape of the contact surface was gradually changed from the spherical to flat. Then flat contact surface changed to spherical with a large curvature. In addition, three vortices were found in the tube which may cause a significant effect on the mixing of hydrogen and air.

Other researchers investigated the effects of different gases doping to hydrogen on the spontaneous ignition occurrence. Rudy et al. [58,59] released high-pressure hydrogen-methane mixtures and hydrogen-nitrogen mixtures into a tube which was full of air. It was found that only 5% methane addition could increase the minimum storage pressure at which the mixture may ignite. It is 2.67 times in comparison to the minimum storage pressure of the pure hydrogen. As for nitrogen additions, 5% and 10% N_2 additions may increase 2.12- or 2.85-times minimum storage pressure at which spontaneous ignition took place. Golovastov et al. [60] investigated the effect of methane impurities on the high-pressure hydrogen spontaneous ignition delay. It was shown that the adding of 18% (mol.) of methane leads to a 6-fold increase of ignition delays. Despite the research mentioned above, there is still lack of experimental data concerning the effects of gases doping to air on the occurrence of the high-pressure hydrogen spontaneous ignition. Relatively little is known about the shock wave properties and the spontaneous ignition conditions under this scenario. This experimental study is trying to investigate the effect of hydrogen additions on spontaneous ignition of high-pressure hydrogen, which is useful for us to better understand the physics and the risk of the high-pressure

hydrogen release and spontaneous ignition. In the paper of Gong et al. [61], the effects of hydrogen additions on spontaneous ignition of high-pressure hydrogen released into hydrogen-air mixture was investigated. Hydrogen and air are premixed with different volume concentrations (0%, 5%, 10%, 15% and 20% H_2) in the tube before high pressure hydrogen is suddenly released. Pressure transducers are employed to detect the shock waves, estimate the mean shock wave speed, and record the shock wave overpressure. Light sensors are used to determine the occurrence of high-pressure hydrogen spontaneous ignition in the tube. A high-speed camera is used to capture the flame propagation behavior outside the tube. It is found that only 5% hydrogen addition could decrease the minimum storage pressure required for spontaneous ignition from 4.37 MPa to 2.78 MPa significantly. When 10% or 15% hydrogen is added to the air, the minimum storage pressure decreases to 2.81 MPa and 1.85 MPa, respectively. When hydrogen addition increases to 20%, the spontaneous ignition even takes place at burst pressure as low as 1.79 MPa inside the straight tube.

5.2 Physical mechanism

5.2.1 An instantaneous opening

The mechanism of spontaneous ignition by the diffusion mechanism is illustrated in Figure 8. For simplicity, the simulations were performed for the case of an instantaneous opening of a burst disk separating hydrogen and air at the same initial temperature but at different initial pressures (hydrogen at 9.6 MPa and air at 0.1 MPa) [12].

Figure 8 shows the dynamics of temperature (left) and hydrogen mole fraction (right) during the first 56 μs after the rupture disk instant opening (non-inertial rupture disk). At the initial moment (t=0) the "rupture disk" boundary, separating high-pressure hydrogen and atmospheric air, located at x=0, is instantaneously removed and a shock wave propagates into the air, heating it up due to the compression. The shock wave is followed by a contact surface separating cold hydrogen and heated air. It is seen that the thickness of the heated air layer between the shock front and the contact surface increases in time [3].

The shock wave propagates along the tube as a plane wave without any curvature outside the boundary layer. The shape of the contact surface changes from plane to slightly convex in the beginning due to the non-slip conditions at the pipe walls. The highest temperature is observed in the boundary layer due to velocity decrease (stagnation conditions). Owing to a counter diffusion of hydrogen and air at the contact surface with a consequent heat diffusion from hot air to cold hydrogen through the contact surface, the spontaneous ignition occurs when critical conditions for chemical reaction are reached. The chemical reaction propagates in the direction from the wall to the tube axis as the contact surface propagates downstream. After 45 μs from the start of the process at distance 20 mm from the non-inertial "rupture disk" location the combustion occupies the whole cross-section area of the pipe. The initiation of the chemical reactions in the boundary layer accelerates the propagation of the reaction front along the wall

compared to the axial part leading to change of the convex shape of the contact surface in most of the tube cross-section to a slightly concave form [3].

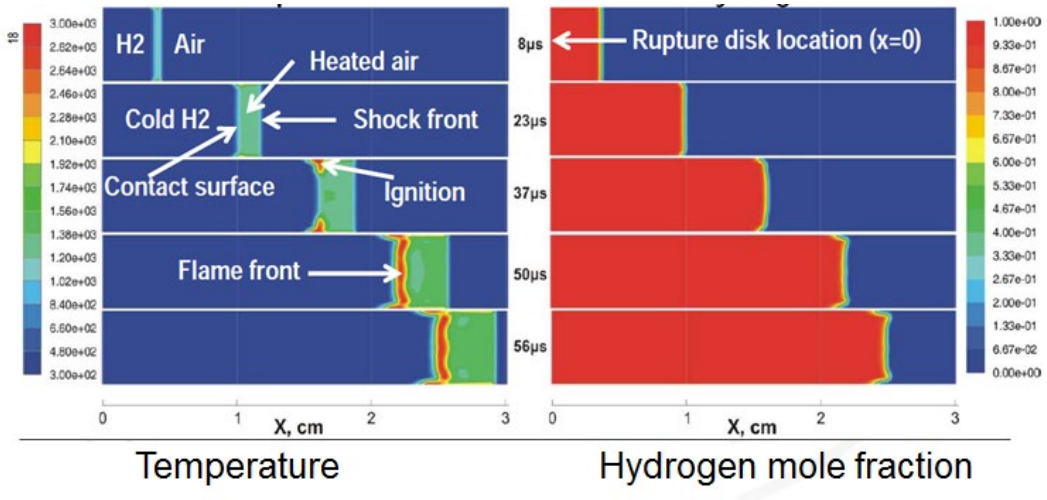

Figure 8. The dynamics of spontaneous ignition: temperature (left) and hydrogen mole fraction (right) [62].

