Hydrogen Safety

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Pure Energy Centre

FOREGROUND

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Contents

List of Figures

List of Tables

1 Safety Challenges and Risks

There are a number of risks and challenges that need to be addressed before using any type of fuel. Hydrogen, currently being considered as one of the main fuel, is by no means different. The main challenge for hydrogen is the cost associated with its production, compression and utilization. The risks are associated with the safe use of the fuel and commercialization acceptance by members of the public. Another challenge faced by the hydrogen community is related to the technology readiness (TRL) of the of the products, being at end of the TRL.

1.1 Risks associated with the safe use of hydrogen fuel

Making the use of hydrogen fuel safe is the most critical aspect to be taken into account when developing a hydrogen project, system, product, etc. The process of making the use of hydrogen safe must not be undermined as any failure could cost lives, lead to the failure of expensive equipment with associated company loss of income, injuries, etc.

As such, any company, entity, and individual involved in designing, developing, manufacturing, installation, commissioning or any other activities related to hydrogen must take every possible to make the end use of hydrogen safe. These can take the form of the use of the latest standard, norm, risk assessment, HAZOP, but also the use of the appropriate mitigation measures and equipment available at the time of developing the hydrogen systems.

Fortunately, there are a number of hydrogen properties that can be used to support the safety case of a project. To this end, it is essential to understand these properties to be able to make full of these when designing a system. The below table provide the different most important H2 properties[1] as compared to both petrol and natural gas.

Property / Fuel	H2	Petrol Vapor	Natural Gas
Ignition Energy (mJ)	0.02 (very small static spark can ignite H2)	0.20	0.29
Flammability Limits (in air)	4 – 74% (wide range)	1.4 – 7.6%	5.3 –15%
Flame Temp in air (°C)	2045 (flame is invisible to the eye)	2197	1875
Explosion Limits (in air)	18.3 – 59% (wide range)	1.1 – 3.3%	5.7 – 14%
Energy density	1 kg of H2 = 33300 Wh (LHV) (higher energy content by weight)	1 kg of petrol = 11760 Wh (LHV)	1 kg of natural gas = 11666 Wh (LHV)
CO2	Zero – can lead to a true net zero emission	CO2 – Global warming	CO2 – Global warming

[1] https://courses.lumenlearning.com/introchem/chapter/properties-of-hydrogen/#:~:text=At%20standard%20temperature%20and%20pressure,such%20as%20hydrocarbons%20and%20water.

	energy system		
Smoke	No smokes - No fumes only water vapor	Dangerous smoke and fumes	Dangerous smoke and fumes
Availability of resource	Infinite (circular H2 cycles from H2O back to H2O)	Finite	Finite
Cost	High costs due to lack of infrastructure at present (cost reduction possible with scale and mass manufacture)	Relatively cheap though no including the cost of illness and death	Extremely cheap as not including the cost of illness and death

Table 1-1 - Common hydrogen properties

1.2 Undesirable H2 properties

Hydrogen has a number of properties that have been qualified as undesirable. However, no matter how much undesirable the properties are, it is vital to devise safety systems that take these into account. The main three properties are:

- H2 gas is odourless.
- H2 has is tasteless.
- Hydrogen gas is colourless.
- Hydrogen is very tiny molecule.

1.2.1 Hydrogen gas is odourless and tasteless

From the above list of properties, it is clear that any standard human being senses including the smell, visual and taste cannot detect a hydrogen leak.

However, hydrogen is not the only gas that has these properties. These are also found in natural gas (NG). To improve the detection of natural gas, the NG community has established a set of mitigation measures. These measures help reduce the risk of accumulating NG, which is the source cause of creating a potential harmful environment.

The most known of these mitigation measures is to add a Sulphur compound. The added compound allows the NG to have a very specific odour that human being can smell. The additive is known as mercaptan. When it is added to NG and there is a leak, a person can smell it. As it is a medium to strong smell, the person smelling the leak will be able to walk away from a potentially hazardous situation[2].

Hydrogen gas does not have such an odorant additive. However, there is research focusing on finding an additive that can could be cost effective. The aim of the research is to also avoid adding an odorant to H2 that can be harmful to human beings. The selected odorant will also have to not contaminate fuel cells or other hydrogen sensitive equipment.

[2] https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4551224/

1.2.2 Hydrogen is colourless even when burning

Hydrogen is a colourless gas, meaning that the gas is not visible to the eye when it leaks. This is also true for both a hydrogen flame and any form of hydrogen combustion. These cannot be directly detected by the human eye. Unfortunately, when burning, Hydrogen does not emit smoke and the heat it produces is not detectable unless the flame is in direct contact with an object. Burning H2 only emits ultraviolet light – It is important to understand that **none** of the human known burning colours such as yellow, orange or blue/red flame are associated with the flame.

Because hydrogen burns with no "colour" known to human (re, orange, yellow, blue, etc.), it is difficult to almost impossible to detect if there is a hydrogen fire. In addition, it is also not possible to detect the direction of the fire, or the length of the fire (the "hydrogen jet flame" length as it is known).

The best course of action that is highly advisable to take when one suspect that there is a hydrogen fire in the vicinity is to move away from the H2 fire and wait till the fire is out. This becomes more of a rule of thumb if the presence of wind, as the fire may not be going in different directions following the wind direction.

Another property of hydrogen that is vital to understand is its flammability and flammability range. Hydrogen is, like any fuel, highly flammable gas even in the presence of the smallest amount of ambient air.

What makes hydrogen a dangerous flammable gas is the very wide range of flammability when compared to hydrocarbon fuels. The lowest flammability starts at 4% and ends at 74% concentration in air. On the other hands, it gets even wider when in the presence of pure oxygen. In this particular case, it starts at 4% and ends at 94%[3].

Of interest is that the lower flammability limit of H2 is 4% which is a little higher than the lower flammability of petrol, which is 1.4%. Effectively, this means that hydrogen has a better safety factor for flammability than petrol as it requires more concentration (though there is only 2.4% difference).

