DOE/CE/50389-502

DIRECT-HYDROGEN-FUELED PROTON-EXCHANGE-MEMBRANE FUEL CELL SYSTEM FOR TRANSPORTATION APPLICATIONS

HYDROGEN VEHICLE SAFETY REPORT

CONTRACT NO. DE-AC02-94CE50389

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MAY 1997

PREPARED FOR:

U.S. DEPARTMENT OF ENERGY
OFFICE OF TRANSPORTATION TECHNOLOGIES

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FOREWORD

This report documents a portion of the results of the project entitled "Direct-Hydrogen-Fueled Proton-Exchange-Membrane Fuel Cell System for Transportation Applications" performed by Ford Motor Company, under contract DE-AC02-94CE50389. The project objective was to design, fabricate, and test a 50-kW direct hydrogen fueled proton exchange membrane (PEM) fuel cell system including onboard hydrogen storage, efficient lightweight fuel cell, gas management system, and complete system controls that can be economically mass produced and comply with all safety, environmental, and consumer requirements for vehicle applications for the 21st century. Specifically, this report presents results of a detailed review of the safety characteristics of hydrogen as fuel for a fuel cell-powered vehicle, with emphasis on high-pressure storage of gaseous hydrogen on-board the vehicle.

Dr. C. E. Thomas, Directed Technologies, Inc., prepared this report. Brian James, George Baum, Frank Lomax, and Ira Kuhn, all of Directed Technologies, Inc., assisted in preparing and editing the report. Ron Sims of the Ford Motor Company guided this effort and coordinated the review of the report by W. J. Koeppel of the Ford Automotive Environmental and Safety Engineering Office.

This work was funded by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Office of Advanced Automotive Technologies. Project and technical management was provided by Mr. Steven Chalk, and Ms. Donna Lee of DOE's Office of Advanced Automotive Technologies with technical oversight and advice provided by Dr. Walter Podolski and Dr. James Miller of Argonne National Laboratory. Mr. Bradford Bates, Manager of the Alternative Power Source Technology Department at Ford Motor Company was responsible for this program.

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Acknowledgments

This safety analysis was performed by Directed Technologies, Inc. for the Ford Motor Company under their prime contract to develop direct hydrogen fuel cell vehicles, contract No. DE-AC02-94CE50389 with the U. S. Department of Energy, Office of Transportation Technologies, under the Assistant Secretary for Energy Efficiency and Renewable Energy. We wish to thank the program manager at Argonne National Laboratory, Dr. Walt Podolski, and Dr. Pandit Patil and Steve Chalk at DOE for their support of this work.

Three of the four Ford hydrogen infrastructure subcontractors also worked directly on this safety analysis. We wish to thank Jim Hansel of Air Products and Chemicals, Inc., Tom Halvorson of Praxair, and Matthew Fairlie of Electrolyser Corporation, Ltd. for their many contributions to this report. In addition, other members of the infrastructure team and the Ford fuel cell subcontractors also contributed to some of our early discussions regarding hydrogen vehicle safety. We also thank Ron Sims of the Ford Motor Company for his continuing help in all aspects of the hydrogen infrastructure work. Brian James, George Baum, Frank Lomax and Ira Kuhn of Directed Technologies, Inc. also assisted in the preparation and editing of this report.

Glossary

AGA = American Gas Association
BLEVE = boiling liquid expanding vapor explosion
BTU = British Thermal Units (1,055 joules)
CGA = Compressed Gas Association
CH_4 = methane (main constituent of natural gas)
CNG= compressed natural gas
DOE = (U.S.) Department of Energy
DOT = (U.S.) Department of Transportation
DTI = Directed Technologies, Inc.
EV = electric vehicle
FCV = fuel cell vehicle
GJ = gigajoules (10^9 joules or 0.9479 million BTUs)
H_2 = hydrogen gas
HHV = higher heating value
ICE = internal combustion engine
kPa = kilopascal [0.14504 pounds per square inch gauge (psig); one atmosphere = 101.325 kPa]
LFL = lower flammability limit
LHV = lower heating value
LNG = liquified natural gas
LPG = liquified petroleum gas (primarily propane)
MBTU = million BTU (1.055 GJ)
MESG = maximum experimental safe gap
MPa = megapascal [145.04 psig]
mJ = millijoules
mps = meters per second
NEC = National Electrical Code
NFPA = National Fire Protection Association
NGV = natural gas vehicle
PEM = proton exchange membrane
PRD = pressure release device
psi = pounds per square inch (6.8947 kilopascal)
SCF = standard cubic feet (0.0283 cubic meters)
SAE = Society of Automotive Engineers
VOC = volatile organic compounds

Executive Summary

This report reviews the safety characteristics of hydrogen as an energy carrier for a fuel cell vehicle (FCV), with emphasis on high pressure gaseous hydrogen onboard storage. We consider normal operation of the vehicle in addition to refueling, collisions, operation in tunnels, and storage in garages. We identify the most likely risks and failure modes leading to hazardous conditions, and provide potential countermeasures in the vehicle design to prevent or substantially reduce the consequences of each plausible failure mode. We then compare the risks of hydrogen with those of more common motor vehicle fuels including gasoline, propane, and natural gas.

Based on an extensive literature review and an evaluation of a hydrogen-powered fuel cell vehicle system, our preliminary conclusions are:

1. The automotive industry has successfully developed the equipment and procedures for the safe use of gasoline by the general public in motor vehicles, such that the risks of death or injury from a gasoline fire during a 4,800 kilometer cross-country trip are less than the risks of other common human activities such as skiing for nine minutes, rock climbing for 41 seconds, working on a farm for nine hours, or flying on a scheduled airline for 33 minutes. The public has accepted these extremely small risks of gasoline, so hydrogen should be considered acceptably safe if it has equal or less risk than gasoline -- gasoline is a good reference point to judge hydrogen safety.

2. In normal operation, a hydrogen-powered fuel cell vehicle and dispensing system, with proper engineering, should be as safe as a gasoline, natural gas, or propane vehicle system.

3. In a collision in open spaces, a safety-engineered hydrogen FCV should have less potential hazard than either a natural gas vehicle or a gasoline vehicle due to four factors. First, carbon fiber wrapped composite storage tanks (the leading high pressure storage tank material due to its low weight) are able to withstand greater impacts than the vehicle itself without rupture, thereby minimizing the risks of a large release of hydrogen as a result of a collision. Second, hydrogen, if released, disperses much faster than gasoline due to much greater buoyancy, reducing the risks of a post-collision fire.[1] Third, the FCV will carry 60% less total energy than a gasoline or natural gas vehicle, resulting in less potential hazard should it ignite. Finally, the design recommended here includes an inertially activated switch in each FCV that, in the event of a collision, will simultaneously shut off the flow of hydrogen via a solenoid valve or valves, and will cut electrical power from the battery.

[1]Hydrogen also has a much higher diffusion rate than gasoline vapor, but diffusion rarely affects vapor dispersal in practical circumstances, according to Michael Swain of the University of Miami.

4. In a tunnel collision, a hydrogen FCV 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 leakage of gasoline and natural gas in a tunnel. Natural gas presents a smaller potential hazard than gasoline in such a hypothetical scenario because its buoyancy and diffusion coefficient are 6.7 and 3.2 times greater than those of gasoline, and its lower limit of flammability is 5.3 times greater than that of gasoline. Hydrogen has 52 times greater buoyancy and 12.2 times greater diffusion coefficient than gasoline. Thus hydrogen will disperse much more quickly than gasoline or natural gas. Similarly, hydrogen's lower flammability limit is four times greater than that of gasoline. Propane is intermediate between gasoline and natural gas.

However, hydrogen will escape faster than natural gas from a punctured high pressure tank due to a nearly three times higher sonic velocity. This higher escape velocity will create a larger but shorter lasting flammable hydrogen cloud, increasing the probability of ignition from nearby fans or lights in the tunnel compared to a natural gas leak. In rank order, gasoline and propane would create the largest and longest lasting flammable gas clouds, followed by hydrogen and natural gas. Thus gasoline and propane would be most likely to be ignited by a fan or light fixture in the tunnel, and natural gas would be the least likely. These conclusions are based on computer simulations of natural gas and gasoline leaks, with hydrogen effects estimated based on known properties of hydrogen. Further computer analysis would be required to more accurately determine the risk from a major hydrogen leak in a tunnel.

5. The greatest potential risk to the public would appear to be a slow leak in an enclosed home garage, where an accumulation of hydrogen could lead to fire or explosion absent hydrogen detection or risk mitigation such as passive or active ventilation, or, possibly, catalytic combustion to safely dispose of any leaking hydrogen. While we consider this the greatest potential risk, it should be noted that a natural gas, propane, or gasoline-powered vehicle with a similar fuel leak also present potential risks that the public accepts without the installation of leak detection or ventilation systems in the home garage. On the other hand, the distinctive odor of gasoline and the odorants added to natural gas and propane warn humans of those leaks, and, once gasoline and propane ignite, the flames are visible whereas hydrogen is odorless and its flames are nearly invisible. One key issue is whether the hydrogen community can develop an effective odorant and flame enhancer for hydrogen that will not contaminate fuel cells.

6. If we consider the total fuel system, including hydrogen production, transportation, storage and dispensing, the total public *exposure* to fuel risks could be less than those of the existing gasoline fuel infrastructure. For example, a hydrogen infrastructure would reduce the public's exposure to gasoline tanker truck fires on our nation's highways, and hydrogen use would cut down the risks associated with large oil spills or leaks from underground storage tanks. The hydrogen infrastructure would depend on some combination of natural gas pipeline distribution to local steam reforming plants and electrical grid distribution to local electrolysis stations. If the steam reforming plants were located at the local dispensing station, or if the hydrogen were shipped to the station by local pipeline, then the public risk exposure equivalent to that caused by gasoline tanker trucks would be eliminated. Large natural gas steam reforming plants might still rely on liquid hydrogen

tanker trucks to transport the hydrogen to the refueling stations, but the hazards associated with a liquid hydrogen tanker collision are considered less than those of a gasoline tanker truck collision, due again to the rapid dispersal of hydrogen in an accident.

7. Overall, we judge the safety of a hydrogen FCV system to be potentially better than the demonstrated safety record of gasoline or propane, and equal to or better than that of natural gas. In effect, the positive safety attributes of hydrogen (high buoyancy, greater lower flammability limit and much higher lower detonation limit) are important in realistic operational and collision scenarios, while the negative safety aspects of hydrogen (low ignition energy, wide flammability range, high flame velocity and resultant tendency to detonate) are not considered as important in likely vehicle accident scenarios.

8. Despite our judgement that hydrogen is likely to be potentially less hazardous overall than gasoline or propane, we must also deal with public perceptions. Strong education and public awareness campaigns may be required before the public *perceives* hydrogen to be an acceptably safe fuel.

Given these preliminary conclusions, we recommend two major actions to address what we have identified as the two potential safety disadvantages of hydrogen compared to alternative fuels. First, we should analyze the home garage hazards of hydrogen in more detail, since this is judged to be the greatest potential practical risk to the public. This should ideally include computer simulations, similar to the tunnel and home gas dispersal programs run previously, and could also include experimental measurements. The objective of this analysis would be to determine if passive garage ventilation is sufficient to disperse the worst likely slow leak from a FCV, or whether active ventilation triggered by a hydrogen detector or catalytic combustion is required to increase the margin of safety. The study should also analyze the corresponding existing risks to the home owner from gasoline, propane, or natural gas leaks in the garage.

Second, to address what may be a greater public *perception* of hydrogen risk related to collisions, we might consider a set of safety demonstrations designed to show that properly engineered fuel cell vehicles pose no additional risk to the public due to onboard hydrogen tanks. One possibility would be to drop old vehicles from a crane to simulate high speed, rear end collisions, with each vehicle equipped with a fully charged high pressure hydrogen tank in the trunk along with a mockup of the fuel cell system. The tank would include safety features such as an internal solenoid shut off valve and inertial switch. Safety would be demonstrated by no loss of pressure in the tanks even when the fuel lines are severed. These simple drop tests could be augmented or replaced by the more thoroughly engineered moving barrier crash tests later in the vehicle development program.

1.0 Introduction

Hydrogen, like any fuel, poses risks if not properly controlled. By definition, any fuel or energy carrier concentrates energy in a small volume in order to do useful work, thereby creating a potential hazard. Overall the safety record for existing fuels is excellent. Society has accepted the relatively rare risks associated with such energy concentrations in exchange for the conveniences and increased standards of living created by fossil fuels and electricity.

We expect energy systems powered by hydrogen to have a similar net impact on society -- there will be risks, but overall the risks will be small, bordering on negligible, compared to the benefits. The specific physical characteristics of hydrogen are quite different from gasoline and propane, and more similar to, but still different than, natural gas. Some attributes of hydrogen make it potentially less hazardous, while other hydrogen characteristics could theoretically make it more dangerous than current fuels if not properly controlled.

In the following section, we discuss the various safety attributes of hydrogen, followed by a brief description of the public's perception of hydrogen in Section 3.0, along with a discussion of the positive safety record of hydrogen in Section 4.0. We present a discussion of safety issues in Section 5.0, including specific suggestions for reducing potential risks onboard the vehicle itself (Section 6.0) and at the refueling station (Section 9.0).

We compare the risks of hydrogen with those of other fuels in Section 10.0, and we analyze different accident scenarios in Section 11.0. Finally, Section 12.0 includes some preliminary concepts for possible hydrogen safety demonstration tests.

2.0 Hydrogen Safety Characteristics

Hydrogen has some attributes that make it potentially less hazardous than gasoline, propane or natural gas, but it also has characteristics that make it more hazardous under some circumstances. Based on a number count, the negative attributes (wider flammability range, lower ignition energy, greater propensity to leak, higher flame velocity and greater propensity to detonate) might seem to outweigh the positive safety aspects of hydrogen (greater diffusion coefficient and buoyancy, lower explosive energy per unit volume or per unit energy.) But we need to assess the practical significance of each of these characteristics in the actual fuel cell electric vehicle (FCV) as well as in the hydrogen infrastructure that supplies the fuel.

2.1 *Propensity to Leak*

Since hydrogen is the smallest element, it has a greater tendency to escape through small openings than liquid fuels or other gaseous fuels. Based on diffusion through a membrane, for example, one would expect hydrogen to escape at a rate that is 3.8 times faster than natural gas, since the diffusion coefficient for hydrogen is 3.8 times greater than that for natural gas. But proper design of the fuel delivery system would eliminate any thin materials[2]. The more appropriate question is how fast hydrogen would leak through actual openings caused by faulty fuel lines, valves, or by a puncture of the compressed storage tank.

Swain and Swain have analyzed and measured the leak rates of hydrogen compared to propane and natural gas for actual natural gas line leaks removed from service[3]. Analytically, leaks through cracks or holes in pipelines can be modeled as either laminar or turbulent flow. For laminar flow, the ratio of leak rates for two gases is theoretically inversely proportional to the ratio of dynamic viscosities for two gases:

$$\frac{Q_{H_2}}{Q_x} = \frac{\mu_x}{\mu_{H_2}} \qquad (1)$$

where Q_{H2} = the hydrogen leak rate,
Q_x = the leak rate of the other gas,
μ_{H2} = the dynamic viscosity of hydrogen, and
μ_x = the dynamic viscosity of the other gas.

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[2]Except for intentionally designed thin components such as the membrane of the storage tank, which is thin to reduce weight but metalized to retard hydrogen diffusion, or the thin fuel cell membranes.

[3]M.R. Swain and M.N. Swain, "A Comparison of H_2, CH_4 and C_3H_8 Fuel Leakage in Residential Settings," Int. J. Hydrogen Energy, Vol. 17, No. 10, pp. 807-815, 1992.

For turbulent flow, the ratio of leak rates theoretically varies inversely as the square root of the gas density:

$$\frac{Q_{H_2}}{Q_x} = \frac{\sqrt{\rho_x}}{\sqrt{\rho_{H_2}}} \qquad (2)$$

where ρ_x = the density of the other gas, and
ρ_{H2} = the density of hydrogen.

The predicted flow rates for hydrogen, methane and propane are summarized in the bottom three rows of Table 2-1, normalized to the leak rate for natural gas, which is predominantly methane.

Table 2-1. Slow Leak Rates of Hydrogen and Propane Relative to Natural Gas

	Methane, CH_4	Hydrogen, H_2	Propane, C_3H_8
Flow Parameters:			
Diffusion Coefficient in air (cm^2/sec)	0.16	0.61	0.10
Viscosity at 0°C (Pa-sec x 10^{-7})	110	87.5	79.5
Density at 70°F, 1 atm. (kg/m^3)	.666	.08342	1.858
Relative Leak Rates:			
Diffusion	1.0	3.8	0.63
Laminar Flow	1.0	1.26	1.38
Turbulent Flow	1.0	2.83	0.6

The Swains' experiments indicate that most leaks from a residential natural gas line are laminar flow. Hence hydrogen would only leak at a rate about 26% higher than natural gas from a given opening. Furthermore, propane would leak even faster, roughly 38% faster than natural gas.

The much higher pressure of the FCV gas cylinders 34.5 MPa (5,000 psi) would undoubtedly produce turbulent flow should a leak develop. We anticipate reducing the pressure to 6.7 MPa (1,000 psi) with a pressure regulator very close to the hydrogen tanks, to minimize the safety hazard associated with long 34.5 MPa fuel lines. The hydrogen pressure supplied to the fuel cell itself will probably be in the 200 kPa (30 psi) range, similar to the home natural gas pressures investigated by Swain. Therefore we may have a range of flow conditions depending on the size and location of any leak on a FCV. For the worst case (turbulent flow), the hydrogen would leak at a rate about 2.8 times faster than natural gas, compared to only 1.26 times faster for laminar flow.

We conclude from these data that the propensity for 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 from the same hole, not the 3.8 times faster frequently assumed based solely on diffusion coefficients. Furthermore, since natural gas has over three times the energy density per unit volume, the natural gas leak would be about 2.7 times more energetic than a hydrogen leak for laminar flow and 1.2 times more energetic for turbulent flow. Therefore a natural gas fire resulting from a leak would have 1.2 to 2.7 times more energy than a hydrogen leak from the same opening. Hydrogen leaks are still a major concern, but not of the same magnitude as is sometimes depicted by quoting the 3.8 times higher hydrogen diffusion coefficient.

For very large leaks from high pressure storage tanks, both hydrogen and natural gas will reach sonic velocity in any puncture hole. However, the sonic velocity of hydrogen (1308 mps) is almost three times that of natural gas (449 mps.) Therefore hydrogen will initially escape much faster than natural gas from a punctured tank. Since natural gas has more than three times the energy density than hydrogen, however, a natural gas leak will always contain more total energy. The mass inside a high pressure tank of any gas, assuming isentropic expansion through a puncture hole is given by:[4]

$$m(t) = \left[m_o^{\frac{(1-\gamma)}{2}} + K_o A_e C_r t \frac{(\gamma - 1)}{2} \right]^{\frac{2}{1-\gamma}} \tag{3}$$

where

$$K_o = \frac{\sqrt{R T_o}}{V_o m_o^{\frac{(\gamma-1)}{2}}}$$

$$C_r = \sqrt{\gamma} \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma+1}{2(\gamma-1)}}$$

A_e = the effective area of the leakage hole = C_D A,
A = the actual hole area (m^2),
C_D = orifice factor,
m_o = the initial mass of the gas inside the tank (kg),

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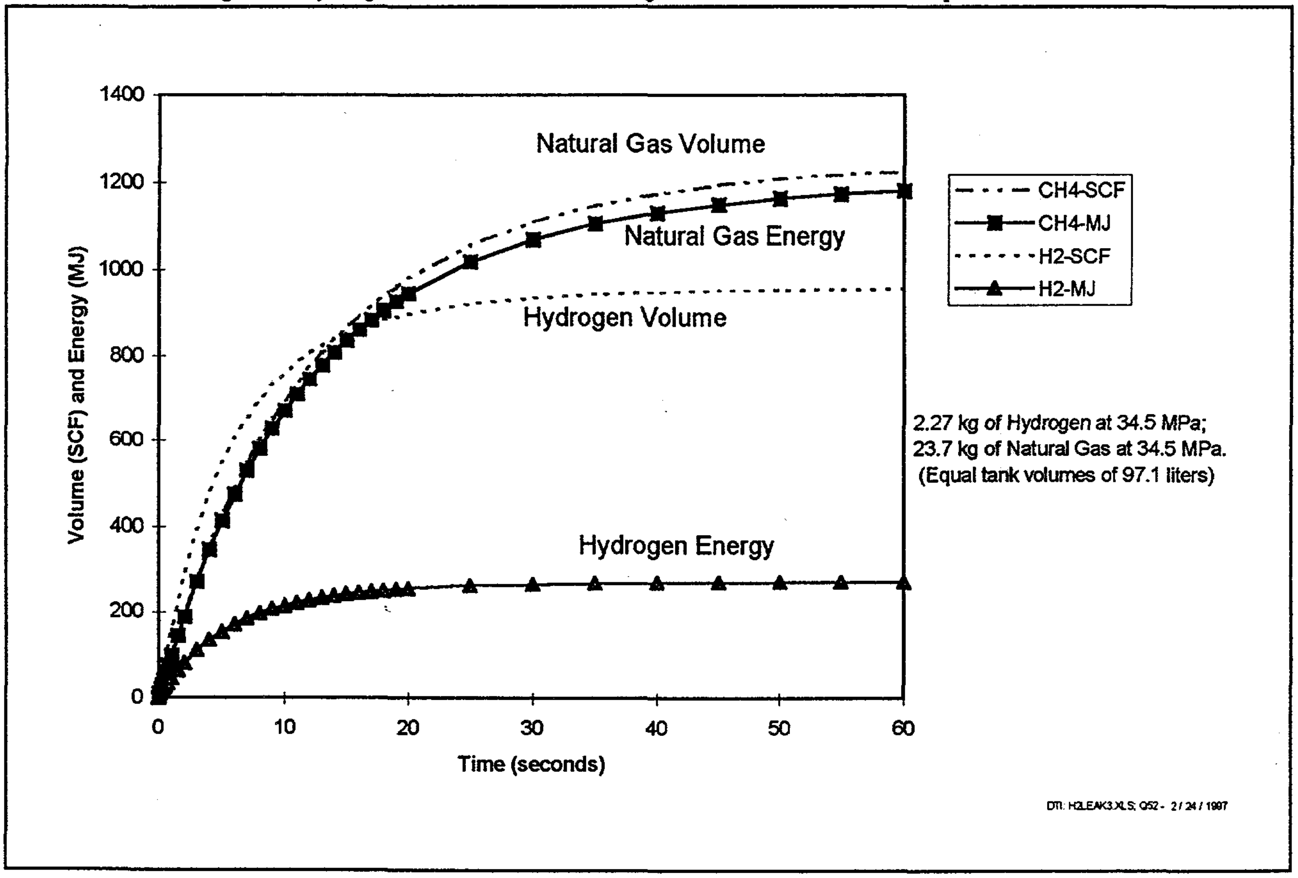
[4]Equation derived by George Baum of Directed Technologies, Inc.

γ = the ratio of specific heats of the gas,
R = the universal gas constant,
T_o = the initial absolute temperature of the gas (°K), and
V_o = the volume of the tank (m^3).

Figure 1 illustrates the cumulative volume and energy flowing from a 6.35 mm hole in two identical tanks filled to 34.5 MPa (5,000 psi), one with hydrogen, the other with natural gas. Due to its high sonic velocity, the hydrogen tank empties faster, with 50% of the hydrogen expelled in 4 seconds. The 34.5 MPa natural gas tank empties to 50% of its initial contents in about 12 seconds. The number of moles of gas contained in a pressurized tank can be more or less than the number of moles calculated for an ideal gas. At 34.5 MPa, for example, an ideal gas is compressed by a factor of 341.1 to one, while natural gas compresses by a factor of 356.9 (slightly more than an ideal gas), and hydrogen compresses by only 279.6, much less than an ideal gas. As a result, the natural gas-filled tank contains 28% more moles than the hydrogen tank at 34.5 MPa, resulting in a 28% greater expanded volume when the two gases escape from the same size of tank.

Figure 1. Hydrogen and Natural Gas Leakage from 6.35 mm Holes in Equal Size Tanks



Although more hydrogen flows from a tank puncture initially than natural gas (dashed lines in Figure 1), the energy content per unit volume of the natural gas is 3.18 times higher than that of hydrogen based on the higher heating value (HHV) of both fuels, and 3.4 times higher based on their lower heating values (LHV). As shown by the solid lines in Figure 1, the energy content of the escaping gas is always higher for natural gas, even though the volume of escaping hydrogen is larger for the first 12 seconds.

The storage tanks in a natural gas vehicle (NGV) will not be the same size as the hydrogen tanks in a fuel cell vehicle (FCV). Tank sizes and pressures will be sized to give the necessary range and performance for each vehicle. Directed Technologies has previously estimated that the FCV will be 2.68 times more energy efficient (LHV) than a gasoline-powered internal combustion engine (ICE).[5] If we assume that an NGV has similar efficiency to the gasoline-powered ICE, then the NGV would carry 2.68 times more energy content than the hydrogen-powered FCV. In addition, NGV's generally store natural gas at 20.7 to 24.8 MPa (3,000 to 3,600 psi), compared to the 34.5 MPa (5,000 psi) assumed in the DTI design for hydrogen. Figure 2 shows the volume and energy leakage rates from a 24.8 MPa (3,600 psi) natural gas tank and a 34.5 MPa hydrogen tank with 2.68 times less total stored energy. We assume that each vehicle has three tanks, both to accommodate packaging on the vehicle and to reduce the impact of any major tank leak. Figure 2 confirms that the hydrogen volume leakage rate would be higher at all times, but energy content of the escaping natural gas will always be larger than the hydrogen energy content from the same size of leak.

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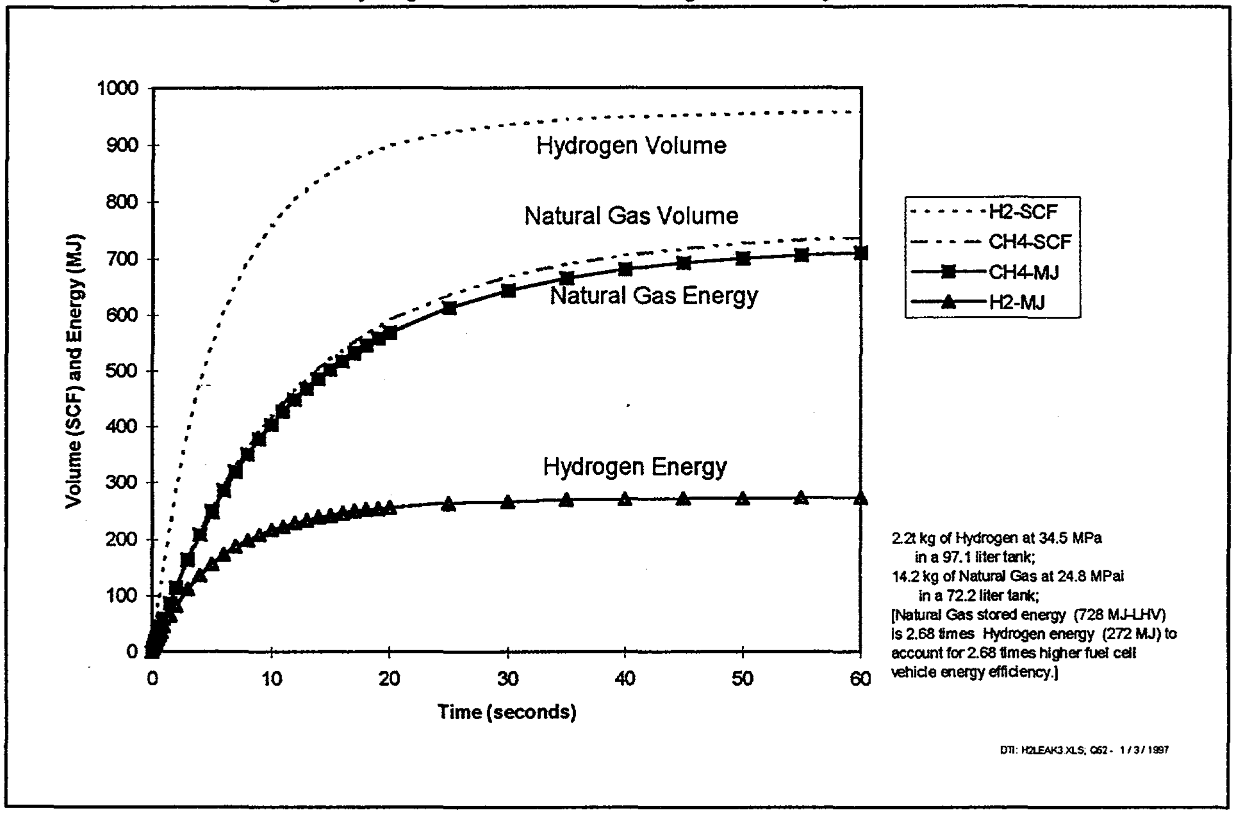
[5]Brian D. James, George N. Baum, and Ira F. Kuhn, Jr., Technology Development Goals for Automotive Fuel Cell Power Systems, Argonne National Laboratory Report No. ANL-94/44, August 1994.

