Fire and Explosion Safety in Hydrogen Containing Processes: State of the Art and Outstanding Questions

Christophe Proust

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ABSTRACT
This paper is intended to be a brief survey of the state of the art about the safety aspects of industrial application using hydrogen. Although hydrogen has been used in the industry for a long time in chemistry, in metallurgy and more recently in the space industry and in electronics, new fields of application emerged at the turn of the century in the energy sector, broadening considerably both the technologies spectrum concerned but also the public exposed to the risks. Experts of the domain admit that the extent of the spreading of hydrogen technologies depends very much on the safety demonstration rendering the implementation acceptable to the public. Considerable effort was done along the two last decades both to develop risk assessment methods specific to hydrogen technologies and to understand better the key physical phenomena: material embrittlement, formation of explosive atmospheres, ignition, high pressure jet fires, unstable combustion, venting, etc. Major outcomes are recalled. But still much has to be done in research and technology development to achieve a massive development of “hydrogen energy applications”. For instance, the question of “spontaneous” ignition is not yet sufficiently resolved, flame front acceleration in congested environments (like in containers) is to be studied so as the efficiency of several mitigation techniques like venting and inerting.

KEYWORDS: Hydrogen safety, ignition, combustion, explosion, mitigation.

INTRODUCTION
Hydrogen has been used for long in a large range of industrial sectors including mainly chemistry (ammonia, fertilizers), oil and gas industry, metallurgy and electronics. More recently, it was used in the space industry [1]. Primarily at the turn of the century, because of the rarefaction of oil resources, climate change but also environmental concerns (toxic emissions from fossil fuels combustion), hydrogen was considered as a new energy vector with a significantly potential impact on the production of energy, use in industry and in transportation [2]. Many R&D initiatives appeared during the two last decades in many places around the world [3, 4, 5]. Going through such information may give the impression, that the potential for development is significant. Nevertheless barriers exist among them safety issues. This question is certainly more acute when hydrogen applications close to the public (cars) are considered. This might explain why the development of hydrogen fueled vehicle is slow although many technological aspects are now solved. The Hindenburg syndrome and the Fukushima accident pictures stand in memories. But even in industry, hydrogen is used with considerable precautions, fires and explosion risks being considered as particularly high. Along the last 15 years, large research programmes were sponsored by the stakeholders (US DOE, EU, etc.) to fill the scientific gaps about fire and explosion risks on one end and to engineering safety in various hydrogen applications on the other end. A large part of the results are available in the journal “International Journal of Hydrogen Energy” created in the
eighties and discussion of this material are going on during the International Colloquium on Hydrogen Safety (first colloquium in 2007).

The main technical challenges are to produce hydrogen efficiently (and environmentally friendly), to transport/store it and to turn in into standard energy (electricity, mechanical energy, etc.). Today, hydrogen is massively produced by steam reforming of methane [6] but within the perspectives of a “sustainable” hydrogen economy other routes are proposed like biomass/coal gasification (with CO₂ capture and sequestration [7]), thermodynamical water splitting using for instance solar energy or high temperature nuclear energy [8], electrolysis (from hydropower, photovoltaic, wind,…) [9] and biological [10]. Transportation and storage are significant challenges mostly because of the material embrittlement difficulty [11] (which could lead to unexpected brittle fracture of storages) and low density of H₂ which requires significant compression rate (tens of MPa) or cooling (liquefaction) which increases the risk of massive leakages. New concepts of carbon fiber reinforced reservoirs emerged enabling storage up to 100 MPa but fire resistance remains an issue [12]. Liquid storage (LH₂) may be better accepted [13] but blowoff limits the duration of the storage and massive liquid spills (due to mechanical shock) may generate very large clouds very rapidly (a 40 m³ container rupture may generate a flammable cloud of tens of thousands of m³ in less than a minute). The survivability of the LH₂ reservoir in a fire is also a question. The recent trends are to use metal hydrides or sorption/desorption [14]. Hydrogen can be turned into electricity using the Fuel Cell technology which seems mature [15].

