

HyResponse

## **BASICS OF HYDROGEN SAFETY FOR FIRST RESPONDERS**

Lecture. Sources of hydrogen ignition and prevention measures



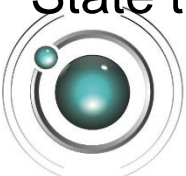
# Content

- Hydrogen ignition incidents and mechanism: an overview.
- Minimum Ignition Energy
- Auto-ignition temperature
- Types of ignition sources
  - Electrostatic discharge
  - Mechanical ignition
  - Ignition by a hot surface
  - Adiabatic compression
- Hydrogen ignition mechanisms
- Spontaneous ignition of sudden releases: diffusion mechanism
- Prevention of hydrogen ignition



# Objectives of the lecture

- Recognise different types of ignition sources;
- Identify mechanisms of hydrogen ignition depending of the ignition source;
- Describe the Joule-Thomson effect on hydrogen ignition;
- Compare the values of minimum ignition energy (MIE) and auto-ignition temperature of hydrogen with those for other common fuels;
- Define the dependence of MIE on 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.



# Hydrogen ignition: incidents analysis

- In the work by Astbury and Hawksworth (2007) it was stated that there have been **reports of high pressure hydrogen leaks igniting for no apparent reason**, 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 (**no rigorous scientific analysis**).
- There are gaps in the knowledge of the exact ignition mechanism for releases of hydrogen.
- The mechanisms which have been considered by Astbury and Hawksworth (2007) include: electrostatic charge generation, reverse Joule-Thompson effect, diffusion ignition, sudden adiabatic compression, and hot surface ignition.



# Hydrogen ignition incidents: statistics

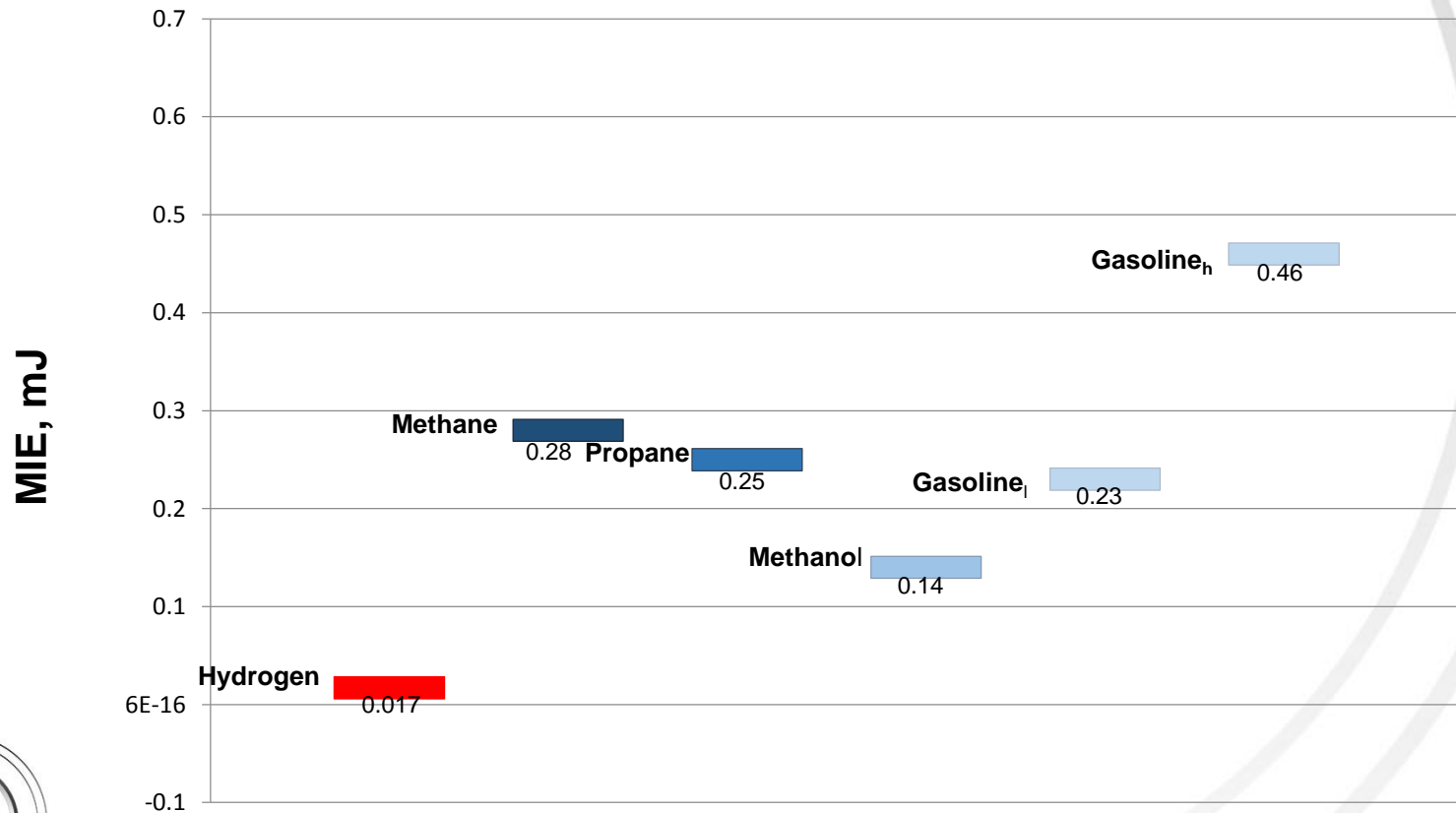
- Analysis of Major Hazard Incident Database Service of the Health and Safety Executive (UK).
- Astbury and Hawksworth (2007) revealed 81 incidents involving releases of hydrogen. Of those, **a delay between release and ignition** was reported only for **4 releases**. The authors assumed that in other cases hydrogen ignited immediately.
- In 11 cases, the source of ignition was identified, but in the remainder, i.e. **86.3%** of incidents, the **source was not identified**.
- The data for **non-hydrogen releases**: 1.5% 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.
- It is worth noting that since this is a Major Hazard Incident Database, releases of hydrogen which simply dispersed and did not involve fire, explosion, or other major hazard are not recorded. So, the **non-ignition being reported as zero** is **not necessarily an indication that all hydrogen releases were ignited**.

