

HANDLING AND SAFETY OF HYDROGEN

Itsuki Uehara

National Institute of Advanced Industrial Science and Technology, Japan

Keywords: Gaseous hydrogen, Liquid hydrogen, Metal hydrides, Safety measures of hydrogen, Fire hazards, Fire damages, Leaked states, Flammability limits, ignition Sources, Quenching Characteristics, Fire damage, Explosion Hazards, Deflagration, Detonation, Explosive Damage, Low temperature hazards, Deflagration, Detonation, Ignition sources, Flammability limits, Detonability limits, Prevention of a fire, Fighting of a fires, Hydrogen embrittlement, Hydrogen detectors, Hydrogen fire detectors.

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Summary

Hydrogen is a highly flammable and explosive gas with wide flammability limits, a low minimum ignition energy and a fast burning velocity. Although its flammable mixture with air rapidly disperses into the atmosphere or deflagrates with a relatively weak impulse in an open space, its deflagration in a totally or partially confined space is

accompanied by a severe pressure impulse and a potential transition to detonation. It is colorless and odorless, and can embrittle some metals. Therefore, for safe handling of gaseous hydrogen, attention must be paid to its possible leakage, likely formation of a flammable mixture, avoidance of ignition sources and selection of appropriate container materials, especially in a confined space. The same considerations apply to liquid hydrogen and metal hydrides, since these yield gaseous hydrogen either spontaneously or during process operation. Liquid hydrogen is accompanied by hazards related to its low temperature, such as fast evaporation, line-blocking due to solidification of moisture and air, thermal stress, cold embrittlement of construction materials, and handlers' frostbite. Metal hydrides allow hydrogen to be stored at moderate pressure and ambient temperature. However, the fine particles produced during repetitive cycles of hydrogen absorption and desorption are often pyrophoric, and may induce an internal stress that causes rupture of the container. Finally, appropriate regulations and protocols for the safe handling of hydrogen in all its forms exist and are properly enforced. As such, there are no grounds to justify the claim that hydrogen is intrinsically more dangerous than any other commodity chemicals and fuels.

1. Introduction

Hydrogen has been an important feedstock and a fuel in various industrial fields for many years, and is expected to be more diversely and widely utilized as an energy carrier in its three forms; compressed gas, cryogenic liquid and metal hydride, in commercial and residential areas. However, hydrogen is one of the most flammable and explosive substances, and makes some metals brittle. Small and large accidents related to hydrogen have actually occurred due to improper handling or control, although the cause of the Hindenburg tragedy, which was regarded as a representative disaster caused by hydrogen, has been shown not to be related to hydrogen. Adequate handling and safety measures of hydrogen are obviously important for both current and emerging uses of hydrogen as a feedstock and a fuel.

2. Safety Aspects of Gaseous Hydrogen

Since gaseous hydrogen is colorless, odorless and tasteless, and burns with a nearly invisible flame, leakage of hydrogen and the resultant fire are not easily perceived. Although hydrogen and its combustion product, water vapor, are not considered to be toxic, leakage and fires of hydrogen cause *suffocation* by decreasing ambient oxygen concentration. Furthermore, the main danger in the handling of hydrogen lies in its *high flammability* in air or oxygen. Its combustible character may result in a fire, a relatively weak explosion (deflagration) or a severe explosion (detonation). For the safe production, storage, transport, and utilization of hydrogen, these dangers must be recognized appropriately. Key properties related to safety aspects of hydrogen are listed in Table 1. The data for methane and gasoline are also given in Table 4 for comparison.

Property	Hydrogen	Methane	Gasoline
Molecular weight	2.016	16.043	<107
NBP ^{a)} temperature (K)	20.268	111.632	310 – 478
Density of liquid at NBP (kg m ⁻³)	70.8	422.6	<702

Density of gas at NTP ^{b)} (kg m ⁻³)	0.0838	0.6512	<4.4
Heat of vaporization (kJ kg ⁻¹)	445.59	509.88	309
Steady state vaporization rates of liquid pools without burning (cm min ⁻¹)	2.5 – 5.0	0.05 – 0.5	0.005 – 0.02
Heat of combustion (low) (MJ kg ⁻¹)	119.93	50.02	44.5
Heat of combustion (high) (MJ kg ⁻¹)	141.86	55.53	48
Diffusion coefficient in still air at NTP (cm ² s ⁻¹)	0.61	0.16	0.05
Diffusion velocity in air at NTP (cm s ⁻¹)	<2.00	<0.51	<0.17
Buoyant velocity in air at NTP (m s ⁻¹)	1.2 – 9	0.8 – 6	nonbouyant
Viscosity of gas at NTP (g cm ⁻¹ s ⁻¹)	8.9 x 10 ⁻⁵	11.17 x 10 ⁻⁵	5.2 x 10 ⁻⁵
Stoichiometric composition in air ^{c)} (%)	29.53	9.48	1.76
Flammability range (limits) in air ^{c)} (%)	4.1 - 75	5.3 - 15	1 – 7.8
Limiting oxygen index ^{c)} (%)	5.0	12.1	11.6
Minimum ignition energy (mJ)	0.02	0.29	0.24
Minimum self ignition temperature ^{d)} (K)	858	813	501 – 744
Hot air-jet ignition temperature ^{e)} (K)	943	1493	1313
Adiabatic flame temperature in air (K)	2318	2158	2470
Burning velocity in air at NTP (cm s ⁻¹)	265 -325	37 - 45	30 - 42
Thermal energy radiated from flame to surroundings (%)	17 - 25	23 - 33	33 – 42
Quenching gap at NTP (mm)	0.6	2	2
Maximum experimental safe gap in air at NTP (mm)	0.08	1.2	0.7
Detonability range in air ^{c)} (%)	18 - 59	6.3 - 13.5	1.1 – 3.3
Detonation velocity in air at NTP (km s ⁻¹)	1.48 – 2.15	1.39 – 1.64	1.4 – 1.78
Energy of explosion of fuel (MJ kg ⁻¹)	<110	<51	<46
Energy of explosion of fuel ^{d)}	<24	<11	<10
Energy of explosion of gaseous fuel ^{b)} (MJ m ⁻³)	9.9	32.3	203.4

- a) NBP = normal boiling point
- b) NTP = normal temperature and pressure (293.15 K, 0.1013 MPa).
- c) in a volumetric ratio.
- d) a stoichiometric mixture.
- e) pure fuel vapor at NTP and a jet diameter of 4 mm.
- f) in a trinitrotoluene TNT to fuel mass ratio.