Figure 2 Hydrogen and Natural Gas Leakage from Likely Vehicle Tanks



2.2 *Hydrogen Embrittlement*

Manganese, some nickel-base and other high strength steels are prone to hydrogen embrittlement. Prolonged exposure to hydrogen, particularly at high temperatures and pressures, can cause these steels to lose strength, leading eventually to failure. Thus hydrogen leaks or fuel line failures could occur with improper choice of materials that come into contact with the hydrogen.

With proper choice of materials, however, hydrogen embrittlement should not contribute to hydrogen safety risks. Aluminum and composite vessels, for example, are not affected by embrittlement. A properly designed hydrogen fuel delivery system should be no more prone to leaks or failures than any other fuel system.

2.3 *Hydrogen Dispersion*

If a leak should occur, hydrogen will quickly disperse, reducing the hazard levels in unconfined spaces to tolerable levels in a much shorter time than with any other fuel. Hydrogen is both more buoyant (rises rapidly) and more diffusive (moves laterally) than either gasoline, propane or natural gas, although molecular diffusion rarely plays a significant role.

Table 2-2. Buoyancy and Diffusion of Gases

	Hydrogen	Natural Gas	Propane	Gasoline Vapor
Buoyancy (Density w/r to Air)	.07	.55	1.52	3.4 - 4.0
Diffusion Coefficient (cm^2/sec)	0.61	0.16	0.10	0.05

As shown in Table 2-2, the density of hydrogen is only 7% that of air, while the density of natural gas is 55% that of air, indicating that they will move upward even without any wind or ventilation. Both gases will rise rapidly, but hydrogen much more so. Propane and gasoline vapors are both heavier than air -- propane has a density 1.52 times greater than air, while gasoline fumes are 3.4 to 4 times heavier than air. Hence propane and gasoline vapors will both tend to remain at ground level as they disperse more slowly or are carried away by the wind.

Hydrogen has a diffusion coefficient that is 3.8 times greater than that of natural gas, 6.1 times greater than propane, and 12 times greater than gasoline vapor. This high diffusion coefficient indicates that hydrogen will diffuse rapidly in all directions in air, quickly decreasing in concentration, while gasoline tends to remain at ground level and diffuse outward at a slower rate from a spill or leak.

Hydrogen's rapid dispersion rate is probably its greatest safety asset in an outdoor environment, although wind and the escape velocity from a high pressure tank may have more influence on the size of a hydrogen flammability cloud. Indoors, high dispersion rates can be both an asset, in the sense that a small leak will rapidly mix with air and stay below the lower flammability limit, but also a potential liability with larger leaks if the expanding gas cloud is more likely to reach ignition sources.

2.4 *Flammability*

Hydrogen is sometimes portrayed as a dangerous fuel because of its wide flammability range in air, coupled with its very low ignition energy. A hydrogen/air mixture can burn at volume ratios between 4% and 75%. The other fuels have much narrower flammability ranges, as summarized in Table 2-3. A hydrogen/air mixture can be ignited with as little as 0.02 mJ of energy, whereas the other fuels require over tens times higher energy for ignition.

Based on these relative data, it would appear that any hydrogen leak would be much more likely to burn than any of the other fuels. For a large release of fuel, hydrogen could potentially be more dangerous, in the sense that a large natural gas release could exceed the 15% upper flammability limit over a larger volume than a hydrogen cloud of more than 75% concentration or gasoline fumes above 7.8% concentration. However, in many practical situations, this may not be valid. For example, the key parameter that determines if a slow fuel leak will ignite is the *lower* flammability limit (LFL). The system designer will always seek to keep the fuel mixture well below the lower limit in any accidental release scenario, either by restricting the maximum likely fuel flow and/or by increasing air circulation to assure that the fuel/air mixture ratio stays well below the LFL.

Hence the LFL is often a better indication of the propensity of a fuel/air mixture to ignite than the total flammability range. The LFL for hydrogen is 4 times greater than gasoline and 1.9 times higher than propane, and only slightly less than that for natural gas. Furthermore, the 4% LFL for hydrogen applies only to upward propagating flames. For downward propagating flames, the concentration of hydrogen must be at least 9% to sustain a flame, according to Berman.[6] This agrees with estimates by Michael Swain of the University of Miami, who reported that about 10% hydrogen is required before a downward propagating flame will continue to burn. That is, if the ignition source is above a 10% or less flammable mixture of hydrogen, then the hydrogen below the source will not be ignited. For methane, the downward propagating LFL is only slightly larger than the upward propagating limit, on the order of 5.6% downward vs. 5.3% upward, although the lower limit for natural gas can be as low as 3.8%.[7]

Table 2-3. Flammability Characteristics of Fuels

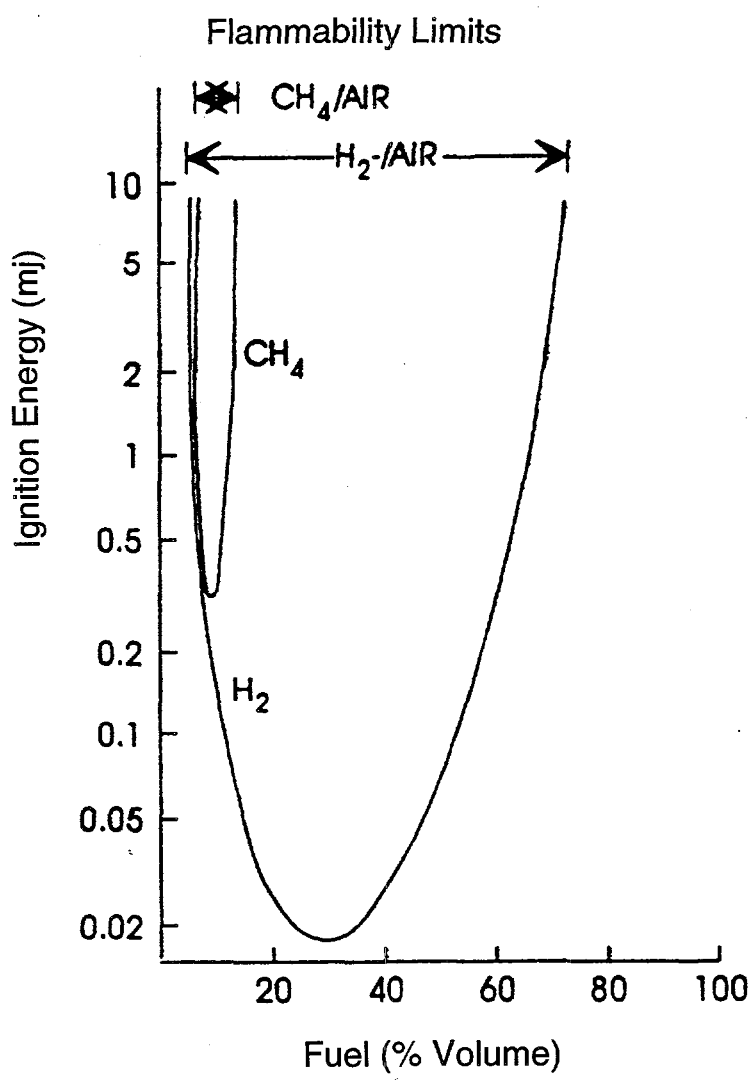
	Hydrogen	Methane / Natural Gas	Propane	Gasoline
Flammability Limits (% in air)				
Lower Limit (LFL)	4	5.3 / 3.8	2.1	1
[Downward Propagating LFL]	[9-10]	[5.6]	-	-
Upper Limit	75	15	10	7.8
Minimum Ignition Energy (millijoules -mJ)	0.02	0.29	0.3	0.24
Autoignition Temperatures (°C)				
Minimum	520	630	450	228-470
Heated Air Jet	640	1040	885	
Nichrome Wire	750	1220	1050	

[6]Marshall Berman, "A Critical Review of Recent Large-Scale Experiments on Hydrogen/Air Detonations," Nuclear Science and Engineering, Vol. 93, pp. 321-347, 1986.

[7]Private communication with Michael Swain, June 12, 1995 and February 23, 1997.

Hydrogen's factor of ten lower minimum ignition energy may also have less of a practical impact than the number would indicate. First, the minimum ignition energy for hydrogen applies only at a fuel concentration of about 25 to 30% in air. At lower or higher fuel air ratios, the ignition energy required for hydrogen to start burning increases sharply, as shown by Fischer (Figure 3).[8] In fact, the energy required to ignite a hydrogen/air mixture is almost equal to the energy necessary to ignite a natural gas/air mixture in the region of the lower flammability limit or 4 to 5% fuel concentration, as shown in Figure 3.

Figure 3. Ignition Energy for Hydrogen and Methane as a Function of the Fuel/Air Ratio



[8]M. Fischer, "Safety Aspects of Hydrogen Combustion in Hydrogen Energy Systems," Int. J. Hydrogen Energy, Vol. 11, No. 9, pp. 593-601.

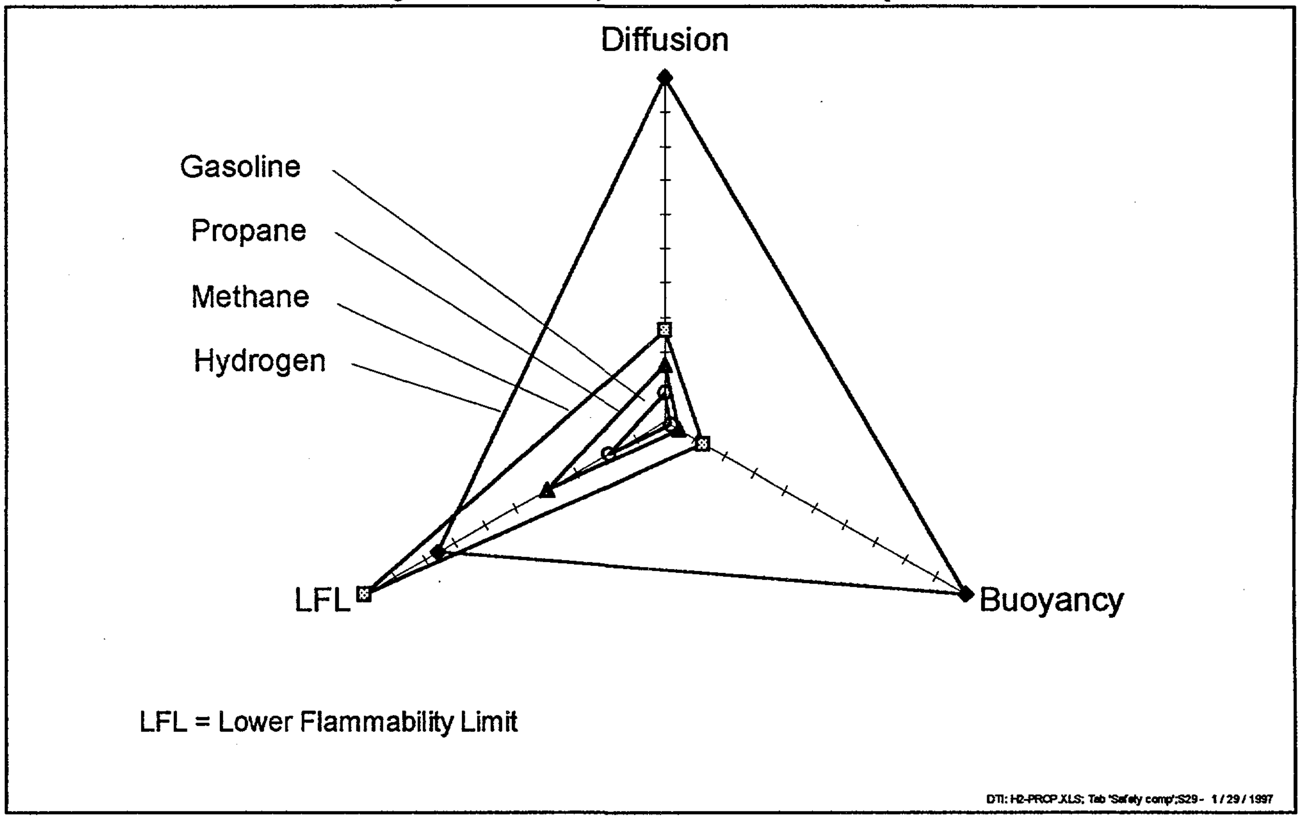
Fischer also points out that the most common ignition source -- weak static electricity from the human body -- will produce a spark with 10 mJ of energy, or 40 times more energy than is needed to ignite any of these fuels. The much lower ignition energy level for hydrogen at 30%fuel concentration is therefore of little practical significance in the most feared circumstance: the accumulation of hydrogen from a slow leak ignited by static electricity from an approaching human.

The higher flammability limit of hydrogen could be detrimental in some circumstances. For example, if hydrogen leaks into a garage and exceeds the lower limit of flammability without ignition, then the volume of air falling within the flammability range could become very large, thereby increasing the likelihood of reaching an ignition source somewhere in the garage. But a similar natural gas leak that was not initially ignited would reach a fuel/air ratio above 20% in much of the room, above the higher flammability limit and hence not prone to ignition. If an ignition source were subsequently introduced into these two rooms, the hydrogen mixture would be more likely to burn since more of the room would be within its wide flammability range.

The autoignition temperature might be important in some circumstances, if a hot surface such as a tailpipe or engine block is the only potential ignition source. As shown in Table 2-3, hydrogen has a slight advantage over gasoline, since hydrogen generally requires a hotter surface to ignite. The practical significance may be slight, however, since the autoignition temperature depends on many variables including the size, shape, and material of the hot source. The last two rows of Table 2-3 illustrate that even the relative ranking of autoignition temperature between the fuels shifts if the hot source is a heated air jet or a nichrome wire instead of a heated glass vessel, the usual method for measuring minimum autoignition temperature.

The practical flammability characteristics for a small leak (diffusion, buoyancy and lower flammability limit) are illustrated in Figure 4 for hydrogen, methane, propane and gasoline . This three-dimensional plot shows that hydrogen (diamond data points) is the safest fuel, since it has the highest diffusion and buoyancy and the second lowest LFL -- being away from the xyz origin of this plot is safe and fuels near the origin are generally more dangerous in terms of flammability characteristics.

Figure 4. Flammability Characteristics of Fuel Vapors



To summarize the flammability issue, both hydrogen and natural gas would be less likely than gasoline or propane to ignite in the case of a small leak discharging into a closed area with a nearby ignition source, due to their higher minimum limits of flammability. Since most ignition sources generate more than 10 mJ, all four fuels would be ignited if the fuel/air mixture reaches the lower limit, so the extraordinarily low ignition level at one hydrogen/air ratio may have little practical significance. If hydrogen does accumulate above the lower limit of flammability without ignition, then it would be more likely to ignite than the other fuels by reaching a distant ignition source within hydrogen's wide flammability range. Hydrogen and natural gas might be slightly less likely than gasoline or propane to ignite due to contact with a hot surface.

2.5 *Detonability*

After ignition, a burning fuel/air mixture can proceed along several paths. In the open atmosphere, the burning velocity remains low, and little physical damage from large overpressure is possible. Thus it is very unlikely that hydrogen would ever explode in an outdoor accident with normal ignition sources. Very high energy such as a lightning strike or a chemical explosive would be necessary to detonate a hydrogen gas cloud.

In confined spaces, however, substantially increased burning velocities are possible. The physical damage from an expanding flame front varies depending on the burning velocity. Transition from laminar to turbulent flow can create a deflagration at subsonic velocities, with overpressures up to 8 to 1. If the expanding wavefront becomes supersonic due in part to shock waves and turbulence generated by the enclosure surfaces, a detonation with much larger overpressures (20 to 1 or larger), and hence much greater physical damage, is possible.

Hydrogen has a burning velocity 7 times faster than that of natural gas or gasoline as shown in Table 2-4. All else being equal, a hydrogen flame would be much more likely to progress to a deflagration or even a detonation than the 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. One source indicates that it is rather difficult to initiate a detonation even with hydrogen in the laboratory, unless the gas is confined in a long, narrow tube with a length to diameter ratio over 100 to one.[9] Another source points out, however, that previous measurements in long narrow pipes may have actually impeded the transition to detonation. In fact, the lower detonability limit in larger enclosures may be closer to 13% than the 18% reported in the literature.[10]

The lower detonability fuel/air ratio for hydrogen is two times higher than that of natural gas, and 12 times higher than that of gasoline. The likelihood of a hydrogen detonation is small if the fuel leak is discharged into a space with a nearby ignition source, such that the fuel burns before it can reach the lower detonability limit. In order for an explosion to occur, the hydrogen would first have to accumulate and reach at least a 13% concentration in a closed space without ignition. An ignition source would then have to be triggered, setting off the detonation. Since any hydrogen system will either be engineered to stay below the lower flammability limit of 4% or have detectors to sound alarms or turn on exhaust fans should that threshold be approached, any accumulation to 13 to 18% would represent a major failure of the safety protection system.

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. As with detonation, these explosive values are difficult to achieve in reality, but they do give another perspective on the relative dangers of hydrogen versus the other fuels.

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[9]J. Hord, "Is Hydrogen a Safe Fuel?", Int. J. of Hydrogen Energy, Vol. 3, p.168.

[10]Ibid., Berman.

Table 2-4. Detonation Characteristics of Fuels

	Hydrogen	Natural Gas	Propane	Gasoline
Detonability Limits				
Lower (% volume in air)	13 to 18.3	6.3	3.1	1.1
Upper	59	13.5	7	3.3
Burning Velocity (cm/sec)	270	37	47	30
Explosive Energy:[11]				
Per Unit Energy (gTNT/kJ)	0.17	0.19		0.21
Per Unit Volume (gTNT/m^3)	2.02	7.03		44.22
Maximum Experimental Safe Gap (cm)	.008	.12		.074

The last row of Table 2-4 lists the "maximum experimental safe gap," which is the maximum size of openings in an enclosure that will prevent a flame from spreading from the enclosure to an unburned flammable mixture outside the enclosure. This concept grew out of the "Davy lamp," a lamp that allowed miners to safely carry a flame into mines containing flammable mixtures of methane and air[12]. The flame of the lamp was surrounded by a fine metal gauze that prevented the ignition of the methane outside the lamp, even though the flammable mixture permeated the metal gauze. In fact, the lamp also served to indicate the presence of flammable methane mixtures, since the flame expanded inside the metal gauze when methane was present above the lower flammability limit (5.3% for methane.) As shown in Table 2-4, hydrogen is the most difficult gas to contain by this technique, since any openings must be less than 80 microns (0.003 inches or 3 mils) to prevent the spread of a flame in a hydrogen/air mixture.

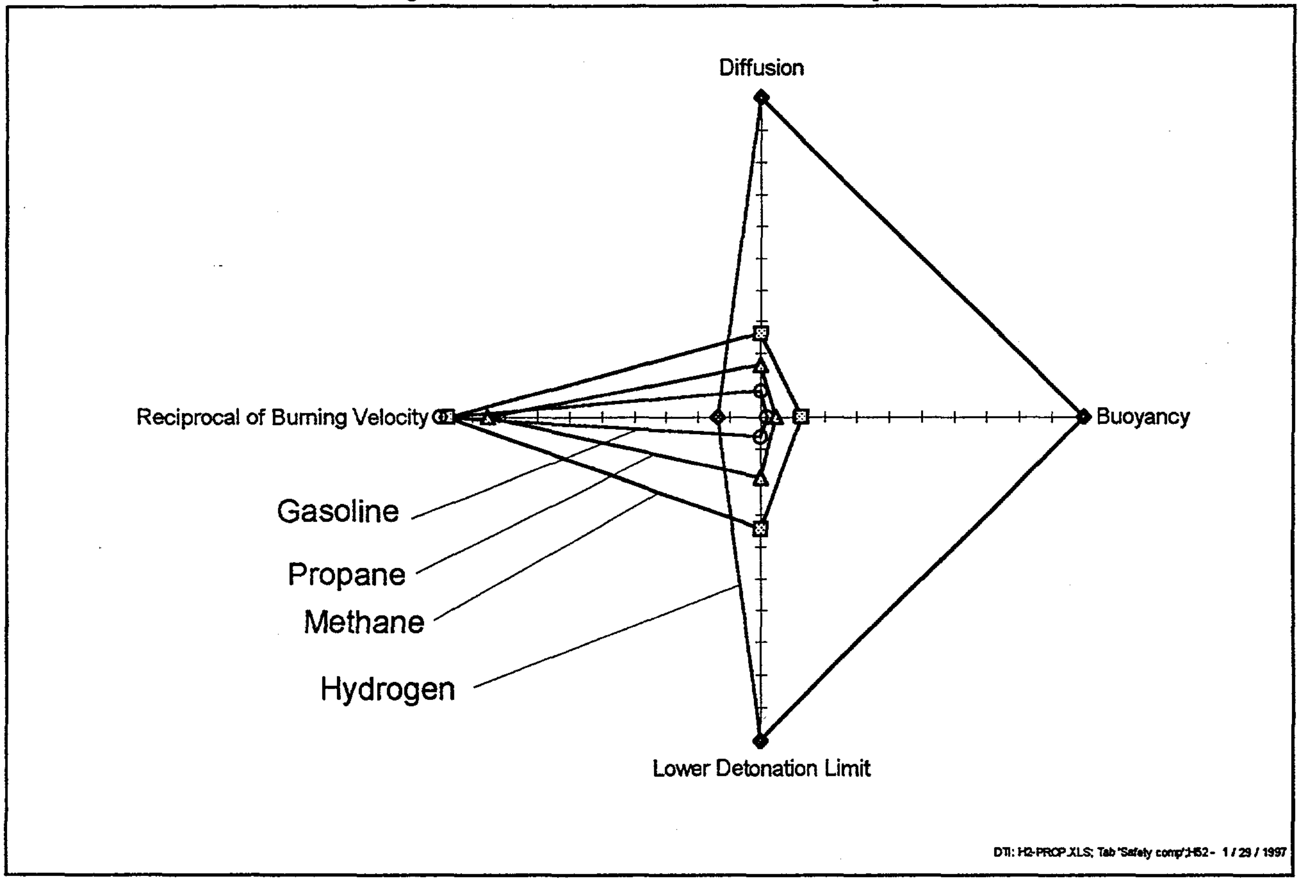
The detonation characteristics of hydrogen are compared with the other three fuels in Figure 5, which is a four dimensional plot of diffusion, buoyancy, lower detonation limit, and the reciprocal of burning velocity. We plotted the reciprocal of burning velocity since high velocity is detrimental, and this visual plot, like Figure 4, has the most dangerous attributes close to the origin of the plot. Figure 5 illustrates that hydrogen is far superior to the other fuels (farther away from the origin) with respect to diffusion, buoyancy and lower detonation limit, but is clearly the worst fuel in terms of burning velocity. Figure 5 graphically illustrates the merits of hydrogen with respect to detonation:

[11]One gram of TNT (symmetrical trinitrotoluene) is equivalent to 4,602 joules of energy.

[12]Peter J. Schram and Mark W. Earley, Electrical Installations in Hazardous Locations, National Fire Protection Association, Quincy Massachusetts, 1993, pg.18.

it is the least likely fuel to form a detonable vapor cloud, but once if it reaches the lower detonation limit, it is the most likely fuel to proceed from deflagration to detonation.

Figure 5. Detonation Characteristics of Fuel Vapors



2.6 *Hydrogen Flame Detection*

Hydrogen flames are nearly invisible, since burning hydrogen does not emit significant energy in the visible portion of the electromagnetic spectrum. In general, the more chemical species in a fuel, the more likely there will be radiation in the visible region. (The Space Shuttle graphically demonstrates the low luminosity of hydrogen during lift-off: the hydrogen flames from the three main shuttle engines are difficult to see, while the two solid rocket booster engines flames are very bright even in daytime launches, due to the complex chemical composition of the solid fuel.) People in the vicinity of a hydrogen flame may not even know there is a fire, thereby increasing the risks to unsuspecting bystanders or rescue workers as they approach an accident.

To reduce the risks accidental contact with nearly invisible flames, an impurity could be added to the hydrogen to create emission bands in the visible spectrum. The challenge is to find a chemical that will provide the necessary luminosity without degrading the performance of hydrogen end-use devices such as fuel cells.

On the positive side, the low emissivity of hydrogen flames means that near-by materials (and people) will be much less likely to ignite by radiant heat transfer. By contrast, a gasoline fire spreads both by the flow of liquid gasoline, and by the radiation from the gasoline fire that heats all adjacent materials. Therefore secondary fires are much more likely with a gasoline fire than with a hydrogen fire. Finally, 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.)

2.7 *Special Properties of Liquid Hydrogen*

While this program is focussed on the storage of gaseous hydrogen onboard the vehicle, the hydrogen might be liquified at a large natural gas steam reforming plant to minimize the costs of transportation to distant refueling stations. Liquid hydrogen presents another set of safety issues that must be addressed in the context of the hydrogen infrastructure tasks. Praxair did conduct a preliminary hazard review of a gaseous hydrogen refueling station supplied by liquid hydrogen. This hazard review is reproduced as Appendix D in this report, beginning with Table D-3.

Liquid hydrogen creates additional hazards, including the risk of cold burns, and the increased duration of leaked cryogenic fuel in the event of a collision. Liquid hydrogen will initially condense air in the vicinity, and must warm up before the rapid dispersal characteristics of gaseous hydrogen come into play. In this regard, a large spill of liquid hydrogen has some of the characteristics of a gasoline spill. However, a liquid hydrogen spill will dissipate much faster than a gasoline spill. Like gasoline, liquid hydrogen could create a "BLEVE" -- a boiling liquid expanding vapor explosion -- a violent explosion should the pressure relief valves fail.

3.0 The Public Perception of Hydrogen Safety

Conveying the reality of hydrogen safety to the general public may be a major challenge. The average person will not sit still for a lecture on lower flammability limits, burning velocities and diffusion coefficients. Mention hydrogen, and most people think of the hydrogen bomb or the Hindenburg "disaster." We may have to overcome these long lasting stereotypes with the more positive aspects of the hydrogen record, possibly supplemented with new safety tests and analytical calculations.

3.1 *The Hindenburg*

The Hindenburg, after completing 35 previous transatlantic flights, was destroyed by fire while docking at Lakehurst, New Jersey on May 19, 1937. The spectacular fire that eventually consumed the entire structure was captured on film, widely publicizing hydrogen as a dangerous substance. The predecessor to the Hindenburg, the Graf Zeppelin, had flown over 1.5 million kilometers in 9 years, crossing the Atlantic 139 times without incident, including one around-the-world trip, stopping only in Lakehurst, Los Angeles, and Tokyo.