Thus, all the required technological bricks seem available to foster the development of industrial applications in the field of the so called “hydrogen economy”. Roadmaps to do so are available in many countries (see for instance the websites of the European JTI-FCH, US DOE and METI in Japan). However, since the storage problem does not seem to be solved satisfactorily road transportation applications remain in the R&D domain. Demonstrators and practical implementation are not in the public domain (cars, houses) but in the industry. They include energy storage, electricity backup, buses, trains, etc. [16], [17] Many of these applications are installed and transported in containers [18].

Academic people are not always fully aware that safety demonstration can be a barrier or a driver in industry. For the specific case of hydrogen technologies (and not only for those under development), safety is the major constrain and a robust demonstration is definitely required before investing in an industrial deployment. There is a need to engineer safety in the same way the mechanical parts of a system are designed. Safety design toolboxes are to be developed [19], [20] which should nominally integrate a probabilistic estimation of the failures, a set of tools to calculate the consequences of the failures (explosive cloud extent, fire and explosions) and, ideally, a mean to integrate the influence of mitigation barriers (shut off valves, vent, etc.). Unfortunately, data, knowledge and even mitigation techniques are still lacking to be able to “engineer safety” as it should be done with sufficient accuracy and reliability.

The gaps to be filled to reach the foregoing goal are tentatively addressed in the following. Surely not all the “burning” questions would emerge. There is always some subjectivity in setting priorities. The present author based his choices on his personal consulting experience in hazardous processes including small and large “hydrogen energy” systems. A focus is made on the physical understanding and phenomenological modelling. Numerical aspects addressed in the conclusions.

Clearly, the most important issue is to quantify the leak scenario both in terms of probability/frequency and in leak size. Usually databases are used, most often originated from the oil and gas industry, which are not really applicable to hydrogen technologies [20], [21]. This important question is not covered hereafter. Other issues concern the physics of explosions and fires and are addressed in the next section following the traditional sequential reasoning in risk management: formation of the explosive atmosphere (ATEX), ignition, flame
propagation/explosions and fires. Some implications for the mitigation techniques are addressed in the conclusions.

**ATEX**

**Physical properties**

Major standard hazardous properties of hydrogen as compared to more traditional fuels are summarized in table 1. The flammability range is 5-10 times larger than for classical hydrocarbons, the minimum ignition energy is 5-10 times smaller and the maximum burning velocity is also about 5-10 times larger. In other words, hydrogen-involved explosions might lead to much larger consequences.

<table>
<thead>
<tr>
<th>Properties:</th>
<th>Unit</th>
<th>Hydrogen</th>
<th>Methane</th>
<th>Propane</th>
<th>Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>g/mol</td>
<td>2.016</td>
<td>16.043</td>
<td>44.10</td>
<td>~110</td>
</tr>
<tr>
<td>Ignition range in air (LFL – UFL)</td>
<td>[% v/v]</td>
<td>4 – 75</td>
<td>5.3 - 15</td>
<td>2.2 - 9.6</td>
<td>0.79 – 8.1</td>
</tr>
<tr>
<td>Detonation range in air (LDL – UDL)</td>
<td>[% v/v]</td>
<td>13 – 65</td>
<td>6.3 - 13.5</td>
<td>3.1 – 7</td>
<td>1.1 - 3.3</td>
</tr>
<tr>
<td>Stoichiometric composition in air</td>
<td>[% v/v]</td>
<td>29.5</td>
<td>9.5</td>
<td>4</td>
<td>1.8</td>
</tr>
<tr>
<td>Minimum ignition energy</td>
<td>[mJ]</td>
<td>0.02</td>
<td>0.28</td>
<td>0.25</td>
<td>0.23 - 0.46</td>
</tr>
<tr>
<td>Combustion heat</td>
<td>[MJ/kg]</td>
<td>120</td>
<td>50</td>
<td>46</td>
<td>45</td>
</tr>
<tr>
<td>Auto-ignition temperature</td>
<td>[°C]</td>
<td>585</td>
<td>537</td>
<td>470</td>
<td>228 – 501</td>
</tr>
<tr>
<td>Vapour/air density</td>
<td></td>
<td>0.1</td>
<td>0.6</td>
<td>1.6</td>
<td>-3</td>
</tr>
</tbody>
</table>

The potential positive side is that because hydrogen at ambient conditions is much lighter than air, the flammable atmosphere may be vented out from enclosures in a much easier way potentially limiting the volume of the ATEX. A significant amount of work was carried out on this item along the past decades investigating the modelling of the flowrate from highly pressurised reservoirs, the formation of the jet/plume and the accumulation of the explosive atmosphere in an enclosure.