5.2.2 Effect of a valve opening rate

Figure 9 shows the dynamics of temperature and hydrogen mole fraction at an initial stage of hydrogen release into the air in a mock PRD with an instant opening (left) and with an inertial opening (right) of the rupture disk for initial pressure of 1.35 MPa in the high-pressure chamber [63]. The inertial rupture disk opening is accompanied by a formation of an under-expanded jet from an increasing with time open area of the disk. A barrel-like structure can be seen for the case of inertial membrane opening (Figure 9, right). Inertial disk rapture results in lower temperature and different shape of hydrogen-air interface compared to instantaneous membrane opening, which made Bragin et al. [63] to suggest that a "slow opening even for fast valves" sometimes eliminates the ignition.

The inertial disk model had 10 radial sections and its rapture was modelled via one-by-one consecutive opening of each of 10 sections of the rupture disk changing the barrel diameter to a larger one and making the temperature field look similar to the multiple diamond-like pattern, which is characteristic for this range of pressures. In the case of the instant opening of an imaginary non-inertial membrane the shock-heated zone in air (red colour) is almost three times thicker compared to the inertial membrane rupture case at the same moment of time. It is obvious that the inertial opening of the membrane generates more intense mixing of hydrogen and air, including in the boundary layer of the axial channel walls. Maximum temperature in the shock-heated air is 50 K lower for the inertial membrane opening case. Thus, modelling of the inertial rupture disk opening is an important part of predictive simulations of spontaneous ignition in complex geometries [3].

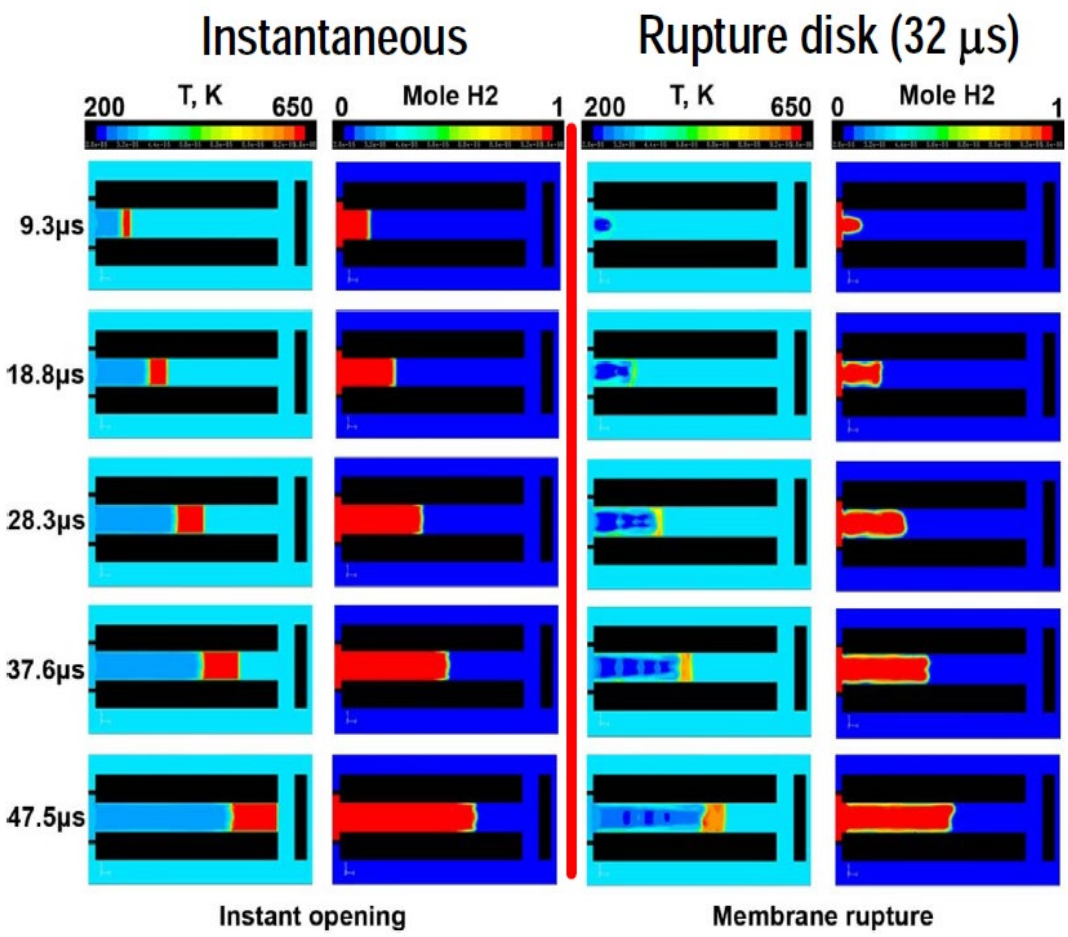

Figure 9. Dynamics of temperature and hydrogen mole fraction at the initial stage following an instant rupture disk opening (left) and an inertial ten-step rupture disk opening (right) for the 1.35 MPa high-pressure chamber case [3].

5.2.3 Transition to a sustained fire

In the series of simulations performed by Bragin and Molkov [64], the focus was shifted from the resolution of spontaneous ignition towards the transition from ignition within the pipe to combustion outside the pipe in the atmosphere. In this study the flame is identified by the mole fraction of hydroxyl groups OH. Hydroxyl concentration coupled with high temperature is widely acknowledged as an indication of combustion taking place. Bragin and Molkov [64] identified the visible flame by the hydroxyl mole fraction higher than 0.001.