# Minimum ignition energy of hydrogen

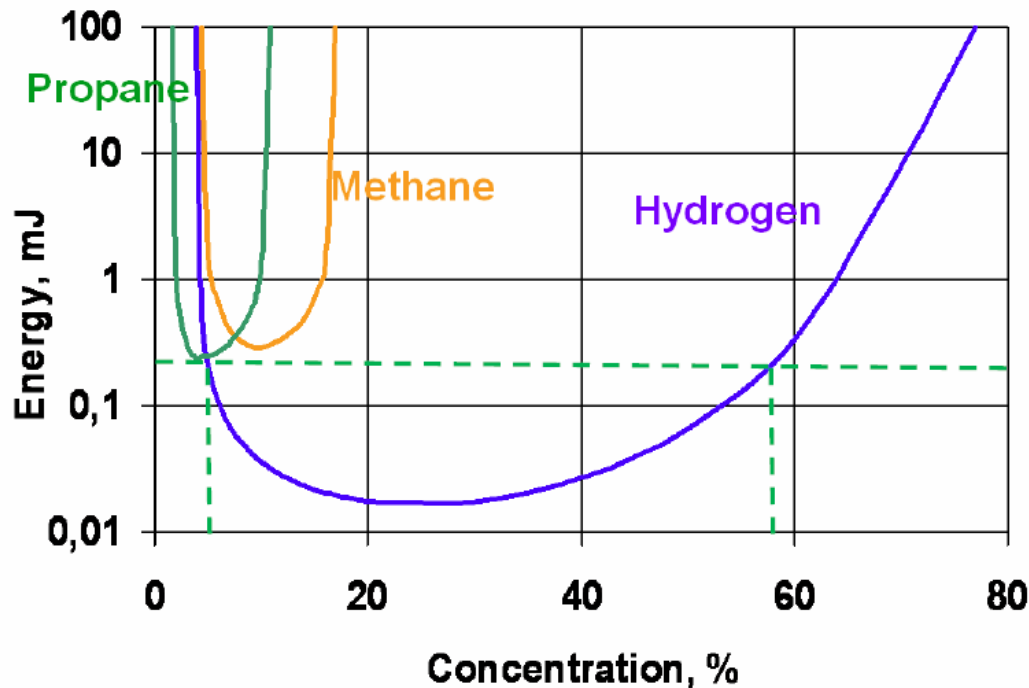
- **Minimum ignition energy (MIE)** of flammable gases and vapours is the minimum value of the electric energy, stored in the discharge circuit with as small a loss in the leads as possible, which (upon discharge across a spark gap) just ignites the quiescent mixture in the most ignitable composition. A weak spark caused by the discharge of a static electricity from a human body may be sufficient to ignite any of the fuel discussed below (Molkov, 2012).
- MIE of hydrogen-air mixture is very low – **0.017 mJ**.

# MIE of hydrogen compared to other fuels

Compared to other fuels hydrogen has the lowest MIE: **0.017 mJ** for hydrogen-air mixtures; **0.0012 mJ** for hydrogen-oxygen mixture.



# Ignition of different fuels



Less energy is needed to ignite a mixture that is closer to its stoichiometric composition.

Source: Schmidchen, 3<sup>rd</sup> ISCARW on Hydrogen Safety, Belfast, 2009

- A source with an 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. %
- **Majority of ignition sources have ignition energy higher than 10 mJ, practically all fuels would be ignited if their fuel/air ratio exceeds the LFL.**



# Triboelectricity

- **Triboelectric charge** is a type of contact electrification, in which a certain material becomes electrically charged after it comes into a friction contact with a different material.
- Hydrogen is essentially an electric **insulator** in both gaseous and liquid phases. Only above some critical “breakdown” voltage, where ionization occurs, it becomes an electrical conductor.
- When high velocity hydrogen flow accompanies high-pressure vessel blow-down this property can potentially be responsible for the generation of **static electrical charge by triboelectricity**. The probability of hydrogen ignition by this mechanism increases with increase of the blow-down time.



# Auto-ignition

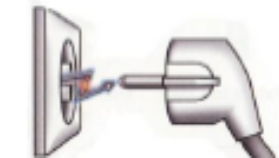
- The auto-ignition temperature is the minimum temperature required to initiate combustion reaction of fuel-oxidiser mixture in the absence of any external source of ignition.
- The standard auto-ignition temperature of hydrogen in air is above  $510^{\circ}\text{C}$ . It is relatively high compared to hydrocarbons with longer molecules. However, it can be lowered by catalytic surfaces. For example, when Pt catalyst is used the ignition can occur at  $T=70^{\circ}\text{C}$ .
- Objects at temperatures from 500 to  $510^{\circ}\text{C}$  can ignite hydrogen-air or hydrogen-oxygen mixtures at atmospheric pressure (Molkov, 2012).
- Hot air jet ignition temperature is  $670^{\circ}\text{C}$  (BRHS, 2009).



# Types of ignition sources (1/2)

## 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 particulates



## Mechanical sources:

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



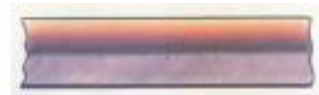
# Types of ignition sources (2/2)

## 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)



# Ignition of hydrogen-oxidiser mixtures

- The mixtures of hydrogen with oxidisers require very low energy to be ignited.
- The result is a flame that propagates throughout the mixture.
- Powerful ignition sources capable of forming shocks, such as high-energy spark discharges and explosives, can directly initiate detonations.
- Due to its low MIE it is often difficult to establish what caused hydrogen to ignite and what was the mechanism.
- [Video1](#): a static spark causes ignition.
- [Video 2](#): ignition without any obvious sources



# Electrostatic discharges

- **Spark discharge** is a single plasma channel between the high potential conductor and an earthed conductor.
- The energy from a spark discharge from an isolated conductor is calculated as  $E = CV^2/2$ , where C is the capacitance of the item, and V is the potential (voltage).
- **Brush discharge** is a discharge between a charged insulator and a conducting earthed point.
- It is characterised by many separate plasma channels, combining at the conductor. As the charged surface is a non-conductor, a capacitance and hence energy cannot be determined.
- **Corona discharge** is a silent, usually continuous discharge which is characterised by a current but no plasma channel.
- A corona discharge is able to ignite a hydrogen–air mixture without there being a discrete spark or single discharge event.

Source: Astbury, GR and Hawksworth, SJ (2007). International Journal of Hydrogen Energy. Vol. 32, pp. 2178-2185.