What is important to remember is the following:

Any room containing hydrogen or where hydrogen is used must be well ventilated. Hydrogen leak detection equipment must be installed. If hydrogen is detected, a sound and visual alarm must be activated. Any means for hydrogen to be quickly diluted is highly advisable and at times mandatory based on the amount of hydrogen being used. Risk of flammability must be reduced quickly to its minimum through the ventilation system. If possible, it is advisable to prevent mixing hydrogen with oxidant (even small amounts).

1.2.2.1 How much energy is needed to ignite hydrogen gas?

Very little energy is needed to ignite hydrogen. As little as 0.02 millijoules of energy can ignite hydrogen in the presence of air. Other hydrocarbon fuels require a much higher amount of energy for ignition of about 0.1 millijoule[4,5]. This is true for butane, ethane, methane, benzene, propane, or petrol. Explosion

[3] https://www.nasa.gov/pdf/513855main_ASK_41s_explosive.pdf

[4] B. Lewis and G. von Elbe: Combustion, Flames and Explosions of Gases, New York, Academic Press, 3rd ed.,1987

limits for hydrogen gas in air are quite wide if compared to other hydrocarbon gases. In this instance, mitigation measures requires a number of sophisticated safety equipment.

1.2.3 Size of hydrogen molecule

Hydrogen is one of the smallest molecules known to human kind. As it is so small, it has the tendency to leak from storage cylinders, tanks, pipes, couplings, etc. As such, preventative measures must be put in place to detect even the tiniest leak.

On the other hand, due to the fact that H2 is a small molecule, it is pretty difficult to store large amount of hydrogen gas in a limited confined storage tank (as a gas). This is why a number of technologies have been developed to pressurised hydrogen and store the gas at extremely high pressure. Some H2 stationary tanks can store H2 up to 1000 bar.

H2 vehicles are now equipped with 700 bar H2 fuel tanks. These high pressures are necessary to attain travelling distances that are in par with incumbent vehicle available on the market place. Note that using high-pressure tanks may lead to an increase potential risk of tank ruptures, or an increased risk of hydrogen leakage. Again, preventative measures are required to avoid this rupture phenomenon.

1.3 Desirable use of hydrogen “positive” properties

The below are some of the most desirable properties of hydrogen, which makes the gas a very attractive proposition, being used as a fuel.

- Hydrogen is the lightest element.
- Hydrogen energy density.
- No CO2.
- Quantity of hydrogen.
- Availability of hydrogen.

1.3.1 The lightest element

Hydrogen may be a very tiny molecule, but it is also the lightest element found on the periodic table. Being the lightest, even lighter than air, means that one can use this property as an advantage when designing hydrogen fuelled systems. If hydrogen gas is allowed to leave a room (meaning there is a ventilation), then any hydrogen molecule inside a room will move vertically up at high speed of up to 72 km/h[6,7]. This means that one can design a hydrogen based on air ventilation flows.

1.3.2 Hydrogen energy content

A 1kg of hydrogen gas contains a lot of energy. It is around 3 times the energy content of 1kg of petrol.

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[5] https://iopscience.iop.org/article/10.1088/1742-6596/301/1/012039/pdf#:~:text=The%20minimum%20ignition%20energy%20(MIE)%20of%20a%20hydrogen%E2%80%93air,and%20von%20Elbe%20%5B1%5D.
[6] https://www.plagazi.com/%EF%BB%BFhydrogen-fuel-safety-essential-facts-for-transit-operators/
[7] https://www.energy.gov/sites/prod/files/2014/03/f9/fct_h2_safety.pdf

1.3.3 CO2 emissions

Hydrogen gas is free from carbon. As such, when burning hydrogen, no CO2 is emitted. There are, however, two by-products. The first by-product is water vapor. The second by-product created during the process of burning hydrogen is NOx, which are more harmful to the environment than CO2. However, there are a number of technologies that help in reducing NOx. Some of these technologies use controlling burning techniques (the temperature of the furnace in controlled, meaning that there is low potential for NOx). Other techniques is to not use air as a feed, but pure oxygen. Air contains nitrogen, and by remove N2 as a feed, then NOx is not produced. Other techniques are using the exhaust and recirculating the exhaust as an input to the process. These techniques lead to 1ppm NOx, which is a very negligeable figure when compare to the use of other fuels and their associated emissions[8].

1.3.4 Quantity and availability of hydrogen

Hydrogen is the most abundant chemical substance of the universe. It is an abundant organic compound, which is found in large quantities in nature, far more plentiful on earth than oxygen. Hydrogen is not only abundant on earth, but also on other planets including on the gas giant Jupiter.

If compared to other carbon-based fuels, hydrogen does not release CO2, is sustainable and infinite when water and green electricity are used to produce it. On the other hand, petrol, natural gas and other carbon-based fuels are all finite. They also release GHG emissions and are responsible for climate change, human health issues, and ultimately premature death.

Finally, Hydrogen can be found in many different forms, some of which are liquid, liquid hydrogen, liquid metal hydrogen, liquid ammonia hydrogen, liquid neon hydrogen, liquid xenon hydrogen, liquid mercury hydrogen, liquid graphite hydrogen or liquid helium hydrogen. Overall, hydrogen is an infinite resource if water is used to produce the gas.

1.4 Some hydrogen risks and risk mitigation measures

The green hydrogen community is developing at a fast pace and many H2 standards are currently being developed. These standards are being put in place to target the different hydrogen risks and provide a set of mitigation measures. It is important to understand the major risks, and the mitigations for them.

1.4.1 Hydrogen leakage and mitigation measures

A hydrogen leak is probably the first risk that anyone would think off apart from the Hindenburg incident. Hydrogen, being a very tiny molecule, requires to be stored at a fairly high pressure. Being a small molecule also means that it can leak quickly and as such one has to plan for hydrogen leakages and aim at preventing these to occur.

It is important to define the impact and severity of an H2 leakage. The best way is to first detect the leak, then apply some mitigation measure. For instance, a leak detection system can be interlinked to a safety system that will take action to alleviate the impact of the leak.

