Liquid hydrogen

Hydrogen is colorless as a liquid. Its vapors are colorless, odorless, tasteless, and highly flammable.

Liquid hydrogen is noncorrosive. Special materials of construction are not required. However, because of its extremely cold temperature, equipment must be designed and manufactured of material that is suitable for extremely low temperature operation. Vessels and piping must be selected and designed to withstand the pressure and temperatures involved and comply with applicable codes and regulations.

Flammability

The wide flammability range, 4% to 74% in air, and the small amount of energy required for ignition necessitate special handling to prevent the inadvertent mixing of hydrogen with air. Care should be taken to eliminate sources of ignition, such as sparks from electrical equipment, static electricity sparks, open flames, or any extremely hot objects. Hydrogen and air mixtures within the flammable range can explode and may burn with a pale blue, almost invisible flame.

Manufacture

Hydrogen is produced by the steam reforming of natural gas, the electrolysis of water and the dissociation of ammonia. Hydrogen is also a by-product of petroleum distillation and chlorine manufacture. The primary method of hydrogen generation is steam reforming of natural gas. Other feedstocks, which are less common, can include ethane, propane, butane, and light and heavy naphtha. The steam reforming process produces syngas, which is a mixture of hydrogen and carbon monoxide. Regardless of the method of production, the product stream is separated into its components. The hydrogen is dried and purified. This gaseous hydrogen is then compressed and cooled to sufficiently low cryogenic temperatures by the use of heat exchangers, along with reciprocating and tube expanders, to form liquid hydrogen.

Uses

Liquid hydrogen is used in large volumes in the space program as a primary rocket fuel for combustion with oxygen or fluorine, and as a propellent for nuclear powered rockets and space vehicles. Although used more commonly in the gaseous state, hydrogen is stored and transported as a liquid. Hydrogen is a raw material for innumerable chemical processes ranging from the manufacturing of high-density polyethylene and polypropylene to the hydrogenation of food-grade oils. In the metallurgical industry, hydrogen is used to reduce metal oxides and prevent oxidation in heat treating certain metals and alloys. Hydrogen is also used by semiconductor manufacturers.

Health effects

Hydrogen gas is odorless and nontoxic but may produce suffocation by diluting the concentration of oxygen in air below levels necessary to support life.

Caution: The amount of hydrogen gas necessary to produce oxygen-deficient atmospheres is well within the flammable range, making fire and explosion the primary hazards associated with hydrogen and air atmospheres.

Table 1: Liquid Hydrogen Physical and Chemical Properties

Chemical Formula	H_2
Molecular Weight	2.016
Boiling Point @ 1 atm	–423.2°F (–252.9°C)
Freezing Point @ 1 atm	–434.8°F (–259.3°C)
Critical Temperature	–400.4°F (–240.2°C)
Critical Pressure	186 psia (12.7 atm)
Density, Liquid @ B.P., 1 atm	4.42 lb./cu.ft. (70.8 kg/cubic meter)
Density, Gas @ 68°F (20°C), 1 atm	0.005229 lb./cu.ft. (0.0838 kg/cubic meter)
Specific Gravity, Gas (air=1) @ 68°F (20°C), 1 atm	0.0696
Specific Gravity, Liquid @ B.P., [water=1 @ 68˚F (20˚C)]	0.0710
Specific Volume @ 68°F (20°C), 1 atm	191 cu. ft./lb.
Latent Heat of Vaporization	389 Btu/lb. mole
Flammable Limits @ 1 atm in air	4.00%–74.2% (by Volume)
Flammable Limits @ 1 atm in oxygen	3.90%–95.8% (by Volume)
Detonable Limits @ 1 atm in air	18.2%–58.9% (by Volume)
Detonable Limits @ 1 atm in oxygen	15%–90% (by Volume)
Autoignition Temperature @ 1 atm	1,060°F (571°C)
Expansion Ratio, Liquid to Gas, B.P. to 68°F (20°C)	1 to 845

Figure 1: Typical Liquid Hydrogen Tanker

Containers

Liquid hydrogen is normally stored in on-site storage systems typically consisting of a tank, vaporizer and controls. Systems are selected in accordance to usage rate, pressure and regulations.

