# Safety issues of hydrogen in vehicles

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## Properties of hydrogen

Hydrogen is an odorless, colorless gas. With molecular weight of 2.016, hydrogen is the lightest element. Its density is about 14 times less than air (0.08376 kg/m$^3$ at standard temperature and pressure). Hydrogen is liquid at temperatures below 20.3 K (at atmospheric pressure). Hydrogen has the highest energy content per unit mass of all fuels - higher heating value is 141.9 MJ/kg, almost three times higher than gasoline. Some important properties of hydrogen are compiled in Table 1.

**Table 1. Selected properties of hydrogen**

| | | |
|---|---|---|
| Molecular weight | | 2.016 |
| Density | kg/m$^3$ | 0.0838 |
| Higher heating value | MJ/kg<br>MJ/m$^3$ | 141.90<br>11.89 |
| Lower heating value | MJ/kg<br>MJ/m$^3$ | 119.90<br>10.05 |
| Boiling temperature | K | 20.3 |
| Density as liquid | kg/m$^3$ | 70.8 |
| Critical point<br>temperature<br>pressure<br>density | <br>K<br>bar<br>kg/m$^3$ | <br>32.94<br>12.84<br>31.40 |
| Self-ignition temperature | K | 858 |
| Ignition limits in air | (vol. %) | 4-75 |
| Stoichiometric mixture in air | (vol. %) | 29.53 |
| Flame temperature in air | K | 2,318 |
| Diffusion coefficient | cm$^2$/s | 0.61 |
| Specific heat ($c_p$) | kJ/(kg ·K) | 14.89 |

Like any other fuel or energy carrier hydrogen poses risks if not properly handled or controlled. The risk of hydrogen, therefore, must be considered relative to the common fuels such as gasoline, propane or natural gas. The specific physical characteristics of hydrogen are quite different from those common fuels. Some of those properties make hydrogen potentially less hazardous, while other hydrogen characteristics could theoretically make it more dangerous in certain situations.

Since hydrogen has the smallest molecule it has a greater tendency to escape through small openings than other liquid or gaseous fuels. Based on properties of hydrogen such as density, viscosity and diffusion coefficient in air, the propensity of hydrogen to leak through holes or joints of low pressure fuel lines may be only 1.26 to 2.8 times faster than a natural gas leak through the same hole (and not 3.8 times faster as frequently assumed based solely on diffusion coefficients). Experiments have indicated that most leaks from residential natural gas lines are laminar [128]. Since natural gas has over three times the energy density per unit volume the natural gas leak would result in more energy release than a hydrogen leak.

For very large leaks from high pressure storage tanks, the leak rate is limited by sonic velocity. Due to higher sonic velocity (1308 m/s) hydrogen would initially escape much faster than natural gas (sonic velocity of natural gas is 449 m/s). Again, since natural gas has more than three times the energy density than hydrogen, a natural gas leak will always contain more energy.

If a leak should occur for whatever reason, hydrogen will disperse much faster than any other fuel, thus reducing the hazard levels. Hydrogen is both more buoyant and more diffusive than either gasoline, propane or natural gas. Table 2 compares some properties and leak rates for hydrogen and natural gas.

**Table 2 Properties and leak rates of hydrogen and natural gas**

| | Hydrogen | Natural gas |
|---|---|---|
| Flow parameters | | |
| Diffusion coef. ($cm^2/s$) | 0.61 | 0.16 |
| Viscosity (μ-poise) | 87.5 | 100 |
| Density ($kg/m^3$) | 0.0838 | 0.651 |
| Sonic velocity (m/s) | 1308 | 449 |
| Relative leak rates | | |
| Diffusion | 3.80 | 1 |
| Laminar flow | 1.23 | 1 |
| Turbulent flow | 2.83 | 1 |
| Sonic flow | 2.91 | 1 |

Hydrogen/air mixture can burn in relatively wide volume ratios, between 4% and 75% of hydrogen in air. Other fuels have much lower flammability ranges, viz., natural gas 5.3-15%, propane 2.1-10%, and gasoline 1-7.8%. However, the range has a little practical value. In many actual leak situations the key parameter that determines if a leak would ignite is the lower flammability limit, and hydrogen's lower flammability limit is 4 times higher than that of gasoline, 1.9 times higher than that of propane and slightly lower than that of natural gas.

Hydrogen has a very low ignition energy (0.02 mJ), about one order of magnitude lower than other fuels. The ignition energy is a function of fuel/air ratio, and for hydrogen it reaches minimum at about 25%-30% hydrogen content in air. At the lower flammability limit hydrogen ignition energy is comparable with that of natural gas [109].

Hydrogen has a flame velocity 7 times faster than that of natural gas or gasoline. A hydrogen flame would therefore be more likely to progress to a deflagration or even a detonation than other fuels. However, the likelihood of a detonation depends in a complex manner on the exact fuel/air ratio, the temperature and particularly the geometry of the confined space. Hydrogen detonation in the open atmosphere is highly unlikely.

The lower detonability fuel/air ratio for hydrogen is 13%-18%, which is two times higher than that of natural gas and 12 times higher than that of gasoline. Since the lower flammability limit is 4% an explosion is possible only under the most unusual scenarios, e.g., hydrogen would first have to accumulate and reach 13% concentration in a closed space without ignition, and only then an ignition source would have to be triggered.

Should an explosion occur, hydrogen has the lowest explosive energy per unit stored energy in the fuel, and a given volume of hydrogen would have 22 times less explosive energy than the same volume filled with gasoline vapor.