As leakage are quite common within the hydrogen industry, several devices have been designed to deal with such problem. The most common device is a hydrogen detector. These devices have been used for

[8] https://www.thechemicalengineer.com/features/hydrogen-the-burning-question/

many years and can substantially reduce risks associated with H2. These are mainly used in confined spaces such as hangars, warehouses, houses, etc. The devices are connected to other essential hydrogen equipment that are use to operate an overall H2 system.

It is common to have the detector directly connected to a number of devices such as valves, ventilation units etc. As a good example, if a hydrogen leak occurs in a hangar, all valves in the supply chain will shut. As an added features, it is common to flush the pipes from hydrogen to a safe area, most likely above the roof of a building. Once the pipes and other equipment are cleared from H2, the alarm will automatically clear.

However, the hydrogen system will not be allowed to re-start till the alarm is manually cleared from the main control system. The reason for this is to force a visual human inspection with the potential help of the hydrogen detector (handheld). During the inspection, and as the system is in off position, any leak potential must be identified, logged, repaired and the system must be tested again.

Most of the times, leaks are found during the installation and commissioning of a system. These are fixed at that time. It is also common to find leaks at autumn, and during winter months due to temperature swings. These swings make the pipes expand and contract, and as such results in leaks.

Note that all of the hydrogen equipment must fail to safe.

1.4.2 Structural rupture of hydrogen tanks and mitigations

The rupture of hydrogen tanks or any type of compressed cylinders is an issue that has been extensively documented throughout the years[9]. Such problems occurs when a tank is over pressurised, or some areas have fatigued, or no standard maintenance checks/certification was performed at appropriate intervals, accidents, etc.

As with most gases, hydrogen can expand with subjected to heat. For instance, when a hydrogen tank is installed without shade and in direct sunlight, the tank can heat up. As the tank heats up, it is will heat up the stored hydrogen. And as hydrogen heats up, it expands. As such, the hydrogen content will the same in terms of energy, but the pressure of hydrogen gas will be higher in the summer than in winter. This is why hydrogen content has to be calculated with pressure, void of the tank, and the temperature that the hydrogen is subjected too.

The tank manufacture industry has developed a number of techniques to deal with ruptures. One of the methods is to design the tanks to handle higher pressure than the pressure they are being used at. For instance, a tank that stores hydrogen at 200 bar must be designed and tested for pressures of 300 bar. Usually, the general rule of thumb is to design and test a tank at 1.5 times its rated operating pressure. For a 200 bar, this is 300 bar (200 x 1.5 = 300).

In addition to the above tank pressure safety design criterion, all installations include a number of other devices to avoid over pressures building up. The most common device is the Pressure Relief Valve (PRV). This valve is designed to open up and release gas to the atmosphere under pre-set conditions. For instance, for a 200-bar tank, the PRV could be set up to release pressure at 210 bar. In some situations, in fact in most installations, the tanks are only partially filled. For a tank of 200 bar, most suppliers will

[9] Hylantic report on safety

fill the tank to 175 bar. In this way, the supplier is allowing a substantial safety margin in terms of the tank pressure.

There is a fourth methodology that has be developed. This methodology focuses on the selection of materials that does not rupture when being put in a fire. The technology has been developed and demonstrated as per the below picture.

A number of studies have shown that in the presence of fire, the tank will rupture quickly. It will take only 4 to 12 minutes for the tank to rupture. However, it will take about 50 minutes for a Thermally Pressure Relief Device (TPRD) to activate and release pressure. This illustrates that current TPRD are not sufficient to protect human lives and equipment[10].