Figure 10 shows the dynamics of temperature, velocity, hydrogen (H_2) and hydroxyl (OH) mole fractions in simulations of high-pressure hydrogen being released from a pipe into open atmosphere [64]. The initial pressure of hydrogen chosen for numerical simulations experiment was 9.7 MPa, the pipe length was 145 mm, the pipe diameter was 5 mm. The field of view in all numerical snapshots is kept constant, where the channel length shown corresponds to 66.5 mm, and the external to the pipe area is 148 mm long and 130 mm wide. All snapshots represent a 2D cross-section along the pipe axis. The maximum and minimum values in each series were fixed to lock the relation between colours and corresponding parameters in all frames. Minimum and maximum values in each set of frames were fixed to 0-2400 K for temperature,

0-3000 m/s for velocity, 0-1 for hydrogen mole fraction, and 0.001-0.01 for hydroxyl mole fraction. If values fall out of these limits, they are coloured according to the colour of limits: red for values above the upper limit and blue for values below the lower limit [3].

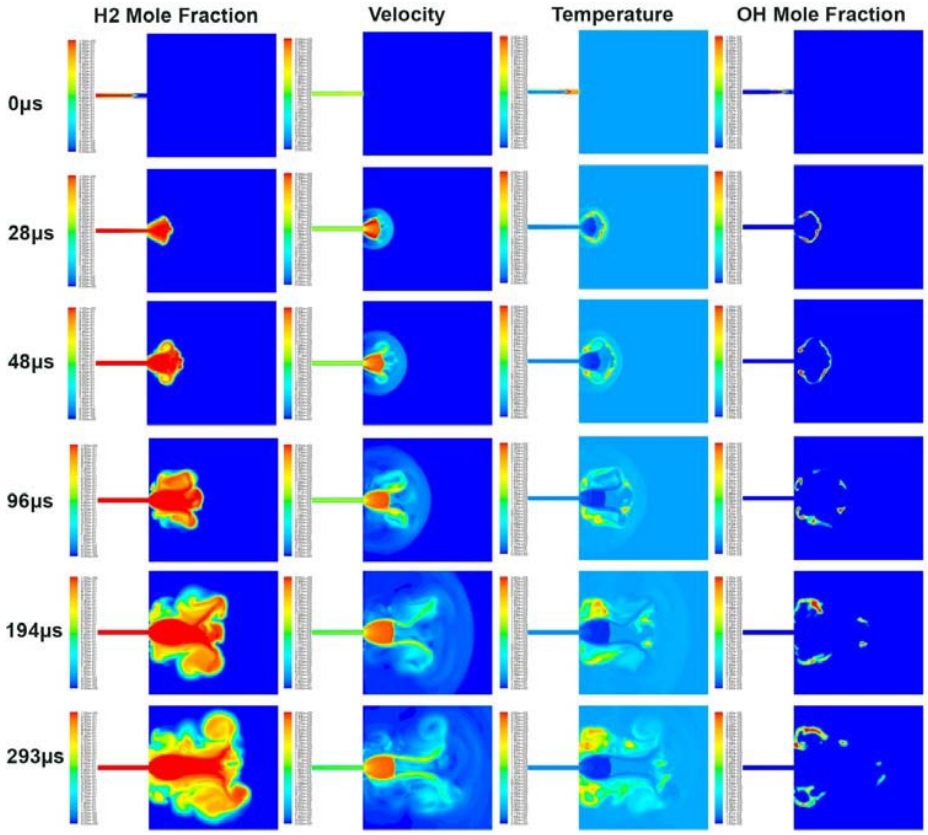

Figure 10. Dynamics of the velocity, temperature and mole fractions of hydrogen and hydroxyl in 2D slice along the pipe axis [64].

The resulting flame front tip gets behind the shock wave by about 7 mm from the end of the pipe. The flame front width is about 3 mm near the pipe axis, while near the wall it extends as long as 35 mm. Combustion is more pronounced near walls, having wider regions with high temperature. The first frame in the time series corresponds to the time of 131.5 μs from the instant opening of the "rupture disk". For ease of interpretation of the transition process the reference time was set to 0 μs at this moment (see Figure 10) [3].

Figure 10 shows that as the shock wave emerges from the pipe exit it diffracts and transforms from a plane to a hemispherical form. The shock propagates outwards and quickly loses its strength. It is followed by the flame front pushed by the expanding hydrogen. Once hydrogen leaves the tube, the expansion starts, and the flame front follows the expansion. The formation of Mach disk commences shortly after (see "28 μs" frame in Figure 10) and the expansion of hydrogen is held back, increasing the separation distance between the leading shock and the contact surface. Sudden deceleration of hydrogen stimulates turbulent mixing, and the contact surface becomes turbulent [64].

5.2.4 Effect of a flame separation by vortex

In parallel to the Mach disk formation, the outer annular flow at the Mach disk's periphery forms. Owing to viscous forces this supersonic annular flow generates a large-scale vortex, which turns the flow back towards the pipe exit. The formation of vortex breaks the combusting gas into two parts: downstream and upstream parts – see the frames of 48 μs in Figure 10. The mole fraction of OH radical (which serves as combustion reaction indicator) and comparison with experimental snapshots in Figure 11 below, which shows a comparison between the experimental and simulated snapshots. Numerical flame propagation can be referenced to experimental dimensions by vertical lines, which are positioned 10 mm apart. Meanwhile, the shock barrel is not yet stabilized. Upstream combustion region is pushed back by the vortex tip (96 μs), while the downstream combustion region in the vicinity of the jet axis is forced out. As the vortex straightens, the supply of hydrogen to the recirculation area dies out and reduction of flow velocity allows necessary induction time for intensification of combustion. It can be seen that combustion affects the gas dynamic evolution of the jet and results in non-axis-symmetrical to some extent flow beyond the Mach disk (194 μs). Shock barrel is stabilized around 200 μs. The annular vortex increases in size, widening the distance from the axis where hydrogen is present. By the time of the last frame in Figure 10 (293 μs) the downstream from vortex combustion is fully ceased (no OH radicals), while the upstream combustion in the recirculation zone is sustained.