Hydrogen flame is nearly invisible, which may be dangerous, because people in the vicinity of a hydrogen flame may not even know there is a fire. This may be remedied by adding some chemicals that will provide the necessary luminosity. The low emissivity of hydrogen flames means that near-by materials and people will be much less likely to ignite and/or hurt by radiant heat transfer. The fumes and soot from a gasoline fire pose a risk to anyone inhaling the smoke, while hydrogen fires produce only water vapor (unless secondary materials begin to burn).

Liquid hydrogen presents another set of safety issues, such as risk of cold burns, and the increased duration of leaked cryogenic fuel. A large spill of liquid hydrogen has some characteristics of a gasoline spill, however it will dissipate much faster. Another potential danger is a violent explosion of a boiling liquid expanding vapor in case of a pressure relief valve failure.

**Hydrogen vehicle hazards**

Hydrogen onboard a vehicle may pose a safety hazard. The hazards should be considered in situations when vehicle is inoperable, when vehicle is in normal operation and in collisions. Potential hazards are due to fire, explosion of toxicity. The latter can be ignored since neither hydrogen nor its fumes in case of fire are toxic. Hydrogen as a source of fire or explosion may come from the fuel storage, from the fuel supply lines or from the fuel cell. The fuel cell poses the least hazard, although hydrogen and oxygen are separated by a very thin (~20-30 μm) polymer membrane. In case of a membrane rupture hydrogen and oxygen would combine, but in that case the fuel cell would lose its potential which should be easily detected by a control system. In that case the supply lines should be immediately disconnected. The fuel cell operating temperature (60° to 90°C) is too low to be a thermal ignition source, however hydrogen and oxygen may combine on the catalyst surface and create ignition conditions. However, the potential damage would be limited due to a small amount of hydrogen present in the fuel cell and fuel supply lines.

The largest amount of hydrogen at any given time is present in the tank. Several tank failure modes may be considered in both normal operation and collision, such as:

- catastrophic rupture, due to manufacturing defect in tank, a defect caused by abusive handling of the tank or stress fracture, puncture by a sharp object, external fire combined with failure of pressure relief device to open;
- massive leak, due to faulty pressure relief device tripping without cause or chemically induced fault in tank wall; puncture by a sharp object, operation of pressure relief device in a case of fire (which is the purpose of the device).
- slow leak due to stress cracks in tank liner, faulty pressure relief device, or faulty coupling from tank to the feed line, or impact-induced openings in fuel line connection.

A similar failure analysis may be applied to both high pressure and low pressure fuel lines.

In a study conducted on behalf of Ford Motor Company, Directed Technologies, Inc., has performed a detailed assessment of probabilities of the above failure modes. The conclusion of the study is that a catastrophic rupture is a highly unlikely event. However, several failure modes resulting in large hydrogen release or a slow leak has been identified both in normal operation and in collision.

Most of the above discussed failure modes may be either avoided or their occurrence and consequences minimized by:

- leak prevention through a proper system design, selection of adequate equipment (some further testing and investigation may be required), allowing for tolerance of shocks and vibrations, locating a pressure relief device vent, protecting the high pressure lines, installing a normally closed solenoid valve on each tank feed line, etc.
- leak detection by either a leak detector or by adding an odorant to the hydrogen fuel (this may be a problem for fuel cells);
- ignition prevention, through automatically disconnecting battery bank, thus eliminating source of electrical sparks which are the cause of 85% gasoline fires after a collision, by designing the fuel supply lines so that they are physically separated from all electrical devices, batteries, motors and wires to the maximum extent possible, and by designing the system for both active and passive ventilation (such as an opening to allow the hydrogen to escape upward).

The risk is typically defined as a product of probability of occurrence and consequences. The above mentioned study by Directed Technologies Inc. includes a detailed risk assessment of several most probable or most severe hydrogen accident scenarios, such as:

- Fuel tank fire or explosion in unconfined spaces
- Fuel tank fire or explosion in tunnels
- Fuel line leaks in unconfined spaces
- Fuel leak in garage
- Refueling station accidents

The conclusion of this study is that in a collision in open spaces, a safety-engineered hydrogen fuel cell car should have less potential hazard than either natural gas or a gasoline vehicle. In a tunnel collision, a hydrogen fuel cell vehicle should be nearly as safe as a natural gas vehicle, and both should be potentially less hazardous than a gasoline or propane vehicle, based on computer simulations comparing substantial post collision release of gasoline and natural gas in a tunnel. The greatest potential risk to the public appears to be a slow leak in an enclosed home garage, where an accumulation of hydrogen could lead to fire or explosion if no hydrogen detection or risk mitigation devices or measures are applied (such as passive or active ventilation).

## Conclusions and recommendations

In conclusion, hydrogen appears to poses risks of the same order of magnitude as other fuels. In spite of public perception, in many aspects hydrogen is actually a safer fuel than gasoline and natural gas. As a matter of fact, hydrogen has a very good safety record, as a constituent of the "town gas" widely used in Europe and USA in the 19th and early 20th century, as a commercially used industrial gas, and as a fuel in space programs. There have been accidents, but nothing that would characterize hydrogen as more dangerous than other fuels.

Nevertheless, further research may be needed in exploring and quantifying both causes and consequences of hydrogen leaks, development of new materials and couplings less susceptible to hydrogen leaks, lifetime and failure modes of fuel cells, etc. The results should be disseminated throughout the scientific community and used to generate the codes and standards for hydrogen use in the vehicles. Selected information should be fed to media and general public, in order to change the image of hydrogen as a dangerous fuel. Practical demonstrations may be extremely valuable in that aspect.

## References

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