

# SAFETY CONSIDERATIONS IN RETAILING HYDROGEN

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*To be used in public, untrained people must be able to handle hydrogen with the same degree of confidence and with no more risk than conventional liquid and gaseous fuels. Physical properties relevant to the safety of hydrogen as a fuel are reviewed and compared to gasoline, LPG and methane. The key parameters are flammability, detonability, ignition energy, materials compatibility, buoyancy and toxicity. For many years, Shell has conducted an experimental programme on gas safety, which has recently been extended to include hydrogen. A selection of results from this programme is presented.*

## 1. Introduction

If hydrogen is to be a fuel used by the general public, untrained people must be able to handle hydrogen with the same degree of confidence and with no more risk than conventional liquid and gaseous fuels. In this context, risk should be regarded as the product of the probability of an incident or accident occurring and the magnitude of its hazardous consequences.

Prevention and control of accidental formation and ignition of large volumes of fuel-air mixtures are crucial to the safe operation of hydrogen systems. Adequate understanding of the overpressures generated in an accident situation is essential for the protection of the public and also of operating plant and safety equipment.

The safe handling and use of hydrogen requires an appreciation of its physical properties in each of the forms in which its use as a vehicle fuel is considered. These include as a gas, liquid and adsorbed to another material, e.g. metal powders, carbon nanofibres, glass beads.

Fire and explosion hazards must be carefully assessed to determine the relative safety of a fuel for each potential application. Hydrogen can be safer than conventional fuels in some situations, and more hazardous in others. The relative safety of hydrogen compared to other fuels must therefore take into consideration the particular circumstances of its accidental release. Several reviews (DTI [1], Barbir[2], Cadwallader & Herring[3], Ringland [4]) have been published that consider the safety of hydrogen as a vehicle fuel. These have concentrated primarily on hydrogen safety related to the vehicle itself rather than the wider context of a fuelling infrastructure. In this wider context it is vital to understand the risks associated with fuel delivery to forecourt or on-site manufacture as well as the risks associated with releases from on-site storage and dispensing operations.

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## 2. Characteristics of Hydrogen

### 2.1 Propensity to Leak

Hydrogen gas has the smallest molecule and has a greater propensity to escape through small openings than liquid fuels or other gaseous fuels.

For releases from pressurised systems the flow is likely to be choked. For the same pressure and hole size, hydrogen would leak approximately 2.8 times faster than natural gas and 5.1 times faster than propane on a volumetric basis. However the energy density of hydrogen is lower than that of methane or propane such that its energy leakage rate would be 0.88 times that of methane and 0.61 times that of propane.

### 2.2 Hydrogen Embrittlement

Prolonged exposure to hydrogen of some high strength steels can cause them to lose their strength, eventually leading to failure. Proper choice of materials to avoid these risks is required.

### 2.3 Dispersion

Hydrogen gas is more diffusive and under most conditions more buoyant than gasoline, propane or methane and hence tends to disperse more rapidly if released. The one exception is for cryogenic releases of hydrogen where the very cold vapour cloud initially formed can be denser than the surrounding air.

At low concentrations the effects of buoyancy become less significant because the density of the fuel-air mixture is similar to that of air. Buoyancy effects are also less significant for high momentum releases. For these releases the orientation of the release will determine the direction in which the hydrogen cloud forms. These releases are the most likely to occur for the high-pressure systems probable for hydrogen storage.

### 2.4 Flammability and Ignition

Hydrogen has much wider limits of flammability in air than methane, propane or gasoline and the minimum ignition energy is about an order of magnitude lower than for other combustibles, Table 1.

Table 1: Flammability and Ignition Characteristics

|                                     | Hydrogen | Methane | Propane | Gasoline |
|-------------------------------------|----------|---------|---------|----------|
| Flammability limits (vol. % in air) |          |         |         |          |
| Lower limit (LFL)                   | 4        | 5.3     | 2.1     | 1        |
| Upper limit (UFL)                   | 75       | 15      | 9.5     | 7.8      |
| Minimum ignition energy (mJ)        | 0.02     | 0.29    | 0.26    | 0.24     |

The wide range of flammability of hydrogen-air mixtures compared to other combustibles is in principle a disadvantage with respect to potential risks. A hydrogen vapour cloud could

potentially have a greater volume within the flammable range than a methane cloud formed under similar release conditions.