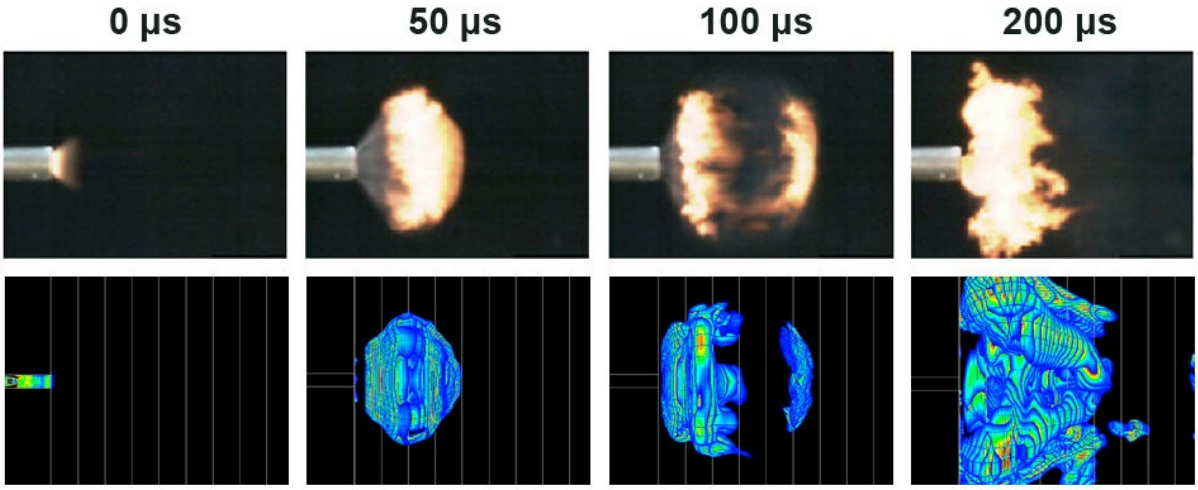

Figure 11. High-speed video camera experimental photographs (top) [33] and numerical 3D snapshots (bottom) [64].

A sequence of photographs taken with a high-speed video camera showing the flame exiting from a pipe, where spontaneous ignition has happened, was published by Mogi et al. [33] and reproduced in Figure 11. This sequence of snapshots shows the combustion of spontaneously ignited hydrogen-air mixture, emerging outside and stabilizing in the vicinity of the pipe exit. The authors observed that once the flame is emerging from the pipe it is stabilized near the nozzle it acts as a pilot flame and ignites/sustains the jet fire afterwards. Therefore, the

numerical simulated flame "stabilization" near the pipe exit [64] may be taken as an indication of the transition from the spontaneous ignition to the sustained jet fire.

Figure 11 shows that the ignited within the pipe jet exits to the atmosphere at 0 μs. It develops into a cocoon of combusting mixture (50 μs). Shortly after this the annular vortex, which cannot be seen here (see Figure 10), causes the cocoon to break into upstream and downstream combusting regions (100 μs). As the downstream combustion region is blown away, the upstream region is stabilized near the tube exit (200 μs). The size of this region, however, is bigger in the simulations. This can be explained by three potential reasons. Firstly, the chosen limit for the numerical visualisation of the flame front of 0.001 of OH (it is often taken as 0.01 of OH). Secondly, there are different conditions for air entrainment in the experiment and simulations. Indeed, the simulations of hydrogen release were carried out not for the pipe with 5 mm internal diameter and 4 mm wall thickness, but for the channel of 5 mm in a wall with "infinite" dimension. Third reason for deviation in size of stabilised flame could be the wetting of the inside surface of the tube between the burst disk and the exit to the atmosphere by the aqueous Na_2CO_3 solution (1%) in order to allow visualization of the flame. This solution could have interfered with heat transfer and chemistry of hydrogen combustion and decreases the visible flame size [3].

It is assumed, following the experimental observations and numerical simulations, that the transition to the sustained jet flame is largely dependent on the initial jet formation stage, where developing annular vortex pushes combusting mixture upstream into the recirculation zone. Once the flame is stabilised near the pipe exit, it can act as a pilot flame to jet fire later [3].

5.3 Spontaneous ignition in a T-shaped PRD

5.3.1 Experimental set-up

The geometry of the experimental set up, including a T-shaped channel mimicking a PRD, is taken from Golub et al. [35] and is shown in Figure 12. The high pressure system consists of a 210 mm long tube with the internal diameter (ID) of 16 mm followed by a 280 mm long tube with the ID = 10 mm, at the end of which a flat rupture disk, made of copper or aluminium with cuts facilitating failure, is located followed by a mock-up PRD (T-shaped channel) open to the atmosphere.

The PRD has a 48 mm long axial channel of 6.5 mm ID with a flat end, and two radial channels on opposite sides of the axial channel to vent hydrogen to the atmosphere. Each radial channel has 6.25 mm length and 4 mm ID (distance from the end connected to the atmosphere of one radial channel to the end of another one is 19 mm). Radial channels are flushed with the axial channel end wall and positioned so that the edge of each radial channel touches tangentially the flat end wall of the axial channel. The rupture disk opening was estimated by Golub et al. [35] as about ten microseconds, thus creating conditions for better mixing of hydrogen with the air during the opening as compared to an unrealistic instant opening. To register the spontaneous ignition a light sensor was installed along the axis of radial channels of the PRD.

Temperature behind the shock wave reflected from the flat end wall was estimated by the authors as more than twice higher than the temperature behind the incident shock wave. Golub et al. [35] stated that when the initial pressure in a high pressure chamber did not exceed 1.2 MPa the light sensor did not record any signal, and when pressure was 2.9 MPa the ignition was registered.