# Sparks and human body (1/2)

## Example of hydrocarbons-air mixtures

- Typical MIE (E) for hydrocarbons-air mixture is 0.029 mJ.
- A capacitance of a person C=100 pF.
- The voltage required to produce the spark that will ignite the mixture  $V=2408$  V. or 2.4 kV.
- Dielectric strength of air is 30 kV/cm.
- The gap between the charged conductor and the earthed point required for the breakdown to occur  $2400/30=0.08$  cm or **0.8 mm**.
- The quenching gap for hydrocarbons is 2-3 mm (investigated by Potter (1960), thus voltage will be equal to 6 kV.
- Typically people cannot feel an electrostatic shock of less than 1 mJ. Therefore they would be unaware of the potential to ignite a mixture of hydrocarbons with air. The same applies to hydrogen-air mixture.

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



# Sparks and human body (2/2)

$$E=CV^2/2$$

## Example of hydrogen-air mixtures

- For hydrogen the corresponding voltages and gaps are much lower.
- The **quenching gap** for hydrogen is **0.64 mm** instead of 2-3 mm for hydrocarbons.
- MIE =0.017 mJ.
- Theoretical dielectric strength of almost stoichiometric mixture (30 vol. % of hydrogen in air) is 26.25 kV/cm.
- The breakdown potential  $V=26.250 \times 0.064 = 1.68 \text{ kV}$ . **2 kV** can be easily generated without people being aware of it.
- $E=0.5 \times 100 \cdot 10^{-12} \times (1680)^2 = 0.141 \text{ mJ}$ , which is significantly higher than MIE of hydrogen 0.017 mJ.

**Thus, electrostatic charging of people 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 (Astbury and Hawksworth, 2007).**





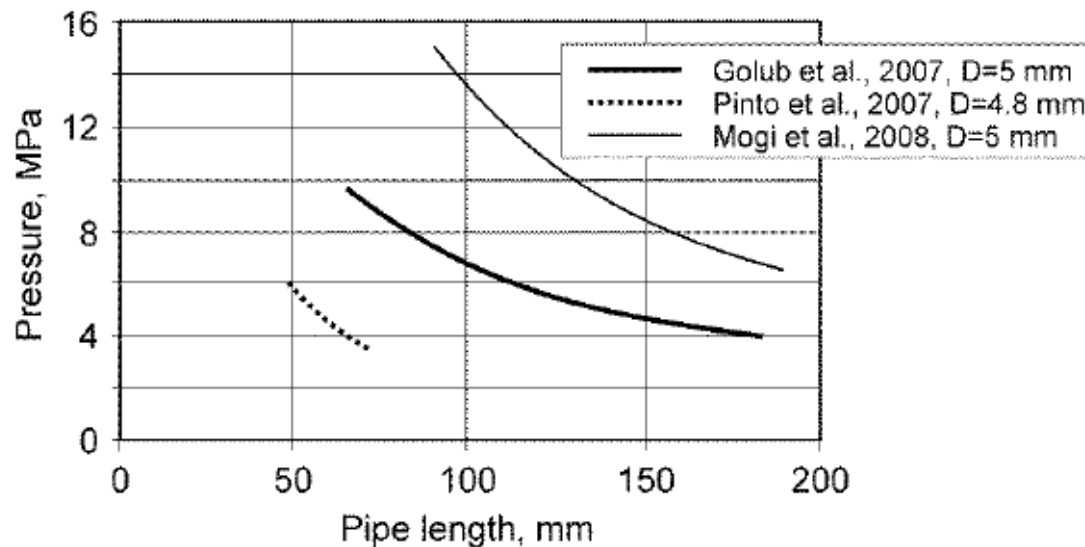
# Adiabatic compression

- The ideal gas, when compressing it at constant entropy, would increase the pressure due to the compression in accordance with the relationship  $PV^\gamma = \text{const.}$
- It can be shown with use of the equation of state for the ideal gas that  $TV^{\gamma-1} = \text{const.}$  For example, for the compression ratio  $V_1/V_2$  of 28 at initial NTP ( $\gamma=1.39$ ), the initial temperature of 293.15 K would increase to  $T_2 = T_1(V_1/V_2)^{\gamma-1} = 1075.2 \text{ K}$ , i.e. the temperature rises by 782 K. In the experiments carried out by Pan et al. (1995), the actual measured temperature realised by a compression ratio of 28 times was only 149 K.
- However, work by Cain (1997) indicates that 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.
- Reverse calculation indicates that a temperature rise from 300 to 1050 K would require a pressure rise ratio of  $P_2/P_1 = (T_2/T_1)^{1/(\gamma-1)} = (1050/300)^{1.39/0.39} = 86.9$ . Thus, adiabatic compression mechanism requires pressure rise ratio greater than that measured by Cain (1997), suggesting that there is another ignition mechanism present (Astbury and Hawksworth, 2007).