Tanks

Tanks are usually cylindrical in shape and placed in a horizontal position. However, some vertical cylindrical tanks and spherical tanks are in use. Standard tank sizes range from 1,500 gallons to 25,000 gallons. Tanks are vacuum-insulated. Pressure relief valves protect the tanks and are designed to ASME specifications.

Transferring liquid

Two persons should be present when liquid hydrogen is being used or transferred or when a container is moved. This does not apply where specially trained employees of the liquid hydrogen supplier, who routinely handle liquid hydrogen, are involved.

Hydrogen is normally vaporized and used as a gas. Withdrawal of liquid from a tanker, tank, or liquid cylinder requires the use of a closed system, with proper safety relief devices, which can be evacuated and/or purged to eliminate the possibility of creating a flammable atmosphere or explosive mixture of liquid air and liquid hydrogen. Purging should be done with helium since liquid hydrogen can solidify other gases, such as nitrogen, and cause plugging and possible rupture of the transfer line or storage vessel. Liquid transfer lines must be vacuum-insulated to minimize product loss through vaporization or the formation of liquid air on the lines with subsequent oxygen enrichment. All equipment must be electrically grounded and bonded before transferring liquid.

Shipment

Liquid hydrogen is transported by liquid semitrailers with a capacity of 12,000 to 17,000 gallons. The stationary tanks are filled from these tankers. Tankers are basically of the same design as the stationary tanks but in addition must meet the requirements of the Department of Transportation. Figure 1 is a typical liquid hydrogen tanker.

Safety considerations

The hazards associated with handling liquid hydrogen are fire, explosion, asphyxiation, and exposure to extremely low temperatures. Consult the Air Products Safety Data Sheet (SDS) for safety information on the gases and equipment you will be using. The potential for forming and igniting flammable mixtures containing hydrogen may be higher than for other flammable gases because:

1. Hydrogen migrates quickly through small openings.
2. The minimum ignition energy for flammable mixtures containing hydrogen is extremely low.

Hydrogen burns with a very pale blue to almost invisible flame, therefore injury may result from unknowingly walking into a hydrogen fire. The fire and explosion hazards can be controlled by appropriate design and operating procedures. Preventing the formation of combustible fuel-oxidant mixtures and removing or otherwise inerting potential sources of ignition (electric spark, static electricity, open flames, etc.) in areas where the hydrogen will be used is essential. Careful evacuation and purge operations should be used to prevent the formation of flammable or explosive mixtures. Adequate ventilation will help reduce the possible formation of flammable mixtures in the event of a hydrogen leak or spill and will also helps eliminate the potential hazard of asphyxiation. Protective clothing should be worn to prevent exposure to extremely cold liquid and cold hydrogen vapors, and also the potential exposure to a flash fire.

3. Cold burns may occur from short contact with frosted lines, liquid air that may be dripping from cold lines or vent stacks, vaporizer fins, and vapor leaks.

Air will condense at liquid hydrogen temperatures and can become an oxygen-enriched liquid due to the vaporization of nitrogen. Oxygen-enriched air increases the combustion rate of flammable and combustible materials, including clothing.

Purging

Gaseous and liquid hydrogen systems must be purged of air, oxygen, or other oxidizers prior to admitting hydrogen to the systems, and purged of hydrogen before opening the system to the atmosphere. Purging should be done to prevent the formation of flammable mixtures and can be accomplished in several ways.

Piping systems and vessels intended for gaseous hydrogen service should be inerted by suitable purging or evacuation procedures. If the piping systems are extensive or complicated, successive evacuations broken first by an inert gas and finally with hydrogen are most reliable.

Evacuating and purging of equipment in gaseous hydrogen service should include the following considerations:

1. Evacuate the equipment and break vacuum with an inert gas, such as nitrogen. If equipment design does not permit evacuation, then pressurize and purge the system with an inert gas.

2. Repeat step 1 at least three times. If analytical equipment is available, purge system until oxygen content of residual gas is either less than or meets the process specification impurity level.