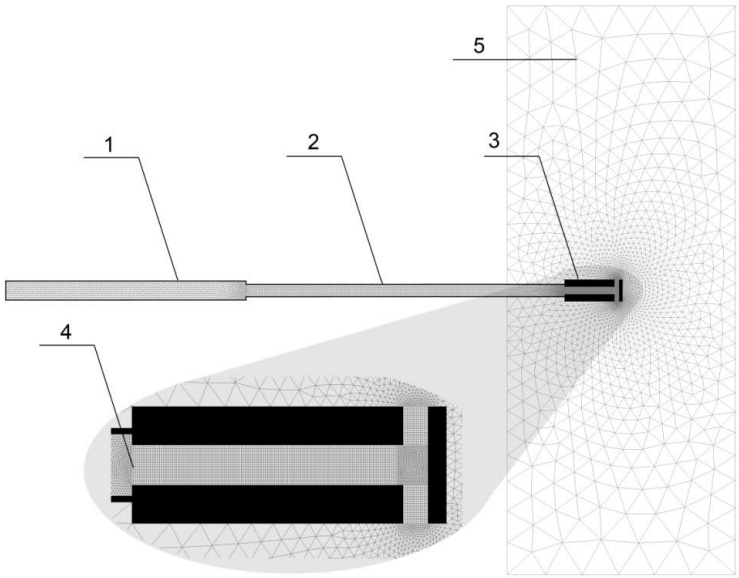

Figure 12. The geometry and computational domain: 1 and 2 – high pressure tubes, 3 – a mock-up PRD (T-shaped channel), 4 – burst disk, 5 – external computational domain.

5.3.2 Effect of a storage pressure

5.3.2.1 Simulation results for 1.35 MPa (no spontaneous ignition)

Figure 13 demonstrates a flow pattern and provides an insight into the process of hydrogen release from a storage at pressure 1.35 MPa through a T-shaped channel mimicking PRD device, in which no ignition was observed. The first snapshot denoted ‘60 μs’ shows a contact surface between hydrogen at near room temperature (in light-blue colour) and the air heated by the pressure wave (in green-yellow) within the horizontal axial channel. The contact surface is inside the axial channel at this moment and it is disturbed by the Rayleigh-Taylor instability. Close to the flat end of the axial channel there is a volume of air heated further by the reflected shock (in red colour). New areas of the heated air (in red) in radial channels are seen in the next snapshot ‘63 μs’ along with the increasing volume of the hot air at the axial channel end. These new areas are probably due to the second reflection from a wall of the radial channel that is opposite to the flat end of the axial channel. At the time of 67 μs “cold” hydrogen starts to exit the axial channel and flows along one side of the radial channel. The hot air temperature in front of hydrogen is reduced (see the snapshots from ‘67 μs’ to ‘77 μs’). There is a drop in the heated air temperature when the hot air exits the radial channel to the atmosphere. The reflected shock is weak at a storage pressure of 1.35 MPa and the hot air in flow following the reflected pressure wave cannot enter the axial channel (only to a small extent at the axial channel axis).

At the time equal to 77 μs hydrogen starts exiting to the atmosphere and its temperature drops further down during this expansion (dark-blue colour) [12].

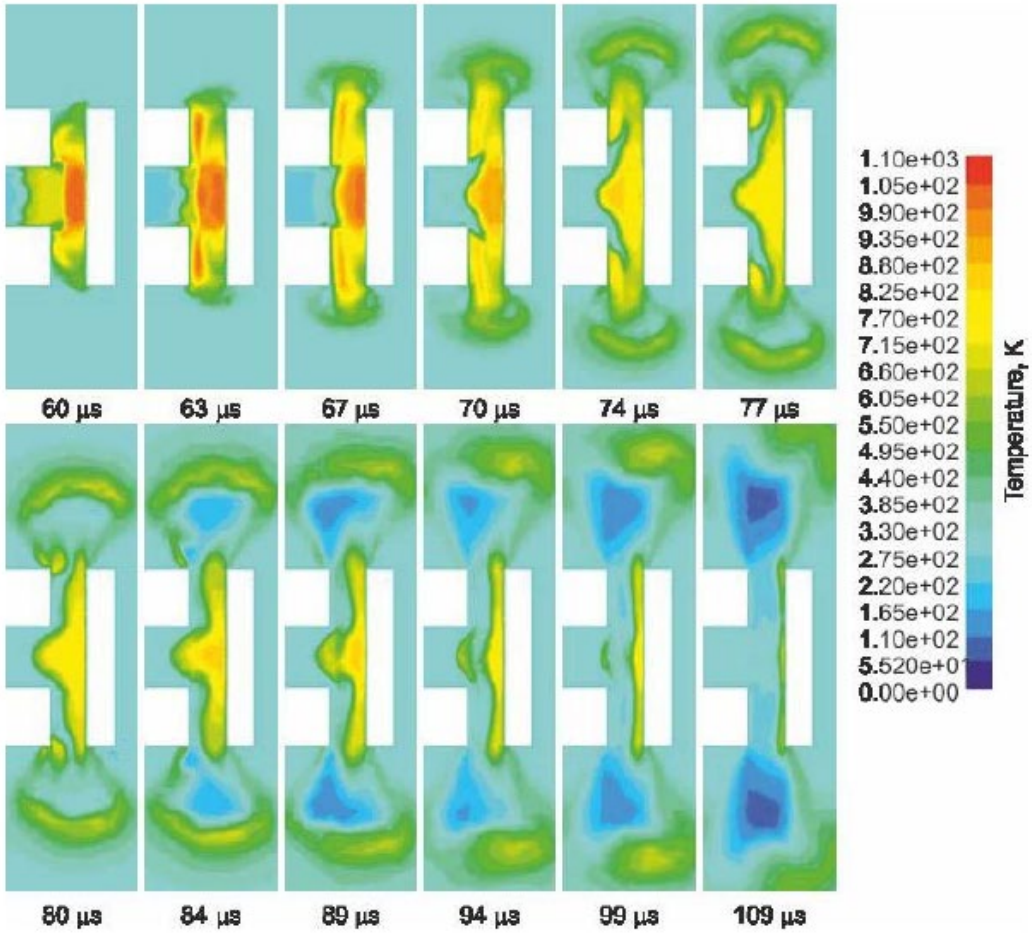

Figure 13. Temperature dynamics of a hydrogen release into the T-shaped channel at a storage pressure of 1.35 MPa - no ignition (yellow – air heated by the shock wave; red – air heated by the reflected shock wave; light-blue in the pipe - flowing hydrogen; dark-blue – hydrogen cooled during expansion to the atmosphere) [12].