# Spontaneous ignition of a sudden release

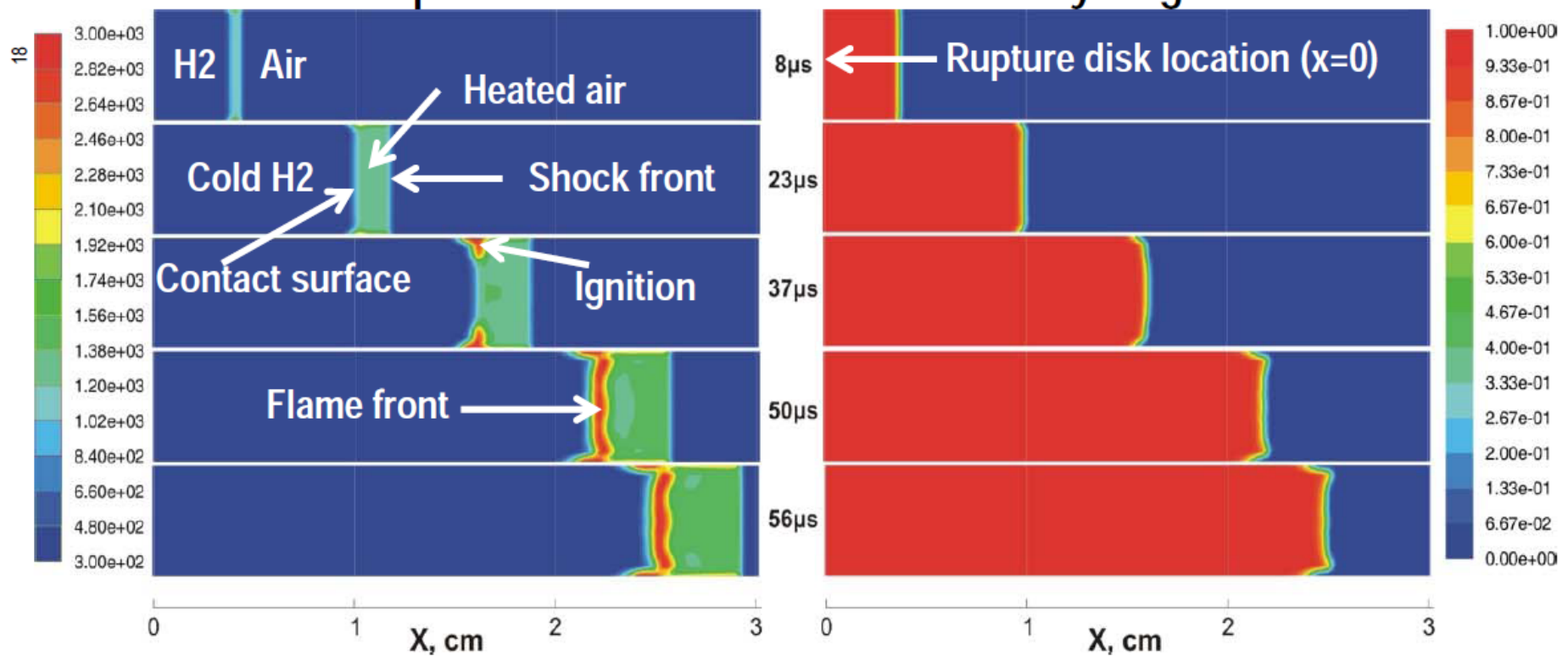
- Hydrogen 'ignition' pressure as a function of a pipe length in series of tests with flat burst disks
- Mogi et al. (2008): min **6 MPa** (wetted by aqueous  $\text{Na}_2\text{CO}_3$  solution (1%) internal pipe surface);
- Golub et al. (2007): min **4 MPa** (dry surface);
- Pinto et al. (2007): min **4 MPa**
- The lowest pressure was reported by Dryer et al. (2007): **2.04 kPa** (not shown on the figure)



# Physical mechanism of spontaneous ignition

A mechanism: a rupture disk separates high pressure hydrogen from the air in a pipe (both gases are at ambient temperature). After the disk rupture a shock wave heats the air. The heated air mixes with hydrogen (cold) at contact surface and ignition occurs. Wolanski and Wojcicki (1972): A diffusion ignition mechanism.

