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Myths and Facts about Hydrogen Hazards

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The anticipated entrance to the hydrogen economy has raised many concerns as regards its safe production, transport, storage and use, not excluding environmental concerns. Although it is true that hydrogen has been safely used for many decades, this has occurred until now in activities mainly in the chemical industry, where skilful and highly trained personnel are engaged. Yet, no one is certain what would happen when a layman handles a potentially hazardous material such as liquid hydrogen to refuel our cars. Such thoughts are sustained by the fact that there is still a significant shortage of knowledge on hazardous properties of hydrogen. Scepticism is also emerging on the environmental effects of large hydrogen leaks when hydrogen will be extensively used worldwide. This paper is a contribution to knowledge of hazardous properties of hydrogen and aims at offering a comprehensive overview on safety issues of this new energy carrier. It is shown that hydrogen safety concerns are not normally more severe, but they are simply different than those we are accustomed to with gasoline or natural gas.

1. Introduction

1.1 Hydrogen hazards

The hazards associated with hydrogen can be (Rigas and Sklavounos, 2008):

- Physiological (asphyxiation, thermal burns, frostbite, hypothermia, and overpressure injury),
- Physical (component failures due to low temperature deterioration of mechanical properties, thermal contraction, and hydrogen embrittlement), or
- Chemical (burning or explosion).

Of them, the primary hazard is inadvertently producing a flammable or explosive mixture with air. Considerable knowledge has been already accumulated on relevant issues, such as flammability and detonation limits of hydrogen-air, hydrogen-oxygen and other hydrogen mixtures, as well as the effect of diluents and inhibitors, ignition sources, autoignition temperature, and quenching gap in air. Yet, a lot more has to be done on deflagration-to-detonation transition (DDT), storage materials, compatibility with other materials, and behavior under extreme conditions of storage and use. The catastrophic hydrogen explosion at the Fukushima Daiichi nuclear power complex in Japan on March 14, 2011 has clearly shown that there is a shortage of knowledge and we have not learned well our lessons from past accidents (Rigas and Amyotte, 2012).

Safety can be obtained only when designers and operational personnel are aware of all hazards related to handling and use of hydrogen. Strangely, most hydrogen hazards stem from the fact that hydrogen gas is odorless, colorless, and tasteless, so leaks are not detected by human senses. This is why hydrogen sensors are often used in industry to successfully detect hydrogen leaks. By comparison, natural gas is also odorless, colorless, and tasteless, but in industry mercaptans are usually added as odorants to make it detectable by people. Unfortunately, all known odorants contaminate fuel cells (a popular application for hydrogen) and are not acceptable in food applications (hydrogenation of edible oils) (NHA, 2006)

1.2 Hydrogen gas properties related to hazards

Considering the hydrogen gas properties which can be related to hazards during transport, storage and use, the following are the most important.

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Detection: In atmospheric conditions, hydrogen gas is colorless, odorless, and not detectable in any concentration by human senses. It is not toxic but can cause asphyxiation by diluting the oxygen in the air.
Volumetric leakage: Leakage of hydrogen from containers and pipelines is expected to be 1.3–2.8 times as large as gaseous methane leakage and approximately 4 times that of air under the same conditions. Thus comes the rule: "airproof is not hydrogen-proof." On the other hand, any released hydrogen has the potential to disperse rapidly by fast diffusion, turbulent convection, and buoyancy, thus considerably limiting its presence in the hazardous zone (Zuettel et al., 2008)
Buoyancy: Hydrogen gas is about 14 times lighter than air in normal conditions (NTP) and this is why any leak quickly moves upward, thus reducing ignition hazards. Yet, cold saturated vapor produced by liquefied hydrogen (LH2) spills is heavier than air and will remain close to the ground until the temperature rises (Rigas and Sklavounos, 2005).
Flame visibility: A hydrogen flame is nearly invisible in daylight irradiating mostly in the infrared and ultraviolet region. Any visibility of a hydrogen flame is caused by impurities such as moisture or particles in the air. Yet, hydrogen fires are readily visible in the dark and large hydrogen fires are detectable in daylight by the "heat ripples" and the thermal radiation to the skin (Hord, 1978).
Flame temperature: The flame temperature for 19.6 % vol. hydrogen in air has been measured as 2,318 K (Zuettel et al., 2008). An obvious hazard resulting from this property may be severe burns on persons directly exposed to hydrogen flames.
Burning velocity: Burning velocity in air is the subsonic velocity at which a flame of a flammable fuel-air mixture propagates. The high burning velocity of hydrogen (2.65 to 3.46 m/s), which is one order of magnitude higher than that of methane (0.45 m/s), indicates its high explosive potential and the difficulty of confining or arresting hydrogen flames and explosions (ANSI, 2004).
Thermal energy radiation from flame: Exposure to hydrogen fires can result in significant damage from thermal radiation, which depends largely on the amount of water vapor in the atmosphere. In fact, atmospheric moisture absorbs the thermal energy radiated from a fire and can reduce it considerably.
Limiting oxygen index: The limiting oxygen index is the minimum concentration of oxygen that will support flame propagation in a mixture of fuel vapors and air. For hydrogen, no flame propagation is observed at NTP conditions, if the mixture contains less than 5 percent by volume oxygen (ANSI, 2004)
Joule–Thomson effect: When gases are expanded from high to low pressure, they usually are cooled. However, the temperature of some real gases increases when they are expanded beyond the temperature and pressure conditions that define their Joule–Thompson (J-T) inversion curve. This maximum inversion temperature for hydrogen is 202 K at zero absolute pressure (Zuettel et al., 2008). So, at greater temperatures and pressures, the temperature of hydrogen will increase upon expansion. Nevertheless, the increase of temperature as a result of the Joule-Thomson effect is not normally sufficient to ignite a hydrogen-air mixture.

