Review of the Safety-related Physical and Combustion Properties of Hydrogen Compared to Natural Gas

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EnergyNews.Biz Webinar

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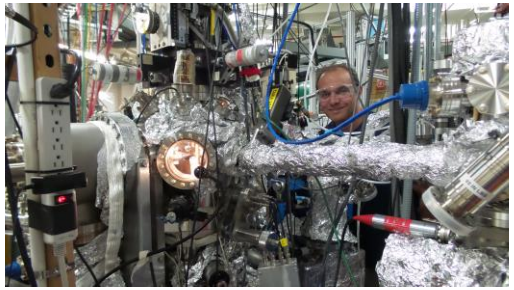
Sandia HQ: Albuquerque NM

Sandia, *Livermore CA, (SF Bay Area). Photo Credit: L.E. Klebanoff*

- Sandia is the 2nd largest National Lab in the U.S.
  - U.S. Department of Energy (DOE) Lab with ~17,000 employees
  - ~ US $5B/yr from DOE, other federal agencies, and private industry
  - H_2 Program is based in Livermore, CA (SF Bay Area)
- Hydrogen program: 70+ years of work on a wide range of topics (H_2 storage, production, delivery, development of science-based safety protocols, evaluating applicability of H_2 fuel cells in different applications).

U.C. Berkeley

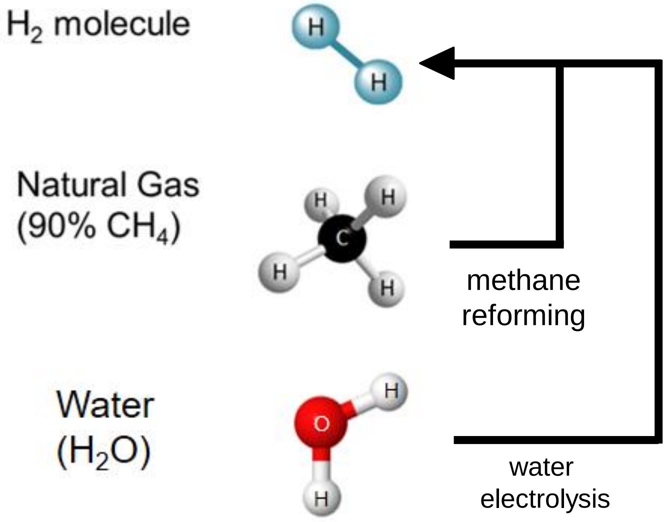


LK doing experiments at the Advanced Light Source

Lennie Klebanoff:

- Ph.D. Physical Chemistry from U.C. Berkeley.
- Chemistry Professor at Lehigh U. for 10 years (Full Prof.)
- I've worked at Sandia for 27 years.
- Worked in H_2 Technology since 2005, deploying hydrogen fuel cell systems.
- Have given H_2 Safety seminars to Port of San Francisco (2015- present), SF Airport first responders, United States Coast Guard (Sector San Francisco, HQ, Sector Delaware Bay), United States Naval Postgraduate School, and several Convention Center Fire Marshalls.

Hydrogen Physical Properties



- Is typically a gas, but can be a liquid (LH_2) if made very cold (20 K, -253 ºC, -424 ºF).
- H_2 is non toxic.
- LH_2 evaporates very fast (seconds).
- More buoyant than helium. Rises very rapidly when released.

Venting very cold hydrogen initially horizontally at the Emeryville H_2 Station, Emeryville CA.

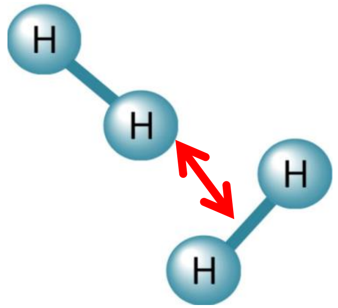
- We will see that H_2 is similar (but not identical to) natural gas (which is 90% methane, CH_4) w/regard to safety.
- If spilled, LH_2 evaporates quickly, leaving no residue.
- H_2/air mixtures can be ignited given an ignition source and the right H_2/air mixture.

One kg of H_2 has about the same energy content as a gallon of gasoline.

LH_2 Evaporates Faster than LNG, Cools Surfaces Less (Spill)

Assume NG is the same as methane (CH_4). Typically, 90% of NG is methane.

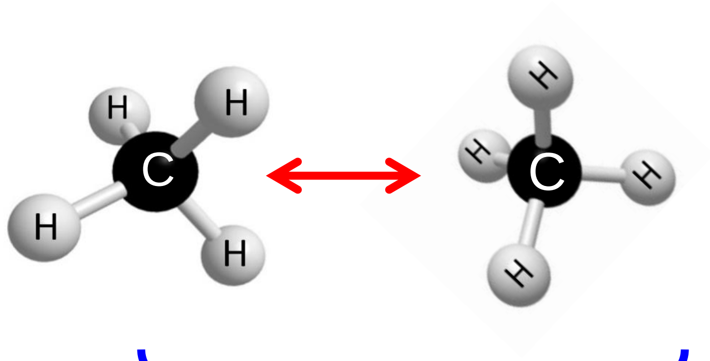
LH_2:



H_2 molecules are small and light, and barely interact at all.

