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NFPA 704 hazard diamond for hydrogen.

Hydrogen Safety

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Introduction

In order to successfully implement a renewable hydrogen economy, the safe production, storage, transport, handling and use of hydrogen is imperative. Like all fuels, hydrogen has inherent hazards and must be handled carefully. However, hydrogen has gained an undeserved reputation as a highly dangerous substance. In fact, hydrogen has been used for years in industrial processes and as a fuel by NASA, and has earned an excellent safety record. Like other fuels, hydrogen can be handled and used safely.

Hydrogen has some unique properties compared to other fuels. Some of these unique characteristics can make it safer to work with, while others make it more hazardous. Therefore, prior to working with hydrogen systems, personnel should have a basic understanding of hydrogen gas properties and associated hazards, and should be properly trained in the safe use of hydrogen systems.

The principal hazard presented by hydrogen systems is the uncontrolled combustion of accidentally released hydrogen. In order for hydrogen to combust, an oxidizer and a source of ignition must be present. Hydrogen is combustible over a wide range of concentrations in air, and various common physical processes (open flames, hot surfaces, friction, electrical spark, static discharge) can serve as sources of ignition. Therefore, one of the most important ways to ensure the safe use of hydrogen is to make sure that there is adequate ventilation to prohibit the creation of a flammable gaseous mixture. In addition, eliminating or minimizing hydrogen leaks and ignition sources are important safety measures. These types of safety measures are best implemented through sound engineering design and proper operation and maintenance practices.

Because hydrogen has an intrinsically low volumetric energy density, storage of hydrogen at high pressure (up to 10,000 psig) and cryogenic liquid storage are being considered for transportation applications. These storage options present there own unique hazards.

The Hindenburg Accident

The Hindenburg accident is probably the one incident that has most contributed to hydrogen's reputation as a very dangerous substance. In fact, hydrogen was not the cause of the Hindenburg accident. Addison Bain, a retired NASA engineer, has studied the Hindenburg disaster extensively. He concluded that the cause of the accident was an electrostatic discharge that ignited the highly flammable skin of the zeppelin. The skin was made of a cotton fabric coated with iron oxide and cellulose butyrate acetate, the latter which included a suspension of aluminum powder. These are essentially the ingredients for a solid rocket propellant.

The Hindenburg used diesel fuel for propulsion and a hydrogen ballast for buoyancy. Once the skin caught fire, the diesel fuel tanks and the hydrogen ballast eventually ignited as well, and the whole thing went up in flames. This truly was a horrendous disaster; however, hydrogen was not to blame. In the words of Addison Bain, the lesson to be learned was "don't coat your air ship with rocket propellant."

Hydrogen Codes and Standards

The safe design of hydrogen systems and procedures for safe operation and maintenance of hydrogen systems can be promulgated through codes and standards. Currently an extensive array of codes and standards covering the safe use of hydrogen as a fuel are under development. This effort is an essential aspect of the U.S. Department of Energy (DOE) Hydrogen Program. The National Hydrogen Association is under contract with the DOE to identify and develop the necessary standards in conjunction with a myriad of industry groups. These groups include the National Fire Protection Association (NFPA), the International Standards Organization (ISO), the Society of Automotive Engineers (SAE), Underwriters Laboratory (UL), the American Society of Mechanical Engineers (ASME), the Canadian Standards Association (CSA), the International Code Council (ICC), the Compressed Gas Association (CGA), the International Electrotechnical Commission (IEC), the American National Standards Institute (ANSI), and the Institute of Electrical and Electronics Engineers (IEEE), among others.

Some Physical Properties of Hydrogen and Methane

	Hydrogen	**Methane**
Autoignition temperature	520° C	630° C

Some Physical Properties of Hydrogen and Methane

Heat of combustion (lower heating value)	120 MJ/kg	50 MJ/kg
Lower flammable limit (in air)	4% by volume	5.3% by volume
Upper flammable limit (in air)	75% by volume	17% by volume
Stoichiometric mixture (in air)	29.5% by volume	9.5% by volume
Density (20C, 100kPa)	0.61 cm2/s	0.16 cm2/s
Viscosity (20C, 100kPa)	8.814 µPa-s	11.023 µPa-s
Flame temperature (in air)	2045° C	1325° C
Minimum ignition energy (in air)	0.017 mJ	0.274 mJ

Properties of Gaseous Hydrogen

Some important characteristics of hydrogen include: its high propensity to leak, its high dispersion characteristics, the difficulty of hydrogen gas and flame detection, its flammability and ignition characteristics, its combustion characteristics, hydrogen embrittlement and material compatibility issues, and associated physiological hazards.

Propensity to Leak

The low viscosity and small molecular size of hydrogen give it a greater propensity to leak than other common gaseous fuels. For a given pressure and hole size, hydrogen will leak approximately 2.8 times faster than natural gas and 5.1 times faster than propane on a volumetric basis. The energy density of hydrogen is much lower than that of methane or propane; therefore, the energy leakage rate for hydrogen would be only 0.88 times that of methane and 0.61 times that of propane for a given pressure and hole size. A gaseous hydrogen plumbing system that is truly leak-free is nearly impossible to build without all welded joints. However, building a system that is as tight as possible and minimizes hydrogen gas leaks is obviously desirable. In addition, adequate ventilation in the vicinity of the hydrogen system is a must.