The Hindenburg carried 96 passengers and crew on that fateful day in 1937. It approached the docking arm at Lakehurst with a lightning storm in the region, which was against normal procedures. Remarkably, only 36 people were killed (including one on the ground). Pictures of the disaster are still etched in the minds of many, reminding them that hydrogen is a dangerous fuel. A live radio broadcast from the scene by a horrified announcer added to the publicity of the event.

Addison Bain, a retired NASA safety expert, has conducted a comprehensive investigation of the Hindenburg incident, searching through archives in both the U.S. and in Germany, interviewing the few remaining witnesses including surviving crew members, and even securing the services of NASA scientists to analyze fragments of the Hindenburg saved as souvenirs.[13] Bain identifies numerous myths regarding the Hindenburg, including the widely stated claim that many victims died from the fall, and not from burns (most did succumb from the flames), that the landing at Lakehurst at high altitude was normal (the Hindenburg came in at 200 feet that day, compared to the normal 50 foot altitude for docking), etc.

But Bain's most startling hypothesis is that hydrogen may not have played a major role in the fire. He sites several witnesses that saw what could have been "St. Elmos fire," -- lightning bolts attracted to the surface of the giant airship. His thorough analysis of the mechanical structure of the dirigible shows that any hydrogen leaking from the inner bags would have been vented to the outside. He shows from historical records and actual analysis of remaining fragments of the ship's gas bags that the construction was either cellulose acetate or cellulose nitrate. Both are flammable. Cellulose

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[13]Addison Bain, "The Hindenburg Incident: Cause and Effect," Keynote Address at the 8th Annual U.S. Hydrogen Meeting, Alexandria, Virginia, March 12, 1997.

acetate is less flammable but was more expensive in the 1930's. In addition, aluminum flakes were added to the covering material to help reflect sunlight to keep the gas bags cool. But Bain points out that cellulose nitrate and metal chips are also the ingredients of rocket fuel, politely suggesting that it might not be wise to paint airships with rocket fuel!

His final slide shows a photograph of another burning airship, engulfed in flames much like the Hindenburg. But with one major difference: this airship was filled with inert helium, not hydrogen, suggesting that the Hindenburg fire could very well have been started by lightning igniting highly flammable fabric on the airship. While hydrogen clearly added to the conflagration, the Hindenburg might have burned even if it had been filled with helium. In retrospect, the Hindenburg was a high risk venture, since the 190,000 standard cubic meters (6.7 million SCF) of hydrogen was carried in a set of rubberized cloth bags, with little protection from outside disturbances. The energy content of the hydrogen was equivalent to about 1,900 gigajoules (GJ), or 19 GJ per passenger.

A modern hydrogen-powered vehicle would be much safer, with energy stored in crash-tested tanks instead of flimsy cloth bags. A fuel cell electric vehicle would carry about 0.8 GJ of hydrogen energy for a four-passenger car, or 0.2 GJ per passenger. The hydrogen would be stored in one or more fiber wrapped composite tanks that could survive 50-mph head-on collisions, engulfment by a diesel fuel fire, and pressures at least 2.25 times design pressure without rupture. These carbon-fiber wrapped tanks have already been approved by the Department of Transportation for use on public highways when filled with natural gas.

The message is clear: a modern fuel cell electric vehicle would have 2300 times less hydrogen energy content than the Hindenburg, or 100 times less per passenger, and the hydrogen container would be immeasurably stronger. In effect, there is no comparison between the safety aspects of the Hindenburg and those of a fuel cell vehicle.

3.2 *Hydrogen Bomb*

The association of hydrogen energy with the hydrogen bomb is an association by name only, but it still affects some people. It should be much easier to refute than the Hindenburg association.

For the record, the term "hydrogen bomb" comes from the use of hydrogen isotopes to produce a thermonuclear or fusion reaction. In a fusion reaction, deuterium, the hydrogen isotope with one neutron (pure hydrogen has none), and tritium, the second hydrogen isotope with two neutrons, are fused together at extremely high temperatures and pressures, similar to conditions in the sun. These extreme conditions could only be achieved in the past by setting off an atomic or fission bomb. Pure tritium (which is radioactive) can also be added to an atomic bomb to boost its yield (i.e., increase its explosive power), and lithium deuteride is used to produce more tritium in a fusion or "hydrogen bomb."

The important point is that hydrogen under normal conditions on earth has zero probability of forming a fusion reaction. (Just ask the scientists who have been struggling for over 30 years with extremely powerful lasers and magnetic confinement devices to harness fusion energy in a controlled reaction.) Therefore there is no scientific credibility to the fear of hydrogen from its association with the hydrogen bomb.

Similarly, hydrogen should not be associated with radioactivity. While tritium, the second isotope of hydrogen, is radioactive with a half-life of 12.5 years, it can only be generated by a nuclear reaction. Normal hydrogen that would be used as an energy carrier will contain no radioactive tritium under any circumstance.

3.3 *National Electrical Code (NEC) Classification*

Given the opportunity, we can absolutely refute the hydrogen bomb connection and significantly diminish the practical implications of the Hindenburg fire. It will be more difficult to explain the fact that hydrogen was enshrined in the National Electrical Code (NEC) in 1937 (the same year as the Hindenburg accident -- presumably a coincidence) as an exceptionally dangerous gas. An electrical engineer, asked to design a system that contains hydrogen, will soon find that the NEC divides Class I hazardous locations (flammable gases or liquids) into four groups, in descending order of hazard[14]:

Group A:	Atmospheres containing acetylene.
Group B:	Atmospheres containing *hydrogen* or equivalent such as manufactured gas.
Group C:	Atmospheres containing ethyl ether vapor.
Group D:	Atmospheres containing most other flammable gases, including gasoline, propane, and natural gas.

By this standard, hydrogen is the second most dangerous gas, after acetylene. The other motor vehicle fuels (gasoline, propane, and natural gas) are all listed in the least dangerous flammable gas group.

This group classification is primarily based on just one factor:[15] the maximum experimental safe gap (MESG) -- the maximum opening that will still prevent the spread of a flame from inside an enclosure to a flammable mixture outside the enclosure. As shown in Table 2-4, the MESG of hydrogen is approximately 9 times smaller than that of gasoline, and 15 times smaller than the MESG of natural gas. From an electrical equipment viewpoint, it is much more difficult to provide a safe enclosure for a switch or motor in a hydrogen environment than in a natural gas or gasoline

[14]Ibid., p. 17.

[15]The group classifications for flammable gases also depends on "explosion pressure," the pressure possible in a long electrical conduit. Prior to 1971, the ignition temperature was also used to classify some gases in more hazardous groups than would be indicated by MESG alone.

environment. As a result, there are no motors or generators that are qualified to operate in a Group A or Group B environment. In an industrial setting, then, some motors and generators can operate in an environment with natural gas, propane or gasoline, but not in areas that might contain hydrogen.

For a residential setting the National Electrical Code Class I designation probably would not be enforced, although the possibility does exist for any of the motor vehicle fuels to leak in the home garage and create a flammable mixture. The NEC designates such an area that could have inadvertent flammable mixtures as Class I, Division 2, whereas Class I Division 1 refers to areas that have flammable mixtures in normal operation. Designation as a Class I area (Division 1 or Division 2) would require explosion proof enclosures or special switches and motors.

The issue might become more important in service stations or maintenance shops that repair hydrogen vehicles. If the local building inspector should interpret the NEC as requiring a Class I, Division 2, Group B rating due to the possibility of a hydrogen flammable mixture when a FCV was repaired, then all of the electrical equipment in the maintenance shop would have to be explosion resistant or enclosed in explosion proof containers. Furthermore, the vehicle itself will contain many switches and motors -- will all vehicle switches and motors have to be explosion proof?

But, even if home garages and hydrogen repair facilities escape the Class I designation, the stigma remains of hydrogen being rated as extraordinarily susceptible to ignition from electrical equipment.

4.0 Positive Hydrogen Safety Experiences

To offset the often negative public perception of hydrogen, we must seek avenues to present the very positive safety record of hydrogen. Most people probably do not realize that hydrogen is used extensively in industry today, nor do they know that hydrogen has been used for over 40 decades, even including use as a home heating fuel.

4.1 *Town Gas*

One of the more comforting facts for those who fear hydrogen may be its use in many homes prior to World War II. Before natural gas became common, many municipalities produced "town gas" by essentially gasifying coal. The manufactured gas was a roughly 50/50 combination of hydrogen and carbon monoxide. Millions of Americans cooked their food, lit their lamps, and heated their homes with hydrogen. One deleterious use for town gas was as a suicide medium, but this was due to CO poisoning, not hydrogen.

Town gas was used extensively in Great Britain (known as "coal gas") for lighting in the 19th century, with 48 km of cast-iron gas lines laid in London by 1815.[16] The composition of this coal gas was listed as 85% hydrogen and methane, and approximately 5% carbon monoxide. Interestingly, wooden gas lines were used to transport this hydrogen-rich gas in the U.S. as late as 1870.

4.2 *Commercial Use of Hydrogen*

Hydrogen gas has been used extensively in certain industries for many decades. Total U.S. hydrogen production was about 108 billion cubic meters in 1988.[17] If used as an energy source, this much hydrogen would be equivalent to 1.2 quads of energy, or about 1.5% of the energy consumed in the U.S. each year. But none of this hydrogen is used as a primary energy source. Rather, it is used predominately for making ammonia for fertilizer and for reducing sulfur in crude oil. Hydrogen is also used in the manufacture of chemicals, electronics components and for food processing. Hydrogen is also used in many hydroelectric plants to cool the large turbine generators, which is one clear illustration that hydrogen can be used safely even in the presence of large electrical ignition sources.

Almost all hydrogen is consumed at the refinery or chemical plant where it is produced. Only two percent or about 2.3 million cubic meters are sold as "merchant hydrogen" to outside customers each year. A safe and reliable hydrogen distribution network has been developed over the years, consisting of liquid hydrogen delivery trucks and dedicated hydrogen pipelines. Worldwide, there are over 800 km of hydrogen pipelines, including 225 km in the Ruhr Valley of Germany that have

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[16] Trevor I. Williams, "A History of the British Gas Industry," Oxford Press, 1981, p.15.

[17] Barbara Heydorn, "Hydrogen Industry and Markets," Proceedings of the First Annual Meeting of the National Hydrogen Association, EPRI Report No. GS-7248, March 1991.

operated safely since 1938, and 210 km of hydrogen pipeline in the vicinity of LaPorte, Texas, owned by Air Products and Chemicals.

The safety record of the commercial hydrogen industry has been excellent. There have been accidents (See Appendix C), but nothing that would indicate that hydrogen is any more dangerous than other fuels with similar energy content.

4.3 *Hydrogen in the Space Program*

Hydrogen has been used as a fuel in the space program. The Space Shuttle main engines are powered by liquid hydrogen and liquid oxygen, which provide the highest specific impulse of any rocket fuel. Hydrogen is also used onboard the Shuttle to provide electricity and water to drink via fuel cells. The NASA program has been instrumental in developing a robust and safe liquid hydrogen production and delivery system. The safety record for the NASA program is briefly summarized in Appendix C, along with other data on hydrogen accidents.

5.0 General Hydrogen System Safety Design Issues

All elements of the hydrogen energy system from hydrogen production, storage, transportation, to the fueling station, maintenance shops, and the vehicle itself must be designed initially to account for hydrogen's unique safety attributes. We can learn much from natural gas vehicles, which more closely resemble hydrogen cars than gasoline-powered vehicles. But hydrogen still has unique features relative to natural gas that require special consideration.

We start with a generic discussion of hydrogen design safety issues, followed by specific safety design considerations for the dispensing station and for the vehicle itself. Praxair has also analyzed the safety aspects of hydrogen production by steam methane reforming, as well as the refueling operation for both stored gaseous and stored liquid hydrogen. Their generic hazard review of these three operations is reproduced in Appendix D of this report.

5.1 *Hydrogen leak prevention*

Of the three legs of the fire triangle (fuel, oxidant, and ignition source), the hydrogen system designer has the most control over the fuel source. Oxygen will always be present in the atmosphere, and we have to assume that ignition sources will always be present indoors or out (although every effort must be made to minimize exposure to ignition sources, too). All system components that come into contact with hydrogen must be designed to minimize leaks. Steels susceptible to hydrogen embrittlement must be avoided.

The general approach used by those converting internal combustion engines to run on hydrogen has been to use components from the natural gas industry. Valves, fittings, fuel lines, dispensing connectors, pressure relief devices and high pressure storage tanks are often borrowed from natural gas vehicles. We need to make sure that this practice is acceptable, that natural gas components are sufficiently durable for long term use in hydrogen fuel delivery systems.

Key issue: can hydrogen vehicles utilize natural gas components? Which ones?

Any hydrogen fuel system must have pipes connecting various components, but every connection is a possible leak source, and must be carefully designed. Hansel et. al. offer the following advice for selection of components for a hydrogen fuel system:[18]

> *"...threaded connections and flanges are highly undesirable and should be avoided. Flared joints and certain crushable seal joints are far better, but welded/brazed lines are considered by far the best for hydrogen use.....Low-melting-temperature metals, plastics and elastomers should be avoided anywhere within the hydrogen fuel line system, as they could easily fail in the event of a fire and permit hydrogen to be released."*

They also recommend that "*Valve design should focus on the tightness of shut-off and resistance to packing leakage. Positive shut-off or isolation of the hydrogen is essential, and packless valves should be considered wherever possible.*"

5.2 *Hydrogen leak detection*

Presumably electronic leak detectors will be used wherever there are large volumes of hydrogen, including production plants and possibly refueling stations. We must decide if detectors are required in the vehicle or in the home garage. Standard flammable gas leak detectors based on catalytic combustion in one leg of a bridge circuit are available, but may be too expensive for widespread use. A standard hydrogen gas detector used in battery rooms of remote communications equipment costs about $600 in single quantities from Trans Sales International. A hydrogen leak detector for use in motor vehicles is available for about $170 from CCI Controls. Presumably these prices will decrease in large quantities, but it is still questionable whether consumers will pay the cost of a hydrogen leak detector in every car or every garage.

Key issue: do we need hydrogen leak detectors in home garages?[19] In FCV's? In refueling stations? Are there less expensive leak detection options (other than odorants?)

In addition, we must decide if odorants should be added to hydrogen for energy applications. Mercaptan is added to both natural gas and propane for safety reasons. If odorants are also required

[18] J.G. Hansel, G. W. Mattern and R.N. Miller, "Safety Considerations in the Design of Hydrogen-Powered Vehicles," Int. J. of Hydrogen Energy, Vol. 18, No. 9, p.787.

[19] NFPA Standard 52 for natural gas vehicle fuel systems states that detectors must be installed in the home garage when the compressor is located in the garage. This industry standard does not require detectors when only the NGV is parked in the garage.

for hydrogen, presumably new chemicals may be needed so that fuel cells are not contaminated (The sulfur in Mercaptan would surely poison fuel cell catalysts). On the other hand, the odorant must not be released during normal operation of the fuel cell to falsely alarm the passengers. If the odorant must be removed just before the fuel cell, then fuel cell contamination would not be an issue. Safety would be compromised to some degree, since a hydrogen leak in the fuel cell would not produce an odor. The ideal odorant would therefore pass through the fuel cell without any contamination, but become deactivated at the fuel cell exhaust. Since PEM fuel cell stacks might otherwise be operated "dead-ended" on the anode side with no exhaust stream, this requirement could increase fuel cell costs.

While hydrogen is odorless, significant leaks from small openings might still create an audible signature. For example, natural gas leaks from a loosened fitting on a 20.7 MPa (3,000 psi) line created a clearly detectable noise, along with fogging and ice buildup at the leak site for leak rates of 0.14 to 0.25 m^3/minute (5 to 9 cfm).[20] Normal ventilation in a bus garage would accommodate up to 0.28 m^3/min (10 cfm) natural gas flow without creating a flammable mixture away from the leaking line in the bus. The normal operating hydrogen flow rate for a FCV would be in the range of 0.14 m^3/min (5 cfm). Therefore there is a possibility that a major fuel line leak could be heard, even if no odorant were added to hydrogen. Odorants would still be desirable for slower leaks, unless normal ventilation would dissipate such slow leaks before the hydrogen cloud reached the lower flammability limit.

Key issue: do we need to develop special odorants for hydrogen that will not poison fuel cells? Or should industry develop a scrubber to remove the odorant before it enters the fuel cell? If so, what organization would do the work? Should this be a DOE hydrogen program element?

5.3 *Ignition prevention*

Should a leak occur, the designer should minimize the sources of ignition. As with detection, ignition prevention will probably be used where ever there is a large volume of hydrogen. Indeed, the National Electric Code requires explosion proof motors and switches in all Class I areas subject to flammable gases either routinely or in the event of equipment failure. Unfortunately, as discussed in Section 3.3, there are no motors certified for use in Group B (hydrogen) environments.

Key issue: will the lack of hydrogen-qualified motors hinder fuel stations that offer gasoline or other fuels in addition to hydrogen?

5.4 *Servicing of hydrogen vehicles*

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[20] "Site Assessment of NGV Bus Operations at the HSR Mountain Garage," prepared by Hatch Associates for the Ministry of Transportation of Ontario, Report No. AT-92-03, March 1993, p. ix.

Maintenance of hydrogen vehicles will require special equipment and expertise. To repair hydrogen fuel systems, shops may need to develop techniques to safely vent all remaining hydrogen from the entire fuel system. Shops may require nitrogen or inert gas to purge the tanks and fuel lines before disassembly, before opening the fuel system to air, unless procedures can be developed to safely exhaust any remaining hydrogen from the system such that no flammable mixture would be produced when it is opened to the air. After repair, the entire system might have to be purged with inert gas to remove air (oxygen) to less than a flammable ratio (4%) prior to filling with hydrogen. Repair shops should be equipped with hydrogen sensors attached to at least warning alarms if not to ventilation systems or electrical power cut-off relays (to remove electrical ignition sources.) Some of the hydrogen maintenance infrastructure may evolve from the natural gas vehicle industry.

5.5 *Technician Training*

Repair shop personnel must be trained at least to disassemble the hydrogen system, including the safe removal and replacement of major components including high pressure storage vessels, valves, pressure regulators, connectors, fuel lines, compressors, heat exchangers, and the fuel cell stack itself. Presumably defective fuel cell stacks would be returned to the factory for repair. The technicians would have to learn how to safely purge hydrogen before and after repair. They would have to be instructed regarding all safety aspect of hydrogen, including the fact that hydrogen flames are invisible.

> Key issue: what organization(s) would be responsible for training (or certifying?) hydrogen qualified technicians? SAE?

5.6 *Labeling*

Warning labels should be developed for key hydrogen equipment, including high pressure storage tanks, refueling pumps, fill connectors, etc. Whenever the public comes into contact with the hydrogen line, they should be warned not to open the lines without proper purging. Manual shut-off valves should be identified, so the hydrogen flow can be cut off in an emergency.

5.7 *Codes and Standards Development*

As stressed by the National Hydrogen Association, international codes and standards for hydrogen vehicles and refueling systems should be developed to help expedite the introduction of FCVs.

> Key issue: how does an industry that does not yet make a profit selling hydrogen for ground-based transportation sustain a national or international effort to develop codes and standards for FCVs and hydrogen infrastructure?

6.0 Vehicle Safety Hazards and Failure Modes

We now consider specific safety risks in the hydrogen-powered FCV, by examining onboard hydrogen systems failures that might lead to hazardous conditions, in both normal operation and during a collision. The hydrogen/PEM fuel cell system has relatively few potential hazards compared to other transportation power systems. There are no toxic chemicals, acids, or hot surfaces that could harm occupants in a collision or abnormal operating sequence (except to the extent that the FCV might have more battery acid onboard than a gasoline ICE vehicle)[21]. There are no flammable liquids, but FCVs, like all electric vehicles, will have relatively high voltage (eg., 350 volts) when the fuel cell system is operating.

We conclude that the only potential hazard to FCV occupants is due to the hydrogen itself, since occupants can be protected from high voltage during normal operation, and the electrical hazard disappears when hydrogen flow to the fuel cell ceases. We will therefore limit hazard discussions to but one issue: what system failure modes could lead to a release of hydrogen? We will then estimate the likelihood of various hydrogen release failure modes (Section 7.0), and describe countermeasures that we can take to minimize the risks of these events (Section 8.0.)

6.1 *Failure Modes for the Compressed Hydrogen Storage System*

As presently conceived, a mid-size (Taurus class) direct hydrogen FCV would have the capacity to carry 3.6 kg of gaseous hydrogen in 34.5 MPa (5,000 psi) cylinders. This amount of hydrogen would provide the 380 mile range, the PNGV goal, assuming that the vehicle body also met PNGV weight, drag and rolling resistance goals. However, more hydrogen would be required if the vehicle body was heavier or had greater aerodynamic drag or rolling resistance. For example, to provide 350 miles range with the current AIV (aluminum intensive vehicle)-Sable, the vehicle would have to store 5.3 kg of hydrogen. We use this larger quantity of hydrogen in this safety analysis to represent the upper bound on the expected amount of stored hydrogen.

To reach the weight goals of this vehicle design, the hydrogen storage cylinders will undoubtedly be constructed with either an aluminum liner or a thin plastic liner covered with a metallic film to retard hydrogen diffusion, covered by layers of carbon fiber wrap, possibly including some glass fibers for toughness. Each tank will be equipped with some type of pressure relief device that will prevent excessive tank pressure and massive ruptures of the tank, should they be subjected to fires or very high temperature.

We consider failure modes in both normal operation and in collisions followed by subsequent fuel-fed fires. "Normal operation" includes the possible failures after long duration (up to 5,000

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[21]Future energy storage devices might include non-acid advanced batteries, ultracapacitors or flywheels -- electromechanical storage devices. These energy storage systems will each have their own hazards, and will not be considered here.

hours) exposure to the motor vehicle environment, which includes vibration, shock, temperature extremes, and possible exposure to chemicals. Possible pressure cylinder failure modes in normal operation include:

1. Catastrophic rupture[22] due to:
   - -manufacturing defect in tank
   - -a defect caused by abusive handling of tank
   - -chemical etching and destruction of the epoxy resin in one area of tank
   - -stress rupture

2. Large hydrogen release[23] due to:
   - -faulty pressure relief device tripping without cause
   - -chemically induced fault in tank wall

3. Slow hydrogen leak due to:
   - -defect in tank
   - -stress cracks in tank liner due to pressure cycling
   - -faulty pressure relief device
   - -faulty coupling from tank to feed line or first valve connected to tank.

During a collision, the tanks could be subjected to both extraordinary impact and to fire fed by fuel spilled from another vehicle. Potential collision failure modes for the storage cylinders include:

1. Catastrophic rupture due to:
   - -collision impact
   - -puncture by a sharp object
   - -external fire combined with failure of pressure relief device to open

2. Large hydrogen release due to
   - -puncture by a sharp object
   - -fire-created hole in tank
   - -operation of pressure relief device in a fire (which is the purpose of the device)

3. Slow hydrogen leak due to:

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[22]A catastrophic rupture is a sudden, massive release of hydrogen due to failure of the cylinder tank walls, and may or may not be accompanied by ignition.

[23]A large hydrogen release is considered to be the flow of hydrogen through the given opening (pressure relief device opening, tank outlet opening, high pressure tubing diameter, projectile-caused hole or defect hole) when the tank is fully charged at 34.5 MPa (5,000 psi).

-fire-induced openings in fuel line connection
-impact-induced openings in fuel line connection

6.2 *Failure Modes for the Hydrogen Delivery System*

A typical hydrogen delivery system might include the fuel tank refilling connection (quick-disconnect?), along with its fuel line to the storage cylinder manifold (including a check valve to prevent hydrogen from flowing from the onboard tank back through the refueling connection), quarter-turn manual shut-off valves at each tank, solenoid operated shut off valves, pressure regulators, high pressure (up to 34.5 MPa) feed lines, intermediate pressure feed lines (6.7 MPa), and low pressure feed lines to the fuel cell system (207 kPa?) (See Figure 6 in Section 8.2 for one possible configuration).

Possible failure modes in normal operation (again, after system aging in the motor vehicle environment up to 5,000 hours) of the fuel delivery system include:

1. Large hydrogen release due to:
   -failure of fatigued connection in high pressure line
   -simultaneous failure of check valve and quick disconnect shut-off

2. Slow hydrogen leak due to
   -connection loosened by vibration, temperature, and pressure cycling, etc.
   -faulty solenoid or shut-off valve (leak through the valve apparatus to the outside)
   -faulty pressure regulator (leak to the outside)
   -fatigue crack in fuel line

Collisions add additional potential failure modes:

1. Large hydrogen release due to:
   -shearing of high pressure fuel line
   -fire-induced melting of solenoid valve (?)
   -rupture of pressure regulator valve

2. Slow hydrogen leak due to:
   -shearing of intermediate pressure fuel line
   -heating of pressure regulator

6.3 *Failure Modes in the Fuel Cell System*

The fuel cell system includes the fuel cell stacks, plus all the auxiliary equipment such as air compressors, humidification equipment, heat exchangers and control electronics.

During normal operation, the fuel cell system could potentially jeopardize the safety of occupants due to combustion of a hydrogen leak in:

-Membranes
-Distribution manifolds
-Humidification system
-High pressure hydrogen expander/air compressor (if any).
-Hydrogen/air heat exchanger (if any)
-Hydrogen recirculation compressor
-Rupture of fuel cell components due to freezing of water.

In a collision, the fuel cell system may not contribute any additional risk, since the solenoid valves will have shut off all hydrogen flow before it could reach the fuel cell. Any severe collision would most likely either sever fuel lines between the fuel tanks and the cell stacks or shut off all flow, as designed. Since the PEM fuel cell contains no toxic chemicals and operates at relatively low temperature (below 100°C), it would not contribute to any hazard to crash survivors, over and above the possibility of mechanical collision with occupants or bystanders.

The fuel cell system must be designed to minimize the risk of hydrogen ignition. The PEM fuel cell operating temperature (70°C to 90°C) is too low to be a thermal ignition source. But electric components such as compressor motors, temperature and humidity sensors and relays, and other control electronics could contribute to a failure mode by igniting the leaking hydrogen. While the FCV traction motor and controller may have more energetic ignition sources, they should also be farther away from hydrogen sources than the fuel cell electrical equipment.

7.0 Failure Mode Risk Assessment

7.1 *Risks of Hydrogen Storage System Failures*

We now consider the three classes of potential storage system failure: catastrophic ruptures, large hydrogen releases without explosion, and slow leaks.

7.1.1 *Catastrophic rupture of storage cylinder.* In normal operation, we assume that the probability of a fiber wrapped tank rupturing would be extremely low. Each tank is tested at 1.5 times its rated operating pressure, and samples from each lot are pressure tested to failure. Each tank design must be qualified at 2.25 times normal operating pressure. Each class of tank is also subjected to gunfire and must not explode but leak only through the bullet-hole.[24] Chemical degradation leading to failure after refueling was observed in two natural gas fiberglass-wrapped cylinders, so this possibility must be considered.

Catastrophic collision failures of the cylinders are also very unlikely. Fiber wrapped tanks have been tested in vehicle drop tests that were equivalent to crashes at up to 52 mph into a solid wall (the earth).[25] The tanks not only survived but did not lose pressure. One cannot rule out a puncture by a sharp object, but, even in this case, tests with high speed projectiles have shown that properly constructed fiber wrapped tanks do not explode-- the gas simply escapes through the puncture wound.