3. Hydrogen may now be introduced to the equipment.

4. Flush system with hydrogen until required purity is reached. Vent all waste hydrogen through a flue or flare stack.

Any purge method should be repeated as often as required to be certain a flammable mixture cannot be formed upon introducing hydrogen or air to the system.

Buildings

Liquid hydrogen is normally vaporized into its gaseous state and piped into buildings for usage. For storage of liquid hydrogen in a building, refer to regional codes or standards (e.g., National Fire Protection Association (NFPA) "Storage, Use and Handling of Compressed Gases and Cryogenic Fluids" - NFPA 55). The following items pertain to a building in which gaseous hydrogen is being used.

1. Provide adequate ventilation, particularly in roof areas where hydrogen might collect. Forced ventilation may be necessary in some applications.

2. The atmosphere in areas in which hydrogen gas may be vented and might collect should be tested with a portable or continuous flammable gas analyzer.

3. Provide an explosion venting surface or vents, taking care to vent a pressure wave to areas where people or other equipment will not become involved. Explosion vents may not be required where small quantities of hydrogen are involved.

4. Buildings should be electrically grounded.

5. Electrical equipment must conform to the existing National Electrical Codes. Electrical equipment not conforming must be located outside the electrical area classified as hazardous. All electrical equipment must be grounded.

6. Building materials should be noncombustible.

7. Post "No Smoking" and "No Open Flames" signs.

Outdoor storage tank requirements

Location—general requirements

1. The storage containers should be located so that they are readily accessible to mobile supply equipment at ground level and to authorized personnel, and where they are not exposed to electric power lines, flammable liquid lines, flammable gas lines, or lines carrying oxidizing materials.

2. It is advisable to locate the liquefied hydrogen container on ground higher than flammable liquid storage or liquid oxygen storage. Where it is necessary to locate the liquefied hydrogen container on ground that is lower than adjacent flammable liquid storage or liquid oxygen storage, suitable protective means (such as diking, diversion curbs, or grading) should be taken.

3. Storage sites should be fenced and posted to prevent entrance by unauthorized personnel. Sites should also be placarded as follows: "Liquefied Hydrogen Flammable Gas – No Smoking – No Open Flames."

4. Weeds or similar combustibles should not be permitted within 25 feet of any liquefied hydrogen equipment.

Location—specific requirements

1. The minimum distance in feet from liquefied hydrogen systems of indicated storage capacity located outdoors to any specified exposure should be in accordance with the current version of NFPA 55: "Compressed Gases and Cryogenic Fluid Code."*

2. Roadways and yard surfaces located below liquefied hydrogen piping, from which liquid air may drip, shall be constructed of noncombustible materials.

3. If protective walls are provided, they shall be constructed of noncombustible materials.

4. Electrical wiring and equipment located within three feet of a point where connections are regularly made and disconnected shall be in accordance with national standards. In the United States the applicable codes are; Article 501 of the National Electrical Code, NFPA No. 70, for Class 1, Group B, Division 1 locations.

5. Electrical wiring and equipment located beyond three feet but within 25 feet of a point where connections are regularly made and disconnected, or within 25 feet of a liquid hydrogen storage container shall be in accordance with national standards. In the United States the applicable codes are; Article 501 of the National Electrical Code, NFPA No. 70, for Class 1, Group B, Division 2 locations. This requirement does not apply to electrical equipment that is installed on mobile supply trucks or tank cars from which the storage container is filled.

6. The liquefied hydrogen container and associated piping shall be electrically bonded and grounded.

7. Adequate lighting shall be provided for nighttime transfer operations.

Personal protection

1. Personnel must be thoroughly familiar with the properties and safety precautions before being allowed to handle hydrogen and/or associated equipment.

2. Full face shield, safety glasses, insulated or leather gloves, long-sleeved shirts, and pants without cuffs should be worn when working on liquid hydrogen systems. Pant legs should be worn outside of boots. Flame retardant clothing is strongly recommended when working on or around liquid hydrogen systems.