Dispersion

Hydrogen is more diffusive and more buoyant than gasoline, methane, and propane and therefore tends to disperse more rapidly. For low-momentum, gaseous hydrogen leaks, buoyancy affects gas motion more significantly than diffusivity. For high-momentum leaks, which are more likely in high-pressure systems, buoyancy effects are less significant, and the direction of the release will determine the gas motion. Localized air currents due to wind or ventilation will also affect gas movement. At low concentrations the effect of buoyancy becomes less significant because the density of the hydrogen-air mixture is similar to that of air.

As a consequence of these dispersion properties, hydrogen gas tends to disperse readily and form an ignitable mixture with air. However, in an unconfined atmosphere this mixture will quickly dilute to levels below the lower flammability limit. Although the rapid mixing properties of hydrogen lead to more rapid formation of a combustible mixture, they also lead to a faster dispersal and generally shorter duration of a flammable hazard than other fuels on an equal volume basis.

Hydrogen Gas and Flame Detection

Hydrogen is a colorless, odorless, and tasteless gas. Its presence cannot be detected by human senses. In addition, the unique characteristics of a hydrogen fire make it difficult to perceive with the human senses. In contrast to other hydrocarbon fuels, which radiate most of their energy as visible light and heat, a hydrogen flame radiates significantly less heat and virtually no visible light. Instead, significant energy from a hydrogen flame is radiated in the ultraviolet region. As a result, hydrogen burns with a pale blue, almost invisible flame that is almost visually imperceptible in artificial light or daylight. Equally important, human physical perception of the heat from a hydrogen fire does not occur until direct contact with the combustion gases.

A broom can be used for locating small hydrogen fires. The idea is to hold the broom out in front of you while approaching the area where the hydrogen fire is suspected. A dry corn straw or sage grass broom will easily ignite when it comes in contact with the flame. A dry fire extinguisher or throwing dust into the air will also cause the flame to emit visible radiation.

Flammability and Ignition

Hydrogen has a much wider range of flammability in air (4% to 75% by volume) than methane (5% to 17% by volume), propane, or gasoline, and the minimum ignition energy (for a stoichiometric mixture) is about an order of magnitude lower (1/16th that of methane).

These characteristics would tend to indicate that flammability is a greater risk for hydrogen than for other fuels. However, these comparisons may not be as significant as they appear. In many accidental situations the lower flammable limit (LFL) is more important. The LFL for hydrogen is similar to that of methane, about twice that of propane, and four times that of gasoline. In addition, the minimum ignition energy for hydrogen at the LFL is also similar to that of methane. Weak ignition sources, such as an electrostatic spark, are often sufficient to ignite a combustible hydrogen-air mixture. However, a weak electrostatic spark from the human body releases about 10 mJ, which is enough energy to ignite methane, propane, gasoline, and other fuels as well.

Combustion Characteristics

Hydrogen-oxidizer mixtures can combust either as a fire at a fixed point, a deflagration, or a detonation. Depending on the rate of release of hydrogen from the source, fires can produce outputs ranging from that of a small candle to a high-pressure jet. At a fixed point hydrogen gas can burn as a jet flame, with combustion taking place along the edges of the jet where it mixes with sufficient air. In a stationary mixture in the open with no confinement a flammable hydrogen mixture will undergo slow deflagration. Deflagration refers to a flame that relies on heat- and mass-transfer mechanisms to combust and move into areas of unburned fuel.

If the flame speed is accelerated, perhaps due to extreme initial turbulence or turbulence induced by obstacles or confinement, the result is an explosion. In the extreme case the flame speed becomes supersonic and results in detonation. Once initiated, detonation is self-sustaining (no further turbulence or confinement is required) as long as the combusting mixture is within the detonatable range. A detonation explosion is capable of causing much greater physical damage due to the significantly higher pressure that is generated (as great as 20 times the initial stoichiometric pressure versus about 8 times the initial pressure for a deflagration).

The lower radiation from a hydrogen flame makes the flame itself hotter than a hydrocarbon flame, and objects engulfed by a hydrogen flame tend to heat faster. However, the lower radiation of heat from the flame means that less heat is transferred to objects or people outside the flame.

The heat of combustion of hydrogen per unit weight is higher than any other material, but hydrogen has a relatively low heat of combustion per unit volume. Thus the combustion of a given volume of hydrogen will release less energy than the same volume of either natural gas or gasoline.

Hydrogen Embrittlement and Material Compatibility

Prolonged exposure of some high strength steels to hydrogen can cause them to lose their strength, eventually leading to failure. This loss of strength is known as hydrogen embrittlement and occurs when hydrogen permeates into the lattice structure of the material. Sensitivity to hydrogen embrittlement is influenced by numerous parameters, including plastic deformation, cyclic loading, hydrogen purity, temperature, and pressure. Hydrogen embrittlement is a particular issue for ferritic steels and occurs at ambient temperatures and elevated pressures. The problem is exacerbated when the steel is subjected to mechanical stresses. The embrittlement processes take place on freshly generated metallic surfaces that are likely to form at surface defects or other stress raisers as a result of stress-induced local plastic deformation processes.

Suitable metals for gaseous hydrogen service include austenitic stainless steel with greater than 7% nickel (such as 304, 304L, 308, 316, 321, 347), copper and its alloys (such as brass, bronze, and copper-nickel), and aluminum and its alloys. Non-metallic materials that can be used in gaseous hydrogen service for valve seats, gaskets, etc. include Buna-N®, Viton®, Kel-F®, and Teflon®.

Physiological Hazards

Hydrogen is non-toxic, but it can cause asphyxiation in a confined area due to displacement of oxygen. Smoke inhalation, a primary cause of injury due to fires, is considered less serious in the case of hydrogen because the sole product of combustion is water. However, secondary fires can cause smoke and other combustion products that present health hazards.

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