## Dynamics of spontaneous ignition (Bragin and Molkov (2011))

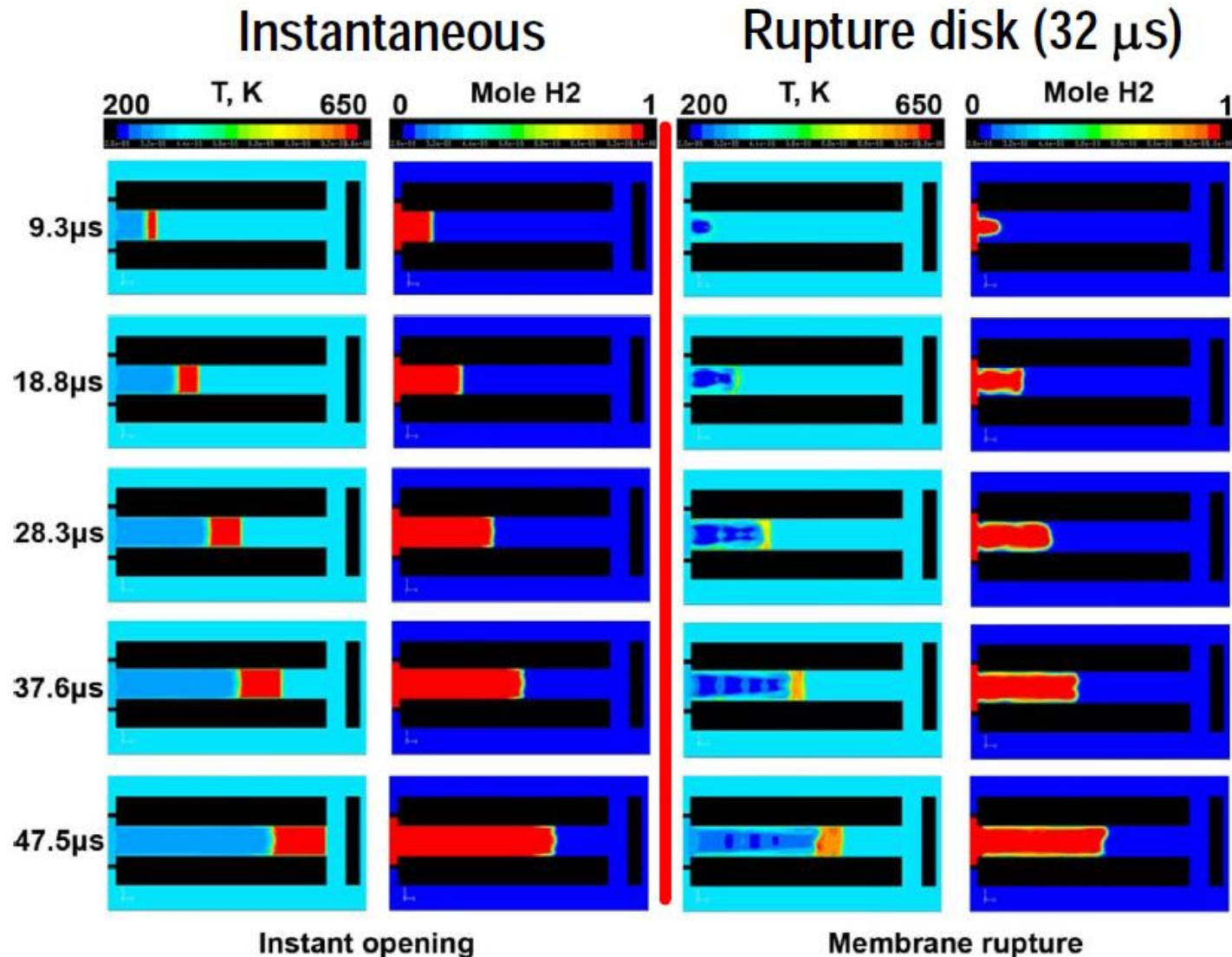


Temperature

Hydrogen mole fraction

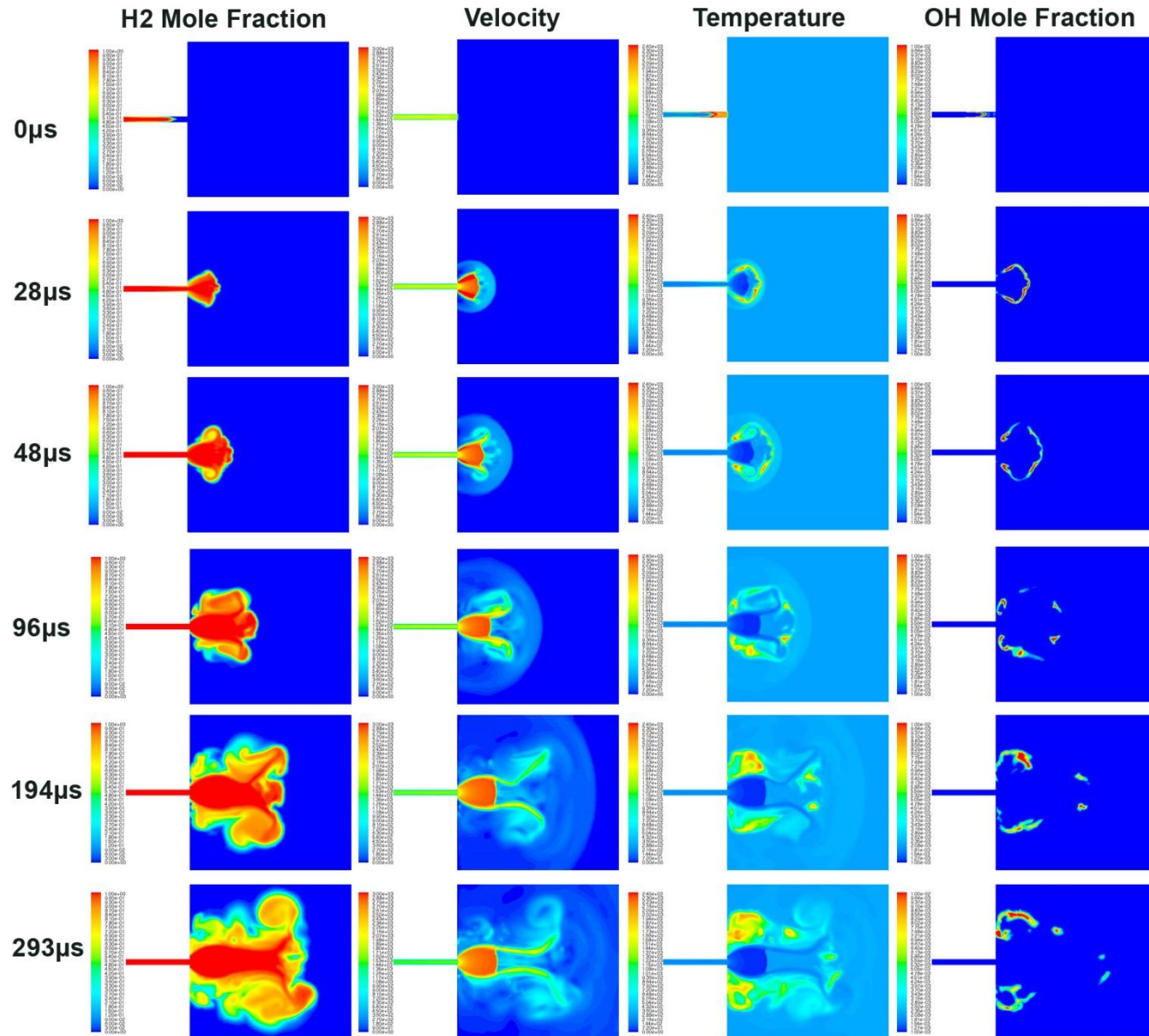
# Effect of a valve opening rate on spontaneous ignition

- The opening time of a rupture disk affects the ignition process.
- The use of valves (“slow opening even for fast valves”) sometimes eliminates the ignition (Bragin et al, 2011).



# Transition to a sustained fire

- LES as a tool for Hydrogen Safety Engineering (PRD design)