On the other hand there are only minor differences between the lower flammable limits (LFLs) of hydrogen and methane, and those of propane and gasoline are even lower. In many accidental situations the LFL is of particular importance as ignition sources of sufficient energy are often present to ignite a fuel-air mixture once a flammable concentration has been reached. In some circumstances (e.g. low momentum releases) the dispersion characteristics of hydrogen may make it less likely that a flammable mixture will form than for the other fuels. In addition the 4 vol.% LFL for hydrogen only applies to upward propagating flames. For downward propagating flames experiments have shown that between 9 and 10 vol.% hydrogen is required [5,6]. For methane the difference between LFLs for upward and downward propagating flames is less, 5.3 versus 5.6 vol.%.

In practical release situations the lower ignition energy of hydrogen may not be as significant a differentiation between the fuels as it first seems. The minimum ignition energy tends to be for mixtures at around stoichiometric composition (29 vol.% for hydrogen). At the LFL the ignition energy for hydrogen is similar to that of methane, Figure 1. In addition many so called weak ignition sources such as electrical equipment sparks, electrostatic sparks or sparks from striking objects involve more energy than is required to ignite methane, propane and other fuels. A weak electrostatic spark from the human body releases about 10 mJ.

Static electricity generation has been implicated as causing ignition in hydrogen venting situations[7]. However there are many spurious ignition sources and phenomena that could cause ignition and this is an area that is poorly understood. Among these is “diffusion ignition” whereby a shock wave from expansion of high-pressure gas into air is postulated to cause local auto-ignition [8,9].

The minimum autoignition temperature of hydrogen at ambient pressure is higher than that of methane, propane or gasoline, Table 2. However the autoignition temperature depends on the nature of the source. The minimum is usually measured in a heated glass vessel, however if a heated air jet or nichrome wire is used the autoignition temperature of hydrogen is lower than the other fuels.

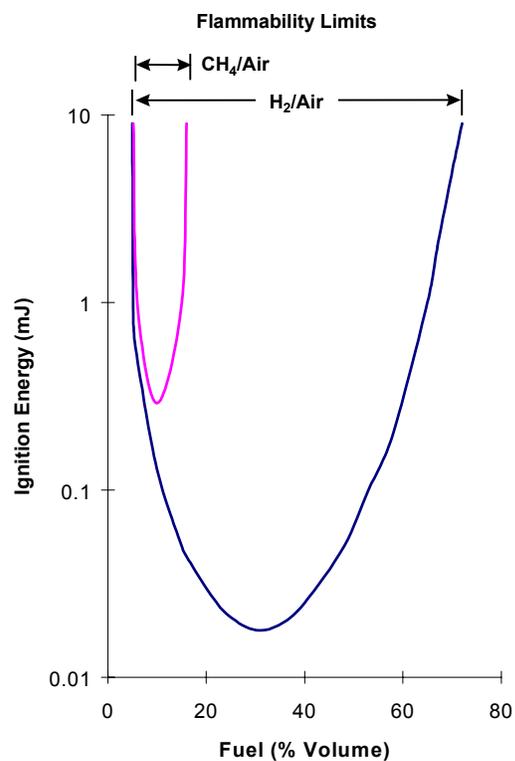


Figure 1: Minimum Ignition Energies

Table 2: Autoignition Temperatures

|                                  | Hydrogen | Methane | Propane | Gasoline |
|----------------------------------|----------|---------|---------|----------|
| Autoignition Temperatures (°C)   |          |         |         |          |
| Minimum                          | 585      | 540     | 487     | 228-471  |
| Heated air jet (0.4 cm diameter) | 670      | 1220    | 885     | 1040     |
| Nichrome wire                    | 750      | 1220    | 1050    |          |

To summarise, in the event of a fuel spill you could expect hydrogen to form a flammable mixture more readily than methane due to its higher buoyancy promoting its rapid mixing in air and due to its slightly lower flammable limit and larger flammable range. Gasoline would be orders of magnitude slower than hydrogen or methane at forming a flammable mixture of the same size and propane would be somewhere in between.