**Leakage flowrate**

It was shown earlier [26] that the quality of the prediction of the leak flowrate define the accuracy of the risk analysis. Even when hydrogen is gaseous, the prediction of the flowrate is not so straightforward. It was shown (Fig. 1) that the deviation from the ideal gas equation of state becomes significant starting from 10 MPa. The often-proposed Abel-Nobel equation of state does not seem to perform so well especially at very high pressure. Deviations up to 10-20% are possible (Fig. 1 from [25]).

The prediction may be more difficult with liquid hydrogen spills especially when flashing occurs. Only very little work is available especially over the droplet size [27].

**Flammable cloud formation**

Some aspects of the formation of the flammable cloud need some consideration too. The phenomenology of gaseous free jets is well understood. It is known that the well-established subsonic free jet theories can be used even with under-expanded flows at the leak point provided the “notional nozzle” approach is used [22, 23, 24]. With this model it is assumed that mixing of the leaking gas with the outside air starts only once the pressure of the released gas is back to atmospheric after adiabatic expansion. Experimental evidence shows that the structure of the plume (axial and radial decay) cannot be obtained this way [28]. Today, there is no consensus on the decay
laws: variations from one to another can result in a factor of two (Fig. 2 from [18]). Recent numerical work [29] suggests that the “notional nozzle approach” may not be universally valid. This may be explain these discrepancies.

**Fig. 1.** Measured compared with calculated density using the perfect gas law and the Abel-Noble equation of state during a vessel blowdown ([25]).

**Fig. 2.** Axial and radial profile of concentration predicted using various decay coefficients from the literature ([18]) claimed to be valid for the release conditions: free jet, hydrogen, 40 bar stagnation pressure upstream of the orifice (orifice diameter 3 mm).

When the momentum of the release is very small, the mixing mechanism is not a jet anymore, totally dominated by the momentum, but a plume into which buoyancy forces dominate. Only very limited evidence is available on such mixing regimes [30].

**Fig. 3.** Concentration of hydrogen in a 4 m$^3$ enclosure equipped with a small vent on the side (0.004 m$^3$), vertical release through a 1 and a 3 mm hole under 10 to 40 bar (ambient temperature). From [37].
Apart from the release characteristics, the composition and size of the flammable atmosphere accumulating inside an enclosure needs consideration. A significant amount of work was done in the last 15 years [31, 32, 33, 34, 35, 36] showing that a more or less stratified layer close to the ceiling of the enclosure or a homogeneous mixture may be formed, depending on a sort of Richardson number. Phenomenological models were issued and tuned against the experimental data. On this latter aspect the proposed models may be valid only for the experimental conditions under consideration. Nevertheless, many practical details may change the physical behaviour and in particular the location of the release point in the enclosure and the presence of obstructions. To illustrate this, recent data obtained changing the location of the vent as compared to the standard situations (vent on the top) are compared to the predictions of the models on Fig. 3 (from [37]).

Clearly this field of research is not closed and improvements are required. The variability of the release characteristics (momentum, location) and of the geometry (congestion) need to be accounted for. Note that nearly no data is available about the turbulence. Preliminary results show, perhaps for the first time, that even rather small leaks may generate a few m/s turbulence intensity ([37]).

IGNITION

As far as hydrogen is concerned, a common belief is that hydrogen leaks have a large probability of ignition and may even ignite “spontaneously” [38] (spontaneously means without any evident source). Following, in risk analysis, it is often assumed that an explosion or a fire would automatically result from a leakage and that there is no need to address the ignition event.