5.3.2.2 Simulation results for 2.9 MPa (ignition) and for 2.43 MPa

Temperature and hydroxyls mole fraction profiles in the axial cross-section for the case with the initial pressure of 2.9 MPa in the high-pressure chamber are presented in Figure 14. Moreover, Figure 15 shows the temperature and hydroxyls mole fraction profiles in the axial cross-section for the case with the initial hydrogen pressure of 2.43 MPa in the high-pressure chamber.

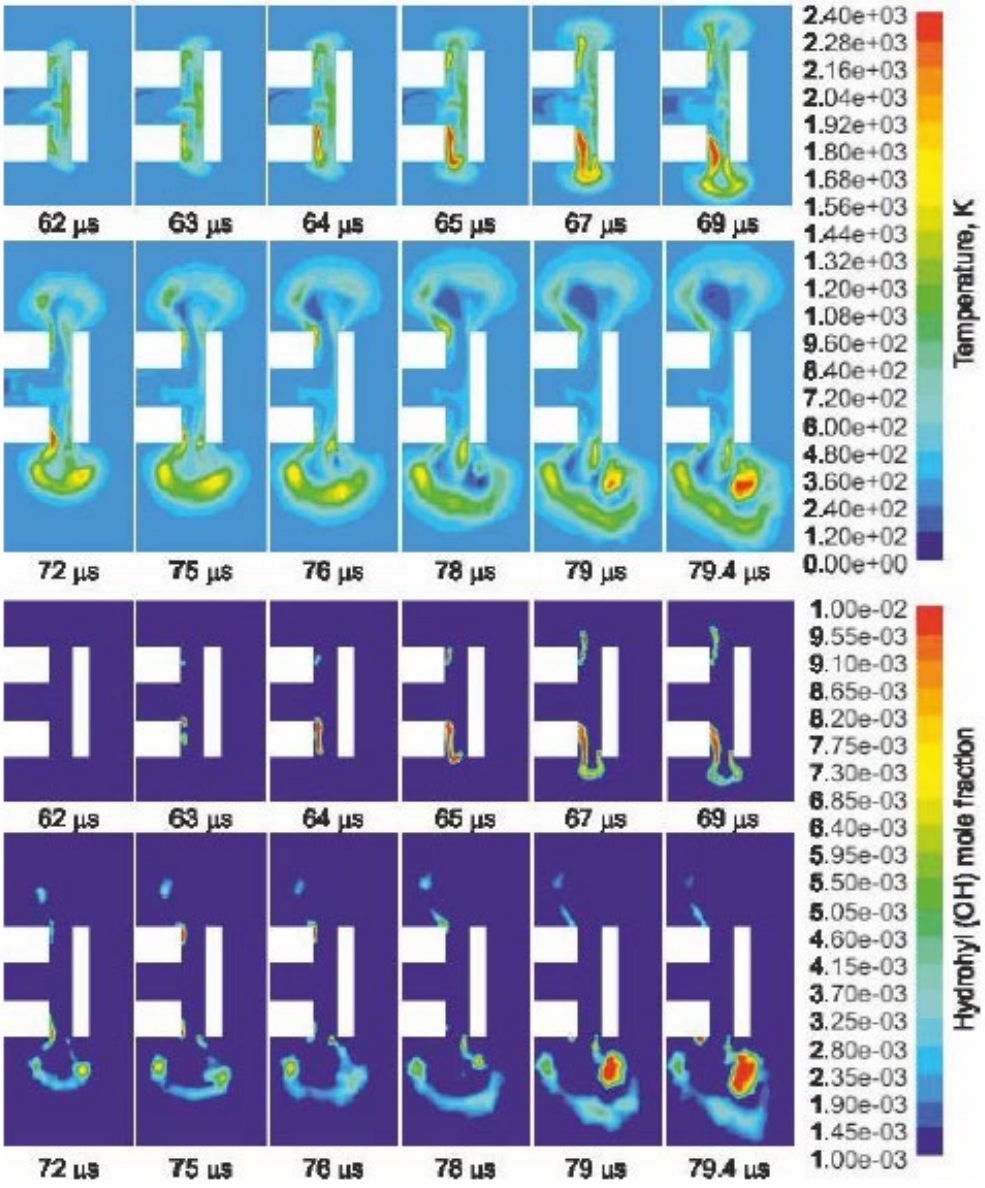

Figure 14. Temperature (top) and hydroxyls mole fraction (bottom) for 2.9 MPa hydrogen storage pressure.

At initial stage of hydrogen release the highest temperature is achieved at the location of the leading shock reflection on the flat end of the axial channel, see snapshots for 62 µs and 63 µs in Figure 14. However, it is clear that the ignition is not possible in this location since hydrogen is not supplied to this area yet. Once the hydrogen flow diffracts around the edge from the axial channel into the radial channels, it starts mixing with the air heated by shocks. This provides the necessary "fire triangle" conditions (i.e. fuel-oxidiser-high temperature) for the ignition of the hydrogen-air mixture. It can be seen that the chemical reaction is initiated in case of both 2.9 MPa (Figure 14) and 2.43 MPa (Figure 15) storage pressure in the radial channel in a location close to the upstream wall and indicated by non-zero hydroxyl mole fraction starting to grow from 63 µs and 67 µs respectively.