Heat of Vaporization = 0.92 kJ/mole

LNG (CH_4):



CH_4 molecules are heavier, and interact more

Heat of Vaporization = 8.5 kJ/mole

Note: the heat of vaporization of water is 40.7 kJ/mole

-- For equal amounts of stored energy, LH_2 takes <u>3 times less</u> energy than LNG to evaporate. In a spill, LH_2 will cool surroundings much less than LNG.

-- Validated models predict that if 2840 kg (10,566 gallons) of LH_2 were instantaneously spilled, it would take only 13 seconds to fully evaporate.

See K. Verfonden et al., Int. J. of Hydrogen Energy **22**, (1997) 649 – 660.

Physical Properties of LH_2 and LNG

LH_2:

Liquid Normal Boiling Point = 20 K (- 253 ºC, - 423.4 F).
Liquid Density = 71 g/L
Lower Heating Value (LHV) = 120 MJ/kg

LNG (LCH_4):

Liquid Normal Boiling Point = 111 K (- 162 ºC, - 259.6 F).
Liquid Density = 422 g/L
LHV = 45 MJ/kg

Per unit of energy (LHV), LH_2 has 0.38 times the mass of LNG, but has 2.4 times the volume.

Per unit of energy (LHV), LH_2 has 0.36 times the mass of diesel, but has 4.2 times the volume.

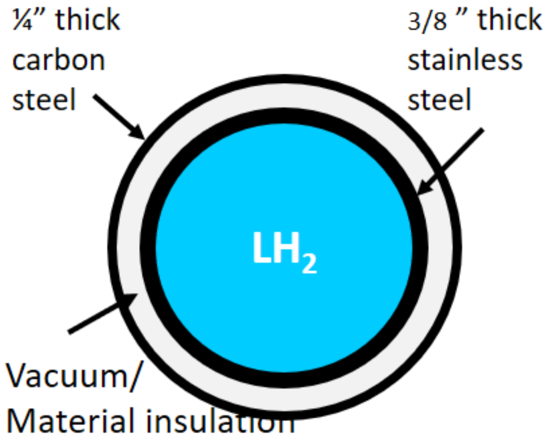
LH_2 can liquify/solidify air; LNG cannot. An important difference for line purging.

LH_2 and LNG are stored in similar ways:

LH_2 Storage Tank on Trailer


LNG Storage Tank on Trailer


Supplying LH_2 to the Kennedy Space Center



Storing H_2 as a High Pressure Gas

H_2 is routinely stored in 250 bar (~ 3,600 psi), 350 bar (~ 5,100 psi), 450 bar (~ 6,500 psi) or 700 bar (~ 10,000 psi) tanks. There are different tank designs, all mature technology.

The densities of H_2 gas at different pressures (ambient T)

250 bar gas = 17.5 g/L

350 bar gas = 23.3 g/L

700 bar gas = 39.3 g/L

900 bar gas = 46.5 g/L

LH_2 (at 1 bar pressure) = 71 g/L

Note: The density of hydrogen in H_2O is 111 gH/L

Research Area: Solid AlH_3 = 149 g/L

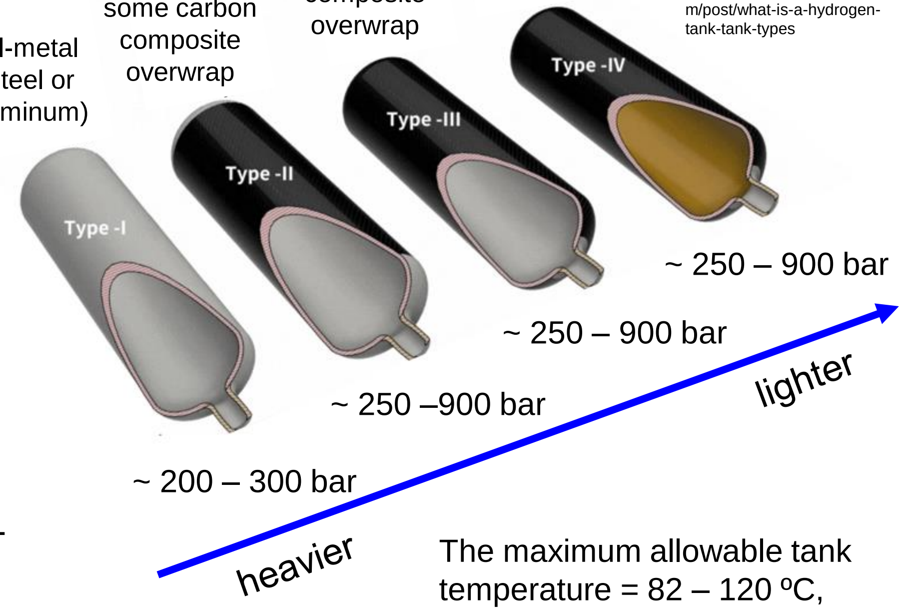
All-metal (steel or aluminum)

Thicker metal liner with some carbon composite overwrap

Thinner Al liner with full carbon composite overwrap

Plastic liner With full composite overwrap

Tank pictures from: https://www.addcomposites.com/post/what-is-a-hydrogen-tank-tank-types



The maximum allowable tank temperature = 82 – 120 ºC, depending on manufacturer.