3. In the event of emergency situations, a fire-resistant suit and gloves should be worn. SCBA is also recommended, but remember that oxygen-deficient atmospheres are within the flammable range and should not be entered. Increase ventilation to areas potentially containing a flammable atmosphere before entering.

* Publication is available from NFPA, 1 Batterymarch Park, Quincy, MA 02169-7471

First aid

Persons suffering from lack of oxygen should be moved to areas with normal atmosphere. **Self-contained breathing apparatus may be required to prevent asphyxiation of rescue workers.** Rescue workers should not enter a flammable atmosphere. Assisted respiration and supplemental oxygen should be given if the victim is not breathing.

Extensive tissue damage or burns can result from exposure to liquid hydrogen or cold hydrogen vapors. Flush affected areas with large volumes of tepid water 105°F–115°F (41°C–46°C) to reduce freezing. Loosen any clothing which may restrict circulation. Do not apply heat. Do not rub frozen skin, as tissue damage may result. Cover affected area with a sterile protective dressing or with clean sheets if area is large, and protect area from further injury. Seek medical attention promptly.

Note to physician

Frozen tissues should be treated promptly by immersion in a water bath at a temperature between 105°F–115°F (41°C–46°C). Avoid the use of dry heat.

Frozen tissues are painless and appear waxy with a pallid yellow color. Tissues become painful and edematous upon thawing, and the pale color turns to pink or red as circulation of blood is restored. Potent analgesics are often indicated. Tissues that have been frozen show severe, widespread cellular injury and are highly susceptible to infections and additional trauma. Therefore, rapid rewarming of tissues in the field is not recommended if transportation to a medical facility will be delayed.

If the body temperature is depressed, the patient must be warmed gradually. Shock may occur during the correction of hypothermia. Cardiac dysrhythmias may be associated with severe hypothermia.

Fire fighting

Hydrogen is easily ignited by heat, open flames, electrical sparks, and static electricity. It will burn with a pale blue, almost invisible flame. Most hydrogen fires will have the flame characteristic of a torch or jet and will originate at the point where the hydrogen is discharging. If a leak is suspected in any part of a system, a hydrogen flame can be detected by cautiously approaching with an outstretched broom, lifting it up and down.

The most effective way to fight a hydrogen fire is to shut off the flow of gas. If it is necessary to extinguish the flame in order to get to a place where the flow of hydrogen can be shut off, a dry powder extinguisher is recommended. However, if the fire is extinguished without stopping the flow of gas, an explosive mixture may form, creating a more serious hazard than the fire itself, should reignition occur from the hot surfaces or other sources.

The usual fire fighting practice is to prevent the fire from spreading and let it burn until the hydrogen is consumed. Dry powder fire extinguishers should be available in the area. A fire blanket should be conveniently located. An adequate water supply should be available to keep surrounding equipment cool in the event of a hydrogen fire. The local fire department should be advised of the nature of the products handled and made aware of the best known methods for combating hydrogen fires.

Pipeline fires, where shutoff is possible and with flame characteristics of a jet or torch, can be effectively controlled as follows:

1. Slowly reduce the flow of hydrogen feeding the fire. Do not completely stop the flow.
2. When the jet is small enough to be approached, put out the flame with a carbon dioxide or dry powder extinguisher.
3. Close off the supply of hydrogen completely.
4. Ventilate the area thoroughly.

Emergency Response System

T 800-523-9374 (Continental U.S. and Puerto Rico)
T +1-610-481-7711 (other locations)
For regional ER telephone numbers, please refer to the local SDS 24 hours a day, 7 days a week for assistance involving Air Products and Chemicals, Inc. products

Technical Information Center

T 800-752-1597 (U.S.)
T +1-610-481-8565 (other locations)
Monday–Friday, 8:00 a.m.–5:00 p.m. EST
F 610-481-8690
gastech@airproducts.com

For more information, please contact us at:

Corporate Headquarters
Air Products and Chemicals, Inc.
1940 Air Products Blvd.
Allentown, PA 18106-5500
T: 610-481-4911

AIR PRODUCTS

tell me more
airproducts.com

 900-13-082-US