- Dynamics of the velocity, temperature and mole fractions of hydrogen and hydroxyl in 2D slice along the pipe axis (Bragin and Molkov, 2011).





# Effect of a flame separation by vortex

- Mogi et al. (2008, top) and LES snapshots of OH (bottom).
- Some difference due to: 1) wetting in the experiment of the inside surface of the tube by aqueous  $\text{Na}_2\text{CO}_3$  solution (1%); 2) surface with channel instead of pipe in LES (entrainment).

0  $\mu\text{s}$



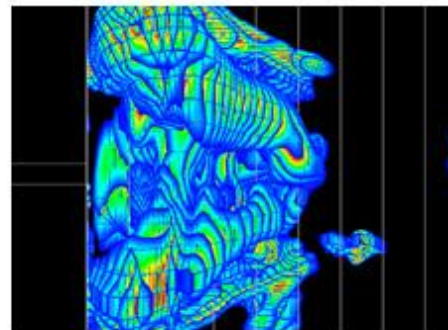
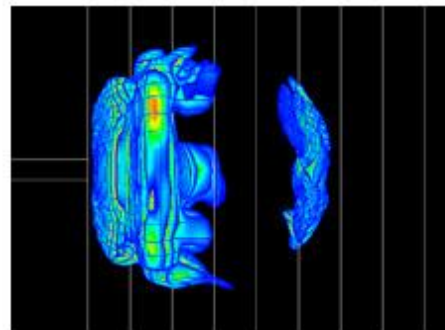
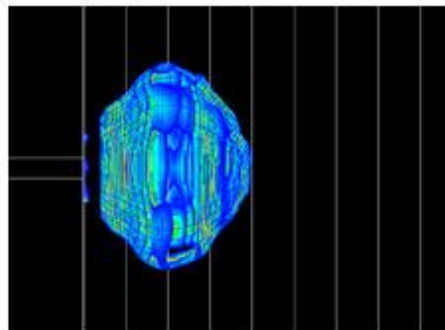
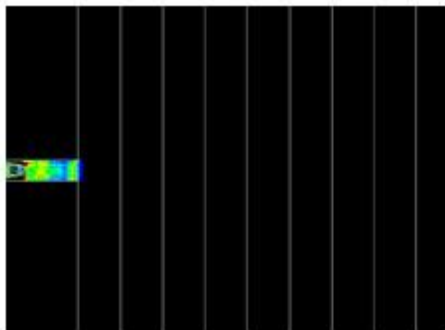
50  $\mu\text{s}$