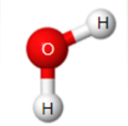
IGX H_2 trailer refueling fuel cell mobile lights at SFO, 2013 – 2021.

Abel-Nobel "Equation of State" for H_2 Gas: $V_m = RT/P + b$
where, V_m = molar volume (L/mole), R = 0.08206 L-atm/mole K, P = pressure in atmospheres, T is Temperature in K, b = 0.01584 L/mole.
One mole of H_2 has a mass of 2.016 grams.

https://www.energy.gov/eere/fuelcells/site-and-bulk-hydrogen-storage

Combustion Properties: Let's Pause for Some Definitions

Combustion of H_2: $2H_2 + O_2 \rightarrow 2H_2O$



Combustion of CH_4: $CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$

Explosion or Detonation: Extremely fast combustion where the flame propagates through the unburned fuel/air mix at supersonic speeds (~ 1000 m/s). Think firecrackers. Explosions produce loud bangs and very damaging overpressures. Explosions are very, very bad.

Deflagration: Fast combustion where the flame propagates through the unburned fuel/air mix at subsonic speeds (~ 100 m/s). Deflagrations are not as loud, and have much less damaging overpressures than explosions. Deflagrations are very bad.

Fire: Ordinary combustion where the flame propagates through the unburned fuel/air mix at slow speeds (~ 10 m/s). Fires are not loud, have no overpressure. Fires are bad. If we work to prevent fires, we also prevent explosions and deflagrations.

Weak (Thermal) Ignition Sources: Matches, sparks, hot surfaces, open flames (< 50 mJ). These are typically the ignition sources that cause accidents.

Strong (Shock Wave) Ignition Sources : blasting caps, TNT, high-voltage capacitor shorts (exploding wires) , lightning (> 4 MJ). Strong sources are ~ 10^8 stronger than weak initiators.

Flammability of H_2 vs NG: Fire

Both H_2 and NG (methane) mixtures with air are easily ignited by "Weak (Heat) Ignition Sources" such as: sparks, hot surfaces, open flames (< 50 mJ).

Fire regulations reference the "Lower Flammability Limit" (LFL) because the greatest fire risk comes from building up gas in initially clean air:

Definition: % by volume = $$\frac{[\text{Volume (Fuel)}]}{[\text{Volume (Fuel + Air)}]} \times 100$$

The LFL to upper flammability limit (UFL) for H_2 = 4.0 – 75.0 % at RT. The LFL to UFL of methane is = 5.3 – 15.0 % at room temp. **Note: the LFL for diesel fuel is 0.6%.**

The minimum ignition energy for CH_4 = 0.29 mJ; That for H_2 is 0.02 mJ. Static discharges from human beings are ~ 10 mJ, **so both CH_4 and H_2 ignite easily.**

H_2 and NG are both easily ignited by weak ignition sources, and start to burn at similar lower flammability limits

Flammability of H_2 vs NG: Direct Explosions/Detonations

The lower explosion limit (LEL) of H_2 at room temperature (% by volume) - upper explosion limit (UEL) = 18.3 – 59.0 % at RT. The LEL to UEL of methane is = 6.3 – 13.5 % at room temperature.

Experiments show that both H_2 and CH_4 require three things to directly detonate:

1. The fuel/air mix in the LEL – UEL range.

2. A strong ignition source.

3. Confinement by physical barriers or concentration by fluid dynamics of jet releases.

-- C.R.I. Bauwens et al. *https://hysafe.info/uploads/papers/2019/279.pdf*

A.D. Little study of LH_2 for the U.S. Air Force: For a series of LH_2 spills up to 5,000 gallons (1342 kg), igniting the unconfined vapor above the pool with spark, flame, or explosive charges produced only fire.

Sandia "Phoenix" Tests of LNG: Ignition of unconfined vapors above a 30,000 gallon pool of LNG produced only fire.

-- A.D. Little, Inc., Report to the U.S. Air Force, C-61092, (1960).
-- L.H. Cassutt, Report to the U.S. Air Force, Report No. 61-05-5182, (1964).

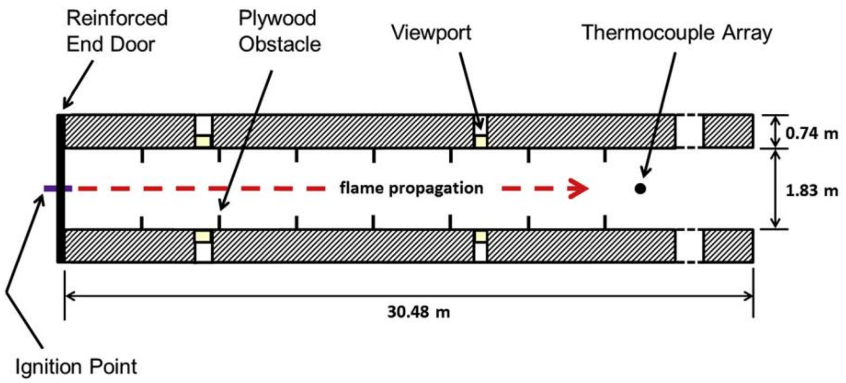
See also: M. Groethe et al. International Journal of Hydrogen Energy **32** (2007) 2125 – 2133 for a more recent study.