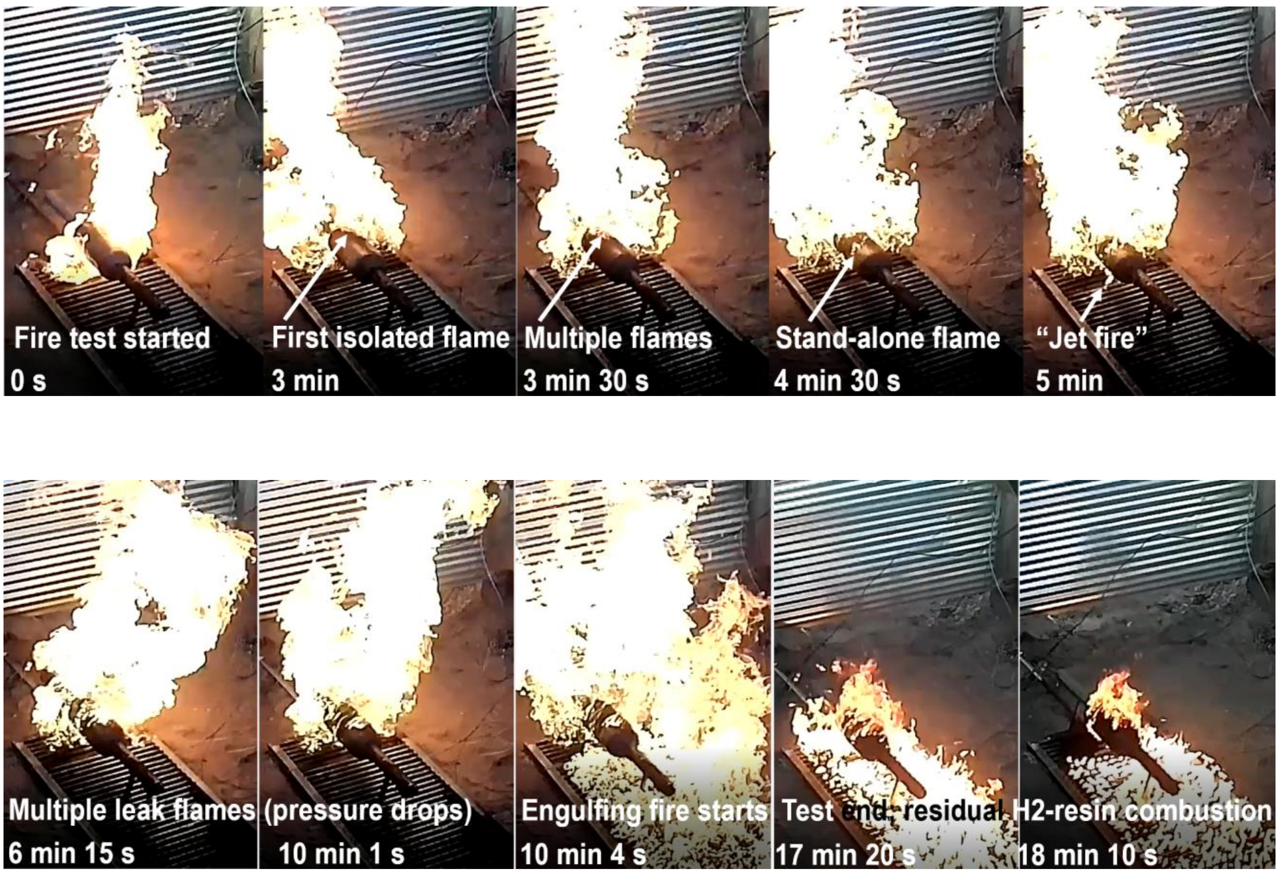

Figure 1.1 - Fire testing of the LNB tanks (Courtesy HySafer centre at the Ulster University)

The innovation in the above explosion rupture free tank during a fire (or high temperature) event is down to the selected composite material. The material melts gradually and as such it allows the hydrogen to filter through at a composed manner. Only a slow portion of hydrogen will evacuate the tank, meaning that no explosion will occur and the hydrogen will burn gently. What the above

[10] Dadashzadeh M, Kashkarov S, Makarov D and Molkov V. 2018. Risk assessment methodology for onboard hydrogen storage. International Journal of Hydrogen Energy 43:6462-6475.

technology offers is a number of benefits that can be added to the prevention of tank rupture. For instance, no catastrophic burst will occur. As a consequence, no blast waves, no fireballs and no projectiles will be resulting from the fire.

1.4.3 Hydrogen fires and mitigations

Hydrogen fires are, like any fire, dangerous. Fortunately, these are extremely rare. Though there are only a few hydrogen fires, these are still a possibility. Therefore, appropriate planning and mitigation measures are required.

However, a hydrogen fire is not visible. This adds to the complexity of a hydrogen detection system. Infrared detectors have developed throughout the years to detect H2 fires. In the case a fire is detected, the whole hydrogen system is shut down and flushed.

What is critical to understand is that when there is a hydrogen fire, it is mandatory to walk away from it. The invisibility factor makes this mandatory as no one can determine where is the flame and what is the direction of the fire.

The different mitigation measures to prevent is to ensure that H2 is not mixing with air or oxygen. At the same time, it is necessary to ground all equipment to avoid static sparks. All sources of ignition must be identified and mitigations put in place.

1.4.4 Hydrogen explosions and mitigations

Throughout the years, a number of hydrogen explosion incidents occurred and have been documented. However, hydrogen explosions are very rare compared to other fuels. Nevertheless, it is still a probable incident that can occur and therefore good planning mitigations must be put in place. Note that most H2 explosions do happen indoor as hydrogen can build up in the presence of air and an ignition source.

A hydrogen explosion requires three main components to occur:

1- Hydrogen fuel in the right quantity. There should be enough fuel concentration.
2- Air / oxygen is available and mixes with H2 fuel.
3- A source of ignition is present.

If the above three conditions are met, then a rapid hydrogen/air combustion occurs as the mixture is ignited. Such a combustion, if contained (e.g., in a confine space), will trigger a sudden over-pressure. The consequence is an explosion. The issue with an explosion is that it can lead to injuries, death, destruction of equipment, properties, and other damages.

It is, therefore, critical to provide appropriate mitigation methods to reduce to a minimal, and if possible cancel, any source of ignitions. Another mitigation measure is to reducing the risks of hydrogen fuel building-up in a confine space. Further to this, fire retarding technology/material/equipment must be used if identified as a potential mitigation measure during the risk assessment. Other techniques to support the reduction of explosion is the use of safe pressure relief, etc.

In summary, the best way to avoid any dangerous explosion is to ensure that hydrogen does not build up in a confine space. As such, continuous ventilation is highly advisable. This mitigation associated with leak detection measures dramatically reduce the potential for the creation of any explosion atmosphere.

Pressure relieve valves (PRV) are also an important aspect of any hydrogen safety system. In the case there is a fire in the vicinity of a hydrogen storage system, then hydrogen pressure will start building up in the tanks. When the hydrogen pressure reaches the PRV's setpoint, then the PRV will open and release the hydrogen to a safe location (usually on top of a roof or at the highest possible point). By releasing the pressure in the tank, the risk for explosion is reduced. In addition, as the hydrogen is released in the atmosphere, the potential for further explosion occur is also reduced.

There are other measures that can be used such as hydrogen infra-red fire detection units, heat detection, smoke alarm systems (to detect fires that are non-hydrogen related), etc. Any of these systems can trigger an alarm. And if this occurs, then hydrogen systems are stopped, flushed and depressurised to avoid any further risks.

The main property that works in favour of hydrogen is it buoyancy. As hydrogen is very light, releasing it in the air will allow it to go upwards at nearly 45 mph. On the contrary, other fuels are heavy, and as such releasing these in the air will not reduce the risk of explosion or fire, but in fact, it will increase it.

In essence, and as a rule of thumb, it is always best to try and evacuate hydrogen to the highest and safest point in the presence of a fire. Also, whenever possible, equipment must be installed outside with plenty of ventilation (including potential for forces ventilation) to ensure the amount of hydrogen is minimal within a given confine space. Similarly, any potential source of static electricity must be removed.

1.5 Safety consideration for HRS and FCVs

The world faces a mammoth challenge in shifting the current hydrocarbon-based supply chain to a new one using green hydrogen fuel. There is a need for a hydrogen production infrastructure (including bulk storage, transport, distribution networks), a hydrogen filling station infrastructure, and hydrogen vehicles to use the fuel (FCVs, FC forklifts, H2 cranes, etc.).