1.3 Liquefied hydrogen properties related to hazards

All hazards accompanying hydrogen gas (GH2) also exist with liquefied hydrogen (LH2) due to its easy evaporation. Additional hazards should be taken into account when handling or storing liquid hydrogen because of that ease of evaporation.
Low boiling point: The boiling point of hydrogen at sea level pressure is 20.3 K. Thus, any liquid hydrogen splashed on the skin or in the eyes can cause frostbite burns or hypothermia. Inhaling vapor or cold gas initially produces respiratory discomfort, and further breathing in can cause asphyxiation.
Ice formation: Vents and valves in storage vessels and dewars may be blocked by accumulation of ice formed from moisture in the air. Excessive pressure may then result in mechanical failure, causing a jet release of hydrogen and potentially a boiling liquid expanding vapor explosion (BLEVE).
Continuous evaporation: The storage of hydrogen as a liquid in a vessel results in continuous evaporation. To equalize pressure, GH2 must be vented to a safe location or temporarily collected safely. Storage vessels should be kept under positive pressure to prevent entering of air, thus producing flammable mixtures. LH2 may be contaminated with air condensed and solidified from the atmosphere or with trace air accumulated during liquefaction of hydrogen. The quantity of solidified air can increase during repeated refilling or pressurization of vessels, producing an explosive mixture with hydrogen.
Pressure rise: Liquefied hydrogen confined, for instance in a pipe between two valves, will eventually warm to ambient temperature, resulting in a significant pressure rise. Standard storage system designs usually assume a heat leak equivalent to 0.5 %/d of the liquid contents. Considering liquefied hydrogen as an ideal gas, the pressure resulting from a trapped volume of liquefied hydrogen at one atmosphere vaporizing and being heated to 294 K is 85.8 MPa. However, the pressure is 172 MPa when hydrogen compressibility is considered (ANSI, 2004).

High vapor density: The high density of the saturated vapor resulting immediately after release from a leaking liquefied hydrogen storage vessel causes the hydrogen cloud to move horizontally or downward for some time. This was shown experimentally by the National Aeronautics and Space Administration (NASA) in the Langley Research Center at the White Sands test facility in 1980 and simulated effectively later using a computational fluid dynamics (CFD) approach (Rigas and Sklavounos, 2005).
Electric charge buildup: Since electrical conductivity of liquefied hydrogen is about 10^{19} ohm-cm at 25 V, the electric current–carrying capacity is small and more or less independent of the imposed voltage. Investigation has shown that electric charge buildup in flowing liquefied hydrogen is not a great concern (ANSI, 2004).