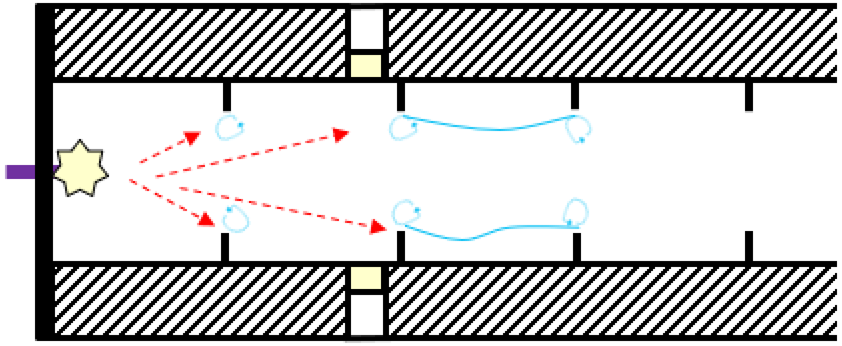
"Phoenix Tests" -- A. Luketa, Sandia National Laboratories Report SAND2011-9415 (2011).

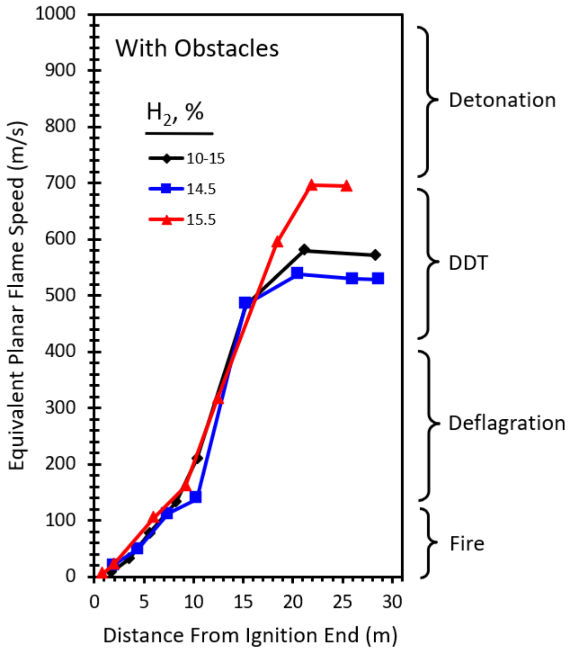
Deflagration to Detonation Transition (DDT)

In a confined environment with a lot of obstacles or internal structures, it is possible to get an explosion or detonation even with weak ignition sources. It's called a Deflagration to Detonation Transition (DDT).

Unlike direct detonation, which requires a strong ignition source, this type of explosion can start with a normal fire. In the confined/obstructed environment, the speed of the combustion accelerates over time and distance to a deflagration. With further acceleration, the deflagration transitions to a detonation because of turbulent mixing of the confined gases caused by the obstructions.





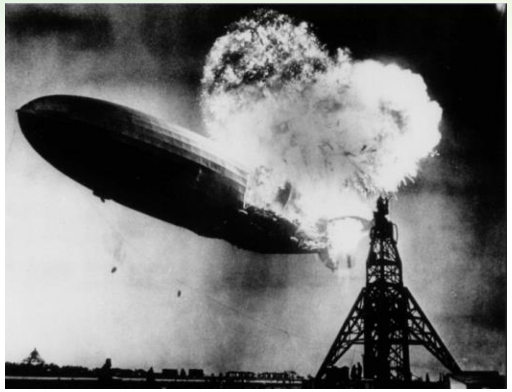


In these studies of H_2, DDT could only occur for 12% fuel /air mix or higher. Both H_2 and NG can experience DDT, although it is easier for hydrogen.

For hydrogen, ~ 10 m of run-up distance was required for the DDT.

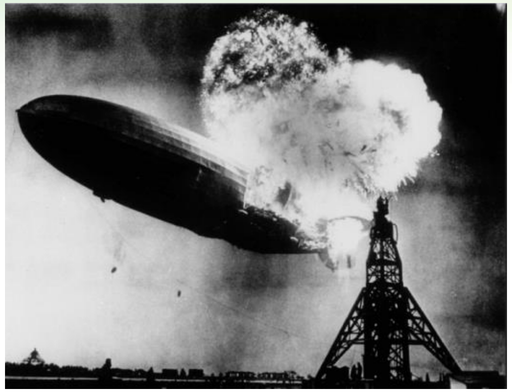
For more info on DDT, see: L.E. Klebanoff et al., Int. J. of Hydrogen Energy **42** (2017) 757 -774.