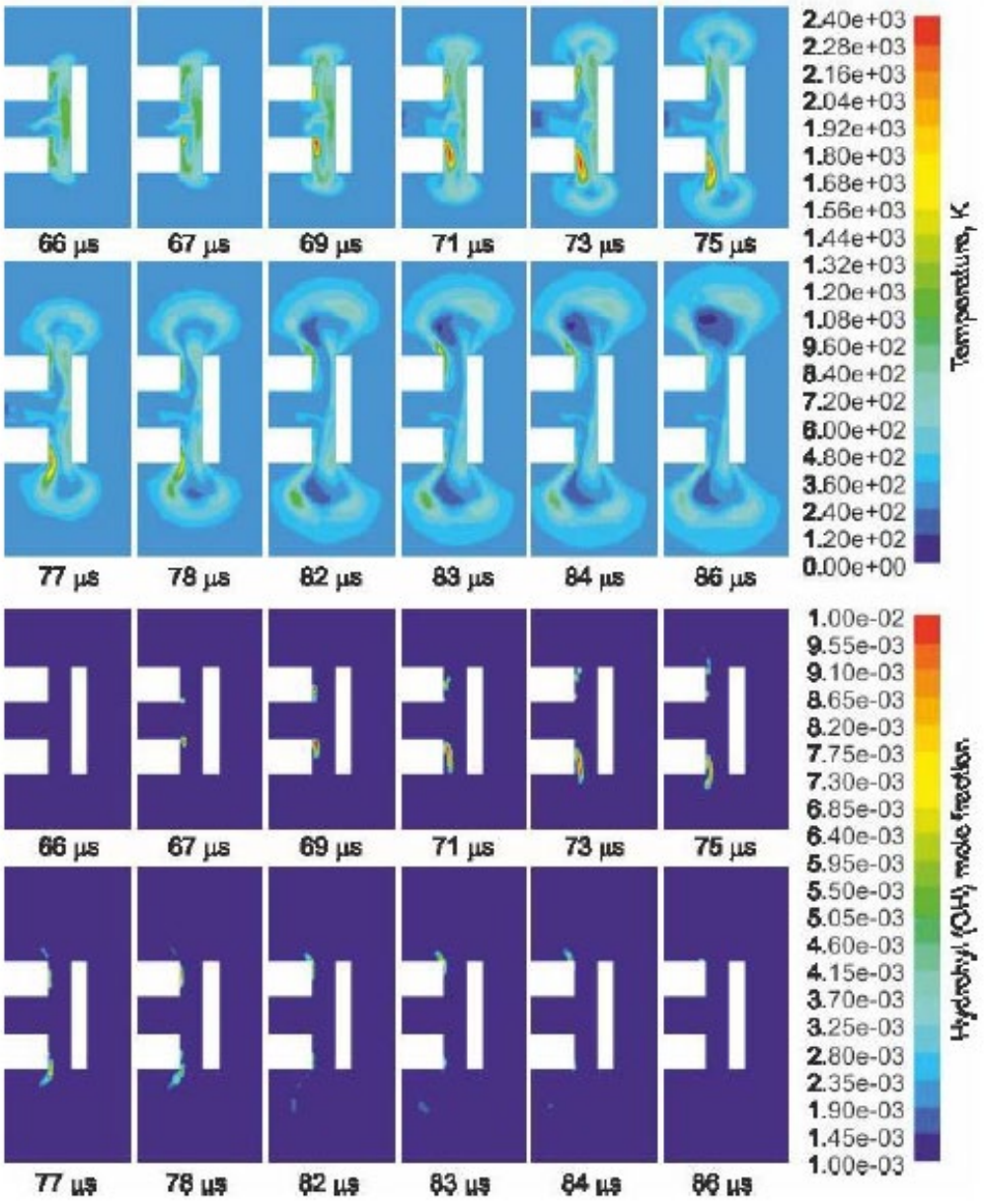

Figure 15. Temperature (top) and hydroxyl mole fraction (bottom) for 2.43 MPa hydrogen storage pressure.

Large high temperature regions can be observed for the storage pressure of 2.9 MPa (Figure 14) compared to the pressure of 2.43 MPa (Figure 15). The difference becomes obvious when combusting mixture is pushed outside. At the pressure of 2.9 MPa a semi-spherical cocoon of a heated to critical conditions flammable hydrogen-air mixture is formed outside the PRD being followed by the expanding hydrogen. The combustion is initiated in several spots within the cocoon (as indicated on the snapshots of temperature and OH mole fraction at 79 µs). The concentration of hydrogen in these spots, outside the PRD, just before the ignition, is in the range between 29 and 36 vol. % (not shown in the Figure). Thus, a conclusion can be drawn that the ignition by the diffusion mechanism takes place in the most reacting near-stoichiometric hydrogen-air mixtures [12].

At the storage pressure of 2.43 MPa (Figure 15) the combustion is rather weak compared to the case of 2.9 MPa pressure, and the reacting mixture is dragged with the adjacent hydrogen flow, which leads to the elongation of combusting regions. Upon the exit from the radial channels of the PRD, the flow undergoes an expansion and high-temperature regions disappear, thus ceasing the reaction and OH concentration, including the cooling role of the expanding pure hydrogen jet on the flammable mixture [12]. The whole process, from the combustion initiation to the self-extinction (i.e. disappearance of high temperature and OH mole fractions region, Figure 15), takes a bit longer than 10 μs. This time is sufficient to register the chemical reaction by a light sensor in the experiments. This explains the uncertainty in the interpretation of the experimental observations by Golub et al. [35]. Indeed, at the pressure of 2.9 MPa the combustion is quite pronounced, but at the pressure of 2.43 MPa the spot of spontaneous ignition is weak, and it disappears due to the self-extinction. However, the light sensors still registered a signal during the spontaneous ignition. Thus, in full compliance with the experimental observation the simulations confirmed the spontaneous ignition at the storage pressure of 2.43 MPa (which is not sustained) [12].

Figures 14 and Figures 15 demonstrate that the process is asymmetrical, i.e. the ignition in the upper radial channel is weaker than in the lower channel. At the pressure of 2.9 MPa the ignition survives the expansion from only the lower radial channel, while the upper part is extinguished. This is caused due to the asymmetrical opening of the rupture disk in the simulations. The results support the previous conclusion about the sensitivity of the spontaneous ignition to the burst disk rupture process that should be investigated further along with the effects of other factors such as the air humidity, etc. [12]. More detailed information on the spontaneous ignition in a T-shaped PRD can be found in [3].