The deployment of FCVs requires the deployment of H2 filling stations. And currently, H2 fillings are in a very low number, not only at country levels, but also global levels. All of the shift of infrastructure will also require a shift in safety cases and safety mitigation solutions which, at times, may be expensive to implement or just a couple of vehicles on the road.

Overall, the deployment of FCVs is blocked by the absence of H2 stations. To be more precise, there are less than 400 filling stations (year 2021) at global level. And most of these stations are currently operating in Japan with a total number of 113 operating refuelling systems. China and South Korea are the other two countries who are starting the deployment of stations with a total of 77 (year 2021 figures)[11].

In comparison, the UK alone has over 8000 hydrocarbon-based filling stating and more are being planned and built[12]. Unfortunately, with the low number of stations available around the world, it is still, today, not viable to own a hydrogen vehicle as it is not possible to travel freely around a country without falling short of a hydrogen filling dispenser.

[11] https://h2tools.org/hyarc/hydrogen-data/international-hydrogen-fueling-stations

[12] https://www.statista.com/statistics/312331/number-of-petrol-stations-in-the-united-kingdom-uk/

The hydrogen council has set a target of 3,000 station worldwide by 2025 in order to start the shift from a hydrocarbon economy to a hydrogen energy one. The council defined that the 3,000 stations will be enough to supply and fill 2 million fuel cell vehicles[13].

Both hydrogen filling stations and fuel cell vehicles have passed the demonstration stage and are ready for wide deployment. The main issue that is currently facing the industry is the price for the hydrogen fuel and for the FC vehicles. As an example, a FCV is currently being sold at around £60,000[14]. This is still fairly expensive when compared to standard petrol/diesel-based vehicles[15].

The increase in hydrogen filling stations and the number of H2FC vehicles will no doubt provide safety challenges to designers. This is why a number of groupings have been created globally to investigate, define and document safety cases and safety potential failure modes which are described in the below section.

1.5.1 Safe design of HRSs and FCVs through failure modes

An investigation of different potential failure modes for various types of filling stations was performed by many experts around the globe. A total of 153 potential failure modes were identified and documented. These modes included the different methods used for transporting and delivering hydrogen to filling station sites. This took into account liquid and compressed state of hydrogen. The study also incorporated onsite hydrogen production from electrolysis and SMR-based filling stations[16] [17].

Of interest was the finding that of the 153 potential failures, the bulk of these were of low probabilities or have low side consequences. However, the highest identified failure modes are associated with the transport and distribution of hydrogen. This is even higher with transporting liquid hydrogen to the filling station. There are three main major issues amongst the 153 potential failures:

1- Collision issues.
2- Relief valve venting – high risk.
3- Potential for overfilling tanks.

1.5.2 Compressed gas failures

Tube trailers are the most common form of transport for pressurised gas. Failures with tube trailers do not occur often and have been identified as a low potential. On the other hand, accidents and collision are of medium potential nature. These accidents could lead to dangerous situations such as leakages, fire, etc.

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[13] Hydrogen Council, How hydrogen empowers the energy transition, January 2017, Page 10

[14] https://www.rac.co.uk/drive/advice/buying-and-selling-guides/hydrogen-cars/

[15] Similar issues are present in the electric vehicle space. However, much of the public discussion ignores the fact that light duty electric vehicles can be charged at the owners' residence. E.g., in the US, the average daily commute is 65 km or less, and 90% of car trips are less than 10 km, so vehicle charging at home is an obvious and common solution. Residential hydrogen refueling will be practical when the cost of electrolyzers is near parity with the cost of residential EV charging.

[16] California Energy Commission. Failure modes and effects analysis for hydrogen fueling options. CEC-600- 2005-0012004

[17] J. Alazemi, J. Andrews, Automotive hydrogen fuelling stations: An international review, Renewable and Sustainable Energy Reviews 48 (2015), 483-499

In terms of pressurised dispensers, failures are extremely rare, but still, these are defined as being of medium failure nature. The reason for such failure mode rating for dispensers is related to their pressure of operation. This filling equipment stay most of the times under pressure, and therefore some equipment will start fatiguing through time. This may result in premature failures. There are also cycling pressure and depressurisation, meaning contraction and expansion cycles. Studies have showed that the metal used in hydrogen pressurised station fatigue through time via the pressurisation cycles and therefore attention should be brought to this failure mode.

The production of hydrogen at a filling station has also been investigated. In these stations, three main failure modes are defined as risks:

- Dryer failure modes.
- Electrical shocks.
- Electrolyte, hydrogen and oxygen leakage risks.

1.5.2.1 Dryer failure modes explained

Dryers can be dangerous as they dry hydrogen and aim to remove any humidity within the gas. Though the technology is well understood, driers do, at times, still leave some moistures passing downstream. This means that rust and other issues can occur, including rapid embrittlement effect on the cylinders, compressors or other downstream equipment.

Driers are also dangerous because they generate some heat. And heat is a source of ignition. Therefore, any dryer could build up enough heat to ignite hydrogen. The smallest presence of an oxidiser (oxygen, air) could lead to catastrophic failures. This is why it is important to control the oxygen flow inside the dryer and to manage the temperature, the pressure, and the flow of the gases.

1.5.2.2 Electrolyser electrical shocks explained

The electrical shock is a real danger as electrolysers operate high voltage, or current, leading to high power. Any electrolyser operation must, therefore, be well protected to deal with electrical potential harmful risks

1.5.2.3 Leaks with electrolysers explained (H2 gas, electrolyte, O2 gas)

Leaks associated with electrolyser operation are common and is a well-known issue. These occur mainly at commissioning time, but also during operation. The least common leak is related with the electrolyte. However, it is still a risk that has potential severe consequences knowing that alkaline electrolyte is corrosive.

In terms of hydrogen and oxygen leakages, these are mainly due to the pressurising and depressurising of the equipment. These are also occurring during temperature swings, say from summer to winter. This means pipes will expand in the summer, but contract in winter. As such, the phenomenon of expansion and contraction will create areas where hydrogen and oxygen will leak. This is why it is important to checks for leaks during temperature swings.