Hindenburg Accident (1937)



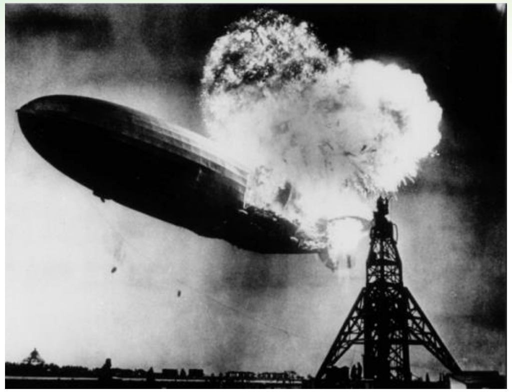
Sandia National Laboratories H2FC Hydrogen and Fuel Cells Program

Hindenburg Accident (1937)



Was it a H_2 Fire, or a H_2 Explosion?

Hindenburg Accident (1937)



It was a fire, NOT an explosion. Explosions are fast (think firecrackers). The airship initially stayed aloft while burning. But fires are bad too and need to be prevented!

The method of storing hydrogen for the airship (rubberized gas bags) in 1937 bears no resemblance to the highly engineered DOT-approved stainless steel LH_2 tanks in use today in many hydrogen fuel cell applications.

Compared to:

NASA has developed extensive experience in the safe and effective handling of hydrogen, the "signature fuel" of the American Space Program since the 1960s.

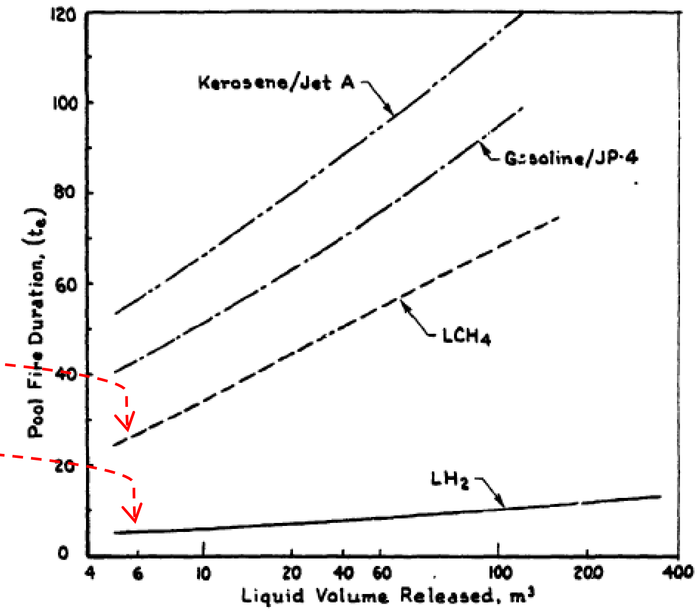
The Nature of Fires: LH_2 vs. LNG

NASA funded a modeling study of the fire safety aspects of LH_2 and LNG (LCH_4) as part of their program in alternative-fuel aircraft in the 1980s.

Pool Burn Times :

LNG = 25 s

LH_2 = 5 s



COMPARISON OF THE FIRE DURATIONS FOR POOL FIRES RESULTING FROM THE INSTANTANEOUS RELEASE OF THE FOUR FUELS

Spilling Equal Volumes of LH_2 and LCH_4:

6 m^3 = 6,000 L = 1585 gallons

= 426 kg of LH_2

= 2532 kg of LNG

A.D. Little, Inc., "An assessment of the crash fire hazard of liquid hydrogen fueled aircraft." Final Report to the National Aeronautics and Space Administration, NASACR-165526. 1982.

LH_2 pool fires burn out faster than LNG pool fires due to the much lower heat of vaporization of LH_2. But both fuels, if spilled, burn themselves out rapidly.

Sandia National Laboratories | H2FC Hydrogen and Fuel Cells Program

LH_2 Fires Radiate Less Heat Than LNG Fires

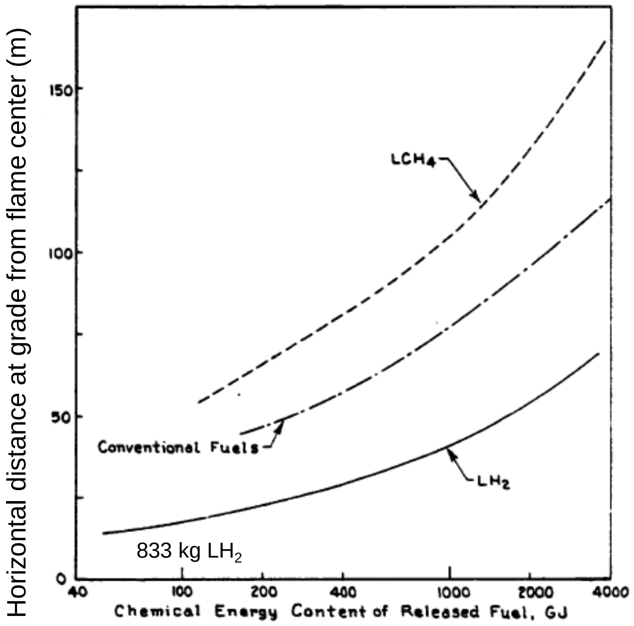
Results from the NASA-funded study:

Note:
5 kW/m^2 is the threshold for skin thermal injury.

For ~ 100 GJ of fuel energy:

~ 833 kg of H_2

~ 2222 kg of LCH_4 (NG)



Comparison of fire thermal radiation hazard distance (5kW/m^2) as a function of the heat content of the released fuel.