This leaves only one credible scenario where a tank might explode: tank overpressurization when it is placed in a fire (originating from spilled fuel after a collision or because the vehicle was parked in a burning structure) and the pressure relief device fails to release the internal hydrogen pressure as the temperature rises. However, these pressure release devices should rarely fail to open under excess pressure (rupture type) or excess temperature (fusible plug). The fusible plugs have materials that are designed to fail (melt) at high temperature. It would be difficult to construct a scenario where these devices failed to fail!

If a 34.5 MPa (5,000 psi) tank should rupture catastrophically, it could cause grave injury to bystanders even if the hydrogen did not ignite. The energy contained in the high pressure gas could propel adjacent objects at high velocity. Fragments of the tank could achieve lethal velocities.

Key issue: how reliable are the pressure relief devices? Is there any mechanism that would possibly prevent them from opening if the cylinder is heated in a fire?

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[24]It has been reported that pure carbon fiber wrapped tanks have shattered in the gunfire test, and that some glass fiber had to be added to increase toughness. (Private communication, John Wozniak of the Applied Physics Lab, August 11, 1995.)

[25]Video produced by EDO Canada on their "LiteRider" NGV fiber-wrapped cylinders.

Tentative conclusion: **the catastrophic rupture of a 34.5 MPa (5,000 psi) fiber wrapped composite storage tank that has passed the NGV-2 tests is very unlikely under any conceivable circumstance, either in normal operation or in a collision or fire.**

7.1.2 *Large hydrogen release from cylinder.* In normal operation, a faulty pressure relief device or a chemical failure are possible, although the probability of either may be very low.

Two fiber glass wrapped natural gas tanks did rupture soon after being filled to 24.8 MPa (3,600 psi) pressure. But these tanks were subjected to extreme chemical exposure through improper design packaging by an after-market NGV converter. In both cases, the tanks were mounted on the bottom of a GM Sierra truck. The installer molded shields over the bottoms of the tanks to protect them from rocks thrown up from the road. Unfortunately, no drain holes were provided for these shields, and the trucks were used to carry lead acid batteries. Over time, acid from the batteries accumulated in direct contact with the fiber glass tanks, eventually etching the glass fibers until the tanks ruptured. In one case, the tank ruptured as it was being filled, throwing the driver backwards without injury. In the second case, the tank ruptured after the driver pulled away from the pumps, reportedly lifting the truck off the road but not seriously injuring the driver.[26]

Although these tanks failed, the natural gas did not ignite in either case. There were no injuries from flying shrapnel. Further, the battery acid would not have damaged carbon fibers, the preferred material for light weight hydrogen tanks.

In a collision, hydrogen could be released as a result of a sharp object penetrating the vehicle and puncturing the tank. Hydrogen will also be released by design if a fire engulfs a FCV. If the tank pressure rises due to a fire, the pressure relief device (PRD) will open to avoid a tank explosion. However, the release rate is restricted by the PRD opening, and might not contribute significantly to the on-going fire. Put another way, if the FCV is for some reason engulfed by flames to the degree that the hydrogen cylinders become very hot, then vehicle occupants would be exposed to serious, perhaps fatal, hazards even without hydrogen release from the tank. Hence the *incremental* hazard of this event may be small. On the other hand, a relatively minor grass fire could set off a hydrogen release and thereby increase the intensity of the original fire.

7.1.3. *Slow hydrogen leak from hydrogen cylinder.* In normal operation, slow leaks could develop at either opening to the tank: the PRD connection or the fuel line connection. With proper design, the probability should be kept very low. A collision would increase the chances of causing a leak, and a fire could also exacerbate small openings.

Table 7-1 summarizes our current judgment of the major risks of a fuel tank hydrogen release.

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[26]Private communication, Rex Haddock, April 7, 1995.

Table 7-1. Possible Failure Modes for High Pressure Storage Tanks

	Normal Operation (Including Fatigue after 5,000 hours)	Collision (Including Post-Collision Fire)
Catastrophic Rupture	Not a Credible Event	Not a Credible Event
Large Release of Hydrogen	1. PRD Failure (PRD = Pressure Relief Device) 2. Chemical Etching of Tank	1. Puncture by Sharp Object 2. Operation of PRD in Fire (As planned; low additional risk in fire)
Slow Hydrogen Leak	1. PRD Connection Leak 2. Fuel Line Connection Leak	1. PRD Connection Leak 2. Fuel Line Connection Leak

7.2 *Risk of Hydrogen Fuel Delivery System Failures*

7.2.1 *Risk of large hydrogen release from fuel delivery system.* In normal operation, the most likely source of a large hydrogen release would be the fatigue failure of one of the connections between the various components and the high pressure fuel lines. While such a fatigue-induced failure may be possible, it would undoubtedly be preceded by a slow leak. Eventually that slow leak would become apparent, either due to odorants, noise of escaping gas, reduced fuel cell performance, reduced vehicle mileage, or a minor fire. It seems unlikely, although not impossible, that a minor leak would lead to a large hydrogen release without detection in a properly engineered system. The other suggested route to a large release -- the simultaneous failure of the check valve and the closure valve on the quick disconnection port -- appears to be extremely unlikely.

In a collision, the high pressure fuel lines will clearly be susceptible to damage. The system design must minimize exposure of high pressure fuel lines, and must attempt to isolate all lines from high pressure during a collision, as discussed in Section 8.0. Fire-induced damage to components such as the solenoid shut-off valves would not seem to be a credible path to increased risk, since the PRD is built into the valve assembly -- the device is designed to release hydrogen pressure in the event of a fire, without leading to a massive, catastrophic rupture.

7.2.2 *Risk of slow leaks in fuel delivery system.* Slow leaks could develop at any of the connections between the fuel line and various components, particularly after many hours of temperature cycling and vibration. Proper design including provisions for flexible fuel line loops to relieve stress should reduce the risks. In addition to the multiple connections, individual components such as valves and pressure regulators could develop internal leaks. While minute leaks of hydrogen by diffusion through very small cracks or openings in these devices are possible, it is unlikely that sufficiently large leaks would develop to cause a significant fire risk.

Table 7-2 summarizes current estimates of the likely risks.

Table 7-2. Possible Failure Modes for the Fuel Delivery System

	Normal Operation (Including Fatigue after 5,000 hours)	Collision (Including Post-Collision Fire)
Large Hydrogen Release	Fuel line connection fatigue failure	Severing of Fuel Lines
Slow Hydrogen Leak	1. Fuel Line Connections 2. Internal Device Leaks (Valves, Pressure Regulators)	1. Collision-induced Device Leaks 2. Fire-induced Leaks

7.3 *Risk of Fuel Cell System Failures*

In normal operation, the greatest risk for fuel cells would appear to be where hydrogen and oxygen normally meet across very thin membranes. In fact, in our push to develop light weight and compact fuel cells, we may be exacerbating the threat by going to very thin membranes. Hydrogen will always diffuse across a few mils of polymer material. The hydrogen normally combines with oxygen catalytically with no harm. But real membranes also have pinholes, which allow greater quantities of hydrogen to leak across. One can imagine a series of these pinholes growing over time with constant use. Initially they would reduce efficiency slightly, and the fuel cell stack temperature would rise as the leaked hydrogen combusted catalytically with oxygen on the air side of the membrane. Fuel cell durability tests will be needed to determine if this pinhole mechanism could exhibit positive feedback, with small leaks raising stack temperature, which in turn might weaken the membranes leading to larger leaks. However, these failure mechanisms would presumably be identified and corrected before fuel cells were qualified for commercial production. Membrane electrode assembly manufacturing irregularities could presumably still lead to leaks in production units, which might lead to overheating. In any case, thermocouples on the fuel cell stacks should shut down hydrogen flow in this case.

Slow leaks might also develop in the hydrogen manifold system that feeds the fuel cells. Again, thinner cells means thinner feed mechanisms and presumably greater propensity to leak after 5,000 hours of vibration and temperature cycling. Leaks are also possible in the humidification system, and in the hydrogen expander used to compress air. Seals could wear out in the hydrogen expander over time, or wear could open up gaps between the expander vanes and the side walls containing the hydrogen.

Table 7-3 summarizes our current assessment of the most likely hydrogen leak sources in the fuel cell system.

Table 7-3. Possible Failure Modes for the Fuel Cell System

	Normal Operation (Including Fatigue after 5,000 hours)	Collision (Including Post-Collision Fire)
Large Hydrogen Release	Membrane Pinhole Enlargement	No Additional Risk
Slow Hydrogen Leak	1. Hydrogen manifold 2. Humidifier 3. H_2 Expander/Air Comp. 4. H_2/Air Heat Exchanger	No Additional Risk

We also need to consider other fuel cell failure modes such as membranes drying out (insufficient humidification), overheating, passages clogging up with water, and freezing of water in humidification channels. For each failure mode, we need to determine if the consequences are dangerous, and, if so, what sensors and countermeasures should be added to prevent that fault mode.

Key issue: are there fault modes such as overheating or drying out of membranes that should be monitored with sensors triggering automatic shutdown to prevent hazardous situations?

8.0 Hydrogen Failure Mode Countermeasures

Given the most likely sources for hydrogen leaks as summarized in Section 7.0, the FCV must be designed to eliminate or reduce the probability of leaks to insignificant levels in both normal operation (Section 8.1) and in collisions (Section 8.2). Despite our best efforts, however, there will always be some finite probability of leaks developing, particularly in a collision. The design should consider the option of using hydrogen detectors to warn occupants or, possibly, to activate ventilation systems (Section 8.3). Finally, the FCV design must eliminate as many ignition sources as possible from the expected hydrogen flammable region in both normal operating and collision conditions (Section 8.4).

8.1 *Leak Prevention in Normal Operation*

Two pressure tank failure modes have been identified that could lead to a large release of hydrogen: failure of the pressure relief device (PRD) and tank deterioration due to chemical action (such as from spilled battery fluid).

There are (at least) three types of PRD's: burst disks that open at high pressure, fusable plugs that melt open at high temperature, and spring loaded valves that open with high pressure. Some PRD's operate on both temperature and pressure: for example, a fusible material must first melt due to high temperature, which then enables a pressure disc to release under high pressure. These composite PRD's have not been reliable in the past, as they have opened prematurely. Millions of PRD's are used in propane tanks, but these operate at pressures of only 600 to 1200 kPa. In the U.S. compressed natural gas tanks that operate up to 24.8 MPa (3,600 psi) are required to have PRD's. They are not required in Italy, however, the country with the most natural gas vehicles (250,000) in operation.

One NGV tank manufacturer, EDO, wrote to the Department of Transportation, urging DOT to specify that only fusable plug PRD's be allowed on high pressure tanks. They contend that the pressure-activated PRD's do have a propensity to open unintentionally under extreme but tolerable conditions of high ambient temperature and high tank internal pressure. EDO believes that the fusable plugs are superior, since they will only open at extraordinarily high temperatures caused by a major fire. The DOT declined to accept this suggestion, however, and the Federal Motor Vehicle Safety Standard No. 301 does not specify which type of PRD to install, which is consistent with DOT/NHTSA philosophy of specifying performance and not design standards.

There have been no failures (false openings) after five years of operation of 16,000 NGV tanks in Ontario equipped with fusible plugs.[27] However, more information is required before a decision regarding the preferred type of pressure relief device can be made.

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[27]Internal memo from Matthew Fairlie of Electrolyser Corp. dated August 11, 1995.

In Section 7.1, high pressure tank openings (PRD and fuel inlet/outlet connection) were identified as possible sources of leaks after 5,000 hours of service.

To prevent fuel line connection leaks, all fuel lines should either be flexible or have loops or other means to accommodate movement from shocks and vibration.

Other components such as shut-off valves, solenoid valves, and regulator valves also need to be leak tested after being subjected to the motor vehicle environment.

The fuel cell system must be similarly scrutinized with respect to long term leak potential, along with the humidification system, and the hydrogen expander/air compressor system, if it is to be used.

8.2 *Leak Prevention in a Collision*

We can avoid hydrogen leaks from the storage tanks in most accidents by placing the cylinders away from the vehicle crush space. The EDO drop tests at simulated speeds up to 52 mph into solid earth clearly show that fiber wrapped composite tanks are extremely durable in even the highest impact crashes.

However, we can never rule out bizarre accidents where a tumbling or careening vehicle strikes a sharp object at just the right angle and position to puncture the tank.

> Key issue: is it practical to consider a deflection plate or plates over the hydrogen tanks to deflect possible protrusions in an accident? Or would they have to be too heavy to be effective?

The hydrogen tank would also release hydrogen by design in the event of a post-collision fire, as the PRD opens at high temperature or pressure. We need to design or select the PRD so that it safely vents the cylinder at the lowest possible flow rate to minimize additional fuel supplied to the fire. Ideally the PRD should be vented in a direction to minimize potential contact with people and to avoid the accumulation of hydrogen beneath the vehicle.

A collision could also knock off the main cylinder fuel line connection, or the closest valve to the tank, emptying the tank within minutes. The FCV design should definitely include mechanical protection for the cylinder input port by proper orientation on the vehicle and possibly an external collar around the input line.

The fuel delivery system is also potentially vulnerable to collision damage. Fuel lines will undoubtedly run over fairly long distances in the best design, connecting the external refueling port with the storage tanks, and connecting the storage tanks with all the fuel cell system components through numerous valves and flow control devices. It would be extremely difficult to protect all of these lines and connecting devices from all possible collision damage. Lines should be excluded from the vehicle crush space to the extent possible, and confined within or along structural body members whenever possible. However, any areas containing hydrogen fuel lines must also be well ventilated, in case of slow leaks, which could conflict with the goal of strong mechanical protection.

The FCV designer must assume that fuel lines will be ruptured in some accidents. The amount of hydrogen in the fuel lines and the fuel cell stack system at the instant of a collision would not be a major threat, but the rapid release of up to 5.3 kg of hydrogen could create a very serious fire. The key is to isolate the storage cylinders from the rest of the system at the instant of the collision.

One concept for a safe fuel delivery system is shown in Figure 6. The two key ingredients of this collision-safe system are the pressure relief device (PRD) discussed earlier and an electrically operated solenoid valve mounted inside each high pressure tank.

The solenoid valve is normally closed. This fail-safe arrangement means that the removal of electrical power closes the valve, stopping the high pressure flow of hydrogen. As indicated in Figure 6, three conditions are required to keep the solenoid valves open:

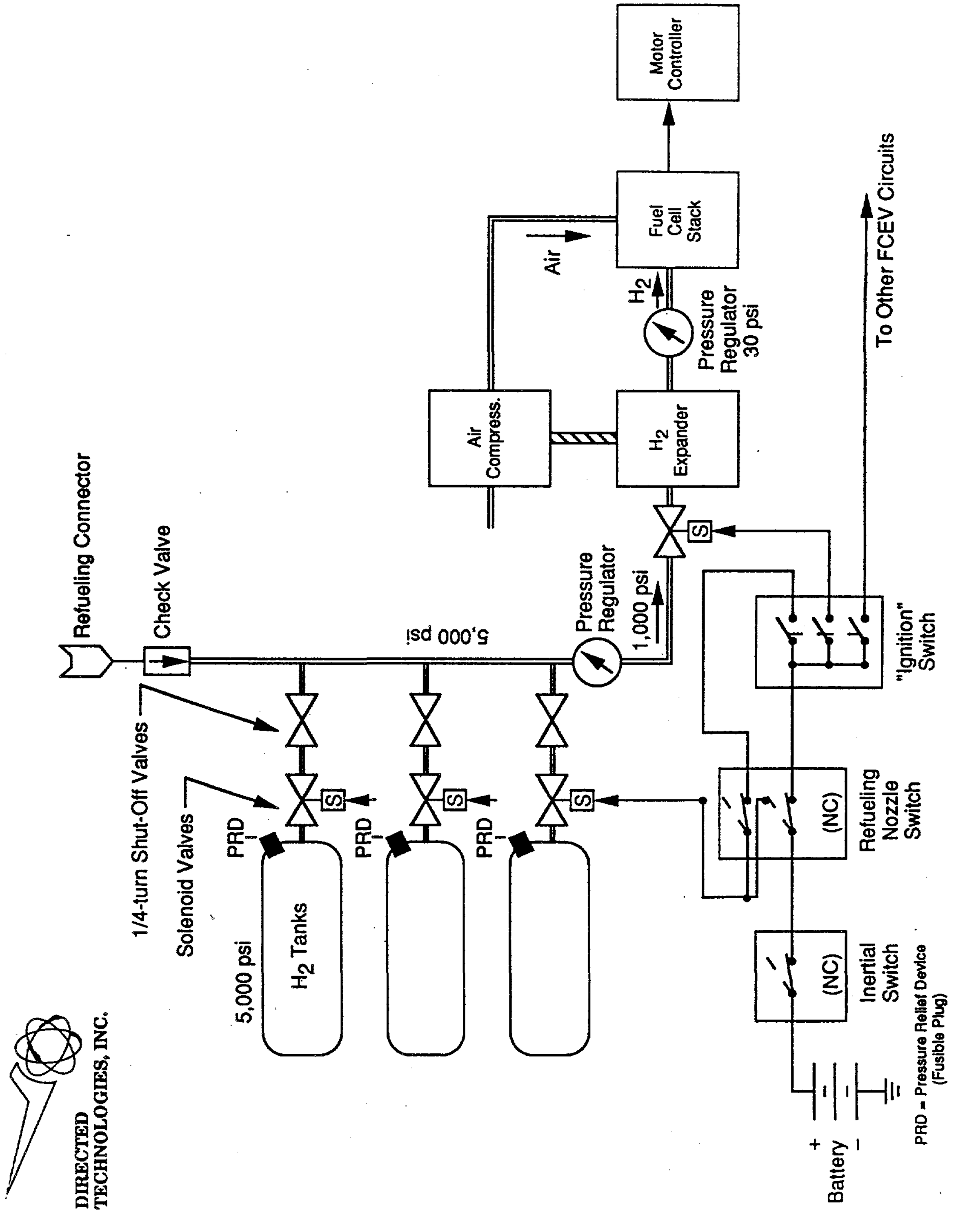
-the FCV "ignition" switch must be on,
-the refueling connector door must be closed[28], and
-the inertial switch must not be activated.

The inertial switch is activated only by a collision above a preset "g" level, usually between 5 and 10 g's. This acceleration threshold eliminates false activation due to normal bumps and shocks, but will shut off hydrogen flow from any serious collision. Upon impact, the switch opens a relay in the solenoid circuit within milliseconds, preventing any escape of high pressure hydrogen from the tank. Note that the electrical circuit is also fail-safe: any circuits cut by the accident will also release the solenoid valves, cutting off hydrogen flow. The inertial switch must be manually reset after an accident to activate the solenoid valve and resume hydrogen flow to the fuel cell.

The safety of this system then depends on the mechanical integrity and reliability of the solenoid valve. The valve would itself have to be protected from impact. We believe that providing impact protection for these valves placed immediately at the storage tank outlet will be less of a challenge than insuring the integrity of many feet of high pressure hydrogen fuel lines

[28]Inserting the refueling nozzle would activate the tank solenoid valves, but not the main fuel line solenoid valve. The refueling nozzle switch would deactivate the other vehicle circuits, preventing the car from being driven away or the main fuel line solenoid from being opened while the tanks were being filled.

Figure 6. Illustration of a Safe Hydrogen Fuel Delivery System



running from the fuel tanks to the fuel cell system. At least one manufacturer builds a recessed solenoid valve that is used on the Ford natural gas vehicles. This valve has been hydro tested to 100 MPa (14,400 psi), higher than the 77.6 MPa (11,250 psi) pressure required with a 2.25 safety factor on a 34.5 MPa (5,000 psi) hydrogen tank.[29] Two other manufacturers have expressed interest in developing such a solenoid valve.

The projected cost of a solenoid valve is $80 to $90 in mass production, which could be too costly. Presumably manufacturing volumes associated with the motor vehicles would drive the cost down further. Costs could be reduced by placing a single solenoid valve after the tank manifold lines, but this would compromise safety by exposing more high pressure line to collision damage.

All high pressure lines might be placed in a special enclosure protected from collision damage, with only low pressure hydrogen lines running to the fuel cell. But low pressure lines would have to be larger to carry the flow, and the hydrogen expander/air compressor system would have to be contained within this enclosure too.

Another alternative would be to place inertially operated valves directly on the inlet line to each hydrogen cylinder, assuming that they could be manufactured for less cost than a 34.5 MPa (5,000 psi) solenoid valve. This approach would have the disadvantage of requiring the driver to manually reset the inertial valves physically located at each tank after a "fender-bender" accident, which is not acceptable to most drivers. (The inertial switch operating the solenoid valve can be located on the dashboard or within reach of the driver for easy reset.)

> Key issue: Is the electrically operated solenoid valve activated by a collision-sensing inertial switch the most cost-effective solution? If not, are there less expensive but effective options to stop the flow of hydrogen in a major accident, such as inertially operated shut-off valves? Alternately, can we protect all high pressure components including the hydrogen expander/air compressor within a collision proof box, with a low pressure solenoid at the output of the enclosure?

One less desirable option would be to place excess flow control valves at each hydrogen cylinder opening. While this might reduce the hydrogen flow rate in the event that a high pressure hydrogen line were broken, it would still allow considerable energy to escape. The energy to keep a 100-hp motor running is significant and could produce a sizable fire. We conclude that excess flow control valves would not be adequate alone to reduce the fire risks of a hydrogen fuel line break.

Another possible option would be to install tear-away closure valves at key points in the high pressure lines. These valves close automatically when the incoming line is removed, much like the

[29]Private communication with Dwight Nofsinger, Superior Valve Company, May 22, 1995.

seal on the fuel refill line connector. If these tear-away valves are reasonably priced and reasonably reliable, they may make a good substitute for the electrically operated solenoid valve.

Key issue: are tear-away valves cost effective?

With these precautions to either shield all high pressure hydrogen components within a solid enclosure, or to provide inertially activated closure of the high pressure hydrogen at the cylinder inlet, we do not believe that any special precautions are needed to protect the fuel cell stack itself in the event of an accident.

8.3 *Leak Detection*

The Department of Transportation does *not* require leak detection systems under their Standard 303 for natural gas vehicles. However, they consider the odorant in natural gas to be a sufficient warning of leaks. The DOT may also expect hydrogen to have an odorant, based on their practice with natural gas. The main natural gas odorant, butyl mercaptan, can be sensed by most humans at concentrations of about 1 part per billion. This odorant is added in sufficient quantity so that most people will smell natural gas at concentrations of 0.04%, or 100 times less than the lower flammability limit of 5.3% for natural gas. However, the sulfur in mercaptan would deactivate the catalysts in fuel cells, so the mercaptan would have to be removed prior to the fuel cell or an alternative odorant would have to be developed for hydrogen.

Major issue: should the hydrogen community develop a fuel cell friendly odorant for hydrogen? Should DOE take the lead?

If we are not able to odorize hydrogen due to fuel cell poisoning considerations, then we may have to revisit the issue of providing electronic leak detectors, either for warning or to activate windows, trunk lids or ventilation systems. Without an effective odorant, electronic leak detection may be necessary in both vehicles and in home garages.

With or without an odorant, we may want to consider some type of leak detector for the fuel cell stack, primarily to avoid the deterioration (and possible development of a hazardous condition) through enlargement of pinholes in the cell membranes. For example, thermocouples might be installed within the stacks to measure temperature rise. Excessive heating would give early warning to increased hydrogen flow through a leaky membrane. In principle, faulty cell stacks could be shut off automatically without shutting down the entire system if the hydrogen lines to each stack contained individual solenoid valves.

Key issue: is there a cost effective method for monitoring the integrity of the fuel cell membranes, such that a leak can be detected before a flammable mixture of hydrogen accumulates in any cell?

8.4 *Ignition Prevention*

Should a hydrogen leak occur despite our best efforts, we can still reduce the probability of the hydrogen igniting. First, as discussed in more detail in Appendix B, one detailed experimental study found that 85% of all gasoline fires after a collision are ignited by electrical sources. Hot surfaces such as exhaust manifolds and catalytic converters cannot ignite gasoline under normal crash circumstances, and even friction sparks caused by dragging metal parts across the pavement rarely ignite fires. But most electrical sparks, battery shorts or overheated wires (including hot headlamp filaments) are possible sources of ignition for gasoline as long as the battery current continues to flow, and such electrical currents will likely ignite hydrogen clouds, too.

One approach to prevent such ignition is therefore to disconnect the battery bank with an inertial switch. This switch, used to turn off the fuel pump on all Ford vehicles and most British cars for many years, would disconnect the main battery lead (through a relay) during any collision of pre-determined magnitude. This same inertial switch would also cut off the hydrogen high pressure line, as discussed above, if solenoid valves are cost effective. The switch is reset manually after the collision to restart the car.

For non-collision fuel leaks, the vehicle should be designed such that hydrogen components and fuel lines are separated physically from all electrical devices, batteries, motors and wires to the maximum extent possible.

All hydrogen components should be located as much as possible so that any hydrogen leaks will be vented to the outside and upward, away from possible onboard ignition sources. In principle, the entire fuel cell system could be enclosed in a container with outside ventilation. When the vehicle is moving, the air exchange alone would keep any conceivable leak below the 4% lower flammability limit for hydrogen. When the vehicle is at rest, the vent design should have an opening to allow the hydrogen to escape upward, while accommodating rain, snow, dust, mud and other contamination without clogging.

> Key issue: should the fuel cell system, including all air compressors, humidifiers, heat exchangers and pressure regulators be placed in a container with a separate ventilation system? Should the fuel tanks have a similar vented enclosure?

9.0 Dispensing Station-Specific Safety Design Issues

The hydrogen dispensing station will have unique hazards and specific countermeasures to assure safe operation.

9.1 *Break-away Hoses & Automatic Shut-off Valves*

All dispensing stations should be equipped with special hoses with appropriate shut-off valves that will automatically cut the flow of hydrogen if the vehicle should be driven away without disconnecting the hose. This will be a redundant safety feature, assuming that all hydrogen-powered vehicles have the refueling nozzle switch that shuts off power to the vehicle fuel cell system while the tanks are being filled.

9.2 *Electrical Grounding of Vehicles*

As noted above, one study found that the ignition source for 85% of gasoline fires was electrical sparks. To minimize the chances of static electricity igniting any leaking hydrogen, all vehicles should ideally be grounded before the fuel is dispensed, eliminating the possibility of static electricity from the vehicle to the pump igniting any fuel vapors. This same hazard exists for gasoline-powered vehicles, however, but regulations do not require that vehicles be electrically grounded before filling up our tanks. Since gasoline fumes are heavier than air and have a lower flammability limit than hydrogen (1% vs. 4%), one would expect a greater hazard from gasoline fumes being ignited by static electricity than hydrogen. On the other hand, high pressure hydrogen may have a greater propensity to leak in the vicinity of the fueling nozzle, requiring greater protection from static electricity.

Key issue: should hydrogen-powered vehicles be grounded before fueling begins?

If static discharge is considered a hazard for hydrogen vehicles, we should consider an electrical interlock, such that the refueling flow is blocked by a solenoid until the ground circuit is complete (making sure that the detection circuit does not itself become an ignition source.)

Alternately, the ground lead could be incorporated into the refueling nozzle, making a mechanical ground interlock. However, combining the electrical grounding with the nozzle connection could create the very hazard we are trying to avoid: if there is a slow leak in either the fueling nozzle or in the vehicle fueling fixture, then closing the electrical grounding circuit adjacent to the nozzle could bring a spark into proximity of an otherwise very small flammable cloud. Therefore a separate grounding connection should be made *before* the fueling nozzle is inserted into the vehicle.

Key issue: can drivers be burdened with a two-step refueling process: attaching a separate grounding wire prior to inserting the fuel nozzle into the vehicle receptacle?

9.3 *Low Pressure Sensors on Storage Tanks*

One safety hazard might be the possibility of air leaking back into nearly depleted hydrogen storage tanks, creating a flammable mixture. This could be mitigated by placing a check valve in the refueling line, or by sensing the pressure in the storage tanks and shutting off any tank that falls below some minimum pressure -- or both.