2. Safety comparisons of hydrogen, methane, and gasoline

Substitution of conventional fuels by alternative energy carriers has been implemented to some extent by the introduction of natural gas as a generalized fuel in the world market. Its use is not limited to industry and the home, but extends to public means of transportation, especially in Europe. The prospects for hydrogen use are similar to those of natural gas and the proposal for their combined use has been made.
Comparing hydrogen, methane and gasoline, gasoline, as shown in Table 1, seems to be the easiest and perhaps the safest fuel to store because of its higher boiling point, lower volatility, and narrower flammability and detonability limits. Nevertheless, hydrogen and methane (the principal ingredient of natural gas) can also be safely stored using current technology.
Despite its lowest volumetric energy density, hydrogen has the highest energy-to-weight ratio of any fuel. Unfortunately, this weight advantage is usually overshadowed by the high weight of the hydrogen storage tanks and associated equipment. Thus, most hydrogen storage systems designed for transport applications are considerably bulkier and heavier than those used for liquid fuels such as gasoline or diesel (Hord, 1978).
Although total score favors gasoline in this attempt to rank these fuels with regard to safety, it should be noted that what is missing in this multicriteria analysis is a severity factor for each one of the safety properties or events, which may change from one fuel application to another. So, in this sense ranking is not complete, yet the table gives an idea of the pros and cons of these fuels on specific safety aspects.

3. Incident reporting

Reporting of incidents related to hydrogen and analyzing the principal causes are useful for sharing with the private and the public sectors the lessons learned. For this purpose the *H2Incidents database* has been created by the Pacific Northwest National Laboratory with funding from the U.S. Department of Energy and can be found in http://www.h2incidents.org/. In this database, incidents and near-misses are reported without including the names of the companies and other details in a way that confidentiality encourages reporting the events. The incidents are classified according to settings, equipment, damage and injuries, probable causes and contributing factors.
Thus, the percentage of hydrogen incidents in various settings as reported in *H2Incidents database* for a total of 209 incidents is depicted in Figure 1(A). It is concluded from this figure that laboratory incidents are nowadays by far the most frequent (32.1 %), but this is expected to change in the years to come when moving from the intense hydrogen research of today to the more widespread utilization of hydrogen. It is clear from Figure 1(B), in which percentages of damage and injuries are shown in hydrogen incidents, that for a total number of incidents equal to 240 only a small proportion results in loss of human life (4.6 %). This is because special mitigation measures are usually taken, knowing the severity of such incidents.
In addition to *H2Incidents database*, many other remarkable efforts have been developed or are under way. These efforts aim at collecting and offering valuable information of past accidents to assist in the composition of new safety regulations, codes of practice and standards, and in the prevention of similar accidents by supplying useful data for both qualitative and quantitative risk assessment (QRA). Among them, the network of excellence project *HySafe* (Safety of Hydrogen as an Energy Carrier) greatly contributes to the successful transition of Europe to a sustainable development based on hydrogen use.

4. Controversy on hydrogen myths and facts

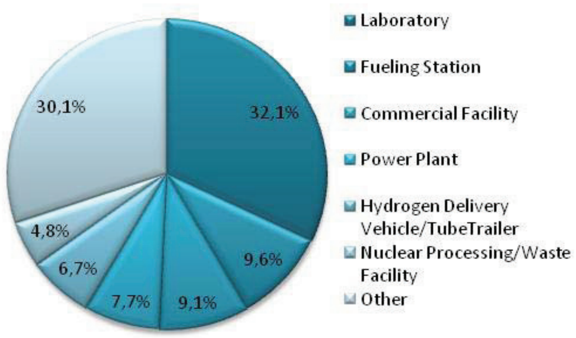
4.1 Safety and security of supply

In his report “Twenty Hydrogen Myths”, Dr. Amory Lovins (2003), CEO of the Rocky Mountain Institute, addresses some of the important issues regarding the proposed future “hydrogen economy”. He describes some of the discussion that has occurred as “conflicting, confusing and often ill-informed” and claims that some issues have been raised solely as reasons for not developing a “Hydrogen Economy”. Among these myths some are referring to hydrogen safety.

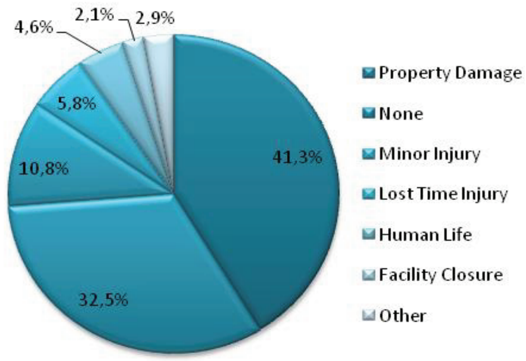
Table 1: Pros and cons of hydrogen, methane and gasoline as fuels with regard to safety issues