For ~ 100 GJ of fuel energy:

Approach limit
for LNG fire = ~ 54 m

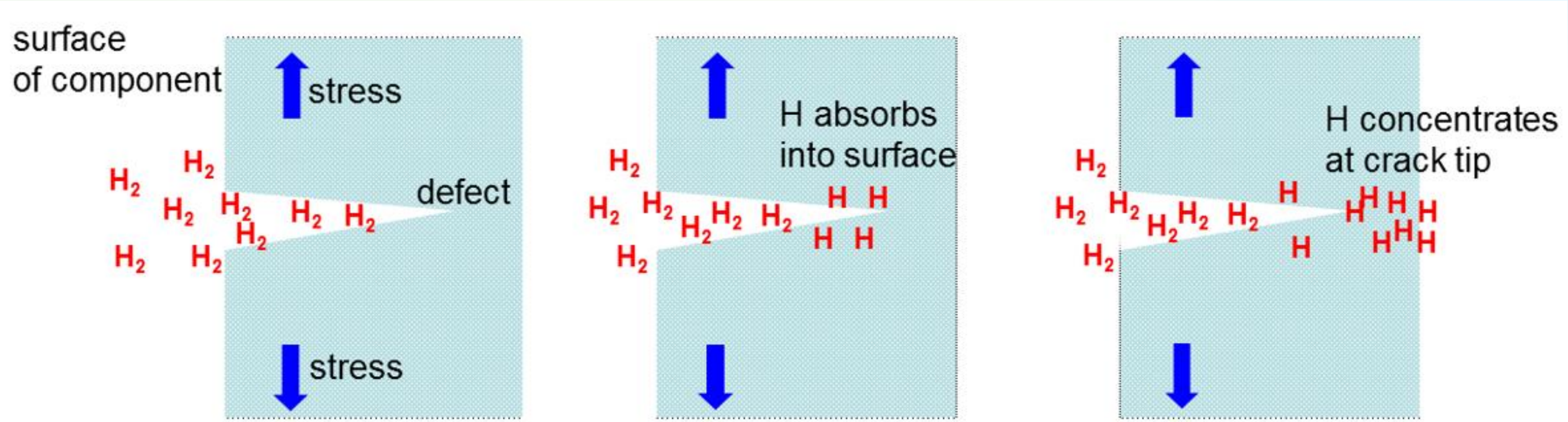
Approach limit
for LH_2 fire ~ 18 m

You can be ~ 3x closer to a H_2 fire than a NG fire for the same safety factor.

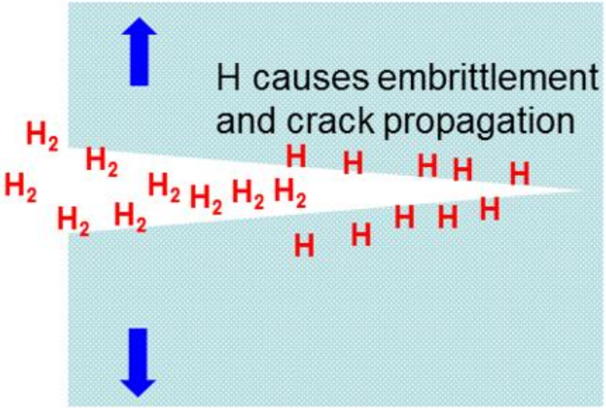
LH_2 fires are radiatively much less hazardous than LNG fires for two reasons:

1. **They don't contain carbon, and so radiate less than NG flames.**
2. **Since the product of H_2 combustion is H_2O, the flame radiation is strongly absorbed by H_2O in air.**

Hydrogen Embrittlement of Steels



For a review of hydrogen embrittlement, see:
D. Sobola et al., Energies **17** (2024) 2972.



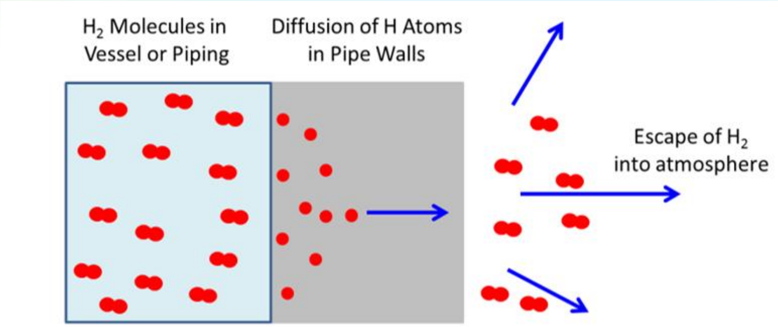
H can accumulate at crack points, promoting crack propagation and eventual material failure in high-strength alloys and steels.

The industry practice is to use 304 or 316 stainless steel in all H_2 plumbing, which is generally satisfactory.

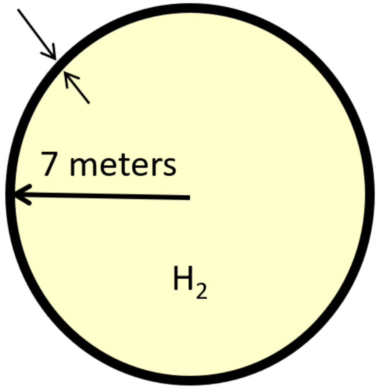
But it is very important to ensure these alloys are used!

