



CRYO-STORAGE AND TECHNOLOGIES (CST)

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SafetyAlert-9 Liquid Hydrogen

General

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 should be designed to American Society of Mechanical Engineers (ASME) Code and the American National Standards Institute (ANSI) Pressure Piping Code or Department of Transportation (DOT) codes for the pressures and temperatures involved.

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, 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 propellant 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.

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



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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 semi-trailers 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 CST Material Safety Data Sheet (MSDS) 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.

Burns may result from unknowingly walking into a hydrogen fire. The fire and explosion hazards can be controlled by appropriate design and operating procedures

Table 1: 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 @ BP, 1 atm	4.42 lb./cu.ft.
Density, Gas @ 68°F (20°C), 1 atm	0.005229 lb./cu.ft.
Specific Gravity, Gas (air=1) @ 68°F (20°C), 1 atm	0.0696
Specific Gravity, Liquid @ BP (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, BP to 68°F (20°C)	1 to 845

Figure 1

Typical Liquid Hydrogen Tanker



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 help eliminate the potential hazard of asphyxiation. Protective clothing should be worn to prevent exposure to extremely cold liquid and cold hydrogen vapors.

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.

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 the most recent edition of the National Fire Protection Association pamphlet *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 Table 2.
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 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 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.

Table 2 Minimum Distance (ft) from Liquefied Hydrogen Systems to Exposures*

Type of Exposure	Total Liquefied Hydrogen Storage (Capacity in Gallons)		
	39,633 to 3,500	3,501 to 15,000	15,001 to 75,000
1. Building/Structure			
a) Wall(s) adjacent to system constructed of noncombustible or limited combustible materials			
1) Sprinklered building/structure or unsprinklered building/structure having noncombustible contents	5 ¹	5 ¹	5 ¹
2) Unsprinklered building/structure with combustible contents.			
Adjacent wall(s) with fire-resistance rating less than 3 hours. ²	25	50	75
Adjacent wall(s) with fire-resistance rating of 3 hours or greater. ²	5	5	5
b) Wall(s) adjacent to system constructed of combustible materials			
1) Sprinklered building/structure	50	50	50
2) Unsprinklered building/structure	50	75	100
2. Wall Openings			
a) Openable	75	75	75
b) Unopenable	25	50	50
3. Air Compressor intakes, inlets for Air-Conditioning or Ventilating Equipment	75	75	75
4. All Classes of Flammable and Combustible Liquids (Above ground and Vent or Fill Openings if below ground) (See 5-1.3) ³	50	75	100
5. Between Stationary Liquefied Hydrogen Containers	5	5	5
6. Flammable Gas Storage (other than hydrogen)	50	75	75
7. Liquid Oxygen Storage and other Oxidizers (See 5-1.3)	75	75	75
8. Combustible Solids	50	75	100
9. Open Flames and Welding	50	50	50
10. Places of Public Assembly	75	75	75
11. Public Ways, Railroads, and Property Lines	25	50	75
12. Protective Structures	5 ³	5 ³	5 ³

¹ Portions of wall less than 10 ft (3 m) (measured horizontally) from any part of a system shall have a fire-resistance rating of at least ½ hour.

² Exclusive of windows and doors.

³ Distances may be reduced to 15 ft for Class IIIB combustible liquids.

* Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids (NFPA 55)
For S1 Units: 1 ft = 0.305 m; 1 gal = 3.785 L.

Personnel Protection

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

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.** 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 (105-115°F (41-46°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 (105-115°F (41-46°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.

Information Sources

- Compressed Gas Association
1725 Jefferson Davis Highway, Suite 1004
Arlington, VA 22202-4102
Phone: 1-703-412-0900
- National Fire Protection Association
1 Batterymarch Park, P.O. Box 9101
Quincy, MA 02269-9101
Phone: 1-800-344-3555

Emergency Response Telephone Numbers

USA

CHEMTRAC

1-800-424-9300 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
703-527-3887 for calls originating elsewhere (Collect calls are accepted)

CHEM-TEL, INC.

1-800-255-3924 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
813-248-0585 for calls originating elsewhere (Collect calls are accepted)

INFOTRAC

1-800-535-5053 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
352-323-3500 for calls originating elsewhere (Collect calls are accepted)

3E COMPANY

1-800-451-8346 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
760-602-8703 for calls originating elsewhere (Collect calls are accepted)

NATIONAL RESPONSE CENTER (NRC)

Call NRC (24 Hours)

1-800-424-8802 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
202-267-2675 in the District of Columbia

MILITARY SHIPMENTS

703-697-0218 Explosives/Ammunition Incidents (Collect calls accepted)
1-800-851-8061 All other dangerous goods incidents

NATIONWIDE POISON CONTROL CENTER (United States Only)

1-800-222-1222 (Toll Free in the U.S.)

CANADA

CANUTEC

613-996-6666 (Collect calls are accepted)
*666 Cellular (In Canada only)

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