Property or Event	Hydrogen	Methane	Gasoline
Size of molecules	Smallest molecule size resulting in highest leakage rate (+)	Small molecule size resulting in high leakage rate (++)	Big molecule size resulting in low leakage rate (+++)
Fire hazard from fuel spills	Fast development (+)	Intermediate development (++)	Low development (+++)
Fire duration	Shortest (+++)	Intermediate (++)	Longest (+)
Flame temperature	About the same	About the same	About the same
Odorization for leak detection	Not allowed if it is used as a fuel cell fuel (+)	Artificially odorized with mercaptans (++)	Normally odorous (+++)
Buoyancy	14.5 times lighter than air at NTP (+++)	1.8 times lighter than air at NTP (++)	Heavier than air (+)
Energy of explosion	Lowest per volume (+++)	Intermediate (++)	Highest per volume (+)
Flammability and detonability limits	Broadest limits (+)	Intermediate limits (++)	Narrowest limits (+++)
Ignition energy	One-fourteenth of methane and one-twelfth of gasoline (+)	Times 14 of hydrogen (yet static electricity discharges from a human body will easily ignite it) (++)	Times 12 of hydrogen (yet static electricity discharges from a human body will easily ignite it) (+++)
Autoignition temperature	Highest autoignition temperature (585 °C) (+++)	High autoignition temperature (540 °C) (++)	Low autoignition temperatures (227-477 °C) (+)
Deflagrations	Confined: Pressure rise ratio <8:1 (+) Unconfined: Usually <7 kPa	Confined: Pressure rise ratio <8:1 (+) Unconfined: Usually <7 kPa	Confined: Pressure rise ratio 70-80 % of hydrogen (++) Unconfined: Usually <7 kPa
Detonations	Pressure rise ratios of ~15:1 (+) Time to peak pressure: 10 times shorter than methane (+)	Pressure rise ratios of ~15:1 (+) Time to peak pressure: 10 times greater than hydrogen (+++)	Pressure rise ratios of ~12:1 (++) Time to peak pressure: 10 times greater than hydrogen (+++)
Shrapnel hazard	Ordinary enclosures (*L/D* < 30): About the same as for methane-air (+) Tunnels or pipes: Greatest risk due to tendency for DDT (+)	Ordinary enclosures (*L/D* < 30): About the same as for hydrogen-air (+) Tunnels or pipes: Lower risk due to tendency for DDT (++)	Somewhat less severe (++) Tunnels or pipes: Lowest risk due to tendency for DDT (+++)
Radiant heat	Lowest (lowest probability for domino effect) (+++)	Intermediate (++)	Highest (+)
Hazardous smoke	Least hazardous (+++)	Less hazardous (++)	Most hazardous (+)
Flame visibility	Lowest (+)	Intermediate (++)	Highest (+++)
Fire fighting	Most difficult (+)	Most difficult (+)	Less difficult (+++)
Total safety score	**30+**	**33+**	**39+**

Note: More plus signs denote higher safety.



(A)



(B)

Figure 1: Percentage of hydrogen incidents in various settings (A) and percentage of damage and injuries from hydrogen incidents (B). (The legend entries ("Laboratory", etc.) go clockwise from the 12:00 position). Data treated from reported incidents in H_2 Incidents database

All of these are disproved by John R. Wilson (2005) in his response to Lovins titled "The truth about hydrogen". Wilson claims that hydrogen safety has not yet been addressed in many items including standards and codes, its use in vehicles, pipeline transmission, and especially small-scale reformer-based gas-station hydrogen generating plants. As regards the security of supply issue of the considerable amounts of water needed for the production of hydrogen when we enter the "hydrogen economy", they both agree that water supplies are sufficient since desalinated water could be used as well; so, this is a non-security issue.

Wilson agrees with Lovins that a distributed, rather than centralized production and use of hydrogen will characterize any future "hydrogen economy". Yet, he claims, this will result in losing economies of scale, and in a great increase of equipment failures. Another problem pointed out by Wilson is the lack of suitable (not leaking too much) large-scale underground storage such as gas-tight former gas wells or even salt caverns that would improve storage safety and diminish environmental concerns.