Permeability is a Non-Issue for 316 Stainless H_2 Storage Systems

Unlike CH_4, H_2 can dissociate on metal surfaces, producing atoms that can diffuse through a metal, reaching the other side and exit as H_2.
The diffusion increases with T and P.



1/16" wall thickness 316 stainless steel



1200 kg of H_2 at 298 K (24.8 C) and 150 psi.

Remove the air, keep the H_2

All H_2 diffusing from the sphere would produce the 4% LFL of H_2 in a phone booth in **60 yrs.**

Remove the air, keep the H_2

149 people exhaling 3 ppm H_2 would produce 4 vol. % H_2 in a phone booth in **10.5 days.**

C. San Marchi, et al.,
Int. J. of Hydrogen Energy
32 (2007) 100 – 116.

H_2 Can't Be Permanently Trapped Underneath Outdoor Structures

Can H_2 somehow get trapped forever underneath Pier structures?
No: Hydrogen by "diffusion" can move and dissipate with time in all directions. Diffusion: molecules move from areas of higher concentration to areas of lower concentration. H_2 will diffuse ~ 3 m over the course of 6 hours.

MV *Sea Change, the world's first 100% commercial H_2 Fuel Cell Ferry*

Pier 68, Port of San Francisco

For more about H_2 Diffusion, see:

K.M. Gitushi, M.L. Blaylock and L.E. Klebanoff, International Journal of Hydrogen Energy **47** (2022) 21492 - 21505.

This means that hydrogen won't stay trapped forever underneath structures even if it gets there, assuming there is a "way out." It will dissipate in hours.

What Happens if H_2 is Released Out in the Open?

Sandia has conducted a lot of “gas dispersion modeling” studies for different types of outdoor hydrogen releases.

See for example: M.L. Blaylock and L.E. Klebanoff, Int. J. of Hydrogen Energy, **47** (2022) 21506 – 21516.

Some general statements can be made:

Without wind:

- Buoyancy will drive H_2 up, where it quickly dissipates below the LFL.
- If released from a high-pressure pipe, momentum will drive it in the direction of the leak for some distance, then buoyancy drives it up for dissipation below the LFL.

With wind:

- A small low-pressure leak will be buoyant (up), while at the same time being driven in the wind direction where it dissipates quickly. Winds aid dilution.
- From a high-pressure pipe leak, momentum will drive it in the direction of the leak for some distance, then buoyancy will drive it up while at the same time the hydrogen is driven in the wind direction and diluted.

Pulling It All Together for Hydrogen (H_2)

H_2 is a fuel that is non-toxic and is typically stored as a cryogenic fluid or high pressure gas.

Because it is light, H_2 is very buoyant. Because the molecules barely interact, spilled LH_2 evaporates very quickly.

LH_2 has a lot of energy per mass, but is 2.4 times bigger than LNG and 4.2 times bigger than diesel fuel for the same stored energy.

The combustion properties of H_2 are well understood. The safety goal is to prevent fires, which also prevents other types of combustion.

H_2 Safety includes leak checking, using the right materials for H_2 contacting surfaces, keeping ignition sources away.

If possible, avoid designing spaces with long “run distances” to discourage DDT.

LH_2 pool fires burn out rapidly due to evaporation, H_2 fires radiate much less thermal energy than other types of fires because there is no carbon.

Hydrogen embrittlement is managed very effectively by using 304 and 316 stainless steel for hydrogen plumbing and manifolds.

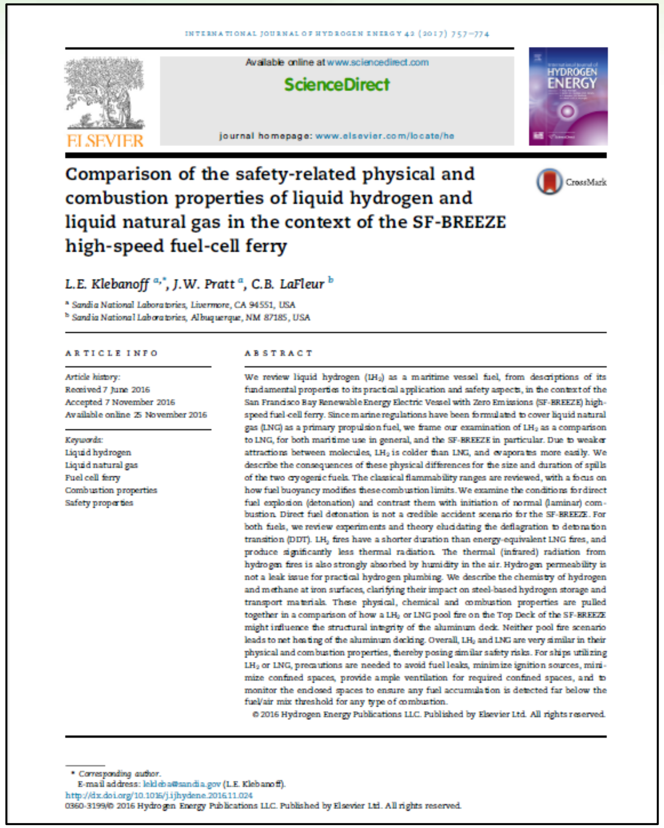
H_2 permeability is not a safety issue when using the right materials (304, 316 stainless steel).