9.4 *Location of Tanks and Refueling Pumps*

Presumably all refueling stations will have to conform to NFPA 50A, "Standard for Gaseous Hydrogen Systems at Consumer Sites." This standard, in addition to specifying the requirement for pressure relief valves, hydrogen compatible components, etc., lists the required distances between storage tanks and other buildings, property lines (5 feet), public sidewalks and parked vehicles (15 feet), or place of public assembly (25 to 50 feet depending on the amount of hydrogen stored.)

10.0 Comparative Risk Assessment

To calculate the *absolute* risk of death or injury due to the use of hydrogen as a motor vehicle fuel, one would construct a fault tree diagraming all conceivable paths that could lead to a fuel fire or explosion. Then the probability of each event and the consequences of each accident would be estimated, with the final risk equal to the product of the probability and the consequence. Given the calculated risks, we would then have to decide what level of risk is acceptable. However, the public is notably averse to the risks associated with unknown events, even while accepting the equivalent risks of common activities. Nuclear power is feared more than coal power by much of the general public, even though over 11,000 miners are injured and more than 60 die in coal mining accidents each year, whereas the worst U.S. nuclear accident at Three Mile Island caused no serious injury and no death.

Evaluated by itself, hydrogen would probably have to meet a very stringent risk level, since it is unknown to most of the public. Walter Stewart of the Los Alamos National Laboratory found a Congressional Record statement from 1875 which illustrates that gasoline once suffered from this unfamiliarity fear:[30]

> "A new source of power...called gasoline has been produced by a Boston engineer. Instead of burning the fuel under a boiler, it is exploded inside the cylinder of an engine...
>
> "The dangers are obvious. Stores of gasoline in the hands of people interested primarily in profit would constitute a fire and explosive hazard of the first rank. Horseless carriages propelled by gasoline might attain speeds of 14, or even 20 miles per hour. The menace to our people of this type hurtling through our streets and along our roads and poisoning the atmosphere would call for prompt legislative action even if the military and economic implications were not so overwhelming...the cost of producing [gasoline] is far beyond the financial capacity of private industry...In addition, the development of this new power may displace the use of horses, which would wreck our agriculture."

One approach to minimize this unfamiliarity-breeds-fear phenomenon is to compare hydrogen directly with more common fuels -- *comparative* risk assessment instead of *absolute* risk assessment. For example, the public has come to accept the small but quantifiable risks involved in personally pumping 20 gallons of gasoline into their car and to piping natural gas directly into their homes. The automotive industry and the home heating industry have properly engineered these products to safely manage these energy sources with very low risk. If we can show that handling and storing hydrogen involves no greater total risk, then the public should be more receptive to using hydrogen.

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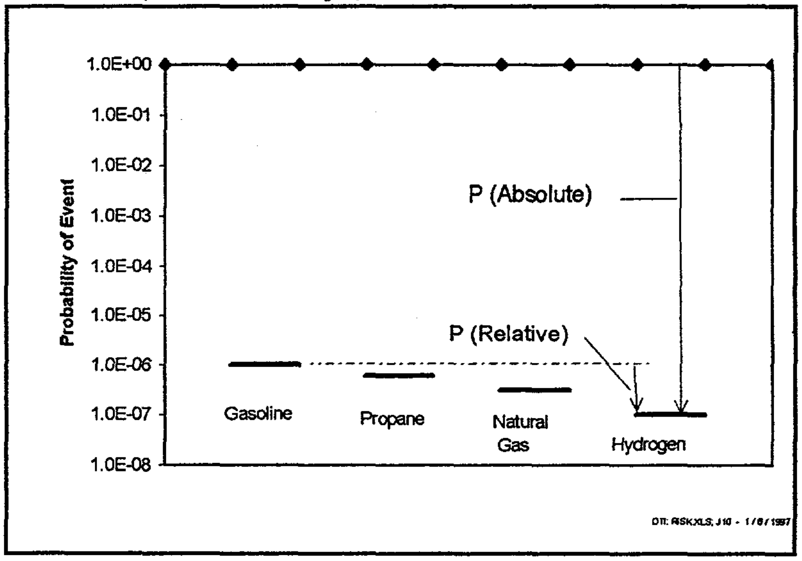
[30]Walter F. Stewart, "Hydrogen as a Vehicular Fuel," Chapter 3 of K.D. Williamson, Jr. and Frederick J. Edeskuty, Recent Developments in Hydrogen Technology, Vol. II, CRC Press, 1986, p.132.

By comparing the risks of hydrogen with those of common fuels, we would not have to try to estimate the absolute risk of hydrogen, and we would not have to choose an acceptable risk level. In effect, we use existing fuels such as gasoline, natural gas, and propane as a baseline for judging the relative safety of hydrogen. This concept of comparative vs. absolute risk assessment is illustrated in Figure 7 for a hypothetical probability of some event occurring. In this case, the probabilities of the event are less than one in a million for all four fuels, but hydrogen is shown as being less likely to experience this hazard than the other fuels. It is often easier to estimate the relatively small difference between hydrogen and the other fuels (a factor of less than ten in this example) than to estimate the absolute probability, a factor of less than one in a million.

10.1 *Gasoline Safety*

Figure 7. Comparative Vs. Absolute Risk Analysis (Illustrative Example)



The conventional motor vehicle is remarkably safe with respect to gasoline related hazards, considering the potential risks involved with moving a half ton of TNT equivalent down a highway at 65 mph. Each year 170 million American drivers propel 190 million vehicles (including 145 million automobiles) more than 3.4 trillion kilometers[31]. There are 33 million accidents, and approximately 45,000 lose their lives annually in traffic accidents, but, remarkably, only one percent involve vehicle fires.[32] Put another way, a gasoline fire fatality occurs once every 7.2 billion kilometers of travel. So the chances of dying in a gasoline fire on a 4,800-kilometer cross country trip are about one in 1.5 million.

Presumably collision rates will be the same for FCVs and gasoline vehicles, since the FCV as presently conceived will have the same performance characteristics. Thus the pertinent questions are whether post collision fires will be more or less probable with hydrogen, and will they be more or less hazardous?

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[31] Statistical Abstract of the United States 1993, U.S. Department of Commerce, p. 616.

[32] Private communication with Alison Miller of the National Fire Protection Association, March 22, 1995.

The annual safety and fire-related statistics for gasoline-powered vehicles are summarized in Table 10-1. The key gasoline-related safety data indicate that a person traveling 17,700 kilometers in the United States faces these risks from a gasoline-related fire:

- a 1.6 chance out of a million of a fire-caused fatality
- a 5.6 chance out of a million of a fire-caused injury, and
- a property damage risk of $1.10 per year caused by a gasoline fire.

For frame of reference, other common activities that produce a one in a million chance of dying include:[33]

-rock climbing for 1.5 minutes,
-skiing for 20 minutes,
-working on a farm for 19 hours, or
-flying on a scheduled airline for 1.2 hours.

In other words, the risk of using gasoline onboard a motor vehicle has proven to be very safe, compared to other human activities.

10.2 *Natural Gas Safety*

Natural gas is also a good reference fuel for comparing hydrogen risks, since it is very common and has also been used relatively extensively as a motor vehicle fuel. In addition, natural gas has more in common with hydrogen than either has with gasoline. It is hoped that hydrogen, like natural gas, will be accepted as a safe fuel. The hydrogen community must demonstrate that hydrogen deserves the same treatment as natural gas.

Natural gas is also used to power about 750,000 motor vehicles around the world. The estimated NGV fleet includes:[34]

Italy	250,000
Ex-Soviet Union	200,000
Argentina	75,000
New Zealand	60,000
Canada	35,000
U.S.	40,000

[33] Larry Laudan, The Book of Risks, John Wiley & Son, New York.

[34] James S. Cannon, Paving the Way to Natural Gas Vehicles, INFORM, 1993, p. 13.

More than 100,000 natural gas vehicles have been operating in Italy since the late 1930's. Most of these NGVs are local conversions made in the Po Valley, which has an abundant supply of natural gas.[35] There are relatively few dedicated NGVs manufactured by automobile companies.

Despite the home-made flavor of these NGVs, and despite the fact that these NGVs have been operating since the late 1930's, the safety record appears to have been excellent. Some early natural gas steel cylinders did fail in Italy. In 1974, for example, there were 6 reported tank failures

[35]Private communication with James S. Cannon, March 23, 1995.

Table 10-1. Summary of Passenger Vehicle Annual Accident Statistics (1988-1992 Average)

		Rate per VMT	Rate/ Vehicle
Registered Motor Vehicles	190,000,000		
Vehicle Miles Traveled (VMT)	2,100,000,000,000		11,000
Total Motor Vehicle Accidents	33,000,000	1.57e-05	1.74e-01
On-Road Accidents	15,400,000	7.33e-06	8.11e-02
Total Fatal Accidents	40,000	1.90e-08	2.11e-04
Fatal non-collision accidents	5,000	2.38e-09	2.63e-05
Fatal collisions with other vehicles	20,000	9.52e-09	1.05e-04
Fatal collisions with fixed objects	13,000	6.19e-09	6.84e-05
Fatal collisions with pedestrians	7,500	3.57e-09	3.95e-05
Total Highway Deaths	45,000	2.14e-08	2.37e-04
Total Fire-related deaths	458	2.18e-10	2.41e-06
Deaths from fires triggered by collisions[36]	(296)	1.41e-10	1.56e-06
Deaths from fires when gasoline was the first material ignited. (Collision and non-collision)	(311)	1.48e-10	1.64e-06
Total Motor Vehicle Injuries	5,400,000	2.57e-06	2.84e-02
Total Fire-related injuries	2,100	1.00e-09	1.11e-05
Injuries from fires triggered by collisions	(487)	2.32e-10	2.56e-06
Injuries from fires when gasoline was the first material ignited. (Collision and non-collision)	(1,100)	5.24e-10	5.79e-06
Total Motor Vehicle Fires	330,000	1.57e-07	1.74e-03
Fires following collisions	(6,000)	2.86e-09	3.16e-05
Fires when gasoline was the first material ignited.	(126,000)	6.00e-08	6.63e-04
Fires of incendiary or suspicious nature	(55,200)	2.63e-08	2.91e-04
Direct Fire-related property damage	$600,000,000	2.86e-04	3.16e+00
Damage from fires triggered by collisions	($24,000,000)	1.14e-05	1.26e-01
Damage from fires when gasoline was the first material ignited.	($211,000,000)	1.00e-04	1.11e+00
Damage from incendiary or suspicious fires	($173,200,000)	8.25e-05	9.12e-01

Ref: Christopher J. Conley, "U.S. Vehicle Fire Trends and Patterns through 1992, Leading Causes and other Patterns and Trends, Passenger Road Transport Vehicle Fires," National Fire Protection Association, October 1994, Tables 4 and 7, and Statistical Abstract of the United States, 1993, U.S. Department of Commerce, Bureau of the Census.

Values in parentheses (--) indicate sample subcategories that are not mutually exclusive and do not add to the total; thus a fire can be caused by a collision and gasoline can be the first material ignited in that same fire -- it is counted in both categories. Other causes of fires and other materials first ignited are not shown in this table.

[36]Authorities are instructed not to include impact-caused fatalities in the category of fire-caused deaths, even though a fire subsequently ensues, but NFPA acknowledges that this fire-caused fatality count may be too high.

out of 408,000 tanks in use, or one failure for every 68,000 tanks. By 1980, the failure rate had dropped to one per every 460,000 tanks, with no failures reported after 1980.[37] Since Italy does not require a pressure relief device on all tanks[38] -- a DOT requirement in the U.S. -- even these few failures might have been avoided with U.S. standards. No deaths or injuries were reported as a result of these early tank failures.

One study in Sweden by the Co-Nordic Natural Gas Project[39] reports that "*there has never been a recorded accident resulting from a faulty CNG system*" and "*CNG components rarely failed and never caused a death or injury*"[in Italy]. If we use U.S. statistics of one gasoline fire fatality per 7.4 billion kilometers traveled, and if natural gas was as hazardous in a collision as gasoline, then we would expect to witness one fatality every 2 years, assuming that Italy's 200,000 NGVs travel 19,300 kilometers per year. The fact that they have not recorded any fatalities in 40 to 50 years might indicate that natural gas has less risk, but the numbers are far too small to be statistically significant, particularly since Italian authorities might easily miss recording one fire fatality every 2 years involving a natural gas-powered vehicle.

World wide, with 750,000 NGV's, we would expect to see two fire related deaths every year, again assuming that NGV's travel 19,300 kilometers per year. The Swedish study uncovered only one fatal NGV fire. In that case, the NGV owner in New Zealand added an extra compressed natural gas tank in the back of his van. He placed the metal fuel line over the battery, which subsequently arced to the fuel line, melting it and eventually setting off an explosion that killed two people.

Overall, the Swedish study concludes that "NGVs are at least as safe as gasoline vehicles," noting that there are too little data to make a statistical comparison with gasoline. They report that only 0.5% of vehicle fatalities are due to fuel fires in Norway, less than the one percent estimated in the United States.

The safety record of NGVs in the U.S. is also excellent, although the relatively few vehicles --30,000 to 40,000 -- mostly in the commercial fleets, do not permit a statistically significant comparison with gasoline-related fires. One often quoted study by the American Gas Association has been used (incorrectly but inadvertently) by several authors to suggest that NGV's might be safer than gasoline vehicles, when in fact the data are far too meager to show *any* relevant difference.

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[37]International Association for Natural Gas Vehicles, A Position Paper on Natural Gas Vehicles, Auckland, New Zealand, 1993, Chapter 6, p.4.

[38]Thomas J. Grant et. al., Safety Analysis of Natural Gas Vehicles Transiting Highway Tunnels, Ebasco Services, Inc., New York, August 1989, p. 6-3.

[39]Mats Ekelund et. al., NGVs and Safety, Co-Nordic Natural Gas Bus Project, 1993.

This AGA study reported no deaths for 8,000 fleet NGV's that traveled 450 million kilometers over a three year period.[40] AGA mentioned (but drew no conclusions) that the total gasoline fleet vehicle death rate was 0.8 per 100 million kilometers, while all registered vehicles had a combined death rate of 1.37 per 100 million kilometers traveled. But only one percent of vehicle deaths is due to fire -- 99 percent are caused by the collision. There is no reason to expect that NGV's will have lower collision impact deaths than gasoline-powered vehicles. In fact, this meager 8,000-NGV fleet would have to wait 50 years (7.4 billion kilometers) before we would expect to see one fire-related accidental death, assuming that natural gas vehicles had the same fire death rate as gasoline vehicles!

AGA also reported a 37% lower injury rate for the NGV fleet. But, again, this was total injuries for all causes, and fires are responsible for only 0.04% of all accident injuries (see Table 10-1), and gasoline causes only 0.02% of all injuries. Changing fuel cannot explain this large drop in injury rate. The drop must be due to some combination of very low data base and the unique features of the natural gas fleet population which is primarily commercial fleets with different demographics and different driving cycles than the average gasoline-powered vehicle.

Natural gas fire results from New Zealand, based on 32,000 NGV's, indicate a total vehicle fire rate (collision and non-collision) between 4% and 16% of the corresponding fire rates for 1.4 million gasoline-powered vehicles in the years 1979-1985. The Fire Commissioner in Vancouver, British Columbia also reported that fire rates for 5,000 NGV's were 40% of the gasoline vehicle rates over a six year period.[41]

We conclude that there is reasonable evidence that natural gas vehicles have lower non-collision fire rates than gasoline, but there are no statistically significant data indicating that natural gas is safer in a collision

While there are 40,000 natural gas vehicles in the U.S., they are far too few to collect meaningful risk statistics, especially compared to 140 million gasoline-powered vehicles. However, natural gas is used extensively as a home heating fuel. While not directly related to vehicle safety, we can compare the risks of natural gas with other home heating fuels such as propane, to act as a rough qualitative check on our later risk assessments based on the physical attributes of these fuels. That is, if the physical safety characteristics of natural gas indicate it to be a safer fuel than propane, and if the home fire statistics verify this relationship, then we would feel more comfortable in relying on physical characteristics of hydrogen to compare it with other vehicle fuels, since we have no experimental vehicle safety data for hydrogen. The relationship is masked to some degree, however, since the vehicle fuel systems operate at much higher pressures than home heating system. So home fire statistics can provide a qualitative feeling as to the relative safety of various fuels.

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[40]The American Gas Association, Natural Gas Vehicle Safety Survey - An Update, Arlington, Virginia, March 20, 1992.

[41]Ibid, Ebasco, p. 6-10.

Natural gas now supplies heat to 47 million homes, or just over half of all American dwelling units.[42] Just under half or 38 million homes also use natural gas for cooking. American homes consume about 5 quads of natural gas energy annually, slightly over half of all residential energy consumption. Electricity supplies about 3 quads of energy to homes, while fuel oil accounts for about one quad of consumption.

The safety record of natural gas is also excellent, considering the risks of piping a flammable gas directly into 47 million homes. According to the National Fire Protection Association (NFPA), there are about 480,000 home fires each year, resulting in 4,100 deaths, 20,800 injuries, and $4.2 billion in property damage.[43] But, despite the fact that natural gas is fed to over half of all dwelling units, natural gas was judged responsible for just 7,200 fires (1.5%), 57 deaths (1.4%), 413 civilian injuries (2%), and $45 million in property damage (1.1%).[44] For comparison, smoking is responsible for 25% of all fire fatalities -- smoking is 17 times more likely to lead to a fire death than natural gas(not to mention all the other health hazards of smoking.)

10.3 *Propane Safety*

Propane (C_3H_8) is also a very common fuel, particularly in rural areas where it is used for crop drying, cooking, heating, and as a motor vehicle fuel. Propane is the main constituent of "bottle gas," or LPG- Liquified Petroleum Gas. LPG may also contain butane, propylene, or butylene. These are gases at standard conditions, but become liquids at room temperature at moderate pressures. At 100°F, propane liquifies at about 1.38 MPa (200 psia), while butane remains a liquid at pressures above 414 kPa (60 psia) at this temperature. LPG can therefore be handled as a liquid at room temperature with moderate pressure cylinders.

LPG is primarily a domestic fuel, produced as a by-product from natural gas processing and crude oil refining. It is used to heat about 5 million homes in the U.S. Like natural gas, an odorant, usually mercaptan, is added to propane before sale.

Propane is the third most prevalent motor vehicle fuel after gasoline and diesel fuel, with 3.5 million propane-powered over-the-road vehicles worldwide.[45] Countries with propane vehicles include:

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[42]Ibid., p. 732.

[43]John R. Hall, Jr. The U.S. Fire Problem Overview Report Through 1993: Leading Causes and other Patterns and Trends in Home, The National Fire Protection Association, Quincy, Massachusetts, January 1995, p. 68.

[44]Alison L. Miller, The U.S. Home Product Report, 1987-1991 (Forms and Types of Materials First Ignited in Fires) - Gases, National Fire Protection Association, February 1994, p. 73.

[45]Private communication with Rick Roldon, Propane Vehicle Council, March 28, 1995.

Italy	750,000
Netherlands	350,000
U.S.	300,000
Belgium	58,000
U.K.	33,000
Japan	(Taxis required to run on LPG)

The U.S. has almost ten times more propane than natural gas vehicles. There were about 782 propane refueling stations nation-wide, compared to 313 natural gas refueling stations in 1993.[46]

Propane is much cleaner burning than gasoline, cutting down exhaust emissions of volatile organic compounds (VOC's) by about 50% compared to gasoline.[47] With the introduction of catalytic converters, tailpipe emissions have been dramatically reduced for gasoline vehicles, raising the percentage of pollution caused by evaporative emissions. But propane, like natural gas, is used in a closed system, so there are no evaporative or refueling emissions. Propane also reduces carbon monoxide emissions, making propane the fuel of choice for many indoor vehicles such as fork lift trucks. Both Japan and South Korea have *mandated* that all taxi cabs be run on propane.[48]

Although propane is transported and stored as a liquid, it becomes a gas when released to the atmosphere. Gaseous propane has two negative safety features compared to natural gas: it is 52% heavier than air (natural gas is 45% lighter), and propane has a lower flammability limit of 2.15%, compared to 5% for natural gas. If a propane leak occurs, it will tend to accumulate on the ground or floor, and will ignite at a lower concentration than natural gas. On the other hand, propane is more buoyant than gasoline, and has a higher flammability limit than gasoline. So propane falls between gasoline and natural gas on both counts.

Fire occurrence data in homes seem to support the assessment that propane is less safe than natural gas. There were an average of 2,400 LPG-started fires in 5 million homes heated by LPG in the 1987-1991 time period (480 fires/million homes), compared to 7,200 natural gas fires in 47 million homes (153 fires/million homes.) In addition, there were 34 LPG-initiated fatalities (6.8 deaths/million homes), and 74 natural gas-initiated deaths (1.6 deaths/million).

Based on these data, one could conclude that propane is 3.1 times more likely than natural gas to start a home fire, and 5.6 times more likely to kill someone. However, the comparison may not be completely valid, in that portable propane heaters were responsible for 200 fires and 2 fatalities. Since there are no comparable natural gas portable heaters, and since these portable units may be more susceptible to accidents regardless of the fuel used, they should probably be removed from the comparison. Excluding portable propane heaters, propane is still 2.8 times more likely to

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[46]First Interim Report of the Federal Fleet Conversion Task Force, DOE/PO-0001, August 1993.

[47]J.E. Sinor Consultants, The Clean Fuels Report, Vol. 3, No. 1, February 1991, p. 142.

[48]Ibid., p. 145.

start a fire than natural gas, and 5 times more likely to cause a death. We will utilize these data later to help calibrate our comparative risk assessments.

11.0 Hydrogen Accident Scenarios

In the following sections, we estimate the risks due to a hydrogen fire by comparing the probabilities and the consequences of a hydrogen fire with those fueled by gasoline, natural gas and propane for four accident scenarios. For each of the four scenarios analyzed in this report, Appendix B includes an estimate of the net probability of a fire starting relative to gasoline, and a consequences factor relative to gasoline (gasoline = 1 in both cases). The risk factor for each fuel relative to gasoline is then the product of the probability times the consequences.

These probability and consequence estimates will be subjective to varying degrees. Some estimates will be on firm quantitative ground, such as the total energy stored onboard the vehicle, which is a component of the consequences estimate. Others will be highly subjective, such as an estimate of the probability of injury due to nearly invisible hydrogen flames. But in all cases the trends will be based on the real physical differences between fuels.

The final quantitative risk estimates will therefore be subject to debate. Some may argue that we should not even try to assign any quantitative values, given the uncertainties involved. We conclude, however, that the exercise is still worthwhile, and the end results are meaningful, as long as the reader realizes that these are subjective but *informed* judgments, showing the risks *relative to gasoline.* At the very least, these quantitative values will show trends and indicate our judgment on the relative safety of the four fuels considered under different accident scenarios. They will also indicate where we need to concentrate our safety efforts.

11.1 *Major Fuel Tank Explosions or Fires in Unconfined Spaces*

Some car owners may fear the worst case scenario: a major collision that sets off a hydrogen explosion. In Appendix B we estimate the relative *probability* that a hydrogen fuel tank would be damaged in a major collision to the extent of releasing a large proportion of the stored fuel, compared to the probability of a gasoline tank being ruptured in a major collision. Similar estimates are made for natural gas and propane tanks. Then we estimate the relative *consequences* of such a major fuel release for the three alternative fuels relative to gasoline.

We conclude from this exercise that there is less potential risk in the use of hydrogen and natural gas as motor vehicle fuels than gasoline or propane, considering a catastrophic release of fuel in open air. Both the probability of a major release and the consequences of that release are judged to be less for the gaseous fuels than for the liquid fuels.

The probability of a catastrophic hydrogen or natural gas release is much less than that of a gasoline release due primarily to the inherent strength of fiber-wrapped composite fuel tanks because of the need to withstand very high internal pressure. In addition, even if the fuel tank should be ruptured, the gaseous fuels may have a lower probability of ignition, since the gases rise away from an accident and away from likely ignition sources.

The consequences of a hydrogen fire could also be less than the results of a gasoline fire, primarily since the fuel cell electric vehicle would carry only 40% or less of the energy content of the gasoline in a similar vehicle for the same range.

Since probability and consequences are both judged to be less in the case of hydrogen, the total risk (product of probability and consequences) of a major hydrogen fire or explosion is even less than that of a gasoline vehicle. Appendix B includes a quantitative estimate of the relative risk of hydrogen, natural gas and propane compared to gasoline in an open-air collision. This analysis predicts that hydrogen would be potentially 300 times less hazardous than gasoline, while natural gas would potentially be 80 times less and propane four times less hazardous. As discussed earlier, these values have large error bars, and should only be used to predict relative trends, and should not be considered statistically valid probabilities. Indeed, the error bars may be so large as to shift the relative rankings of fuels.

11.2 *Major Fuel Tank Explosion or Fire in Tunnels*

A major explosion or detonation of a flammable fuel is virtually impossible in the open atmosphere. Hydrogen is susceptible to detonation with its high burning velocity, but actually instigating such a detonation is very difficult without at least partial enclosures to channel and constrain the expanding flame front . One possible scenario that might lead to such a detonation would be a collision of one or more FCVs inside a tunnel resulting in a large release of hydrogen.

Natural gas vehicles were originally banned from tunnels and even the lower levels of double-deck bridges in New York and Boston for this very reason. Subsequent measurements and analytical studies showed conclusively, however, that natural gas is no worse than and, in most circumstances, less of a hazard than gasoline. Officials have since lifted the bans on natural gas vehicles transiting tunnels in both cities. These natural gas analytical studies provide a strong basis to predict the hazards of a hydrogen release under similar circumstances, since hydrogen behaves much more like natural gas than like gasoline.

We conclude in Appendix B that both natural gas and hydrogen would have a higher probability of ignition inside a tunnel than in the open air, since both gaseous fuels might reach electrical ignition sources such as fans or lights in the tunnel ceiling. However, the analysis also predicts that this increased risk of ignition does not change over all risk values significantly. Hydrogen would drop from 300 times less potentially hazardous than gasoline to 250 times less, while natural gas would decrease from 80 to 60 times less. The probability of propane causing a fatality would be unchanged from its open-air estimate of four times less.

11.3 *Fuel Line Leaks in Unconfined Spaces*

We conclude in Appendix B that hydrogen loses much of its potential safety advantage relative to gasoline with respect to slow leaks. While hydrogen tanks have a large potential advantage over gasoline tanks in a collision, leakage rates during normal operation could be higher with compressed hydrogen than with atmospheric pressure gasoline. We have estimated that hydrogen might be twice as likely as gasoline to leak during normal operation, while natural gas might be 1.3 times more likely to leak.

Hydrogen might be four times less likely to ignite than gasoline due to its four times higher lower flammability limit, and a FCV would not have any hot surfaces to ignite a fire. However, hot surfaces are not a major ignition source, and FCVs would have a significant disadvantage relative to the primary ignition source: electrical sparks. With the high voltage necessary to power the electric motor, the FCV would be more susceptible to ignition. A natural gas vehicle, on the other hand, has the advantage of higher LFL, without any higher risk of electrical ignition than a gasoline ICE.

The net result is that the natural gas vehicle still has an eight to one advantage in total potential risk of fire by fuel line leaks compared to a gasoline ICE, while the hydrogen-powered FCV is rated only marginally less risky (factor of 1.6, which is not significant, given the error bars on these estimates.) We conclude that the hydrogen FCV may be somewhat more susceptible to fuel line fires than an NGV, and about equal to a gasoline ICE vehicle fuel line fire risk.

11.4 *Fuel Leak in a Garage*

One of the greatest potential risks to the public could come from the accumulation of hydrogen in an attached garage due to a slow fuel line leak. In the worst case scenario, the hydrogen would not immediately ignite, but would accumulate and fill a large percentage of the garage volume with a flammable mixture. This mixture would then be ignited in the morning as the car owner opened the door from the house to the garage, either by static electricity or a spark from activating the garage light switch or the garage door opener.