1.5.2.4 SMR potential failures

There is one main SMR potential failure that must be mitigated in all systems. This failure is related to the condensate separator. In the case that the separator is not well controlled or the potential for failure is well mitigated, then a fire and/or explosion could occur. Note that this is a frequent issue in SMRs and as such has been defined as medium-frequency potential failure.

Note that within the 153 failures mode, the different risks described above can have the greatest adverse costs on human lives and equipment alike.

1.5.2.5 Hydrogen fuel cell vehicles potential failures

Hydrogen fuel cell vehicles (H2FCVs) have several potential risks. The most critical risks are:

1. Rupture of a hydrogen tank causing an explosion, deflagration and potential fire.
2. Release of pressurising hydrogen.

Several studies have investigated the above potential failures. These focused on the Failure Modes and Effect Analysis (FMEA) of manufacturing and using a H2FCVs. These studies showed that risks increase dramatically of the FCVs lack safety equipment redundancy. For instance, PRDs, shut-off valves, regulators are required to be redundant because these tend to fail due to embrittlement, pressure, temperature swings, rust, etc. Each and every one of these equipment failures could lead to severe injuries and fire/explosion[18].

1.5.2.6 Safety standards and regulations to reduce potential of H2 hazardous failures

Codes and standards are constantly being produced to ensure safe design, manufacturing, installation, commissioning and operation of assets are achieved. In addition to standards, procedures, processes, and safe working practices are usually produced for each hydrogen site deployments. These are focused on the safe production, transportation, distribution, and consumption of hydrogen.

The fast-growing hydrogen field is now dictating new requirements for standards. The reason for this is related to the fact that in the past none of the hydrogen gas applications were used in the public realm. Today, hydrogen is being considered for cooking, heating homes, vehicles, while none of these existed. This is also true for filling stations, storage of H2 outside big manufacturing plants, etc. These new applications illustrated the vacuum in standard and legislation at global level, and the industry as well as public sector are focused on providing new products with the highest safety mitigation solutions, all based on years of experience in the field by industry experts. The introduction of such standards is aimed to unlocking barriers to entry for hydrogen products.

The new legislation and standards being introduced is also investigating highly conservative risk mitigation measures. The aim is to, through research, add some mitigations or remove obsolete ones such as the requirement for long separation distances between hardware[19].

Standard and legislation professionals are also looking at making sure that the different national and international standards are more harmonised to ensure the lowest number of deviations between countries, thus increasing the deployment speed for hydrogen technologies.

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[18] https://www.fmea-fmeca.com/fmea-hydrogen-fuel-cell-vehicles.pdf

[19] A. P. Harris, Daniel E. Dedrick, Chris La Fleur, Chris San Marchi, Sandia National Laboratories, Safety, Codes and Standards for Hydrogen Installations: Hydrogen Fueling System Footprint Metric Development, April 2014

In the last couple of years, the hydrogen community has created a new field related to standards and codes known as the “hydrogen safety engineering”[20] (HSE). The sole focus of this new field is to lead in the development of new specifications code and standards.

HSE is aiming at login any recurrence of failures from hardware, software or other system issues such as lack of training, documentation, operation, etc. All data is currently being gathered through open databases to ensure most of the information is shared with the public and hydrogen community. The overall aim is to increase safety performance, but also to reduce the number of failure and occurrence of common problems.

1.5.2.7 Planning, permitting and authorising hydrogen system

Though there is substantial amount of work being done on safety, standards and legislation, there is still a substantial vacuum that adversely affect the deployment of hydrogen systems. This legislative vacuum is in the planning, permitting and authorising hydrogen deployment such as hydrogen houses, hydrogen filling stations, etc.

Currently, there is no clarity and formal process that can be followed to authorise and apply for a permitting for a hydrogen system to be installed. This is left at the discretion of local authorities, and at times, left at the discretion of the national authority. There are, today, no efforts in developing a global standard that describe the process of permitting and planning for a hydrogen development.

No formal procedure is available defining what is required to comply with to obtain a formal approval to construct an H2 house, station, building, etc.

This has been recognised by the community, but still governments around the world are not providing instructions to planners to define the different procedures, processes, or guidelines to obtain such permitting. The vacuum is, therefore, threatening the deployment of hydrogen solutions by slowing down any new development.

1.6 Safety case studies for HRSs

Refuelling stations are dangerous by default. They have fuel, oxidant and potential sources of ignitions. Putting all of these three togethers means that there are potential for fires, explosions, deflagrations, etc. at any filling station.

In the United States alone, there has been more than 287,000 car fires between the year 2006 and 2010. This is equivalent to 1 fire per 880 vehicles[21], which is quite substantial.

Unfortunately, fires at petrol stations are a common feature. A good example is the Jieyang, China. This station caught fire in 2019 (April)[22]. Another good example is the fire in the state of Virginia. A fuelling station exploded in May 2019[23] [24].

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[20] J.-B.Saffers, V.V.Molkov, Towards hydrogen safety engineering for reacting and non-reacting hydrogen releases, Journal of Loss Prevention in the Process Industries, Volume 26, Issue 2, March 2013, Pages 344-350

[21] Marty Ahrens, U.S Vehicle Fire Problem, by Type of Vehicle 2006-2010 Annual Averages, Fire Analysis and Research Division National Fire Protection Association, January 2013

[22] https://www.dailymail.co.uk/news/article-6955231/Man-causes-hue-explosion-driving-gas-pump-petrol-station.html

The reason for these fires and explosion relates to the fact that hydrocarbon fuel are heavy gases. As such, any vapor from these fuels will stay at ground level and not disperse quickly if there's no wind. Considering that there is no wind, the fuel vapour will mix with air and even a small source of ignition (static discharge) will lead to fires and potential explosion/deflagration, smoke, pollution, etc.[25].