100  $\mu\text{s}$



200  $\mu\text{s}$

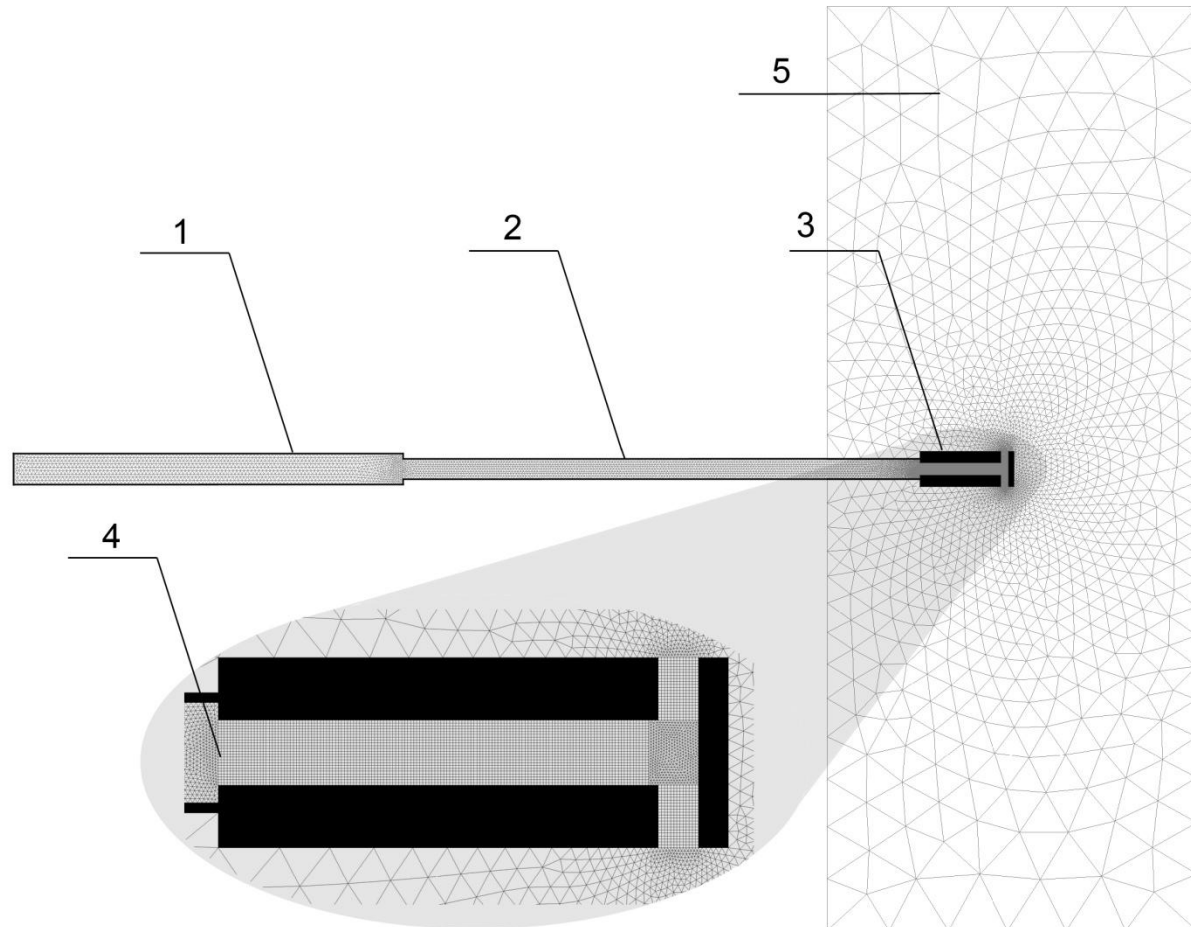


# Spontaneous ignition in a T-shaped PRD

## Experiments by Golub et al. (2010):

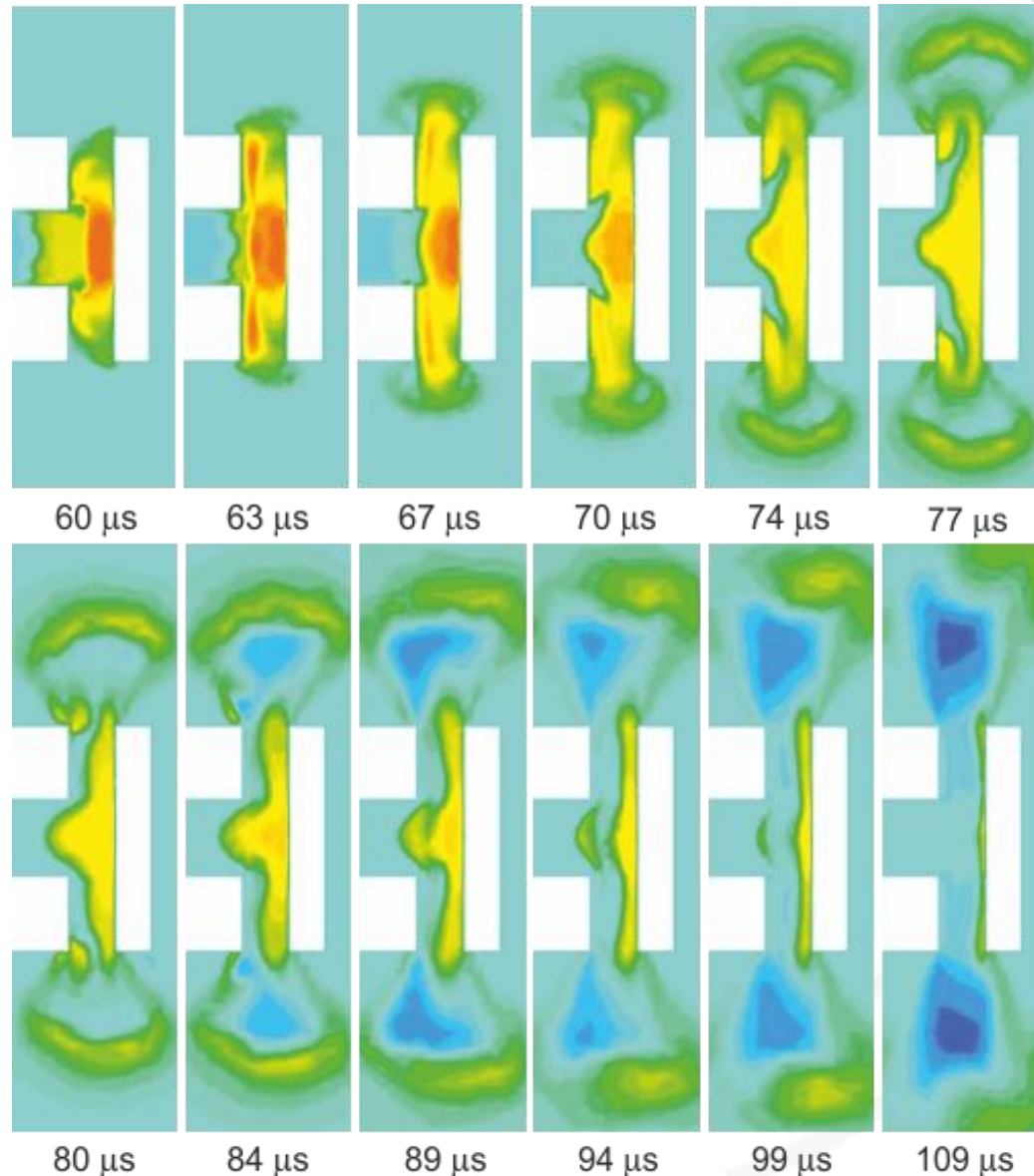
- 1 – 210 mm long 16 mm ID tube;
- 2 – 280 mm long 10 mm ID tube;
- 3 – T-shape PRD;**
- 4 – burst disk
- P=13.5-29 bar
- Ignition at 29 bar**
- Pressure gauges
- Light sensors