Wilson agrees with Lovins on the safety issue of buoyancy of hydrogen when it escapes in the open but he reminds us of the hazards of hydrogen escape in confined areas, insisting that in this way hydrogen should not be characterized as inherently safe as Lovins insists. With regard to hydrogen flames, Wilson agrees that the flame is not highly irradiant, yet intensely hot on contact, and the difficulty of seeing the flame makes fire fighting very difficult. Wilson considers the broad range of explosive limits and violence of hydrogen explosions to be a major hazardous issue.

As regards storage of hydrogen in cars, Wilson totally disagrees with Lovins that composite tanks are safe enough, but he insists on their poor resistance to penetration by sharp objects in a collision. According to Wilson, auto industries have essentially zero experience with accidents involving cars with composite tanks, other than through computer simulations.

Furthermore, Wilson disagrees with Lovins on other than safety issues and especially on the efficiency of using hydrogen to produce electricity or as a fuel for vehicles instead of mineral fuels such as gasoline, diesel fuel and natural gas. He also insists that diesel/capacitor hybrid cars can soon obtain efficiencies of between 1.75 and 2.25 that of current gasoline vehicles, a figure which is at least as good as that actually achievable by a hydrogen fuel-cell vehicle. All of that can be obtained without the complexity, lack of reliability and safety concerns of a "hydrogen economy".

4.2 Environmental hazards

Although hydrogen is considered environmentally friendly compared to hydrocarbons as a transportation fuel, a study by researchers from the California Institute of Technology (CalTech) has shown that if we pass to a hydrogen economy, the hydrogen leakage from its extended use will be as much as 10 to 20 % (Tromp et al., 2003). This, according to the authors, would result in the rapid escape of huge quantities (estimated as 60,000 to 120,000 t) of this extremely light gas to the ozone layer, resulting in doubling or tripling of hydrogen input into the atmosphere from all current natural or human sources. The output will then be the creation of additional water which would cool and dampen the stratosphere, finally thinning the stratospheric ozone layer by as much as 10 %. On the other hand, the combination of hydrogen with oxygen to form water would create increased noctilucent clouds (high wispy tendrils) appearing at dawn and dusk which would accelerate global warming (GW). If the CalTech study is finally verified, hydrogen impact in the environment would resemble the catastrophic effect chlorofluorocarbons (CFCs) had on the stratospheric ozone layer. Since no one would like to repeat the errors of the past, there is still time to fully investigate this eventuality and develop cost-effective technologies to minimize leakage before entering a global hydrogen economy. Nevertheless, there still remain many uncertainties about the hydrogen cycle in the atmosphere.

On the other hand, the anticipated accumulation of hydrogen in the air is questioned by other scientists and organizations, such as the U.S. Department of Energy (Office of Energy Efficiency and Renewable Energy) and the U.S. National Hydrogen Association, claiming that the increase in the total hydrogen concentration would be at least one order of magnitude less than the CalTech researchers estimate. This would result in less than a 1 percent increase in ozone depletion considering the worst case scenario.

With regard to environmental concerns on the GW issue, Wilson (2005), as some other scientists, doubts that carbon emissions are the cause of global warming and believes this phenomenon is the result of a natural increase of solar irradiance accompanied by a related increase in atmospheric water vapor levels. The latter is more effective as a GW forcing agent than carbon dioxide and is present in the atmosphere in far greater quantities. In this scenario, hydrogen use would not affect GW to a significant level. According to both, Lovins and Wilson, release or consumption of too much water with hydrogen use are non-issues, because their contribution to global effects like global warming and depletion of stratospheric ozone is insignificant.

With regard to a supposed shortage or surplus of water on earth due to its production or use, respectively, it should be noted that hydrogen is mainly stored on earth in water of any form, whereas its combustion produces again water; therefore, the cycle closes without environmental deficits of any kind.

5. Conclusion

Hydrogen has been used and stored safely in industry for quite a long time as compressed gas or liquefied hydrogen. Yet, its low accident rate may be due to the stricter safety measures taken for this hazardous material as is the case in other industrial sectors such as the explosives industry. Incident reporting shows that nowadays laboratory incidents are the most frequent (32.1 %) due to intense research currently, but this will probably change with the anticipated extended use of hydrogen. The incident reports also show that from the total number of incidents of today only a small proportion results in loss of human life (4.6 %). Consideration of future hydrogen applications reveals apparently manageable safety problems in the industrial and commercial markets. Although hydrogen safety problems have been efficiently controlled in the industry till now, additional safety analyses will be needed in the transportation and residential fuel markets with the expansion of hydrogen use in these applications.

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