It is the present author’s experience, that hydrogen leaks or flow do not ignite “spontaneously” each time a hydrogen flow is emitted in the open air. Over the last 20 years, the present author performed a few hundreds of pressurised hydrogen leakages in the open air, at large scale, and only 3 ignited spontaneously! Thus, the ignition of a hydrogen leak can be controlled and this is an appealing possibility for the industry.

To enable an efficient ignition prevention policy, the fundamental ignition mechanisms and their links with the practical situations have to be understood. Significant work was devoted to the first aspect in the past 10 or 15 years. Hydrogen-air mixtures have in common with hydrocarbon-air mixtures the two basic ignition mechanisms [39]: “spark ignition” for which the relevant ignition parameter is the Minimum Ignition Energy (MIE -table 1) and “volumetric ignition” for which the relevant ignition parameter is the Auto Ignition Temperature (AIT-table 1). Another fundamental ignition mechanism, different from the previous two should be included describing the flame initiation by a heated surface inside a cold atmosphere [40]. The relevant ignition parameter is a critical surface temperature or a critical power when the heated surface is particularly small (as compared to the flame thickness for instance). Only very limited experimental evidence is available about this particular ignition mechanism. Available data [40, 41] suggest that the critical ignition temperature should lie between 400°C and 700°C at atmospheric pressure (Fig. 4). Note that this ignition mechanism is not well known and in particular the influence of the convective current flowing over the hot surface. The minimum power for ignition measured up to now is 100 mW [42] but there is no guarantee, it is the absolute minimum (Fig. 4). A fourth ignition mechanism was discovered by Wolanski forty years ago [43] according to which ignition can appear in the diffusion layer between hydrogen and air following a sudden release of pressurized hydrogen in air. Since this pioneering work, experimental and theoretical studies were performed [44, 45, 47, 47, 48, 49, 50]. The prominent factors are the initial pressure of hydrogen and the length of the discharge tube. Secondary factors are the geometry of the release pipe, but other parameters might also intervene like the temperature of hydrogen. Critical release pressures to trigger this ignition mechanism are in the range of 2-4 MPa while the typical storage pressures of gaseous hydrogen range between 20 and 70 MPa.
It is more difficult to make a link between the fundamental ignition mechanisms and the practical circumstances leading to an ignition in the industry. A link was made for instance between mechanical friction and sparks and the hot surface ignition mechanism but it is still difficult to deduce the ignition probability from mechanical characteristics [51]. Similarly, optical sources may ignite hydrogen-air mixtures via a hot surface ignition mechanism but predicting the optical ignition thresholds remain a touchy subject [42]. Furthermore, many accidental hydrogen release ignition events cannot be properly explained by the ignition mechanisms described above. Ashbury and others [38, 50] suggest that several of them may intervene depending on the configuration. Electrostatics is regularly called for [52, 53]. Merilo at al. demonstrated that very limited amounts of particles (0.1 g iron oxide) may be sufficient to produce enough electrostatic energy (while flowing with the hydrogen into the release pipe) to ignite hydrogen jets, while emerging into the open air. No need to have a strongly underpressurized jet for this. In many practical cases, this could explain ignitions. But other aspects need also be considered. Mechanical vibrations either produced by a high-speed flow of ultrasounds may heat up significantly tiny bits of metals as those appearing during sudden ruptures. A rapid estimation from the present author would indicate that a sonic flow vibrating (via vortex shedding) a 1 mm diameter-10 mm long steel pin would dissipate a few watts mechanical energy and could heat up by hundreds of °C. Recent experiments [54] suggest that such mechanical excitation may heat up “targets” up to the critical hot surface temperature with incident powers in the range of a few watts.

Thus, significant progresses were made on the fundamental ignition mechanisms of hydrogen-air mixtures. Certainly, more should be done about the hot surface mechanisms. Nevertheless, only limited information is available on the influence of the process conditions (initial pressure, temperature, diluent). Much effort would be required to establish a clear link between the various practical situations and the ignition mechanisms.

**EXPLOSIONS**

The literature devoted to flame propagation and explosion development in premixed hydrogen air mixtures is considerable. Only the main trends could be addressed and the discussion will be organized along the following lines: combustion properties, flame propagation regimes and explosion development.