Although the rapid mixing property of hydrogen leads to the rapid formation of flammable mixtures, they also lead to its ready dispersal and thus generally shorter duration of the flammable hazard than for the other fuels (on an equal volume basis). Despite the UFL of hydrogen being much higher than that of methane, its higher buoyancy leads to it dispersing to concentrations below the LFL more quickly. However this does not apply to spills of cryogenic liquid. At its boiling point the density of hydrogen vapour approaches that of air, while for methane it is greater. This can lead to the formation of transiently non-buoyant flammable mixtures extending considerable distances from the spill.

### 2.5 Combustion characteristics

Hydrogen gas can burn as a jet flame with combustion taking place along the edges of the jet where it mixes with sufficient air. In the open flammable mixtures undergo slow deflagration (also known as a cloud or flash fire). Where the flame speed is accelerated e.g. by extreme initial turbulence, turbulence from obstacles, or confinement, the result is an explosion. An extreme example is a detonation where the flame speed is supersonic. Once initiated a detonation is self-sustaining (i.e. turbulence or confinement are not required) as long as the combusting mixture is within the detonable range.

Hydrogen flames are different to hydrocarbon flames in that there is little or no soot formation and the lower radiation from the flame makes the flame itself hotter than hydrocarbon flames. Objects engulfed by a hydrogen jet flame tend to heat up faster than when in the same size methane flame because the convective component is considerably greater. However the lower radiative component means that there is less radiation transferred to objects (or people) outside the flame.

The quenching gap for hydrogen is smaller than for methane, propane and gasoline. The quenching gap is the largest passage that can prevent propagation of a flame through that passage when it is filled with a flammable fuel-air mixture. When the dimension of a passage is less than a critical width a flame front is extinguished because heat transfer and/or free radical loss become great enough to prevent flame propagation. The quenching gap depends on gas composition, temperature, pressure and passage geometry. The design of flame arrestors and flame traps are dependent on quenching gap measurements. The small quenching gap for hydrogen requires

tighter tolerances, which makes equipment capable of containing hydrogen flames more difficult to build than equipment for hydrocarbon flames.

Table 3: Quenching Gap

|                           | Hydrogen | Methane | Propane | Gasoline |
|---------------------------|----------|---------|---------|----------|
| Quenching gap at NTP (mm) | 0.6      | 2       | 2       | 2        |

The *laminar burning velocity* of a gas-air mixture is the velocity of the cold reactants (without flame stretch) relative to the plane comprising the flame. The *flame speed* is the speed of the flame front as would be observed by a stationary observer outside the flame. This will be higher than the laminar burning velocity because the position of the flame front is driven by the expansion of hot combustion products, (particularly where the hot combustion products can not be vented). The flame speed may increase further with the effect of turbulence, from the either the gas release mechanism or from the interaction of the flame front with obstacles.

In extreme cases of flame acceleration, the mode of combustion may switch from deflagration to detonation. A detonation explosion is more severe than a deflagration explosion, the overpressures generated are higher (in the region of 20 to 1 versus up to 8 to 1 [10]) and hence much greater physical damage is possible.

Generally, the propensity for a combustible mixture to support the transition from deflagration to detonation (DDT) is related the laminar burning velocity (table 4) . The higher the laminar burning velocity is the greater is the tendency for DDT to occur.

Table 4: Explosion Characteristics

|  | Hydrogen | Methane | Propane | Gasoline |
|--|----------|---------|---------|----------|
| Detonability limits (vol. % in air)              |          |         |         |          |
| Lower limit (LDL)                                | 11-18    | 6.3     | 3.1     | 1.1      |
| Upper limit (UDL)                                | 59       | 13.5    | 7       | 3.3      |
| Maximum laminar burning velocity (m/s)           | 3.46     | 0.43    | 0.47    |          |
| Concentration at maximum (vol. %)                | 42.5     | 10.2    | 4.3     |          |
| Laminar burning velocity at stoichiometric (m/s) | 2.37     | 0.42    | 0.46    | 0.42     |
| Concentration at stoichiometric (vol. %)         | 29.5     | 9.5     | 4.1     | 1.8      |

A deflagration can make the transition to a detonation if the concentrations in the flammable cloud are within the detonable range and the flame front can accelerate to a speed above the sonic velocity in air. The flow driven by the expansion of hot combustion products means that DDT is a particular concern for one-dimensional cases, such as pipelines. However, even for spherical gas clouds, DDT can occur in principle if the dimensions of the cloud are large enough to provide sufficient run-up distance for the flame to accelerate, and if there are turbulence promoting structures to accelerate the flame or there are pressure wave reflecting bodies such as walls.