H_2 diffusion is your friend, removing H_2 from trapped spaces if there is a way out (e.g., underneath piers).

Since H_2 is very light compared to air, H_2 will blow in the direction of the prevailing wind, while also rising due to buoyancy and diluting.

NFPA 2 is the science-based industrial regulation that considers the physical and combustion properties of H_2 in establishing site requirements for the safe use of H_2 at facilities.

Further Reading…..



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Comparison of the safety-related physical and combustion properties of liquid hydrogen and liquid natural gas in the context of the SF-BREEZE high-speed fuel-cell ferry

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ABSTRACT

We review liquid hydrogen (LH_2) as a maritime vessel fuel, from descriptions of its fundamental properties to its practical application and safety aspects, in the context of the San Francisco Bay Renewable Energy Electric Vessel with Zero Emissions (SF-BREEZE) high-speed fuel-cell ferry. Since marine regulations have been formulated to cover liquid natural gas (LNG) as a primary propulsion fuel, we frame our examination of LH_2 as a comparison to LNG, for both maritime use in general, and the SF-BREEZE in particular. Due to weaker attractions between molecules, LH_2 is colder than LNG, and evaporates more easily. We describe the consequences of these physical differences for the size and duration of spills of the two cryogenic fuels. The classical flammability ranges are reviewed, with a focus on how fuel buoyancy modifies these combustion limits. We examine the conditions for direct fuel explosion (detonation) and contrast them with initiation of normal (laminar) combustion. Direct fuel detonation is not a credible accident scenario for the SF-BREEZE. For both fuels, we review experiments and theory elucidating the deflagration to detonation transition (DDT). LH_2 fires have a shorter duration than energy-equivalent LNG fires, and produce significantly less thermal radiation. The thermal (infrared) radiation from hydrogen fires is also strongly absorbed by humidity in the air. Hydrogen permeability is not a leak issue for practical hydrogen plumbing. We describe the chemistry of hydrogen and methane at iron surfaces, clarifying their impact on steel-based hydrogen storage and transport materials. These physical, chemical and combustion properties are pulled together in a comparison of how a LH_2 or LNG pool fire on the Top Deck of the SF-BREEZE might influence the structural integrity of the aluminum deck. Neither pool fire scenario leads to net heating of the aluminum decking. Overall, LH_2 and LNG are very similar in their physical and combustion properties, thereby posing similar safety risks. For ships utilizing LH_2 or LNG, precautions are needed to avoid fuel leaks, minimize ignition sources, minimize confined spaces, provide ample ventilation for required confined spaces, and to monitor the enclosed spaces to ensure any fuel accumulation is detected far below the fuel/air mix threshold for any type of combustion.

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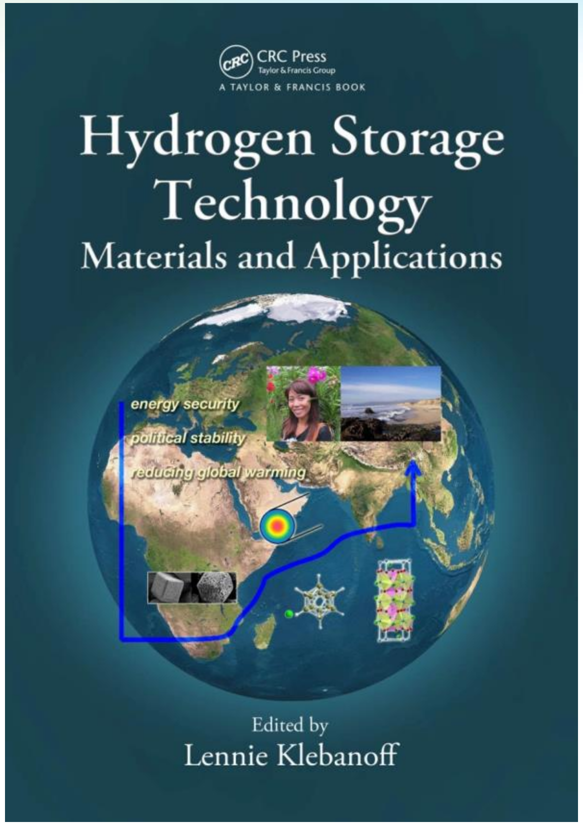
http://dx.doi.org/10.1016/j.ijhydene.2016.11.024

More information about the safety properties of H_2 gas and LH_2 can be found in:

L.E. Klebanoff et al., International Journal of Hydrogen Energy **42** (2017) 757 - 774.



More information about H_2 Technology in general.

Topics:

- H_2-based Energy
- H_2 Energy Conversion Devices
- All methods of H_2 Storage
- Engineered H_2 Storage Systems
- H_2 Codes and Standards

--published by CRC Press in 2012

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For more information on H_2/Fuel Cell Maritime Projects visit:
https://maritime.sandia.gov

- Past and current maritime projects
- Download reports

Thank You!

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