This is also true for compressed natural gas stations and vehicles[26]. Over 250 deaths have been reported in Pakistan alone while using CNG fuelled vehicles. Investigations on the different accidents demonstrate that human being is at the source of the accidents. Lack of testing and poor quality of CNG storage cylinder are the number reason for accidents. Other issue is related to driver negligence[27].

In contrary, hydrogen gas is very light. As such, even if it leaks at stations, it will go upwards fast and not stay at ground level. And this is true even if there is no wind. Nevertheless, hydrogen systems can still be associated with safety incidents and these must not be undermined. In fact, investigating each incident can lead to substantial learnings to improve the safety case for hydrogen compared to other fuels. Two hydrogen safety incidents are described below with the mitigation solutions provided too.

1.6.1 Failure of a Bus Fuelling Station

On the 4th May 2012, a PRV (Pressure Release Valve) failed at the regional transit agency district of Emeryville hydrogen filling station in California[28,29]. The PRV failed during normal operational conditions where no pressure or overheating or fire where present.

The PRV failure triggered the release of hydrogen in the atmosphere. Both hydrogen and air mixed, air being an oxidant, there was only a need for a source of ignition for a fire or explosion to happen. The inevitable occurred, the leaked hydrogen ignited. An explosion was followed with a fire, both, the explosion and fire, deemed to be small in intensity.

The fire did not propagate neither did it last for a long period of time. While burning the fire created a flame which was defined as being horizontal. The flame was located at the end of a pipe orifice.

The local staff contacted the fire bigrade and emergency services. They also shut the H2 down supply lines so that the fire can be contained. However, the staff decided not to shut down the isolation valve on the vent storage system, and this valve was left in operation. The reason for this was that the staff deemed the access to the valve being dangerous and highly risky.

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[23] https://eu.usatoday.com/story/news/nation/2019/05/11/gas-station-explosion-in-virginia-three-dead-authorities/1179178001/

[24] A. Burgess, Real and phantom risks at the petrol station: The curious case of mobile phones, fires and body static, Health Risk Soc. 2007, 9, 53-66.

[25] R. Coates, R. Review of Alleged Mobile Phone Incidents - The Fact, The Fiction and the Perception of Risk, in Institute of Petroleum, Technical Seminar Proceedings: Can Mobile Phone Communications Ignite Petroleum Vapour?, Institute of Petroleum, London: 2003; pp. 43-49.

[26] Hylantic safety storage report references

[27] M. I. Khan, T. Yasmeen, N. B. Khan, Safety issues associated with the use and operation of natural gas vehicles: learning from accidents in Pakistan, J. *Braz. Soc. Mech. Sci. Eng.* 2015, 38, 2481-2497.

[28] Hydrogen Safety and Event Response, Subcommittee Report Hydrogen and Fuel Cells Technical Advisory Committee, June 2017

[29] http://www.actransit.org/environment/

A number of learnings can be taken from the above:

1- The staff understood the seriousness of the event. They also understood the risks associated with a - hydrogen fire and the dangerous areas not to be accessed.
2- The staff quickly called the emergency services, which were quick to arrive (within 10 minutes of the call).

Other learnings can be taken from what happen after the above events:

1- Emergency units were only provided information about the state of the hydrogen filling station after an hour has passed. This is too long for the emergency services to be able to define the risks and set up appropriate measures to reduce/mitigate/prevent other potential risks to arise. Communication procedures during emergency incidents were lacking at the site.
2- The lack of communication procedures led to a major delay in evacuation of the surrounding area. It took two hours from the first explosion event for the evacuation to take place.
3- The incident lasted nearly three hours. The emergency services deemed the site to be safe at the three-hour mark. Local operation staff were safe to enter the zone where the isolation valve was situated. The valve that was on the leaking vent storage system was shut manually. In the three hours of leaking hydrogen, about 300 kg of H_2 was released to the atmosphere.
4- The safety system put in place acted as per the designed and mitigation plan. The 300 kg released to the atmosphere did not lead to other incidents such as bigger explosion, more fire, casualties, injuries, or other negative effect on nearby hardware. Note that 300 kg of hydrogen is equivalent to nearly 9900 kWh of energy.
5- A comparison can be made between H_2 and other fuels. Considering 9900 kWh of petrol or diesel or other form of hydrocarbon energy were used instead of hydrogen. If this hydrocarbon energy was released in the atmosphere and ignited, then severe damages could have resulted. The reason for this is that hydrocarbon are heavy fuels. Releasing these in the atmosphere and ignited them would result in environment damage. CO_2 would be released and land or water pollution could be the consequence of the event. However, other potential adverse risks could result because the fuel is heavy. A wider fire and explosion could develop which could lead to loss of lives, equipment and more. On the contrary, hydrogen is really light, and as such, by allowing hydrogen to escape at a high-level location, none of the above risks were even going to occur. The morality of the incident is that hydrogen characteristics must be used for all designs to lead to a safe operation of filling stations or other installations.

At the end of the incident, an organisation was appointed to investigate what had happened. The Sandia National Laboratories was tasked to define the origins and reasons for the H_2 fire. Advanced analysis of the equipment used locally illustrated that metal embrittlement was at the origin of the leakage and subsequent fire, explosion, etc.

Embrittlement is a phenomenon of premature aging caused by hydrogen and found in many different installations. This phenomenon must not be taken lightly as it can cause severe incidents. Though embrittlement is a slow process, it can be accelerated in a number of instances by the use of low-grade stainless steel (SS). In the case of the installation at the filling station, SS-440-C was used. This is a low-grade SS used in the PRV.

In addition to the use of low-grade SS-440-C steel, the PRV was wrongly assembled which was the main root cause of the above events.