A further concern is whether the turbulence in an emerging high pressure hydrogen gas jet release coupled with its exceptionally high burning velocity may also provide the conditions for detonation rather than deflagration to occur on ignition. Direct detonation of a hydrogen gas cloud is less likely than a deflagration as the ignition energy required is in the 10 kJ range (c.f. figure 1), the minimum concentration is higher and the detonable range is narrower than the flammable range.

### 3. Shell Hydrogen Experiments

As was discussed in the last section, hydrogen has a much higher laminar burning velocity than conventional hydrocarbon fuels such as gasoline, methane and propane. It is much more buoyant than these other fuels and so the build-up of a significant flammable gas cloud is less likely. Nevertheless, following an accidental release occurring on a retail forecourt if a flammable gas cloud can build up and find an ignition source, then one might expect to see much higher overpressures for hydrogen-air explosions in comparison to the other fuels discussed. Moreover, the risk of a DDT occurring cannot be completely discounted *a priori*.

The question as to whether there are any credible scenarios associated with a forecourt release of hydrogen which could give rise to detonation is vital therefore to properly assess the risks associated with retailing hydrogen as a fuel. Shell Hydrogen has sponsored an experimental programme, conducted by Shell Global Solutions (UK) to address these concerns.

#### 3.1 Explosion experiments with quiescent gas mixtures



Figure 2 Test rig with example configuration

Mixtures of hydrogen and air were constrained within an open box containing obstacle grids (figure 2). This was achieved by wrapping polythene sheets to the side of the box and affixing them with magnetic strips. The polythene sheets come away immediately following ignition. The largest dimension of the rig is 1.2m and the rig may be considered to be representative of lengthscales of dispensing equipment on a forecourt. The flame front is accelerated by obstacles in the array. Experiments were conducted with varying levels of obstacle “congestion”.

For these experiments, hydrogen was compared to ethylene and acetylene, which are known to be more reactive gases than methane or propane. The laminar burning velocity reported in the literature [11,12] for each fuel is presented in Figure 3. As can be seen from the figure and from table 4, the maximum in the hydrogen laminar burning velocities occurs for somewhat rich fuel air mixtures. Nevertheless for the whole range of fuel-air ratio the laminar burning velocity of hydrogen is higher than acetylene or ethylene. Based on the discussion in section 2.5, one might expect therefore that explosion severity would be in the rank order Hydrogen>Acetylene>Ethylene.

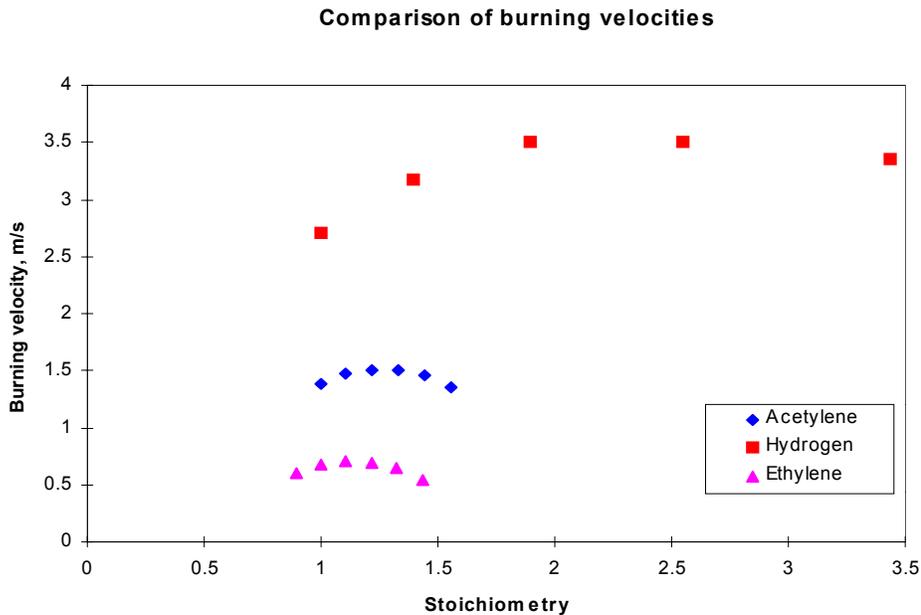


Figure 3 Laminar Burning velocities of hydrogen, acetylene and ethylene as a function of stoichiometry.