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 [65]:

- 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 Ex-zone classification

The description of equipment ex-zone classification and the frequency of leaks (in hrs per annum) are indicated in Table 1. The equipment used in Zone 0 has to be intrinsically safe. The equipment must be controlled by a certifying body to get the appropriate marking. Regular maintenance is required to ensure the equipment remains intrinsically safe.

Table 1. Ex-zone classification.

Zone	Description	Frequency
0	An area where an explosive gas atmosphere is present continuously or for long periods	>1000 h/a
1	An area where an explosive gas atmosphere is likely to occur in normal operation	>10 h/a but <1000 h/a
2	An area where an explosive gas atmosphere is not likely to occur during normal operation, or if it occurs will only exist for a short period	<10 h/a
No zone	Safe area	No Ex-Atmosphere present at any time

Electrical equipment can be a source of ignition. The main prevention principle is to limit the presence of ignition sources in hazardous locations/areas. If this is not possible three basic protection methods are used to ensure safety and compliance with the regulations:

1. Explosion containment. This method allows the fire or explosion to occur but confines it to a well-defined area. This aims to avoid the propagation of the hazardous conditions to a surrounding atmosphere. It is possible to use:
   - An explosion-proof enclosure, when the explosion will remain confined in an enclosure specially designed to resist the overpressure. It is applicable to the equipment located in Zones 1 and 2, but not in Zone 0 and referenced with the symbol Ex ‘d’
2. Segregation. This method attempts to physically separate or isolate electrical parts or hot surfaces from the explosive mixture. It is possible to use:
   - Pressurisation protection method, when a protective gas is contained inside the enclosure in order to maintain a pressure slightly higher than in the external atmosphere. It is applicable only to the equipment located in Zones 1 and 2, but not in Zone 0 and is referenced with the symbol Ex ‘p’.
   - Encapsulation protection method when a resin is used to segregate electrical parts. It is applicable only to the equipment located in Zones 1 and 2, but not in Zone 0 and is referenced with the symbol Ex ‘m’.

- Oil immersion protection method when all electrical parts are submersed in oil. It is applicable only to the equipment located in Zones 1 and 2, but not in Zone 0 and is referenced with the symbol Ex ‘o’.
- Powder filling protection method when powdered material (usually quartz powder) is used to segregate electrical parts. It is applicable only to the equipment located in Zones 1 and 2, but not in Zone 0 and is referenced with the symbol Ex ‘q’.

3. Prevention. It is a method that limits the energy content, both electrical and thermal, to safe levels under both normal operation and in fault conditions. It is possible to use:
   - Increased safety protection method when electrical apparatus is designed to prevent the generation of the excessive temperatures, arcs and sparks inside and outside the apparatus during normal conditions. It is applicable only to the equipment located in Zones 1 and 2, but not in Zone 0 and referenced with the symbol Ex ‘e’.
   - Intrinsic safety protection method. There is a limitation in the energy stored in an electrical circuit making it incapable of generating arcs, sparks or thermal effects that are able to ignite an explosion of hydrogen-air mixture, both during normal operation and in specific fault conditions. The kind of protection labelled as Ex ‘ia’ is applicable to the equipment located in Zones 0, 1 and 2, while the one labelled as Ex ‘ib’ – only to the equipment in Zones 1 and 2, but not in Zone 0 [66].

6.2 Electrostatic spark ignition prevention

Hydrogen belongs to the flammable gas Group IIC. European Committee for Electro-technical Standardization [67] restricts the widths of narrow materials (pipes, cables sheaths, etc) depending on the zones and gas categories, which are given in Table 2.

Table 2. CENELC restrictions on width of narrow materials.

Zone	Maximum width, cm		
	Group IIA	Group IIB	Group IIC
0	0.3	0.3	0.1
1	3.0	3.0	2.0
2	No limit	No limit	No limit

CENELC also imposed restrictions on the chargeable surfaces, depending on the zones and gas categories, which are shown in Table 3. This document restricts areas of insulating materials that may become charged and limits the maximum charge that can be transferred from the surface in the form of a brush discharge (maximum tolerable charge transferred for hydrogen is 10 nC).

Table 3. CENELEC restrictions on chargeable surface.

Zone	Maximum area, cm^2		
	Group IIA	Group IIB	Group IIC
0	50	25	4
1	100	100	20
2	No limit	No limit	No limit

The prevention of ignition of hydrogen, deliberately vented to the atmosphere, can be applied by using a polished toroidal ring in the end of the vent. In practice, corrosion and dirt deposits on such rings are effectively small radius protrusions [12]. Control of static electricity might require a change of material in the employees' overalls and adoption of antistatic footwear. In addition, battery-powered devices such as radios, mobile phones, cameras are also considered as potential ignition sources [12].

Different guidelines such as [68] and [69] describe the methods to prevent the charge generation and accumulation, and electrostatic discharge as required by ATEX [70]. They include:

- Avoid or restrict the charge generation: for non-conductive liquid, such as liquid hydrogen, it is recommended not to exceed 1 m/s transport speeds by increasing diameter or by decreasing the flow rate.
- Remove or decrease the charge accumulation: this can be done by avoiding the use of insulating materials and also by grounding and bonding the elements of the installation.
- Organizational measurements: the control of static electricity depends on the training of staff involved as mentioned in ATEX 137 [70].

6.3 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 ºC even for a few mm^2 according to the experiments conducted within the European project MECHEX (please note that hydrogen auto-ignition temperature, 510 ºC, is still lower than specified above).

Physical separation of ignition sources, such as welding, flames or hot working is preferable. An additional classification of electrical equipment is based on the maximum surface temperature of apparatus at atmospheric pressure shown in Table 4 [71]. Any type of apparatus from T1 to T6 can be used in a flammable hydrogen-air mixture.

Table 4. Classification of electrical apparatus depending on their maximum surface temperature [71].

Temperature class	Maximum surface temperature, °C
T1	450
T2	300
T3	200
T4	135
T5	100
T6	85

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 [66]. 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 [66]:

- 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 [66]:

- 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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