Although the garage scenario may create the greatest risk for the public, we do not have enough information to make even a qualitative comparison between gasoline and hydrogen risks. Leakage rates would be determined by two entirely different mechanisms: hydrogen would leak as the result of multiple failures of the proposed safety system. That is, a leak would have to develop somewhere in the hydrogen fuel supply system, and, simultaneously, the solenoid shut-off valve would have to fail to close or develop a slow internal leak itself. The simultaneous occurrence of these two failures would likely be extremely infrequent. Furthermore, Mike Swain at the University of Miami has suggested that the operation of the solenoid valve could be periodically checked by the vehicle computer system.[49] For example, the valve could be momentarily closed (power turned off) during fuel cell operation and the resulting drop in downstream pressure measured. If the valve failed to close and no pressure drop was measured, then the vehicle monitoring system would issue a

[49]Private communication, Mike Swain, August 6, 1996.

maintenance warning to the driver. The faulty valve could then be replaced, further reducing the probability of a leak developing later in an enclosed space.

A gasoline leak, on the other hand, would most likely develop as a result of a puncture or corrosion (assuming steel fuel tanks; as more vehicles switch to high density polyethylene tanks, even this failure mode is eliminated) of the tank itself. Any leak developing in the gasoline fuel line would not generate a major risk at atmospheric pressure. We simply do not have adequate statistical data to compare the probability of a gasoline tank leak with the probability of a solenoid valve leak in conjunction with a hydrogen fuel system leak.

Similarly, we cannot at this time estimate the relative risks of ignition between the gaseous fuels and gasoline. Further work is required to better understand these relative risks.

11.5 *Refueling Station Accident Scenarios*

Tom Halvorson of Praxair has conducted a detailed hazard review of three hydrogen fuel systems:

* An on-site steam methane reformer to produce hydrogen.
* A gaseous hydrogen dispensing system.
* A gaseous hydrogen dispensing system from on-site liquid hydrogen.

For each system, failure modes are listed for each component, along with causes, consequences and recommended actions to avert the failure. No quantitative risk assessment is attempted, pending a detailed system design. The results of the Praxair hazard reviews are included as Appendix D.

12.0 Potential Hydrogen Safety Demonstration Tests

12.1 *Impact or Drop Tests*

One fiber wrapped tank manufacturer has videotaped old cars dropped on their trunks, showing that the enclosed fiber-wrapped tanks survive collisions up to 50 mph. While the tanks may survive, other fuel delivery system and fuel cell system components are much more vulnerable. We recommend a series of vehicle moving barrier impact or drop tests, with fully charged hydrogen tanks plus mockups of the fuel delivery system. Hydrogen fuel lines from the tanks would contain as much hydrogen as the proposed FCV. These lines would be filled before the drop test. The hydrogen fuel system would be equipped with the recommended safety features, including recessed solenoid shutoff valves on the tanks and inertial switches to stop flow from the tanks after a crash. The impact or drop tests and post-test inspection and measurement of the tanks would therefore demonstrate the safe operation of the complete hydrogen storage, delivery and fuel system even in the worst collision scenarios.

12.2 *Bullet Tests*

We might extend the NGV-2 bullet tests to include larger caliber bullets, or other projectiles to simulate larger objects penetrating a tank during a collision. The goal would be to demonstrate that fiber wrapped tanks would not create a shrapnel threat if punctured by objects larger than the usual test bullets.

12.3 *Garage Leak Tests*

Mike Swain of the University of Miami has measured and simulated the risk of leaking gas appliances in a home kitchen. He compared hydrogen, propane and natural gas. We recommend that this analysis be extended to the home garage, and that gasoline be added to the list of comparative fuels. The goals would be to determine, through some combination of measurements and computer simulation , the risk of hydrogen leaks in a home garage accumulating to a flammable mixture. If the risk is high, then we need to determine how much ventilation is needed to preclude reaching a flammable condition with the worst plausible hydrogen leak. A secondary goal would be to compare the risks of a hydrogen leak with those from other motor vehicle fuels.

12.4 *Accelerated Life Testing*

Once the vehicle and fueling systems have been designed, all components should be life tested under accelerated conditions, if possible, to estimate their durability over the life of the vehicle or the refueling station. In some cases, acceleration can be achieved by rapid cycling. The solenoid valves can be cycled on and off many times per minute, compared to the real life situation when they might be turned on and off only four or five times per day. Ten years of operation could then be simulated in a day or two. Other failure modes are much more difficult to accelerate, such the fatigue failure due to shock and vibration on the road. Test protocols should be established for key failure mechanisms once the vehicle and fueling designs are completed.

Annotated Hydrogen Safety Bibliography[50]

Marshall Berman, "A Critical Review of Recent Large-Scale Experiments on Hydrogen-Air Detonations," Nuclear Science and Engineering, Vol. 93, pp. 321-347, 1986.

(Debunks previous theory that hydrogen/air mixtures can only detonate in long tubes. Gives examples of detonations occurring in large enclosures [1x1x4 meters] when gas jets or fans are present. Concludes that detonation process is too complicated to predict which enclosures or geometries will permit deflagration to detonation transition. Also notes that lower detonability limit may be as low as 13% hydrogen, vs. 18.3% reported in the literature. Finally, comments that downward propagating lower flammability limit is 9% , compared to the usual estimate of 4% for upward propagating flames. [This is in agreement with Mike Swain's estimate of about 10% LFL for downward propagating flames.])

L.M Das, "Safety Aspects of a Hydrogen-Fueled Engine System Development," Int. J. Hydrogen Energy, Vol 16, No. 9, pp.619-624, 1991.

(Includes some discussion of embrittlement, plus the fact that flame arrestors for hydrocarbon flames will not work with hydrogen due to its small quenching distance -- it can sneak through small holes!)

Fred J. Edeskuty, "Safety," Chapter 5 of Hydrogen: Its Technology and Implications, Vol IV, Utilization of Hydrogen, Edited by K.E. Cox & K.D. Williamson, Jr., p. 203-219, CRC Press, 1979.

(Good survey article on safety, beginning with the first H_2 fatality in 1785 when he placed a hydrogen balloon above his conventional hot air balloon, believing that hydrogen would always rise if a leak developed -- it didn't and he died in the fall to the ground after the explosion. Fred points out that a lighted cigarette will not ignite hydrogen since a cigarette burns below the 500°C ignition point for hydrogen.

Fred notes that gas flowing out of a high pressure tank is *cooled* by tens of degrees, even though the Joule-Thompson effect would warm the gas a few degrees.

He makes the interesting point that safety rules should not be too strict, since they will cause workers to become too lax, possibly ignoring or underemphasizing other safety rules that are needed.)

M. Fischer, "Safety Aspects of Hydrogen Combustion in Hydrogen Energy Systems," Int. J. Hydrogen Energy, Vol. 11, No. 9, pp 593-601, 1986.

(***Excellent review of hydrogen safety issues. Shows hydrogen ignition energy, burning velocities, and flame temperatures as a function of %hydrogen in air. Good discussion of hydrogen's propensity to detonate, but also points out that the lower limit for detonability at 18.3% is three times greater than for natural gas at 6.3%, once again illustrating that hydrogen is safer *if* the safety system catches any leaks before they accumulate to the 4% flammability level.)

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[50]This bibliography is not the result of an exhaustive literature search, but represents the key books and documents recommended or referenced by hydrogen safety experts such as Addison Bain, Fred Edeskuty, Jim Hansel, Mike Swain and Bob Zalosh.

James G. Hansel, G.W. Mattern, and R.N. Miller, "Safety Considerations in the Design of Hydrogen-Powered Vehicles," Int. J. Hydrogen Energy, Vol. 18, No. 9, p.783-790, 1993.

(Includes data on auto-ignition temperature of H_2, methane and propane under three different conditions -- heated glass, heated wire and heated air jet. Good discussion of hydrogen vehicle safety issues.)

J. Hord, "Is Hydrogen a Safe Fuel?" Int. J. Hydrogen Energy, Vol. 3, pp. 157-176, 1978.

(One of the primary hydrogen safety articles that fully reviews the safety attributes of hydrogen, methane and gasoline. Includes details not discussed elsewhere, such as the MESG -- Maximum experimental safe gap -- the largest gap through which an ignited fuel-air mixture will not pass. For H2, the gap cannot be larger than 0.008 cm, while methane will not pass through a 0.12 cm gap and gasoline through a 0.07 cm gap. Thus it is much more difficult to stop a hydrogen flame with flame arrestors.

Fire detection idea: use "intumescent" paints which char, swell, and emit pungent gases at low temperature (200°C). Major conclusion: "The tendency of hydrogen to detonate from spark ignition is perhaps the most significant deterrent to its widespread use." Hydrogen is definitely more prone to detonation than methane or gasoline.

On the positive side, the explosive energy of hydrogen *per unit energy of fuel* is lower than methane or gasoline: H2=0.17 gTNT/kJ; methane=0.19, and gasoline=0.21. Of course, hydrogen also has the least explosive potential per unit volume by an even larger margin.)

Paul M. Ordin, "Review of Hydrogen Accidents and Incidents in NASA Operations," NASA Lewis Research Center, #749036, p. 442 (1974).

(Survey of 96 events involving hydrogen in NASA operations. Only five of the 96 involve road accidents, with hydrogen released in three of the five. None ignited. Four of the 96 episodes were related to hydrogen released from charging batteries.)

H.-J. Pfriem, "Overview of the Cooperative Program on Hydrogen Storage, Conversion and Safety of the International Energy Agency,", Int. J. Hydrogen Energy, Vol. 16, No.5, pp 329-338, 1991.

(Review of international activities, with references regarding hydrogen embrittlement, including the result that adding 8% methane suppresses detonation.)

R. Reider and F.J. Edeskuty, "Hydrogen Safety Problems," Int. J. Hydrogen Energy, Vol. 4, pp 41-45, 1979.

(Brief article includes description of several detonation experiments in small block houses. In some cases it was difficult to initiate a detonation, even when 25 liters of liquid H2 were spilled and a detonator used as the ignition source. With larger quantities of spilled LH2, however, the resulting detonation overpressure was twice that expected from a deflagration and "considerably more than the pressure to be expected in a blockhouse equipped with a weak (1/8th inch masonite) wall.)

James T. Ringland, "Safety Issues for Hydrogen-Powered Vehicles," Sandia National Laboratories, SAND94-8226, March 1994.

(Excellent summary of hydrogen safety issues, including a good interpretation of hydrogen's apparent flammability and ignition characteristics -- in practice the very low ignition energy and wide flammability range are not significant, since only the lower limits apply, where hydrogen is superior to gasoline fumes and propane. He summarizes the two major (only?) hydrogen accident reports by Zalosh (industry) and Ordin (NASA). Jim is no longer working on hydrogen issues.)

D. Shooter & A. Kalelicar, "Benefits and Risks Associated with Gaseous Fueled Vehicles," Arthur D. Little Report to the Massachusetts Turnpike Authority, Boston, Massachusetts, May 1972.

(Ebasco study quotes this report to state that "a well-designed and maintained gaseous-fueled vehicle presented no more risk in the Boston Harbor Tunnels than a gasoline-powered vehicle.)

M.R. Swain and M.N. Swain, "A Comparison of H_2, CH_4 and C_3H_8 Fuel Leakage in Residential Settings," Int. J. Hydrogen Energy, Vol. 17, No. 10, pp. 807-815, 1992.

(Excellent analysis of hydrogen flow rates compared to natural gas and propane; main conclusion is that laminar flow, not diffusion, defines typical natural gas line leaks, and hydrogen flow rates from such a leak are only 1.26 times natural gas in volume rate of leak, not the 3.8 times higher rate predicted by diffusion. Report also reports on computer simulations of gas clouds in typical kitchens, concluding that *propane is the most dangerous and hydrogen the least dangerous, with natural gas in the middle*.)

M.R. Swain and M.N. Swain, "Passive Ventilation Systems for the Safe Use of Hydrogen." (undated, unreferenced manuscript.)

(They point out that the lower flammability limit of 4.1% for hydrogen does not always indicate combustion. Concentrations less than 10% will not support a downward propagating flame, for example, and even an upward propagating flame in a 4% to 10% mixture will not consume all of the hydrogen. Main conclusion: for leakage rates of 40 liters/min, which is 16 times the largest NG leak found in previous work, hydrogen would not reach the 4% combustion limit if passive ventilation is 0.3 SCF/ft^2, the lowest recommended circulation for homes by ANSI/ASHRAE standards.)

Robert G. Zalosh and Thomas P. Short, "Compilation and Analysis of Hydrogen Accident Reports," Factory Mutual Research Corporation, October 1978.

(They analyzed 409 hydrogen related accidents, including 88 from Paul Ordin's NASA list. There were a total of 22 fatalities resulting from these accidents and 101 injuries. Explosions were almost twice as likely as fires with hydrogen 211 (51%) to 117 (28%). The report cites an earlier study that concluded that there is *no significant difference* between the frequency or severity of "town gas" -- H_2+CO -- and natural gas. They come to a similar conclusion. However, they also note two subsets of data that would seem to contradict their main conclusion. Data from the ferrous metal industry show that hydrogen is 21 times more likely to create an accident than natural gas. A similar comparison for oil refineries shows that

hydrogen is 4.5 times more often involved in an accident than NG, and 2.4 times more likely than propane, all on a per unit energy basis.)

Natural Gas Safety Bibliography

Mats Ekelund, "International Operational Experiences with Heavy-Duty Natural Gas Vehicles," Nordiska GasBuss projektet, August 1993.

(Summarizes various NGV heavy duty experiences around the world. Includes NGV refueling station cost of $560 K installed for 24.8 MPa (3,600 psi) station, and describes Sweden's carbon fiber plastic NG tanks (37 kg for 70 liter tanks))

Mats Ekelund, "Safety Assessment of Methane Operated Vehicles," for the Co-Nordic Natural Gas Bus Project, Report # 92-3537, September 1993.

(Good survey of NGV safety experience from around the world, including rare examples of NGV fires and failures. Their main conclusion is that there is no increased risk with NGV's relative to gasoline or diesel, but the data base is too small for statistically significant conclusions.)

T.J. Grant, S.H. Shaaban, M. Zuzovsky, & R. Anigstein (Ebasco Services), Safety analysis of Natural Gas Vehicles Transiting Highway Tunnels, New York State Energy Research and Development Authority Report 90-2, August 1989.

(Good analysis comparing gasoline and natural gas fires in tunnels. They conclude that fire-related death and injury from NGVs to be "substantially less than gasoline vehicles," and in the body of the report they conservatively estimate NGVs would have at most 20% of gasoline major fires leading to injury or death -- gasoline vehicles are five times more likely to produce injury or death from fire or explosion. Overall risk of NGVs in a tunnel "is comparable to or less than a gasoline vehicle depending on the hazard category." They cite 500,000 NGVs with 40 billion kilometers traveled with"no evidence of a DOT-approved cylinder ever failing in a CNG vehicle application." There were no reported deaths or injuries due to CNG in U.S., Canada or Italy; gasoline rate would have implied 30 deaths or injuries due to fire over the distance traveled had they been gasoline vehicles [see page 6-8.]

This report also includes good statistics on gasoline vehicle fire [less than 1% of collisions result in fires, and hot exhaust or sparks from friction do not usually ignite gasoline -- only electrical shorts and hot headlight filaments are good gasoline igniters] and a good summary of FMVSS 301, the fuel loss standard for liquid fueled vehicles [no more than 5 to 15 ounces of gasoline must be spilled after a 30 mph front or rear collision or a 20 mph side collision.])

Hatch Associates, Site Assessment of NGV Bus Operations at the HSR Mountain Garage, AT-92-03, March 1993.

(This assessment, provided by Matthew Fairlie of Electrolyser, analyzes the risks of storing natural gas buses in a diesel maintenance garage in Ontario. They use a fault tree analysis plus a hazard analysis, concluding that 25 NGV buses stored in the garage would have a

0.017/year chance of "occasional window breakage." Appendix C contains a detailed list of failure rates for NGV components including cylinders (2 x 10^{-5}/yr.), check & solenoid valves (1.8 x10^{-4}/yr.), 1/4 to 1/2 inch fuel line tubing (1.8 x10^{-5}/meter-year), pressure regulator (1.1 x 10^{-2}/year,) and fusible plugs (PRD's: 1.7 x10^{-4} per year.) Most of these failure rates have been doubled to account for increased stress in the bus/motor vehicle environment.)

G. A Karim, "Some Considerations of the Safety of Methane, (CNG), as an Automotive Fuel - Comparison with Gasoline, Propane and Hydrogen Operation," SAE Technical Paper Series 830267, February 28-March 4, 1983.

(He starts out asserting that CNG is safer than any other fuel, including hydrogen, and proceeds to compare NG with gasoline or propane only when NG is superior, and mentions but a few cases where hydrogen might be less safe (e.g. higher flame temperature, but he neglects to mention that H2 doesn't radiate, so it should create less ancillary damage, etc. He declares that methane has less chance for detonation, failing to note that hydrogen has 3 times higher minimum detonation percentage -- 18.3% vs. 6.3% lower detonation level for NG.)

M. Krupka, A. Peaslee and H. Laquer, "Gaseous Fuel Safety Assessment for Light-Duty Automotive Vehicles," LA-9829-MS, Los Alamos National Laboratory, November 1983.

(Ebasco reported that this study evaluated a CNG collision in a tunnel and concluded that "the CNG vehicle posed less of a hazard than a gasoline-fueled vehicle." However, the full report is much more "on the one hand, and other the other hand," stating that gaseous fuels (CNG, LNG, LPG) are more dangerous in closed environments such as garages, but less dangerous in open air. The report does not consider hydrogen. It does comment that Italy has no example of an NG explosion despite over 30 years of NGV experience with the public (as opposed to primarily fleet NGV's in the states.) For the residential garage, they estimate that LPG and NG would both be more likely to explode and to burn than gasoline or particularly diesel (which is the safest fuel by far since it's vapor pressure is so low). The report also notes the rarity of explosions, even with gasoline vehicles.)

Robert Zalosh, James Amy, Craig Hofmeister, and Weining Wang, "Dispersion of CNG Fuel Releases in Naturally Ventilated Tunnels," Center for Fire Safety Studies, Worcester Polytechnic Institute, November 1994.

(Excellent computer simulation comparing gasoline and natural gas fuel line leaks in *unventilated* tunnels under the Boston harbor. They measured the natural ventilation rates in these tunnels during the night when the traffic-generated wind was least. Using these data, they then ran fluid dynamic computer models, comparing the lower flammability limits in the tunnels for gasoline and natural gas, assuming that the fuel line ruptured in both cases. The results are very graphic. The flammability region around the NGV is very small, whereas the flammability region for the gasoline spill often fills the entire tunnel down wind from the leak. The weakest measured ventilation rates are still 7 to 10 times more than the ventilation rates where natural gas flammability region becomes significant.)

Natural Gas Vehicle Coalition Member Business Guide, November 1994
(comprehensive list of companies that manufacture NGV components, including tanks, compressors, NGV conversions and refueling stations.)

Appendix A - Hydrogen and Related Codes and Standards

A-1. National Fire Protection Association

NFPA 30A - Automotive & Marine Service Station Code
NFPA 50A - Standard for Gaseous Hydrogen Systems at Consumer Sites
NFPA 50B - Standard for Liquified Hydrogen Systems at Consumer Sites
NFPA 52 - CNG Vehicular Fuel Systems
(*Prohibits* any storage of CNG for residential dispensers, and limits refueling rate to less than 5 SCF/minute, or 7.7 hours to transfer 5.4 kg of hydrogen! Only 10,000 SCF (23.6 kg of H_2 storage) allowed for commercial dispensers)
NFPA 55 - Compressed & Liquified Gases in Portable Cylinders
NFPA 58 - Storage & Handling of Liquified Petroleum Gases
NFPA 70 - National Electrical Code
NFPA 496 - Purged & Pressurized Enclosures for Electrical Equipment
NFPA 497A - Classification of Class I Hazardous Locations
NFPA 497M - Classification of Gases, Vapors and Dusts for Electrical Equipment in Hazardous (Classified) Locations (autoignition temperatures for many materials)
NFPA MY-HLH -88 - Electrical Installations in Hazardous Locations

A-2 Compressed Gas Association

CGA G-5-1991 - Hydrogen
CGA G 5.4 - Standard for Hydrogen Piping Systems at consumer locations
CGA S 1.1 - Pressure Relief Device Standards, Part 1 - Cylinders for Compressed Gases
CGA S 1.2 - Pressure Relief Device Standards, Part 2 - Cargo and Portable Tanks for Compressed Gases
CGA S 1.3 - Pressure Relief Device Standards, Part 3 - Compressed Gas Storage Containers

A-3 Natural Gas Vehicle Coalition

NGV1 - CNGV Fueling Connection Devices (1994)
NGV2 - Basic Requirements for CNGV Fuel Containers (1992)
(Includes safety margins -- 2.25 for carbon, 3.0 for aramid and 3.5 for glass fiber tanks, along with the required tests. Qualifications tests include chemical exposure to hydrogen sulfide, pendulum impact, drop tests, a bonfire test (with NG), high temperature creep, and gunfire (pressurized with air or nitrogen -- not NG -- using a 0.30 caliber armor-piercing projectile.)
Codes and Standards Applicable to NGV fuel stations and fuel systems primarily for CNG, Feb. 9, 1990.

(Summary of applicable codes and standards, including tabular list of conflicting and supporting provisions of Canadian, NFPA, CSA, DOT and other codes)

A-4 Department of Transportation

(National Highway Traffic Safety Administration - NHTSA)

FMVSS No. 301 - Fuel System Integrity

(Defines front, rear and side crash tests for conventional vehicles. Gasoline tanks must loose no more than ? ounces of gasoline after the stationary vehicle is hit from the rear with a 78-inch wide, 1,814 kg flat rectangular barrier traveling at 30 mph.)

FMVSS No. 303 - Fuel System Integrity of CNGVs

(Defines crash tests to limit fires after crashes; fuel system nitrogen pressure must not decrease by more than 1.06 MPa (154 psi) -- 10 times the measurement sensitivity -- in one hour after 30-mph crash, or the amount of fuel leakage equal to the allowed gasoline leakage in FMVSS No. 301, whichever is greater; final rule published 4/25/94; takes effect 9/1/95)

FMVSS No. 304 - CNG Fuel Containers

(Requires pressure cycling, burst tests, and bonfire test for NGV tanks; complied with NGV2 specs *except for carbon fiber tanks,* where the safety factor was increased from 2.25 to 3.33. [NGV2 requires safety factor of 3.0 for aramid fibers and 3.5 for glass fibers and 2.25 for carbon fiber tanks.] DOT eventually reversed this change, allowing the 2.25 safety factor for carbon fiber tanks for at least two years.)

Appendix B - Detailed Probability and Consequence Estimates

This appendix presents the detailed assessment of the potential risks of hydrogen, natural gas and propane as motor vehicle fuels, all relative to the potential risks of gasoline. While we assign quantitative values to both the probabilities and consequences of a given accident, the reader should be warned that many of these values are highly speculative, often based on engineering judgment or even intuitive reasoning. Lacking any reliable data for vehicles that have yet to be built, using a fuel like hydrogen that has only powered a few dozen land-based vehicles, we cannot calibrate many of our estimates with real world safety data. We have taken into account the physical characteristics of the various gases whenever possible, but in some cases these estimates are probably correct to only a factor of ten -- we are simply trying to determine where to put the decimal point! Consequently, the final estimated risk factors should be taken as a rough order of magnitude assessment of relative risk. These are really qualitative estimates clothed in quantitative numbers.

These factors should be interpreted as our best judgment at DTI at this point in time regarding the relative risk potential of the three alternative fuels relative to gasoline. Given the paucity of hard data, others would undoubtedly assign much different values for some of these risks, possibly even reversing the relative safety order between the fuels for some accident scenarios. Yet we have found this exercise helpful in determining the most likely risks and in identifying areas needing improvements.

This appendix includes the detailed estimates of probabilities and consequences for four of the six accident scenarios selected for analysis:

- Catastrophic fuel tank rupture in open air.
- Catastrophic fuel tank rupture in a tunnel.
- Fuel line leak in open air.
- Fuel line leak in a home garage.
- Refueling station accident.
- Hydrogen production plant accident.

The hydrogen infrastructure contractors did not conduct a thorough safety analysis of hydrogen production, since they have completed many such reviews each time they build a new hydrogen plant. Praxair did conduct a preliminary hazard review of an on-site hydrogen refueling station as well as a liquid hydrogen based fueling station, both reproduced as Appendix D.

B-1 Detailed Risk Assessment for the Tank Rupture in Open Air

B.1.1 *Probability of major fuel tank failures.* A very strong case can be made that the fuel tank for a compressed hydrogen system is much stronger than the standard gasoline tank. Modern fiber wrapped composite tanks must be very strong to withstand the high pressure, currently 24.8 MPa (3,600 psi) for natural gas tanks, and 34.5 MPa (5,000 psi) for the planned FCV tanks. Tank manufacturers are required by Department of Transportation regulations to subject these tanks to a series of tests, including firing bullets at the tanks, placing them in bonfires, pressurizing them to more than double their normal operating pressure, and cycling the tanks 18,000 times to their design pressure.[51] The natural gas vehicle industry requires even more tests, including exposure to hydrogen sulfide, impact tests, drop tests, and 1,500 pressure cycles after the tank has been intentionally flawed by cutting a groove in the side.[52] No such tests are required for gasoline or diesel fuel tanks.

The net result is that fiber wrapped composite tanks are much stronger than conventional steel gasoline tanks. One manufacturer has video taped a series of drop tests, where the composite tanks are installed in the rear of vehicles.[53] The vehicles are then lifted by a crane and dropped on their trunks from various heights up to 90 feet, simulating rear end collisions at speeds up to 52 mph. The composite compressed gas tanks survived in all cases without rupture or loss of pressure, even though the rear ends of the vehicles were totally demolished.

We conclude that the probability of a fiber wrapped composite tank rupturing as the result of a collision is very low, and definitely less than the chances of a gasoline tank rupturing. We therefore assign a relative probability of 0.05 for both hydrogen and natural gas tanks relative to gasoline.

Propane tanks are designed for only a few thousand kPa, but NFPA Standard 58 specifies that they be tested at four times their service pressure. Propane steel tanks are typically four times thicker than their gasoline counterparts.[54] We assign a probability of 0.25 for the propensity of propane tanks to rupture relative to gasoline tanks.

B.1.2 *Probability of ignition.* Given a tank failure, the next question is whether the fuel would be ignited. We must independently consider the likelihood of different ignition sources. For example, gasoline released in a collision may have a high probability of flowing to the ground where a grass fire started by a hot catalytic converter could ignite the gasoline, while hydrogen might be more susceptible to ignition by sparks or static electricity. For each ignition source, we also need to estimate the probability of a flammable mixture of the fuel reaching that source.

If there are "N" possible ignition sources, then the probability of hydrogen flammable mixture igniting relative to the probability of a gasoline flammable mixture being ignited by the same set of "N" ignitions sources is given by:

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[51]National Highway Traffic Safety Administration Standard 304, *Compressed Natural Gas Fuel Containers* as published in the Federal Register, Vol. 59, No. 185, September 26, 1994, p. 49010.

[52]Basic Requirements for Compressed Natural Gas Vehicle (NGV) Fuel Containers, American Gas Association ANSI/AGA NGV2-1992.