1.6.1.1 Site mitigating measures developed after the investigation

Following the safety audit conducted by Sandia National Laboratories, several new measures were introduced to ensure better safety and mitigation were in place. These are:

1- New emergency protocols and procedures have been developed to allow for quicker and faster decisions to be made under a safety emergency call. The protocols put in place mainly focus on how to share information with emergency services. They also identified what kind of information was critical to share in the event of a safety call.
2- New evacuation procedures were produced again to speed up the evacuation process.
3- SS-440-C PRVs were all replaced.
4- Vent lines for PRVs were further elevated in order to protect the storage system.
5- New alarms (evacuation sirens) were installed. The aim is to provide audible emergency signals.
6- The number of emergency shut down systems have been increased. These were installed at the maintenance building but also in the 24/7 control area.
7- The number of isolation valves were increased to segregate and separate the main hydrogen storage system into 3 different banks.

1.6.1.2 Offsite mitigation measures

There are number of offsite mitigation measures that can be undertaken in order to support better decision making during an emergency event. The below measures were adopted at the filling station site after the review from Sandia National Laboratories:

- Training emergency responder teams was highlighted of high importance. Therefore, emergency staff were offered training on hydrogen fuel properties and how the technologies work.
- The training included knowledge build up on the difference between H2 gas and H2 in liquid form, but also on the main difference between H2 and liquefied natural gas (LNG). The aim is to dismay any confusion between the different gases, their properties and how to handle these in the event of emergency call.
- A new Hazard and operability (HAZOP) were performed. A full assessment of the control and operation was deemed to be a critical action to be undertaken. The HAZOP revealed the need to check and validate each of the equipment manufacture materials as being appropriate for use with hydrogen gas (the aim is to avoid embrittlement). All manufacturer were requested to confirm the types of materials they use in the manufacture of their equipment and the appropriateness of the material for us with hydrogen.
- Periodic training was identified as an important feature of any filling station so that operators get a refresh course on the different aspects of H2 properties and technologies.
- Periodic drills were introduced for operators.
- Annual open doors to the member of the public are critical to alleviate fears of hydrogen from nearby population.

1.6.2 Tube trailer hydrogen incident

The incident occurred in February 2018. At tube trailer was sent to deliver hydrogen at the H2 fuelling station in Diamond Bar, California (owned by South Coast Air Quality Management District). The trailer was made of 25 tubes of carbon fibre cylinders. These are reinforced aluminium-lined cylinders type. 24 cylinders were filled with 240 kg of compressed hydrogen while the last one was empty.

An incident occurred during the delivery of the H2. Pressurised hydrogen was released from one of the tubes. Hydrogen mixed with the air and caught fire. The incident occurred at a traffic junction while the truck was in a stop position (no motion – red traffic light). The driver defined the incident by describing he heard a small explosion. He then saw flames coming at the end of a cylinder tube.

The driver followed the safety procedures for these types of events. He left the truck and informed other population nearby to move away from the trailer.

1.6.2.1 Post analysis of the incident after an investigation was conducted

The main cause for the above incident comes from the PRDs (Pressure relief Devices). 12 out of the 25 PRDs activated and hydrogen was released before igniting with the presence of air (oxidant) and a source of ignition.

A total of 120 kg of hydrogen was released in the atmosphere, most of which burnt in the air. The local Los Angels County Fire Department decided to evacuate the vicinity of the incident due to its potential severity (potential for explosion of the hydrogen tanks). The department managed to evacuate between 1,400 to 2,000 people. The analysis defined that there were no injuries neither casualty associated with the release of hydrogen and subsequent H2 fire. The analysis also valued that the cost of incident at $175,000[30].

The detailed analysis showed that the first PRD to activate was the one mounted on cylinder No. 14. The PRD activated for no apparent reason as it operated under normal conditions, that is no presence of over pressure in cylinders.

As no overpressure of the gas was present, the investigation focused on the PRD. The analysis of the PRD showed that it was of the wrong type.

In addition to the above, in normal operation and under normal hydrogen safety practices, hydrogen should be evacuated away from the cylinders. On this particular tube trailer, this was not the case. The hydrogen gas was not released upwards (like it is in standard practice). The hydrogen was released towards the inside of the tube trailer and as such the gas spread around the different cylinders.

As the hydrogen gas caught fire, the temperature around the cylinders increased. This led to the actuation of other PRDs as hydrogen pressure built up inside the cylinders (due to the heat). More hydrogen was therefore released, and more caught fire. This led to 21 tube cylinders being damaged.

The investigation identified that the trailer undertook a requalification inspection just weeks before the incident (requalification undertaken on December 2017). Each inspection provides the tube trailer with

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[30] National Transportation Safety Board, Hazardous Materials Incident Report, Oct. 10 2019

a new 5-year certificate for operation. The inspection has a number of criteria to test including a pressure test which was completed successfully.

During the post incident investigation, it was found that four new PRDs were replaced at requalification time of the trailer. The four PRDs installed were not of the right specification. These were designed to activate at 5,000 psi. However, each hydrogen cylinder on the trailer had an operating pressure of 10,000 psi. The organisation that performed the requalification described that the 5,000 psi PRDs were unintentionally mixed with the 10,000 psi one. This was not detected by the inspector.

In addition to the above, seven compression fittings used to connect PRDs and the vent lines (pipes) were not properly tightened. The technician performing the inspection did not check these compression fittings, which led to them being undetected.

From the findings, a set of recommendations were summarised and implemented. Some of the most critical ones are:

1- Training: as with most of the recent hydrogen incidents, it was clearly identified that emergency responders must be better trained to deal with hydrogen safety including the transport of H2 in tube trailers.
2- Training: the investigation identified that the documentation on safety for first responders was too general and required more practical and operational focus.
3- Improve on the design/procedural criteria used for tube trailer components: new design guidelines and procedures must be developed all focused-on PRD vent systems. The procedure must involve inspectors to check the type of material used for the PRD. It also involves the verification and validation of the operating pressures of the different components used within an H2 trailer system to avoid the use of lower pressure equipment in a higher-pressure setup.
4- Standard and codes: add to the codes and standards the requirement for all inspectors to check that the correct pressure rating for the different components of an H2 trailer are installed. This includes the rating for PRDs and pipe, etc. The certifying tube trailer inspectors must check these ratings and test the pressure of the equipment (perform a pressure test).

There are a number of measures that have been implemented but not made publicly available by the different organisations involved in the investigation process.