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



# Effect of storage pressure on spontaneous ignition in a T-shaped channel (1/3)

- 1.35 MPa – no ignition

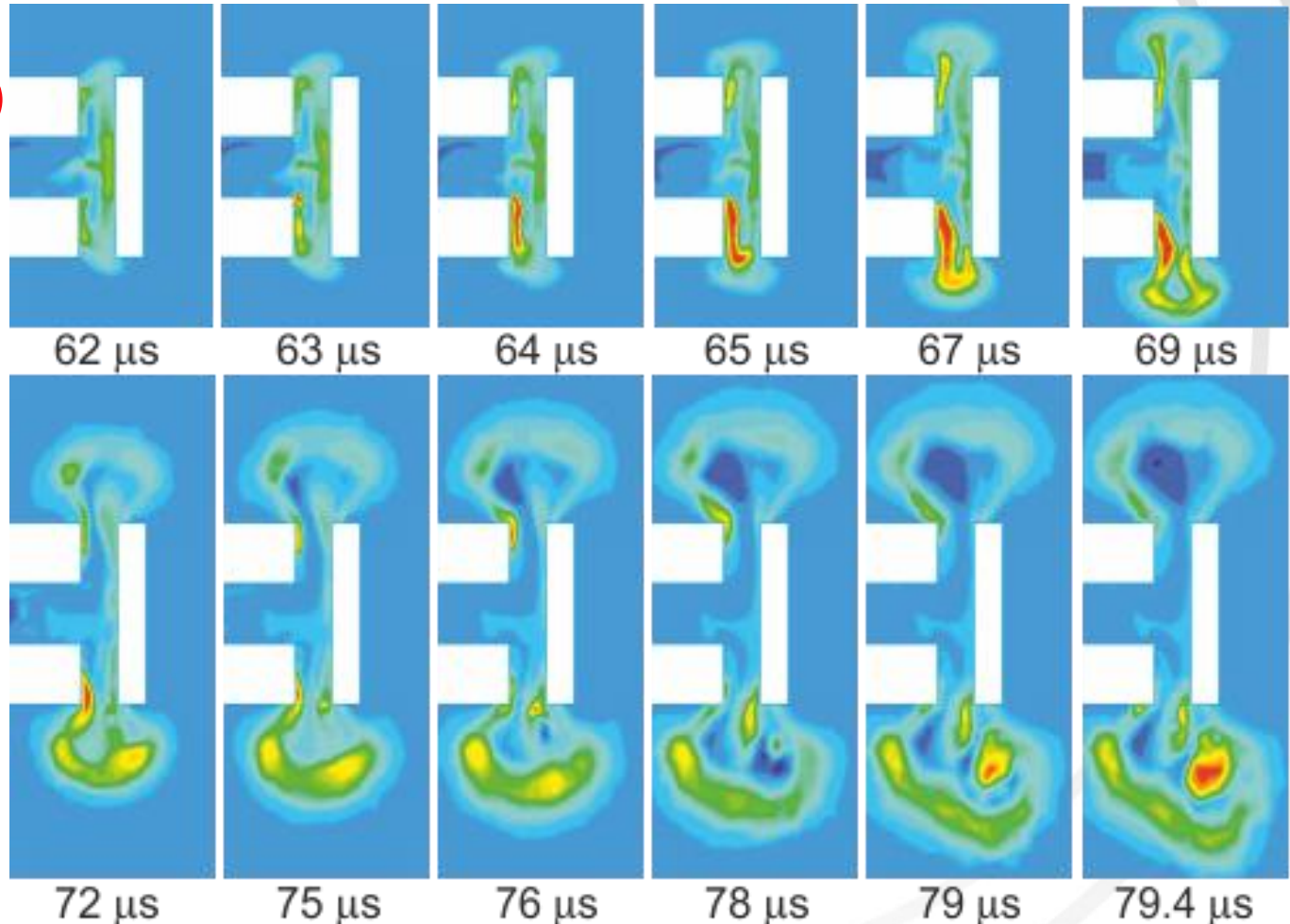


Temperature scale: 0-1100 K



# Effect of storage pressure on spontaneous ignition in a T-shaped channel (2/3)

2.9 MPa –  
ignition (T)



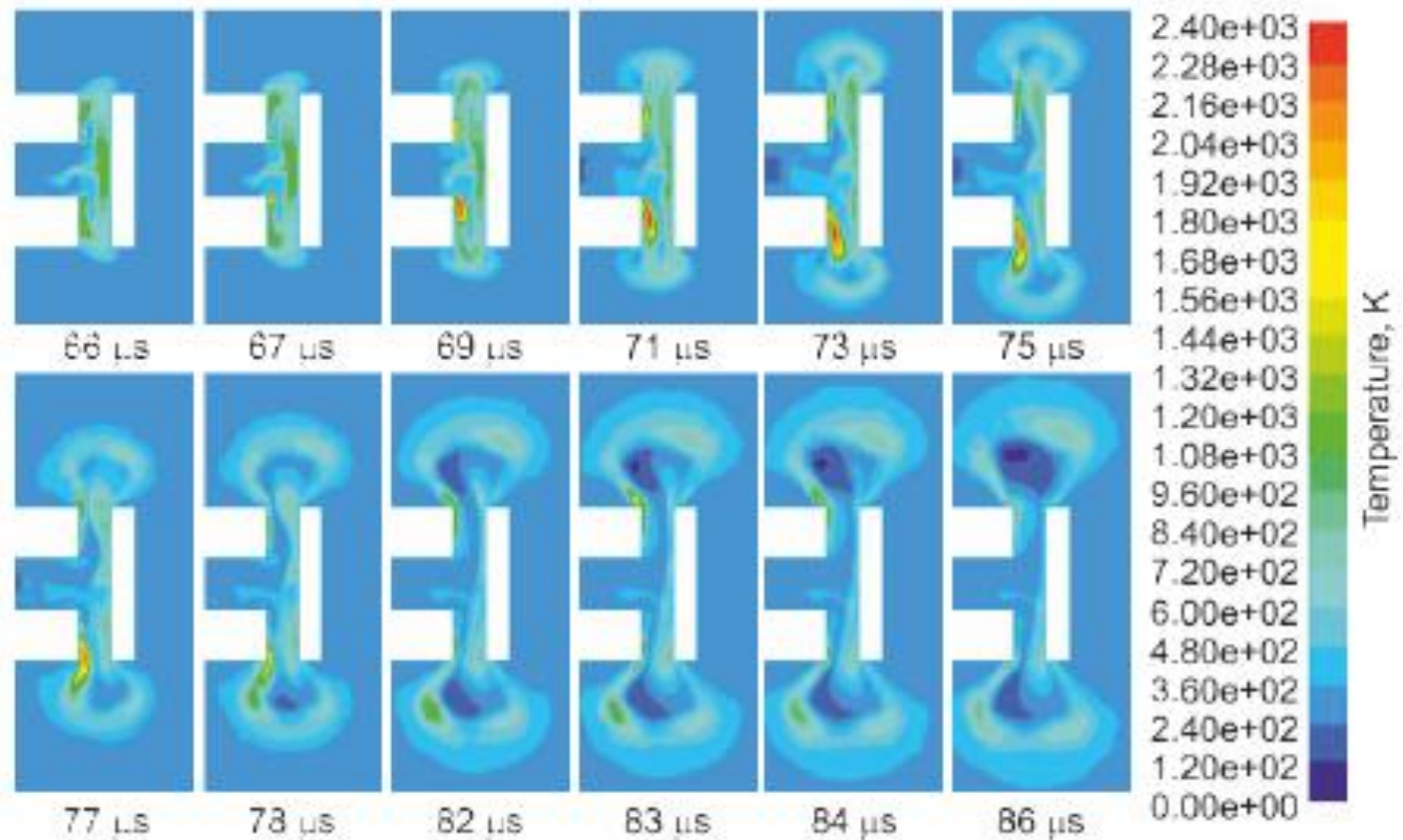
Temperature scale: 0-2400 K



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# Effect of storage pressure on spontaneous ignition in a T-shaped channel (3/3)

- **2.44 MPa**
- **Ignition –YES, sustained fire - NO**



# Prevention of ignition

- Ignition sources must be eliminated or isolated in appropriate way and **operations should be conducted as if unforeseen ignition sources could occur.**
- **Grounding methods** should be evaluated 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.



# Ex-zone classification



- Health and Safety Executive, UK: Ex-zone classification.
- Equipment used in zone 0 has to be intrinsically safe. The equipment has to be certified by a notified body in order to get the marking.
- This information adapted from the HyFacts project (<http://hyfacts.eu/>).

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



Note that the use of spark free tools is not an absolute guarantee that no spark will occur. Even these tools might convey enough energy to a material or a material combination to create a hot spot or to rip off a burning particle.

# Prevention of ignition with electrostatic sparks

This information adapted from the HyFacts project (<http://hyfacts.eu/>)

- ❖ **Hydrogen** belongs to the flammable gas **Group IIC**.
- ❖ CENELEC (2003) restrictions on **widths** of narrow materials depending on zones and gas categories (**left**).
- ❖ CENELEC (2003) restrictions on chargeable **surface** depending on zones and gas categories (**right**) – 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).

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

Zone	Maximum area, cm <sup>2</sup>		
	Group IIA	Group IIB	Group IIC
<b>0</b>	50	25	4
<b>1</b>	100	100	20
<b>2</b>	No limit	No limit	No limit



# Control of thermal sources of ignition

- Hydrogen-air mixtures can be ignited by a hot surface if its temperature is higher than the auto-ignition temperature. Thus, the temperature of hot surfaces or hot spots should not exceed 585 °C even for a few mm<sup>2</sup>.
- An adequate electrical and non-electrical equipment is shown in Table below.

## Classification of electrical apparatus depending on their maximum surface temperature.

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

As an ignition of hydrogen occurs at  $T > 560^{\circ}\text{C}$  any type of apparatus from T1 to T6 can be used in flammable hydrogen-air mixture.

Source: IEC, Electrical apparatus for explosive gas atmospheres – Part 0: General requirements. EN60079-0 (2006).

# Control of mechanical sources of ignition

- Careful design of equipment:
  - Limiting rotating speed
  - Provide a sufficient distance between fixed and rotating parts
  - Set up temperature sensors
- Prevention of ignition by impact:
  - Use of spark-free tools
  - Purge hydrogen before any intervention
  - Avoid contact of aluminium and steel

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