[53]Ibid., EDO Canada

[54]Private communication with Rick Bolden, Propane Vehicle Council, March 28, 1995.

$$P_{H/G} = \frac{P_H}{P_G} = \sum_{i=1}^{N} \left[\frac{P(H_2, i)}{P(Gasoline, i)} \right] F(Gasoline, i) \quad (6)$$

or

$$P_{H/G} = \sum_{i=1}^{N} P_{H/G}(i) \times F(Gasoline, i) \quad (7)$$

where $P_{H/G}$ = the probability of hydrogen ignition relative to gasoline for all "N" ignition sources,
P_H = the absolute probability of hydrogen igniting from all "N" sources,
P_G = the absolute probability of gasoline igniting from all "N" sources,
P (H_2, i) = the probability of hydrogen igniting from the "i^{th}" ignition source,
P (Gasoline, i) = the probability of gasoline igniting from the "i^{th}" source,
$P_{H/G}$ (i) = the probability of hydrogen igniting from the "i^{th}" source relative to gasoline, and
F (Gasoline, i) = the fraction of gasoline fires started by the "i^{th}" source.

Three possible ignition sources after a major collision are hot surfaces, friction sparks, and electric sparks (or static electricity). They have to be treated separately since gasoline and hydrogen might have different probabilities of ignition from these sources. We have to consider both the likelihood of sources being near a collision, and also the likelihood that a flammable mixture of the fuels will reach those sources.

Consider first ignition by hot surfaces. We need to estimate $P_{H/G}$(Thermal Ignition) -- the probability of hydrogen igniting by hot surfaces relative to the probability of gasoline igniting by hot surfaces after a collision, and F (Thermal Ignition) -- the fraction of gasoline fires started by hot surfaces.

The gasoline-powered car will have two very hot sources: the exhaust manifold and the catalytic converter. Neither source will be present in a FCV. The PEM fuel cell operates in the range from 70°C to 90°C, far below the autoignition temperature for any fuel. (Gasoline has the lowest autoignition temperature, which can be as low as 228° C, depending on the gasoline composition, while hydrogen has a nominal autoignition temperature of 520°C.) The electric motor(s) on the FCV will be rather warm, operating at 130°C with a maximum rated temperature of 180°C, or still below the autoignition temperature of any fuel. Thus the FCV will not normally have any large area hot ignition surfaces. (After a crash, the hot filaments of headlights, brake lights, etc. could be an ignition source, assuming that the battery continued to supply current.)

While a direct hydrogen FCV will not have major hot surfaces to ignite a hydrogen flammable mixture, hot surfaces could be close by in the case of a FCV colliding with a gasoline vehicle.

Jim Hansel of Air Products and Chemicals has shown, however, that a large hydrogen leak, such as a puncture of a high pressure tank, could create a large plume of gas with a concentration above the flammable limit. If this hydrogen plume were directed upward after an accident, it would continue to rise with little risk of intercepting an ignition source. If a FCV with a ruptured fuel tank (a very low probability event) came to rest on its side after a collision, and *if* the high pressure tank hole was unobstructed by any other nearby debris or objects, then the hydrogen plume could extend for 9 to 36 meters away from a 1/16 to 1/4 inch hole.[55] This plume would be larger with hydrogen than for an equivalent natural gas high pressure leak, primarily because the sonic velocity of high pressure hydrogen exiting a leak is almost three times the sonic velocity of natural gas. The hydrogen gas velocity is so great that buoyancy has little effect -- the hydrogen plume from a horizontal high pressure leak gradually drifts upward, but not until the flammable cloud has traveled 9 to 36 meters from the vehicle.

Hansel has calculated the gas plume size for hydrogen and natural gas escaping from a 3.175 mm hole. Both gas tanks are pressurized to 20.7 MPa (3,000 psi). The approximate cross sectional area of the resulting flammable gas mixtures is shown in Table B-1 for simulated daytime conditions with 7.6 m/s wind, and for night conditions with 0.5 m/s wind.

Table B-1. Flammable Gas Cloud Surface Areas Due to Gas Leaks from 20.7 MPa (3,000 psi) Tanks (3.175 mm holes)

	Hydrogen Plume Area (m^2)	Natural Gas Plume Area (m^2)	Ratio (H/NG)
Night Conditions (0.5 m/s wind)	23.5	1.9	12.5
Day Conditions (7.6 m/s wind)	8.2	0.97	8.5

We conclude that a hydrogen flammable gas cloud will be 8 to 12 times larger than natural gas under these circumstances. However, in order for the gas to reach any ignition source, three sequential events are required:

- the carbon fiber wrapped tank is punctured by a sharp object;
- the vehicle comes to rest (presumably on it's side) with the hole oriented horizontally; and
- no objects block the pathway in front of the hole.

Hansel's computer simulations show that the gas plumes have a cone angle of about 14 degrees (half angle) for both natural gas and hydrogen, independent of hole size. If we assume that all gas plume angles are equally likely after a collision (probably a conservative assumption since vehicles will be less likely to end up on their sides or tops than on their wheels after an accident), then the probability of an ignition source being within a 28 degree full cone angle would be

[55]James G. Hansel, "High Pressure Jet Releases from an Onboard Hydrogen Storage System," Air Products and Chemicals, Inc., July 1995.

28/180=0.16 -- the flammable gas cloud would encompass an ignition source located near the ground only 16% of the time.

Next, we need to compare hydrogen and natural gas flammable clouds with those of gasoline and propane. Zalosh et al. have used computer simulations to estimate the size of gasoline flammable clouds after a fuel leak inside a tunnel under various wind or air movement conditions. The gasoline spills on to the ground, and slowly evaporates. One of their simulations analyzed a 0.65 m/s wind inside the tunnel, which is very close to the 0.5 m/s assumed by Hansel for his gas jet plume calculations. The comparison is not exact, since the tunnel walls may have constrained the movement of the gasoline vapor, but the results are striking as summarized in Table B-2 . For small holes, the hydrogen potentially flammable cloud is relatively small, but the cloud lasts for up to two minutes. For larger holes, the cloud extends up to 140 m^2, but only for nine seconds. For comparison, the gasoline potentially flammable cloud lasts for more than six minutes as the liquid pool feeds the flammable mixture, which extends over 495 m^2 in the tunnel scenario. The gasoline cloud therefore covers more than five times the area and lasts more than 40 times longer, increasing the chances of ignition by a source far from the vehicle.

Table B-2. Flammable Cloud Size and Duration for Gasoline and Hydrogen

	Hole Size (mm)	Flammable Area (m^2)	Duration (seconds)
Hydrogen [34.5 MPa (5,000 psi)] (Open air)	1.59	9.4	150
	3.18	38	38
	6.35	140	9
Gasoline (Tunnel)	-	495	400

With this background, we need to estimate the likelihood that a flammable mixture of any gas will reach the hot surface. Hydrogen has three major advantages over gasoline: hydrogen has a larger lower flammability limit (LFL) of 4%, compared to 1% for gasoline. Hydrogen is lighter than air, and will rise rapidly away from the crash site, once the effects of the high sonic velocity are overcome by adjacent objects. Finally, hydrogen has a higher autoignition temperature than gasoline, further reducing the (already low) chances of ignition by a hot surface. The computer simulations of total area of flammable mixture reported above take the first two factors into account (larger LFL and buoyancy), but not the higher autoignition temperature.

If we assume that the only hot surface would be on the (gasoline) vehicle which collided with the FCV, then the large extent of the flammable clouds is not significant once the cloud grows large enough to reach the gasoline vehicle. If the hot manifold from an ICE is within 10 meters of the leaking hydrogen tank on the FCV, for example, then it doesn't matter if the gasoline flammable mixture extends for 60 meters while the hydrogen flammable mixture reaches only 20 meters -- either flammable mixture will reach the hot surface.

We make the following assumptions to estimate the probability of hydrogen being ignited by a thermal source relative to gasoline:

1. About 58% of all fatal automobile accidents and about 58% of fatalities involve just one car[56]; assume that the probability of thermal ignition for a one-car FCV crash is zero.

2. For the other 42% involving two or more cars, assume that both hydrogen and gasoline vapors will have the lateral expansion to reach the hot source on the other ICE vehicle, but the gasoline travels down-wind with a 50% probability of intercepting the other ICE, while the hydrogen flammable gas cloud has a 16% probability of being oriented horizontally within an 14 degree half angle cone necessary to intercept the other ICE vehicle. For a two-car ICE collision, the gasoline can be ignited by its own hot surfaces, or by the hot surfaces on the other vehicle. Assume that 70% of hot surface ignitions originate in the owner's vehicle, producing a total probability of 0.7 + 0.3 x 0.5 = 0.85. The FCV has no hot source, so its probability is 0 + 0.3 x 0.16 = 0.048. The probability of hydrogen igniting relative to gasoline in a two-car crash is therefore 0.048/0.85 = 0.056.

The net relative probability of hydrogen thermal ignition is then the product of 0.056 times 0.42, the probability of a two-car crash, which gives a final probability of 0.024 - hydrogen is 40 times (1/0.024) less likely to ignite from hot surfaces than gasoline as a result of a collision that causes a fuel tank rupture.

For natural gas, the flammable gas cloud would not extend as far from the tank rupture. For example, a natural gas plume would extend about 5 meters from a 3.18 mm hole at 20.7 MPa (3,000 psi), compared to a hydrogen plume reaching 20 meters from the same size hole at 34.5 MPa (5,000 psi). We assume that natural gas would not have the range to reach the other vehicle in a crash 30% of the time. A natural gas vehicle would have its own hot surfaces, however, so its total probability of ignition from thermal sources would be 0.7+0.3 x 0.16 x 0.7 = 0.73, compared to 0.85 for the gasoline vehicle, or a relative probability of 0.73/0.85 = 0.86.

Propane has some favorable characteristics compared to gasoline, including 65% higher LFL, slightly higher buoyancy, and slightly higher thermal ignition temperature. But propane has one major disadvantage: some propane will flash to a vapor immediately after release from the tank since propane is a gas at standard temperature and pressure, creating a larger flammable mixture, whereas gasoline takes much longer to evaporate. For thermal ignition sources associated with vehicles involved with the accident, time duration is not that important -- the vehicle surfaces will be hot at the time of the crash, and will slowly cool afterwards. Gasoline does not receive a penalty on this basis for lingering long after the crash. Lacking any computer simulations for propane leaks, we assign a value of 0.65 for the probability of propane being ignited by a hot surface compared to gasoline, based solely on propane's higher LFL.

Next, consider the relative probabilities of friction sparks igniting a fire. The FCV will still generate friction sparks, so hydrogen loses its advantage of having no high temperature thermal source. Hydrogen and natural gas still maintain the advantage of rising, which should be even more

[56]Ibid, Statistical Abstract 1993, p. 621.

advantageous than for thermal sources located on the vehicles, since the friction sparks will be on the road surface. The ignition energy replaces the autoignition temperature as the measure of ignition, further reducing hydrogen's advantage. Since the friction sparks only occur while the vehicles are moving after the collision, the long term effects of flammable gas cloud formation are not important. We have to predict the relative importance of liquid gasoline vs. the gaseous fuels coming into contact with friction sparks. All four fuels could immediately come into the vicinity of sparks from the vehicle as it careens away from a collision. Hydrogen and natural gas could be at a disadvantage since the high pressure gas could be expelled into the vicinity of sparks at any position of the vehicle dragging across the pavement, whereas the liquid fuels would be initially constrained to the area near the fuel tank leak.

In a sense, we are comparing two "plumes" -- the physical gas jet plumes from a ruptured high pressure tank, and the "plume" of gasoline spilling from the ruptured gasoline tank of a moving vehicle after the crash. We need to predict which plume will most likely intercept the friction sparks from the vehicle as it drags across pavement. Given the inertia of the high pressure gas leaks, we assume that the initial area of the flammable cloud immediately after a collision-induced rupture would create a larger flammable area near the road surface than spilling gasoline. We assume here that hydrogen would have three times the probability of gasoline, while natural gas with a lower sonic velocity would have 2.5 times greater probability of reaching friction sparks before the vehicle came to rest. Propane would be more likely than gasoline to reach the sparks due to its propensity to "flash" to a vapor immediately after a puncture; we assume propane would be 1.5 times more likely to reach a spark than gasoline.

Next, consider the relative probability of ignition by electrical sparks or by static electricity. The FCV design includes an inertial switch that cuts off the battery pack within milliseconds of an impact, eliminating any vehicle electrical spark ignition sources. A heated filament lamp or other electrical spark from the other car in a two-car crash could still ignite the hydrogen, however. The relative probability of hydrogen being ignited by an electrical spark from another vehicle in a two-car crash is therefore $0.42 \times 0.3 = 0.126$, assuming that 30% of electrical sparks come from the other vehicle in a crash (and 70% from the owner's vehicle). For natural gas and propane, flammable clouds would reach both vehicles, so the probability would be equal to one compared to gasoline.

Static electricity could come from many sources near a crash scene, increasing the risk in terms of both increased area for a possible ignition source and also increased time of exposure -- static electricity may not be associated with the accident and could ignite the flammable mixture long after the crash. For example, rescuers or other vehicles or persons approaching an accident scene could generate static electricity. The long duration of gasoline flammable clouds relative to hydrogen and natural gas would therefore increase risk for conventional vehicles.

However, the probability of ignition should not increase linearly with flammable cloud area or with time duration. The most likely ignition sources would still be in the vicinity of the accident immediately after a crash. We therefore arbitrarily assume that the probability of static electricity ignition varies as the square root of the flammable area times the flammable cloud duration time, to represent less than linear functionality. For gasoline, this product is 495 m^2 times 400 seconds, or 198,000 m^2-seconds. For hydrogen, the factor is 1,260 m^2-seconds, and 140 for natural gas. The probabilities of ignition are therefore 0.08 for hydrogen $(1{,}260/198{,}000)^{0.5}$ and 0.027 for natural gas, both relative to gasoline. Assume that propane has similar flammable gas cloud dynamics to gasoline, and equal probability of ignition by electrical sources.

To combine vehicle electrical sparks and static electricity, assume that 80% of the ignition sources are due to static electricity and 20% to electrical sparks. The net probability of ignition for electrical sources is then 0.089 for hydrogen and 0.22 for natural gas, both relative to gasoline.

Finally, we need to estimate the relative occurrences of thermal-ignited, friction spark-ignited, and electrical spark-ignited gasoline fires, to plug into Equation 2. Hot surfaces such as catalytic converters or exhaust manifolds are often listed in the literature as possible ignition sources for gasoline. Judging from minimum autoignition temperatures, this seems reasonable. Gasoline can have an autoignition temperature as low as 228°C, while catalytic converters can reach 540°C, and brake linings have been measured as high as 425°C.[57] However, Johnson and Sanderson[58] conducted detailed measurements and experiments on gasoline. They found that the autoignition temperature for gasoline (n-Hexane) varies from 228°C for a large (2.93 inch) heated pyrex vessel to 550°C for a small (less than one inch) vessel. The low gasoline autoignition temperature only applies to large surface areas.

They also attempted to ignite gasoline on a large flat plate, simulating a large area exhaust manifold. They raised the temperature gradually up to 550°C, but could not ignite the gasoline. They speculate that the liquid gasoline droplets evaporate before they reach the ignition temperature, concluding that:

> "*It is unlikely that a sufficient quantity of fuel would be trapped on the surface of a hot component long enough for autoignition to occur.*"[59]

Although gasoline cannot be ignited directly by hot surfaces, it can be ignited indirectly by another substance. For example, dry grass can be ignited by the catalytic converter after a collision vehicle comes to rest. The field fire subsequently ignites the spilled gasoline. Or, more likely, transmission fluid or motor oil, both of which have lower autoignition temperatures than gasoline, spills on to the exhaust manifold and ignites, setting off the leaking gasoline.

Johnson and Sanderson also made numerous tests of electrical ignition sources, and concluded that they are most likely the cause of most gasoline fires. In a collision, electrical sparks from shorting the battery are very likely sources, as are the filaments of headlamps. However, the lamp seal must be broken, and the current must continue to flow. The hot filament without electrical current is not a plausible ignition sources in most cases. But if the lamp is broken, and if the current from the battery is still flowing through the filament, it will continue to burn in air for about 30 seconds, enough to ignite any nearby gasoline (another good reason to install an inertial switch that

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[57]N. Johnson and S. Sanderson, Spilled Fuel Ignition Sources and Countermeasures, Department of Transportation Document No. HS 801 722, September, 1975.

[58]Ibid.

[59]Ibid., p. 3-43.

cuts off the battery within milliseconds after a crash). Surprisingly they found that headlamp filaments are intact in 25% of 30 mph front end crashes.

Finally, they found from their experiments that mechanical friction sparks (really small metallic particles heated to incandescence) are less likely than electrical sparks to ignite gasoline. Their final assessment of the probability of gasoline ignition sources are as follows:

-Hot surfaces: 5%
-Frictions sparks: 10%
-Electrical sparks: 85%

We will use these estimates in Equation 7. The final probability of hydrogen igniting relative to the probability of gasoline igniting is:

$$P_{H/G} = P_{H/G}(Thermal) \times F(Thermal) + P_{H/G}(Friction) \times F(Friction) + P_{H/G}(Spark) \times F(Spark)$$
$$= .024 \times 0.05 + 3.0 \times 0.1 + 0.089 \times .85 = 0.38 \quad (8)$$

The relative probabilities for the three alternative fuels are summarized in Table B-3.

Table B-3. Ignition Probabilities of Fuels Compared to Gasoline in Open Air

	Thermal Ignition Probability		Friction Spark Ignition		Static Electricity Ignition		Composite Ignition Probability
	$P_{H/G}$ (Thermal)	F(Thermal)	$P_{H/G}$ (Friction)	F(Friction)	$P_{H/G}$(Static)	F(Static)	$P_{H/G}$
Hydrogen	0.024	.05	3	0.1	0.089	0.85	0.53
Natural Gas	0.86	.05	2.5	0.1	0.22	0.85	0.56
Propane	0.65	.05	1.5	0.1	1	0.85	1.08
Gasoline	1	.05	1	0.1	1	0.85	1.00

Hydrogen would be 2.6 times less likely to ignite than gasoline, according to this methodology. The relative ignition probabilities for natural gas and propane would be 0.48 and 1.03 respectively -- natural gas would be two times less likely to ignite and propane would have about the same probability as gasoline to ignite. As a calibration check on this process, recall that the reported fire rate for propane heated homes was about 2.3 times the natural gas fire rate, which compares favorably with the 2.1 ratio derived here.[60]

[60] Although we are using numerical values to represent risk, in reality these are qualitative estimates, and agreement with actual field data within an order of magnitude should be considered acceptable. In other words, we are attempting to determine where to put the decimal point in these risk assessments! The fact that the ratios came out so close is coincidental.

B.1.3 *Consequences of a major fuel tank fire.* The magnitude of any fire or explosion will be limited by the amount of energy stored in a full fuel tank. While most collisions would never release all or even a major portion of the stored energy, this at least sets an upper bound on the risks involved.

A fuel cell electric vehicle (FCV) will inherently carry less stored energy than a gasoline-powered ICEV, due to the increased efficiency of the fuel cell compared to the internal combustion engine. Directed Technologies has designed a FCV based on the Ford Taurus[61]. The onboard hydrogen energy (LHV) would be about 2.7 times less than the energy required of gasoline for the same range on the 1.25 times faster combined driving schedule. The FCV would require about 5.8 kg of hydrogen, while the gasoline version of the Taurus requires about 15.4 gallons of gasoline to travel 611 kilometers (380 miles) on the 1.25 times faster combined driving schedule.

Hydrogen also has slightly less explosive power per unit of stored energy (.17 gTNT/kJ) than gasoline (0.21 gTNT/kJ). So the theoretical explosive power of a FCV would be *only* 118 kg of TNT, compared to 392 kg of TNT equivalent in 15.4 gallons of gasoline. Here is a clear example of the virtue of comparative risk assessment. We would fail our objective of convincing the public that hydrogen is relatively safe if we asked citizens if they would want to park a vehicle in their garage that contained the equivalent of 118 kg of TNT. The more appropriate question is: would they consider putting a FCV with 118 kg of TNT *in place of* their current vehicle that is equivalent to 392 kg of TNT?

In practice, neither fuel would likely ever result in an explosive release of these magnitudes. Any reasonable scenario would release at most 10 percent of this stored energy.[62] But the ratio is still important: the conventional gasoline vehicle carries about 3.3 times more explosive energy than a hydrogen-powered FCV for the same range. We therefore assign a factor of 0.3 for hydrogen consequences relative to gasoline -- any catastrophic release of the full contents of a fuel tank will be 70% less dangerous for the hydrogen FCV compared to the gasoline ICE, assuming all else were equal.

But all fires are not equal with respect to the chances of major injury or death to the car driver, passengers, by-standers, or rescue workers. The next step in our comparative risk assessment process is to estimate the relative consequences of a hydrogen fire versus a gasoline fire to people in the vicinity. We assume equal energy fires here, since the final estimate will be multiplied by the 0.25 factor to account for less total hydrogen explosive energy.

In general, a hydrogen fire will be less dangerous to people on the ground than a gasoline fire of equal energy release. Hydrogen buoyancy and dispersal will tend to move the flammable mixture and resulting fire ball upward, away from people, whereas the gasoline fire will tend to remain on the ground. The gasoline fire will have a greater tendency to ignite secondary materials at the crash site, both due to liquid gasoline spreading on the ground and due to thermal radiation. Both of these

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[61]Ibid., James et al...

[62]Ibid., Fischer, p. 597.

effects are absent or minor with hydrogen. In short, the percentage of gasoline fire energy consumed in the vicinity of people is much greater than that for hydrogen.

A hydrogen fire could be more dangerous in some respects. Hydrogen has a greater tendency to detonate than gasoline, but this probability is so small in unconfined spaces that it can be ignored. Second, the nearly invisible hydrogen flame could lead to serious injury or even death if survivors or rescue workers move into an invisible hydrogen flame jet. Third, a jet of hydrogen emanating from a ruptured tank could be very intense for a short period of time. If this ignited, and if the fire jet were aimed at a person, it could be lethal.

We consider independently three fire dangers to people: direct fire exposure, radiation or induced secondary fires, and inadvertent exposure to fires (particularly for hydrogen).

For direct flame contact, we need to estimate the relationship of the fire location to the likely victim location. Following a crash, liquid gasoline from a ruptured tank will accumulate on the ground, probably in the vicinity of the vehicle and its occupants. Gasoline fires will last longer than the gaseous fuels, since the liquid fuel continues to feed the flames, once ignited. In short, much of the gasoline energy will be consumed near the crash site, maximizing the likelihood of exposure to people.

Hydrogen and natural gas fires will tend to be of much shorter duration, and the spatial extent of the flames will tend to be upward, away from the crash scene with much less lateral spreading. To the degree that some gases escape before ignition, the total energy consumed in the fire will be less, whereas unignited gasoline will likely remain near the crash site until the fire starts. We assign a factor of 0.5 to both gaseous fuels: on the average, the potential direct flame exposure to vehicle occupants will be half that of gasoline.

Propane will be intermediate between gasoline and hydrogen: it will not remain on the ground as a liquid, given its low boiling point (-43.7°F), but gaseous propane is heavier than air, and will not rise like hydrogen or natural gas. Assign a value of 0.8 relative to gasoline for victim flame exposure.

For radiation hazard and the threat of secondary fires, all three carbon fuels have high emissivity. Only hydrogen has low emissivity and low likelihood of injuring nearby survivors or of starting secondary fires. However, their relative roles are reversed for the case of inadvertent exposure to fires: hydrogen is the only fuel that is not readily visible. For this analysis, we will assume that these two hazards cancel: reduced damage due to the lower radiation hazard of hydrogen will equal the increased possibility of injuries and deaths due to inadvertent contact with invisible hydrogen flames.

The final risk assessment estimate (probability times consequences) for the case of a major fuel tank rupture is summarized in Table B-4 for the three fuels:

Table B-4. Estimate of Total Risk of a Major Fuel Tank Rupture in Open Air (all Relative to Gasoline)

	Probability of Occurrence		Consequences		**Net Risk**
	Tank Rupture	Ignition	Energy Content	Flame Hazard	**P x C**
Hydrogen FCV	0.05	0.38	0.3	0.5	**0.003**
Natural Gas ICEV	0.05	0.48	1	0.5	**0.012**
Propane ICEV	0.25	1.03	1	0.8	**0.21**
Gasoline ICEV	1	1	1	1	**1.00**

According to this analysis, the net potential risk from a major fuel tank fire is 300 times less with a hydrogen-powered FCV than a gasoline-powered conventional vehicle. A natural gas vehicle would be 80 times less, and a propane ICE vehicle would be 5 times less. While the exact numbers are not relevant, the relationships are clear: hydrogen is the least risky, with natural gas, propane, and gasoline progressively more risky in terms of fatalities or injuries from a major fuel tank rupture in unconfined spaces.

With respect to the real fire death data comparison between natural gas and propane, recall that propane caused about 4 times more fatalities in home fires, while the analysis above indicates a 17 to one ratio. However, the different storage tanks - unique to the vehicle comparison here - account for a factor of five. The product of ignition likelihood and flame hazard shows a 3.5 to one ratio between natural gas and propane in this assessment, somewhat less than the real fire data of 4 times increased risk of fatality in propane-heated homes relative to natural gas-heated homes.

B-2 Detailed Risk Assessment for a Catastrophic Tank Failure inside a Tunnel

B.2.1 *Probability of fuel tank rupture in a tunnel.* We can use the estimate from Section B.1.1 for a fuel tank rupture in unconfined spaces. The probability of a tank rupture with respect to gasoline is estimated as:

Hydrogen: 0.05
Natural Gas: 0.05
Propane: 0.25

B.2.2 *Probability of ignition in a tunnel.* The tunnel environment adds some new dimensions to the chances for ignition. The gaseous fuels are somewhat constrained, which might increase the volume of gas/air mixture within flammable limits before ignition (less air dilution), and the tunnel itself might provide ignition sources (circulation fans, lights, etc.). In addition, we will assume that all crashes are two-car collisions, removing the slight advantage of the FCV in a one-car crash of not having hot surfaces available for ignition.

One major concern is that a flammable mixture of hydrogen would accumulate in the tunnel, and that a fan or light would ignite this mixture. Detonation would require at least an 18% mixture of hydrogen and air (the lower detonability limit), but a 4% mixture could ignite. If we can show that hydrogen rarely reaches the 4% level at the ceiling of a tunnel, then reaching the 18% level is much less likely. Furthermore, a flammable mixture above 4% will most likely reach any constant tunnel ignition source such as a light or fan and ignite the hydrogen mixture before it can reach the 18% lower detonability limit -- hydrogen would most likely burn before it could detonate.

Robert Zalosh and his colleagues at the Worcester Polytechnic Institute have previously measured air circulation patterns in Boston tunnels. They have also simulated flammable gas clouds from a ruptured gasoline line and a ruptured natural gas line, using finite element computer fluid dynamic and dispersion models.[63] Their results, reproduced in Figures 8 through 10, illustrate that a gasoline spill will create a much larger flammable region than a natural gas leak. Figure 8 shows the flammable gas clouds for a 0.65 meter per second tunnel ventilation rate, which is less than the average measured natural ventilation rates between 0.74 m/s and 1.39 m/s. Under this condition, the simulated gasoline spill creates a flammable mixture that extends the length of the 50 meter tunnel downwind from the crash site. The gasoline spills onto the road, and continues to evaporate for over 400 seconds. Natural gas from a ruptured fuel line escapes in about 68 seconds, and creates a much smaller flammable cloud, as shown on the bottom of Figure 8. The flammable mixture is limited to the immediate vicinity of the vehicle. No flammable mixture reaches the ceiling of the tunnel, so the tunnel has no adverse affect on the likelihood of ignition.

At a lower ventilation rate of 0.3 m/s, gasoline flammable mixture fills the downwind portion of the tunnel, as shown in Figure 9, while the natural gas flammable cloud is still confined to the vicinity of the van. At 0.2 m/s (Figure 10), natural gas flammable mixture does reach the tunnel ceiling, but this air circulation flow rate is 3 times less than the minimum flow rate measured in actual tunnels. These flow rate measurements were taken after midnight with minimal traffic, often less than 2 to 3 cars per hour. Air flow rates will generally be much greater with more traffic.

