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Compilation of Existing Safety Data on Hydrogen and Comparative Fuels

Executive Summary

An overview of the safety characteristics of hydrogen compared to methane, propane and gasoline is presented. The relative safety of hydrogen compared to other fuels must take into consideration the particular circumstances of its accidental release and its reactive nature. Hydrogen can be safer than conventional fuels in some situations, and more hazardous in others.

The primary hazards associated with unintentional fuel releases are those of fire and explosion. Over-simplistic hazard evaluations have been found in the literature that neglect the differing behaviour of fuels on ignition. Quantification of the fire and explosion hazards cannot be based solely on the relative energy content of the fuel.

1. Introduction

1.1. Objectives

This study aims to collate existing data relating to hydrogen safety and compare it with data on other fuels commonly used in the transport sector, methane, propane and gasoline.

1.2. Background

The use of hydrogen as a fuel inevitably results in risks to the public, as is the case for use of any combustible material. Currently hydrogen use is predominantly limited to highly trained individuals. If it is 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. 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 (DTI¹, Barbir², Cadwallader & Herring³, Ringland⁴) 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 some scenarios hydrogen may be safer than conventional automotive fuels, in others more dangerous. Hence a meaningful comparison must be based on comparing all relevant situations. Cadwallader and Herring³ quote the National Hydrogen Energy Association as having qualitatively determined that methane was less dangerous than hydrogen and that hydrogen was less dangerous than propane⁵. That assessment was based on tests showing that a hydrogen gas release in a confined space was the quickest to form a flammable mixture and that hydrogen has the lowest ignition energy. In vented spaces a propane release still formed a large flammable mixture, methane resulted in a small flammable mixture and hydrogen gave virtually no flammable mixture as it easily vented from the space. However this assessment is not a useful judge of the overall risk associated with the use of hydrogen. It has not accounted for the fact that in a particular scenario hydrogen may have a different leak frequency, in congested areas ignition of a flammable cloud of hydrogen may generate significantly different overpressures than methane or propane, hydrogen is more likely to detonate than methane or propane and liquid hydrogen has the additional hazard of cold effects.

Simplistic comparisons of fuel hazards on the basis of the relative energy content of fuels stored have also been found in the literature (DTI¹). Again this approach is unsatisfactory, a release of hydrogen of less energy content than a release of methane could still do more damage if the conditions were such that the hydrogen could detonate whilst the methane could

not. The manner in which the energy in the fuel is dissipated is as important as the energy content of the fuel.

2. Basic Safety Characteristics

There are several reviews of hydrogen safety characteristics relative to other fuels available in the open literature (e.g. DTI¹, Cadwallader & Herring³, Fischer⁶, Hord⁷, Ringland⁴). This section gives a brief overview of these characteristics compared with those of methane, propane and gasoline.

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 transfer through a membrane the relative rate is governed by the relative diffusion coefficients of the materials. For subsonic releases through openings the rate is dependent on whether the flow is laminar or turbulent. For laminar flow the relative molar leak rates of two gases are theoretically inversely proportional to the ratio of their dynamic viscosities. For turbulent flow the molar leak rates are theoretically inversely proportional to the square root of the relative gas densities. For sonic releases the molar leak rates are proportional to the sonic velocity of the gases. For perfect gases the ratio of molar flow rates equals the ratio of volumetric flows.

Predicted theoretical flowrates of methane and propane relative to hydrogen are given in Table 1.

Table 1: Leak Characteristics

	Hydrogen, H ₂	Methane, CH ₄	Propane, C ₃ H ₈
Flow Parameters:			
Diffusion coefficient in air at NTP ^a (cm ² /s)	0.61	0.16	0.12
Viscosity at NTP (g/cm-s x 10 ⁻⁵)	89	11.7	80
Density at NTP (kg/m ³)	0.0838	0.6512	1.870
Ratio of specific heats, Cp/Cv at NTP	1.308	1.383	1.14
Relative leak rates (volumetric):			
Subsonic flow			
Diffusion	1	0.26	0.20
Laminar Flow	1	0.77	1.11
Turbulent Flow	1	0.35	0.21
Sonic flow	1	0.34	0.20
Relative leak rates (energy basis ^b):			
Subsonic flow			
Diffusion	1	0.87	1.63
Laminar Flow	1	2.66	9.38
Turbulent Flow	1	1.18	1.80
Sonic flow	1	1.14	1.63

^a Normal temperature and pressure - 1 atm and 20°C

^b Based on lower heating value of the fuel

For the high pressure systems likely to be used for hydrogen storage the flow from any leaks is likely to be sonic therefore 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 for sonic flow 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 2.

Table 2: 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^{8,9}. 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.