A large body of data is available concerning the combustion properties of hydrogen air flames and
especially about the laminar burning velocities. A review was proposed recently by Dahoe [55] (Fig. 6). Data are available mostly at moderate pressures (up to 1 MPa) and at ambient temperatures. In practice, very cold mixtures may be produced for instance because of the blow down cooling or because simply liquid hydrogen is leaking and very little information is available about the burning velocity for temperatures as low as -150°C [56]. Furthermore, lean mixtures are more likely in industrial processes. It is known from the experimentalist (see below) that when the hydrogen concentration in air is lower than about 10% v/v, the explosion resembles more a flash fire with nearly no pressure rise. Kumar and more recently Bradley [57, 58] focused their work on the burning velocity of lean mixtures to provide more accurate data about the laminar burning velocity.

The flame propagation regimes is a key point in safety. All in all, the larger the laminar burning velocity, the larger the propensity of the flame to accelerate fast and to go to the detonation regime. Clearly, detonations of choked flames (flames with the maximum possible velocity when the dimension of the equipment does not allow for detonation transition) are unacceptable from the safety point of view because all the combustion energy is transformed into pressure. Because of this a large effort was devoted in the past to understand the premixed flame acceleration processes and to find “simple” criteria to decide whether a premixed flame will or will not accelerate in a congested environment. A very interesting analysis was proposed by Dorofeev and al. [59, 60]. The authors assume that the transition from slow regimes to fast flames (detonations or choked flames) results from the self-ignition of pockets of reactants mixed with burnt gases by the turbulence, the latter resulting by the flow induced by the piston effect of the flame. This provides reasonable estimates. On Fig. 7, it can be seen that lean enough mixtures (below 10% H2 v/v) would not lead to a flame acceleration in line with the experimentalist observations.

Nevertheless, flame acceleration may not only result from the turbulence of the flow and in situations where turbulence of the flow dominates, other flame acceleration processes (than the reactant pocket self-ignition) may be at work as well, as recognized by Dorofeev [60]. On this last point the analysis proposed by Valiev et al. [61] is particularly interesting. The authors show that standard flame propagation between the obstacles may justify the acceleration of the flame. The understanding of the mechanisms producing a turbulent and accelerating flame is really a key for safety. When only the influence of the turbulence of the flow is considered, the literature proposes several turbulent burning velocity correlations, providing significantly different results, typically within a ratio of 2 [18] even when the turbulence intensity is low (1 to 3 m/s).

It is more and more acknowledged today that the various instabilities of the flame front are not only
active when the flow is quiet but also intervene when the flow is disturbed by acoustics, congestion or turbulence [62, 63, 64]. There is certainly a need to revise/complete our vision of what a “turbulent” hydrogen-air flame is.

![Fig. 7. Flame acceleration criteria in H2-airsteam mixtures from [59].](image)

![Fig. 8. Comparison of the vented H2-air explosion models [65, 66, 67, 68] with some experimental data [69, 70, 71, 72] from [18]](image)

Clearly, such uncertainties may affect drastically the prediction of the explosion inside a process. The typical situation, widely studied during the last decades, is that of a vented container filled with a H2-air mixture [65, 66, 67, 68]. A number of models were proposed [69, 70, 71, 72] showing a large scattering as compared to the experimental results (Fig. 8). Clearly an effort to understand the flame dynamics is these practical, but simple, configurations is still required.

In the real life, congestion may be very significant in containers. This aspect was not sufficiently covered until now [73]. The questions are: what is the influence of obstacles on the flame propagation inside a confinement and is it possible to incorporate their influence in a simple manner?

**FIRES**

Hydrogen flames are said to be transparent, hardly visible and only weakly radiative. This is however not true for highly turbulent jet flames. The quantity of water vapor is so large that the flame plume is reddish (Fig. 5).