Figure 4 shows a representative hydrogen explosion test in progress. Flame speeds and explosion overpressures were recorded as a function of time. Experiments were conducted for each of the fuels at various values of stoichiometry and levels of congestion. For a given set of conditions, the repeatably observed rank order for explosion severity was found to be Acetylene>Hydrogen>Ethylene.

It appears therefore that for the length scales we have investigated, the severity of hydrogen explosions is not as great as indicated by the magnitude of the laminar burning velocity of hydrogen relative to other hydrocarbons. Also for length scales representative of dispensing

equipment, there appear to be no credible events in which ignition of a quiescent hydrogen-air cloud could lead to a deflagration to detonation transition.

We are currently looking for joint industry partners to investigate unconfined hydrogen explosions in length scales that would be representative of onsite hydrogen manufacturing equipment.



Figure 4 Example of hydrogen explosion experiment 28 ms after ignition.

### **3.2 Jet Release Experiments.**

The previous section described the combustion of quiescent hydrogen air mixtures. Although the situation allows an experiment to be properly characterised and understood, it does not represent a completely realistic scenario, since a gas cloud will most likely have been formed by the mixing with air of a jet of pressurised hydrogen or the evaporation of a liquid spill.

We have therefore undertaken a series of experiments releasing a hydrogen jet into a congested region. This serves as a “demonstration” rather than an experiment since it is difficult to characterise. Nevertheless for congested regions of size 1-1.5m, although local high overpressures were observed on jet ignition, there was no evidence of any event likely to lead to a deflagration to detonation transition from a 25 bar release. We are in the process of confirming this conclusion at pressures up to 150 bars. We are also seeking joint industry funding to investigate the hazards associated with jet releases of hydrogen at 350 bar and 700 bar.

## **4.0 Conclusions**

The comparative safety of hydrogen can only be judged based on the particular circumstances in which it will be used. In some instances hydrogen's propensity to dissipate quickly, relatively high LFL and low energy density may make it a safer fuel than the alternatives considered. In other cases hydrogen's wide flammable range, small quenching gap and propensity to detonate might make it less safe.

Detailed safety analyses will be required to establish the relative safety of different fuels for each specific application and potential accident scenario.

The high laminar burning velocity of hydrogen compared to other hydrocarbon fuels is a reason to be concerned about the possible severity of an explosion following ignition of an accidental hydrogen release in a congested region. In particular there has been a concern as to whether there are any credible forecourt accident scenarios in which a detonation could occur. Our experimental programme suggests a detonation is unlikely for gas clouds of the length scale of dispensing equipment. Moreover for the length scales that we have investigated, the severity of hydrogen explosions is not as great as indicated by the magnitude of the laminar burning velocity of hydrogen relative to hydrocarbons.

### **Acknowledgements**

The author thanks Shell Hydrogen for permission to publish.

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### **Curriculum Vitae**

Roger Cracknell joined Shell in 1994. He joined the Fuels Business Group of Shell Global Solutions in 1999. He is currently a Senior Scientist leading hydrogen related projects within

Shell Global Solutions (UK). Before joining the Fuels Business Group, he worked in the HSE consultancy of Shell Global Solutions where he specialised in fire and explosions hazards posed by inadvertent releases of hydrocarbons. Roger Cracknell has a Ph.D. in Physical Chemistry from Imperial College (University of London). Between 1990 and 1992 he was a Postdoctoral Research Associate in the School of Chemical Engineering of Cornell University, New York, USA. Between 1992 and 1994 he continued as a postdoctoral scientist at Imperial College.

During his career, Roger has published over 30 refereed journal and conference papers.