Hord J., *International Journal of hydrogen Energy* Vol. 3, 157-176 (1978). International Association of Hydrogen Energy.

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Table 1. Properties of hydrogen, methane and gasoline related to safety and handling.

2.1 Fire Hazards and Related Damage

A fire hazard means an existing or potential condition or situation that may result in a fire. Most fire hazards in handling of hydrogen result from formation of a flammable mixture with air through its accidental or inadvertent leakage that is attributed to mishandling or mechanical failures of equipment, construction materials, erosion, physical abuse, improper maintenance, or collision.

When leaked hydrogen ignites in an open space, it usually deflagrates with a flame propagating as an expansion wave at a relatively fast velocity below the speed of sound, or it can burn as an open flame or a fireball near its leaking site. In the case of totally or partially confined spaces, the flammable mixture deflagrates mostly by ignition. Under more explosive conditions, the deflagration can transform to a detonation, in which combustion waves coupled with shock waves propagate at supersonic speeds.

It is obvious that these deflagrations and detonations also cause fires. Explosive hazards and damage based on deflagration and detonation phenomena are described in later subsections.

2.1.1 Leaked States

Gases leaking from holes, cracks, valves or pipes form a laminar, turbulent or sonic flow. Leaks through narrow passageways at relatively small pressure differences tend to be laminar flows, whereas those at relatively large pressure differences tend to become turbulent or sonic.

In the case of turbulent and sonic leaks, the volumetric leak rates of hydrogen are much larger than those of gaseous methane and gasoline. However, leak rates in terms of the combustion energy are smaller for hydrogen than for either organic fuel in all three types of leak because hydrogen has a considerably lower heat of combustion per unit volume.

Leaked hydrogen is expected to mix with surrounding air more rapidly than other gaseous fuels, since hydrogen has faster *diffusion* and *buoyant* velocities than other fuels. At the same time, buoyant hydrogen can disperse more quickly without remaining near the leak point.

In open areas, the quick dispersion rate of hydrogen probably reduces the duration of a fire hazard, although the fire hazard may be much influenced by the leak rate and wind velocity. In confined spaces, mixing of leaked hydrogen with air is promoted by convective diffusion caused by its buoyant current, thereby exacerbating any fire hazard. In radical situations such as the impact rupture of a hydrogen tank in an automobile, the fire hazard is created instantaneously regardless of gas flow characteristics.

2.1.2 Flammability Limits

For mixtures of fuel and air, propagation of flames is sustainable within a composition range between the so-called *lean* and *rich* flammability limits. These depend on combustion factors such as ignition energy, initial pressure, initial temperature, and relative humidity. The flammability limits of hydrogen–air mixtures are between 4.1 and 75% by volume of hydrogen in air at atmospheric pressure and room temperature, and increase almost linearly with increasing temperature. The large value of 75% for the rich flammability limit is linked to the small value of 5% for the *limiting oxygen index*, which is the minimum concentration of oxygen that can support flame propagation in a mixture of hydrogen, air, and nitrogen. The wide flammability limits of hydrogen are a disadvantage, especially for hydrogen leakage in totally or partially confined spaces, from a safety point of view. However, hydrogen in air is likely to ignite only when the local concentration of hydrogen reaches the lean flammability limit, which is slightly lower than for propane but much higher than for gasoline.

2.1.3 Ignition Sources

Hydrogen in air is very susceptible to ignition, although it exhibits a higher *self-ignition temperature* than methane and gasoline. The *minimum energy for ignition* at a volumetric hydrogen concentration of about 30% is only 0.02 mJ, an order of magnitude less than that for methane or gasoline. The ignition energy sharply increases at leaner or richer hydrogen concentrations, and is almost equal to that for methane at a concentration of 4–5%. However, even a weak discharge of static electricity from a human body can produce a spark of 10 mJ.

The ignition energies of all these fuels are so low that their flammable mixtures with air can ignite in the presence of weak ignition sources such as sparks, friction heat, and hot surfaces. In addition, jets of hot air or combustion products emitted from the surroundings can cause to ignite a gaseous fuel or its mixture with air. Hydrogen can ignite at a lower hot air-jet temperature than methane and gasoline. The *hot air-jet ignition temperature* decreases with increasing jet diameter and depends on the composition of the combustible mixture and the velocity of the jet.

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Biographical Sketch

Itsuki Uehara, born April 4, 1950, in Kyoto Prefecture, Japan, graduated from Nagoya Institute of Technology in 1973. He received his ME degree in chemical engineering from Nagoya University in 1975 and Doctor of Engineering degree in electrochemistry from Kyoto University; has worked for Osaka National Research Institute on hydrogen energy systems and applications of hydrogen storage alloys (1975–1999); has worked as the Chief of the Central Research Institute, Toyama Industrial Technology Center (1999–2001); is presently the Human Resource Coordinator, National Institute of Advanced Industrial Science and Technology; and has published some 100 papers and 5 books.