Detailed measurement of the flame size and radiative properties were performed recently [25, 74, 75]. When the Froude number of the leakage is large (typically as soon as the driving pressure is above the sonic conditions), the flame length is reasonably obtained using the correlation of Delichatsios [73] as shown on Fig. 5 (L* is the non-dimensional flame length as defined by Delichatsios).

Estimating the radiant fraction is more complicated. Data from different sources seems difficult to reconcile. With smaller orifice sizes, Proust and al. [25] obtained a much larger radiant fraction (10-15%) than Schefter et al. [75] (5-10%) with similar driving pressures.

Effort are still needed to clarify this important safety question since fires rapidly induce catastrophic failures and escalating effects. Note also that some categories of hydrogen fire are not momentum driven and may rather be strongly buoyant (liquid hydrogen fires for instance). The Froude number (following the Delichatsios definition) might be as low as 10⁻³. Nearly no data are available for this.
CONCLUSIONS

This review cannot be exhaustive. It is established bearing in mind the safety issues associated to the industrial “hydrogen applications” in development. As explained in the introduction, the possibility to deploy hydrogen technologies outside the present industrial domains (spatial, electronics, chemistry) depends to a large extent on the safety demonstration. Safety must be engineered. Many gaps need to be fulfilled to reach this objective.

The fate of hydrogen leakages in hydrogen systems and outside is to be better assessed; the question is would a flammable atmosphere accumulate or not. If yet how rich and turbulent will it be and how fast and where will it appear. Data and engineering tools are available but not complete enough.

It is the present authors (large) experience that hydrogen leakages, even highly pressurised and very brutal do not by far systematically ignite. Speaking about spontaneous ignition is exaggerated. The reality is that hydrogen mixtures ignite easily because of the diversity of ignition mechanisms and reactivity. Electrostatic ignition due to the turbo charging of solid impurities swept by the hydrogen flow is certainly to be further considered. But other sources like mechanical vibrations should be looked at too.

As far as explosions are concerned, research work is deeply needed to clarify the flame acceleration mechanisms. Probably the influence of flame instabilities should be considered. It may help to explain the behaviour of the flame in presence of perturbations likes acoustics, congestion and flow turbulence. Detailed experimental on vented explosion in realistic containers may help to guide this work in addition of providing valuable data for the practice.

The fire situations are not yet sufficiently covered especially concerning the radiant fractions and buoyancy driven fires (liquid hydrogen fires for instance).

Because of these lacks, it is still difficult to propose tools sufficiently accurate to “engineer” the safety of a hydrogen system.
One option would be to cover the lacks identified above thanks to CFD computations. To make it simple, RANS or LES CFD codes do not really solve the Navier-Stokes equations but an approximation of them. Sub models are included to “close” the physics (for instance k-epsilon in RANS, Smagorinski in LES, etc.) and approximate solvers are used to solve the differential equations. If it can be agreed that the right physics is embedded, then numerical simulations can be used to close the experimental gaps. This might be the case for the formation of the explosive atmosphere [77, 79]. Note however that performing a “clean” simulation is resource demanding but in manpower and CPU time especially when the geometry is very complicated. As far as combustion is concerned, using CFD to close the gaps is still outstanding. If reasonable combustion mechanisms of hydrogen in air seem available [79], the flame propagation problem including instabilities and turbulence is not solved. Because of this, agreed flame propagation model are not available.

It is the opinion of the present author that CFD tools are very useful in interpreting experimental results, testing models and, when sufficiently comprehensive, in closing experimental gaps.

Saying this, the present author is aware that such work will remain an expert/scientific activity and probably not an engineering work. Engineers might prefer fast but accurate and validated design methods enabling some standardization, facilitating decision making and communication.

The last point concerns the mitigation techniques. Venting would certainly remain the ultimate protection means. For hydrogen air explosions, rapid flames may be produced and if the flame speed is larger than a few tens of m/s, venting may become inefficient and resulting in container rupturing, debris projections and large flame ball. A combination of safety barriers may be required including passive or active ventilation [80, 81, 82] to reduce the amount of explosive atmosphere and perhaps partial inerting [83]. Standard venting may however be unpractical because of the large outside flame ball and secondary explosion [84]. New design is desirable.

REFERENCES