For releases of hydrogen stored above atmospheric pressure the NFPA 1991 have suggested that the static electricity generated by the flow of pressurised gas is large enough to cause discharge to the ground and ignite the gas jet. This effect is reported to have occurred in hydrogen venting situations¹⁰. However there are many spurious ignition sources that could have been responsible for these ignitions and this is an area that is poorly understood.

The minimum autoignition temperature of hydrogen is higher than that of methane, propane or gasoline, Table 3. 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.

Table 3: 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 properties 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

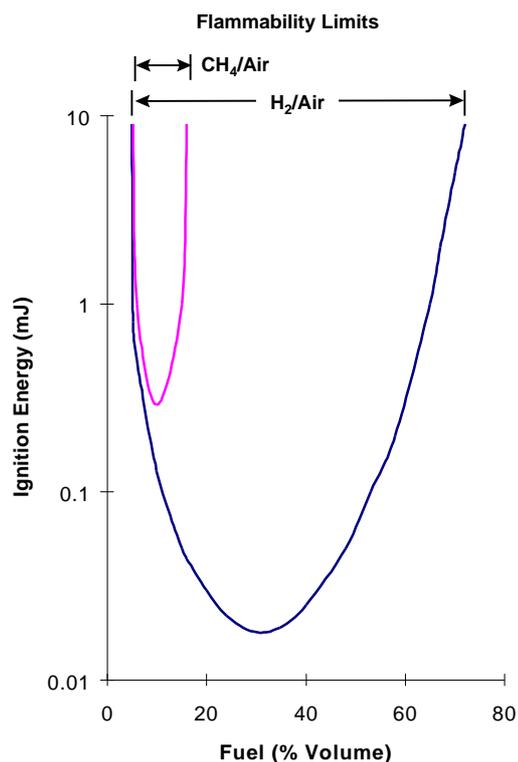


Figure 1: Minimum Ignition Energies

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. Hydrogen Combustion

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.

A hydrogen flame is almost invisible, emits less radiation than a hydrocarbon flame and burns without producing smoke. However inhalation of the hot combustion products can still damage the lungs. 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. The heat from hydrogen flames is emitted in narrow infra-red bands, mainly from water vapour and/or CO₂. Most of the heat radiated will be absorbed over short distances by the cold CO₂ and water vapour in the atmosphere. The adiabatic flame temperatures in air of hydrogen, methane, propane and gasoline and the percentage of thermal energy radiated to the surroundings are given in Table 4.

Table 4: Adiabatic Flame Temperatures and % Thermal Energy Radiated

	Hydrogen	Methane	Propane	Gasoline
Adiabatic Flame Temperature in Air (K)	2318	2158	2198	2470
% Thermal Energy Radiated from Flame to Surroundings*	5 to 10	10 to 33	10 to 50	10 to 50

* For hydrocarbon flames the majority of radiation is due to soot formation and emission and is therefore highly dependent on the combustion efficiency. A sonic gas flame is more efficient than a sub-sonic gas flame which is in turn more efficient than a pool fire. The values quoted cover the range of combustion efficiencies.

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 5: Quenching Gap

	Hydrogen	Methane	Propane	Gasoline

Quenching gap at NTP (mm)	0.6	2	2	2
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An explosion is always accompanied by a fireball and a pressure wave (overpressure). The fireball can ignite combustible materials in the vicinity or fuel released by the explosion so that a fire may follow an explosion. If the flammable mixture is partially or totally confined the explosion may propel fragments of the enclosure material over great distances.

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 1¹¹) and hence much greater physical damage is possible.

Direct detonation of a hydrogen gas cloud is less likely than a deflagration explosion as the ignition energy required is in the 10 kJ range, the minimum concentration is higher and the detonable range is narrower than the flammable range. The propensity for a combustible mixture to support the transition from deflagration to detonation (DDT) is indicated by the burning velocity. The higher the burning velocity is the greater is the tendency for DDT to occur.

Table 6: Detonation 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 burning velocity (m/s)	3.46	0.43	0.47	
Concentration at maximum (vol. %)	42.5	10.2	4.3	
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. This can occur 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. 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.

Hord⁷ notes that experimental data indicate that a U-shaped enclosure plus the ground comprise sufficient confinement to support “strong” explosions in detonable hydrogen-air mixtures ignited by thermal ignition sources.

The hydrogen concentration range required for a detonation is normally quoted as being between 18 and 59 vol.% in air. However recent experiments with large scale hydrogen clouds¹² and elevated initial temperature or pressure conditions¹³ have shown that DDT can occur even at concentrations as low as 11 %vol. For gasoline in air the detonable range is much narrower (1.1 to 3.3 vol.%) but the lower detonable limit is less (1.1 vol.% versus 18 vol.%). The detonability of methane and propane lie in between.

In the open detonation of a flammable hydrogen-air mixture is much less likely than a deflagration since a high energy ignition source is required and the minimum concentration in air to support it is higher, 18 %vol. as opposed to 4 %vol.

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