These simulations assumed that a single tank of natural gas was released through a severed one quarter inch fuel line. The tank contained 24 kg of natural gas, with a heating value of about 1.35 GJ (HHV). This tank was one of several on a natural gas van in this simulation. The corresponding gasoline-powered van had 35 gallons of gasoline, which leaked after the collision through a one half inch fuel line.

For a hydrogen-powered FCV, we assume that the 5.3 kg of onboard hydrogen would be stored in three tanks to permit reasonable packaging within the vehicle. Each tank would include a normally closed solenoid valve that would close within milliseconds of a collision via an inertial switch. If one tank were punctured in the accident, the contents of the other two tanks would be confined. The current vehicle design uses one large tank with 2.2 kg of hydrogen, and two smaller tanks. We therefore assume that the worst possible release would be 2.2 kg of hydrogen, equivalent

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[63]Robert Zalosh, James Amy, Craig Hofmeister, and Weining Wang, "Dispersion of CNG Fuel Releases in Naturally Ventilated Tunnels," Center for Firesafety Studies, Worcester Polytechnic Institute, November 1994.

to 0.31 GJ (HHV), or approximately 4.4 times less than the energy content assumed by Zalosh in the natural gas tunnel simulations.

Figure 8. Flammable Cloud Comparisons: Natural Gas and Gasoline in a Tunnel with 0.65 m/s Air Motion[64]

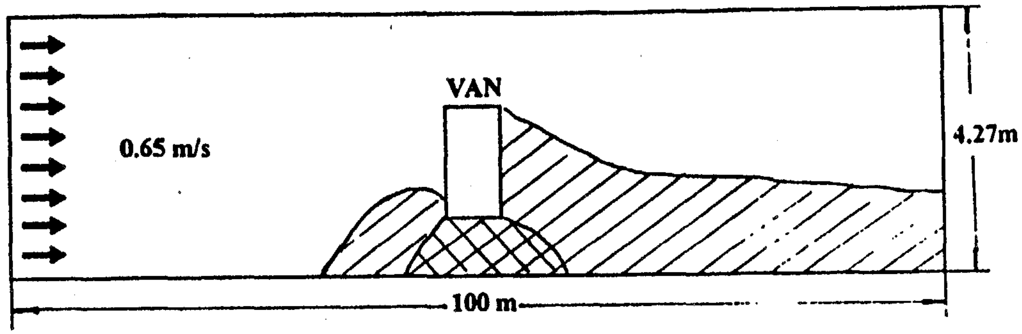


FIGURE 11(a). Gasoline Flammable Vapor Region Downstream of Van in Tunnel with 0.65 m/s Ventilation Velocity Region under Van Has Vapor Concentrations above the Upper Flammable Limit.

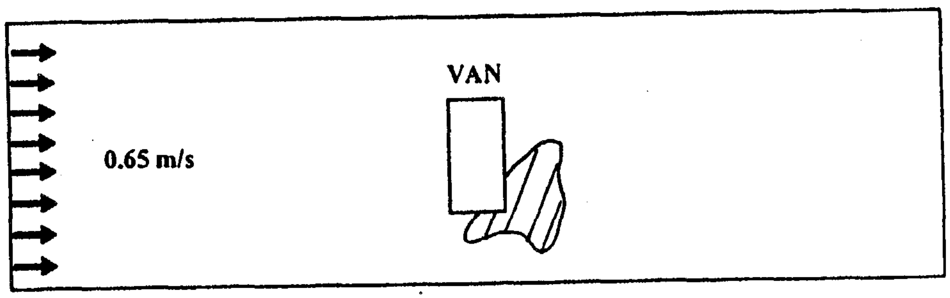


FIGURE 11(b). CNG Flammable Region Downstream of Van at a Ventilation Velocity of 0.65 m/s

[64]Ibid., Zalosh et. al.

Figure 9. Flammable Cloud Comparisons: Natural Gas and Gasoline in a Tunnel with 0.30 m/s Air Motion

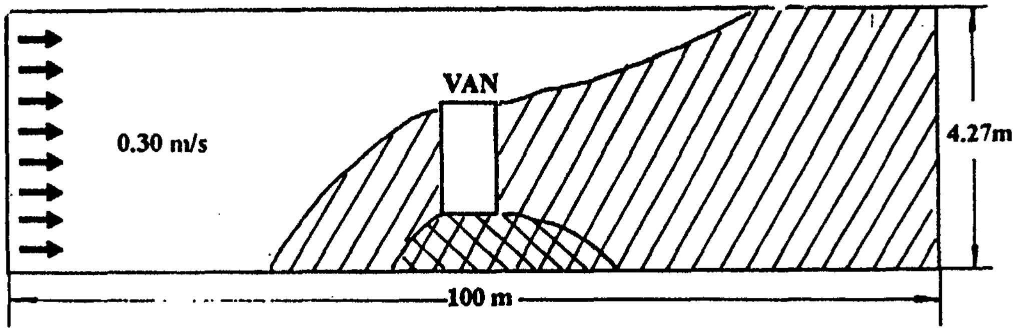


FIGURE 12(a). Gasoline Flammable Vapor Region Downstream of Van in Tunnel with 0.30 m/s Ventilation Velocity
Region under Van Has Vapor Concentrations above the Upper Flammable Limit.

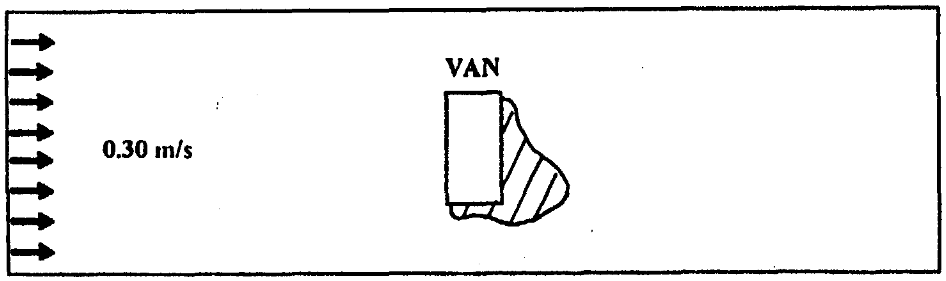


FIGURE 12(b). CNG Flammable Region Downstream of Van at a Ventilation Velocity of 0.30 m/s

Figure 10. Flammable Cloud Comparisons: Natural Gas and Gasoline in a Tunnel with 0.20 m/s Air Motion

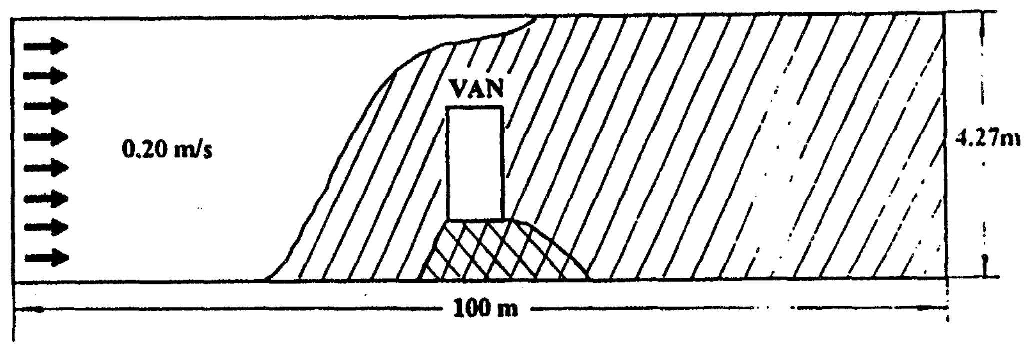


FIGURE 13(a). Gasoline Flammable Vapor Region Downstream of Van in Tunnel with 0.20 m/s Ventilation Velocity Region under Van Has Vapor Concentrations above the Upper Flammable Limit.

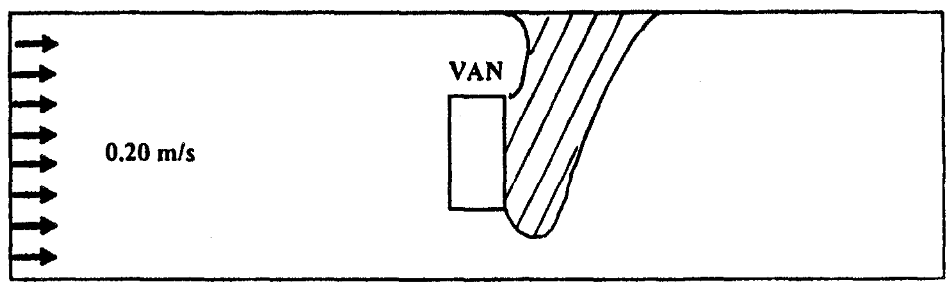


FIGURE 13(b). CNG Flammable Region Downstream of Van at a Ventilation Velocity of 0.20 m/s

As shown by Figure 2 of Section 2.1 of this report, hydrogen energy leaking from a hydrogen-powered fuel cell vehicle would be about three times less than that from a natural gas vehicle with equal range capability, and 4.4 times less than Zalosh assumed for the natural gas leaking in his tunnel simulation. For the one quarter inch hole assumed in Figure 2, 90% of the hydrogen would escape in about 15 seconds, while 90% of the natural gas would escape in about 30 seconds, both less than the 68 seconds time assumed by Zalosh.

While a hydrogen leak will disperse less total energy than a natural gas tank, the hydrogen will escape at much higher velocity (1,307 mps) compared to natural gas (438 mps). As discussed earlier, Jim Hansel of Air Products and Chemicals has shown that hydrogen will therefore create a larger plume of flammable gas mixture than natural gas. Under some circumstances, this flammable plume might reach a distant ignition source more readily than natural gas. Further simulation or modeling would be required to clarify this issue.

In the meantime, for thermal ignition sources, assume all 2-car crashes, increasing the hydrogen thermal source ignition probability relative to gasoline from 0.024 to 0.056. Natural gas and propane are unchanged from the open air case at 0.86 and 0.65, both relative to gasoline. Assume no changes to the friction spark ignition probabilities.

For electrical ignition sources inside a tunnel, assume equal probability density of electrical sources on the tunnel ceiling (due to fans and lights) as on the roadway (from electrical sparks from other vehicles and static electricity.) For vehicle electrical sparks, assume 70% from owner's vehicle and 30% from the other vehicle. For the gasoline ICE, the other vehicle will be downwind 50% of the time, or the total probability of gasoline fumes reaching electrical sparks would be 0.7 x 1 + 0.3 x 0.5 = 0.85. Both natural gas and hydrogen would have 16% probability of their gas jets intersecting the other vehicle. Hydrogen would have no electrical source from the FCV, and a probability of 0.3 x 0.16 = 0.048 from the other vehicle. Natural gas would have a combined probability of 0.7 x 1 + 0.3 x 0.16 = 0.748.

For static electricity, assume the same ratios estimated for the open-air case: 0.08 for hydrogen and 0.027 for natural gas, both relative to gasoline at 1.0, based on the square root of the flammable gas cloud areas times the cloud time duration.

The probability of the gas jets intersecting the tunnel ceiling depends on the maximum reach of the jet, which is estimated by Hansel at 4.8 meters for natural gas (3.2 mm hole and 20.7 MPa (3,000 psi)) and 36 meters for hydrogen (6.4 mm hole and 34.5 MPa (5,000 psi)). For a tunnel 4.3 meters high, the hydrogen jet would intersect the ceiling for tilt angles above 6.8°. For natural gas, the tilt angle of the jet plume would have to exceed 62.8° relative to horizontal before the flammable jet cloud would reach the ceiling of the tunnel. If we again assume that any (unobstructed) gas jet from a tank puncture would have a random orientation after a tunnel crash (meaning that the car would have equal probability of landing in any orientation), then the hydrogen jet would reach the ceiling in 46% of all puncture accidents, while the natural gas jet would reach the ceiling 15% of the time. Gasoline will only reach the ceiling if the air motion falls below 0.3 m/s, as shown in Figure 9. Since the average tunnel air velocities are in the range of 0.74 to 1.39 m/s, this occurrence would be relatively rare. Assume a one percent probability for gasoline reaching the ceiling.

The probability estimates for the three sources of electrical ignition inside the tunnel are summarized in Table B-5. To find a composite probability, we have to assign probabilities to each of the three sources. We have assumed 30% probability for vehicle electrical ignition sources and for ceiling ignition, and 40% for static electricity. The final probabilities of electrical ignition normalized to gasoline are 0.27 for hydrogen and 0.41 for natural gas. Note that the estimated ignition probability for hydrogen is less than that for natural gas, even though the gas jet plume estimated for hydrogen is larger than that of natural gas for two of the three sources (ceiling and static electricity). However, the composite probability is dominated by the much larger probability of natural gas igniting from an electrical source on the vehicle, while the hydrogen FCV has no such source (due to the inertial switch cut-off), and could only be ignited if the hydrogen jet plume reached another vehicle in a crash.

Table B-5. Relative Post-Collision Ignition Probabilities from Electrical Sources Inside a Tunnel

	Vehicle Electrical Source	Ceiling Electrical Source	Static Electricity	Weighted Sum	**Sum Normalized to Gasoline**
Hydrogen	0.048	0.46	0.08	0.18	**0.26**
Natural Gas	0.75	0.15	0.027	0.28	**0.41**
Gasoline (& Propane)	0.85	0.01	1	.685	**1**
Weighting Factors	0.3	0.3	0.4		

The composite ignition probabilities from all sources (thermal, friction spark and electrical) are summarized in Table B-6 for the tunnel scenario. The relative probability of ignition for hydrogen has increased from 38% in open air to 53% in a tunnel, while natural gas has increased from 48% to 64%.

Table B-6. Ignition Probabilities of Fuels Compared to Gasoline in a Tunnel Collision

	Thermal Ignition Probability	Friction Spark Ignition	Static Electricity Ignition	Composite Ignition Probability
Hydrogen	0.056	3	0.27	0.53
Natural Gas	0.86	2.5	0.41	0.64
Propane	0.65	1.5	1	1.03
Gasoline	1	1	1	1.00

B.2.3 *Consequences of fuel tank fire in a tunnel.*

The consequences of a tunnel fire are similar to those in open air. Hydrogen vehicles will have about one third of the total explosive energy onboard compared to a gasoline ICE vehicle, and both hydrogen and natural gas will both rise and tend to burn away from the vehicle and passengers, while gasoline and propane will all burn on the ground, near victims. The consequences of a major hydrogen release could be much worse if the hydrogen accumulated inside the tunnel and reached the lower detonation limit before ignition. The tunnel would provide some confinement that could help to promote growth from deflagration to detonation with very large overpressures. However, the likelihood of detonation seems very small based on the computer simulations of Zalosh et al., which show that a major leak of natural gas from a vehicle results in a flammable natural gas mixture that extends at most one to two meters from the vehicle. The lower flammability limit of natural gas is 5.3 percent, while the lower detonability limit for hydrogen is 18.3 %. Furthermore, the hydrogen tank of a FCV would hold 4.4 times less energy than the natural gas tank simulated by Zalosh. The chances of hydrogen reaching the 18.3% concentration inside the tunnel with the correct geometry to produce a detonation seem remote.

We therefore use the same consequences estimates as in the open air case. The resulting net risks for a tunnel crash are summarized in Table B-7. The only changes from the open air to the tunnel case are the slightly higher ignition probabilities for natural gas and hydrogen, resulting in only minor changes in the over all risks of hydrogen (from 0.002 to 0.003) and of natural gas (from 0.012 to 0.016).

Table B-7. Estimate of Total Risk of a Major Fuel Tank Rupture in a Tunnel (all Relative to Gasoline)

	Probability of Occurrence		Consequences		**Net Risk**
	Tank Rupture	Ignition	Energy Content	Flame Hazard	**P x C**
Hydrogen FCV	0.05	0.53	0.3	0.5	**0.004**
Natural Gas ICEV	0.05	0.64	1	0.5	**0.016**
Propane ICEV	0.25	1.03	1	0.8	**0.21**
Gasoline ICEV	1	1	1	1	**1.00**

B-3 Detailed Risk Assessment for Fuel Line Leaks in Unconfined Spaces

B.3.1 *Probability of fuel line leak.* Similarly, fuel lines could develop leaks during normal operation without any collision. There is no inherent reason why gaseous fuel lines will be any different than gasoline fuel lines in this regard. However, just as high pressure hydrogen storage tanks will necessarily be constructed to be much more durable than gasoline tanks, the various hydrogen plumbing lines and components will be more durable than conventional gasoline fuel lines. The hydrogen fuel lines and connections must be fabricated to withstand in excess of 34.5 MPa (5,000 psi) pressure.

On the other hand, hydrogen pressurized to 34.5 MPa (5,000 psi) will be more likely to escape from small orifices than liquid gasoline near atmospheric pressure. Ideally we wanted to utilized historical leak rate data to compare these fuels. However, we have not been able to locate any reliable data on hydrogen vs. gasoline leak rates. Some publications list historical leak rates for various fuel line connectors, pressure regulators, solenoid valves, but frequently do not specify the type and size of component, the pressure, nor the magnitude of the leak.

Instead, we have simply assigned the following relative leak rates for the four fuels, based on the assumption that high pressure hydrogen will leak more than gasoline due to its high pressure, despite higher quality components than gasoline fuel lines:

Hydrogen:	2.0
Natural Gas:	1.3
Propane:	0.5
Gasoline:	1.0

We assume that natural gas leaks less than hydrogen due to lower pressure and larger molecular weight, while propane will leak less than gasoline due to lower pressure and a more robust (closed) fuel delivery system. That is, the propane tanks and fuel lines are built to withstand the several thousand kPa internal gas pressure, while liquid tanks have no such design requirement.

B.3.2 *Probability of fuel line leak ignition in unconfined spaces.*

Possible ignition sources in the vehicle include electrical sparks, hot surfaces, and static electricity. Hydrogen will have an advantage since the FCV will have no hot surfaces, although the net effect will be small since hot surfaces account for only five percent of gasoline fires according to the study quoted previously. In addition the FCV will have much higher voltage to power the electric drive motor, so electrical ignition sources should dominate the hydrogen FCV ignition list.

We assume initially that the probability of ignition is inversely proportional to each fuel's lower flammability limit. Normalized to gasoline, the relative probabilities of ignition would be

Hydrogen:	0.25
Natural Gas:	0.19
Propane:	0.5
Gasoline:	1.0

For electrical ignition of hydrogen, assume four times higher risk for the FCV due to high voltage, which cancels out hydrogen's lower flammability advantage. For thermal ignition of natural gas, multiply natural gas's 0.19 factor (based on LFL ratio) by the inverse of its higher autoignition temperature compared to gasoline and propane (470°C/630°C = 0.75), or a net ignition factor of 0.14. Finally, assume that 50% of vehicle fires are ignited by electrical sparks, 10% by hot surfaces, and 40% by static electricity. The net ignition probabilities are summarized in Table B-8.

Table B-8. Ignition Probabilities of Slow Fuel Leaks

	Electrical Sparks	Hot Surface	Static Charge	Net Ignition Probability
Hydrogen	1	0	.25	.60
Natural Gas	.19	.14	.19	.18
Propane	0.5	0.5	0.5	0.5
Gasoline	1	1	1	1
Weighting Factor	0.5	0.1	0.4	

B.3.3 *Consequences of fires in unconfined spaces.*

Assume the same relative consequences uses previously for the four fuels.

The final estimates of total risk of a fuel line leak vehicle fire are summarized in Table B-9:

Table B-9. Estimate of Total Risk of Fuel Line Leak Fire

	Probability of Occurrence			
	Leak	Ignition	Consequences	**Net Risk**
Hydrogen FCV	2.0	0.60	0.5	**0.6**
Natural Gas ICEV	1.3	0.18	0.5	**0.12**
Propane ICEV	0.5	0.50	0.8	**0.2**
Gasoline ICEV	1	1	1	**1**

The risk of a hydrogen vehicle fire is only slightly less likely than the risk of a gasoline fire, according to this analysis. Compared to a catastrophic tank rupture, hydrogen loses its big advantage, since the hydrogen fuel lines are not considered more leak proof than gasoline fuel lines.

Hydrogen is also considered to be more risky than natural gas, due primarily to the assumption of higher exposure of any hydrogen leak to high voltage and the higher probability of electrical spark ignition.

B-4 Detailed Risk Assessment for Fuel Leak in a Garage

A slow leak of gasoline from conventional vehicles parked in a home garage could in principle lead to the accumulation of a combustible mixture. Similarly, hydrogen, natural gas and propane vehicles could also produce flammable or even explosive mixtures of gas that went undetected until an unsuspecting car owner turned on the garage door opener or light switch. We attempt to estimate the relative risks from vehicles powered by these four fuels.

B.4.1 *Probability of a fuel leak in a garage*. The fuel lines and various hydrogen control devices such as check valves, solenoid valves, pressure regulators, and hydrogen expanders could develop slow leaks after years of fatigue. If these leaks grew, they would eventually be detected, either by reduced vehicle performance or through hydrogen leak detectors or odorants, if used. But a small leak could go unnoticed in normal operation. Once parked in the garage, these small leaks could conceivably lead to the accumulation of a flammable mixture.

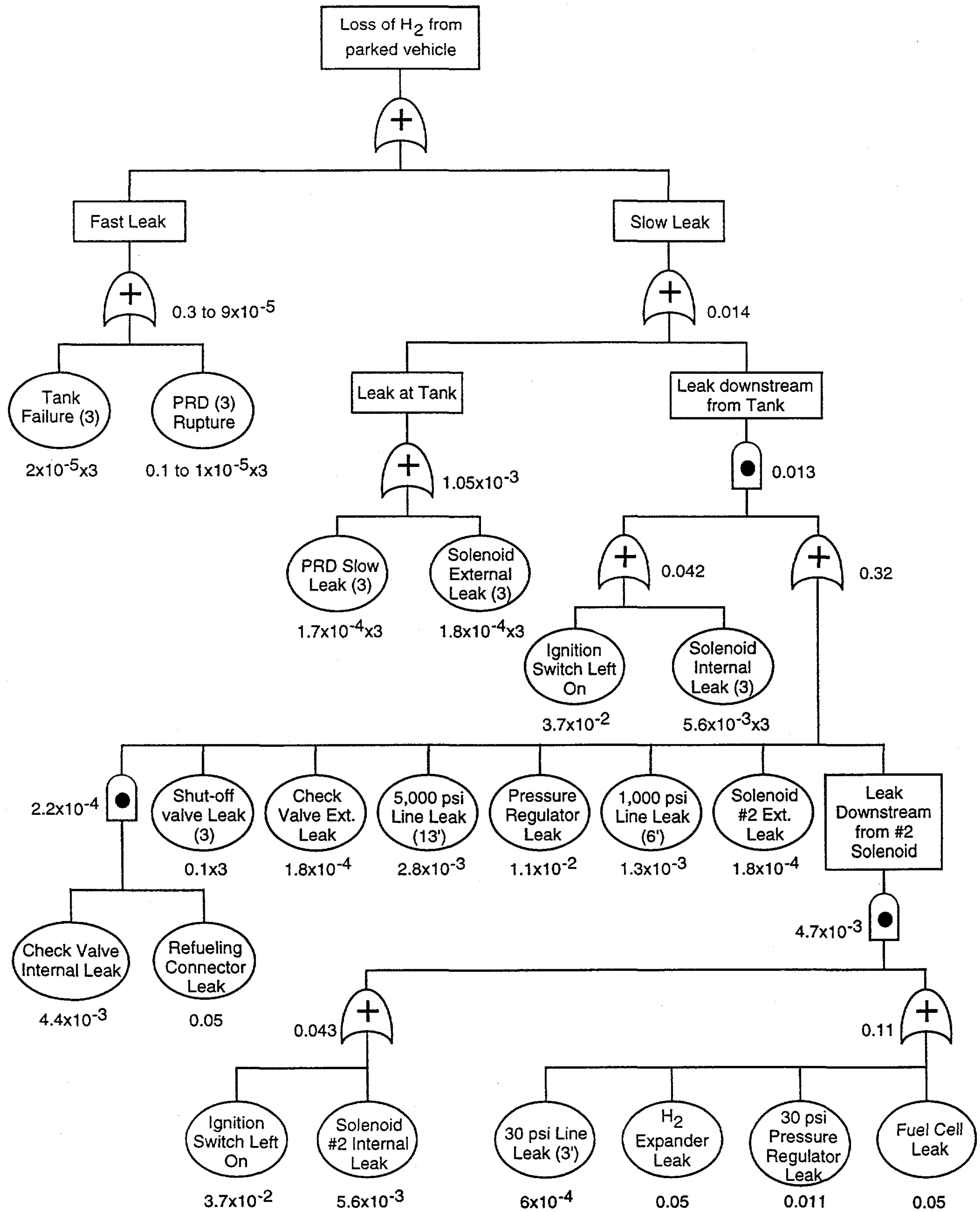
However, the FCV as currently envisioned would include solenoid shutoff valves on each hydrogen tank (See Figure 6 in Section 8). Even if a leak did occur during operation, only the hydrogen stored in the fuel delivery system would escape into the garage -- access to the hydrogen storage tank would be blocked by the internal solenoid valve, unlike the fuel line leak during vehicle operation that was considered in the previous section. The probability of an undetected leak would have to be multiplied by the probability of a failure of this solenoid valve safety feature. The driver might also leave the vehicle ignition switch in the "on" position when he or she parked the car in the garage, but even this human failure could be eliminated by an interlock with the vehicle doors: opening any door would automatically shut off the fuel cell system, which could only be turned on again by the action of the driver inserting and turning the ignition key.

Possible failure modes leading to a hydrogen release (beyond the release of hydrogen in the fuel lines at shutdown) include:

* driver fails to turn off "ignition key" after parking vehicle, *and* the door interlock cutoff fails, *and* a fuel line leak develops.
* solenoid valve fails to close after current is removed, *and* a fuel line leak develops in any one of the components in the fuel cell system downstream from the solenoid valve.
* solenoid valve closes but develops an internal leak, *and* a fuel line leak develops.
* pressure relief device leaks or ruptures in error.
* solenoid valve case or fitting to tank develops an external leak.

The various combinations of events that could lead to a leak from the FCV hydrogen system are summarized in the fault tree analysis of Figure 11. This fault tree is based on the hydrogen delivery system shown in Figure 6. The component failure rates for the fault tree were taken from

Figure 11. Fault Tree Analysis for Loss of Hydrogen from a Fuel Cell Vehicle Parked in a Garage



(ref: Figure 6)

a report on natural gas buses.[65] These component failure rates have great uncertainty. In most cases, no information is given regarding the type of failure or the size of any resulting leak. Jim Hansel of Air Products & Chemicals conducted a fairly exhaustive literature search under this Ford/DOE infrastructure project to find better component failure rate statistics.[66] He concluded that most of the data in the 38 references he uncovered come from very old nuclear plant design, and most often do not indicate the type of leak or failure mode. For example, a failure of a valve might indicate internal leakage or external leakage. Even when the failure mode is specified, the leakage rate is not identified -- a failure could mean a slow weeping leak of little consequence or a massive rupture of the component. Hansel also noted extraordinary variation in the data. Failure rates for a given component often varied by factors of 200 or more. Hence the fault tree values are highly speculative, and subject to change over time as more relevant data are developed.

The fault tree of Figure 11 shows a probability of a slow leak of 0.014/year, which means that a vehicle would develop a slow leak once every 70 years. With millions of cars, this failure rate would be unacceptably high. However, closer scrutiny of this fault tree indicates that the two main leak modes are due the driver leaving the ignition switch on, and the leakage of the manual shut-off valves. Both of these effects can be moderated. As mentioned above, the ignition switch power can be interrupted whenever a car door is opened, shutting off the solenoid valve until the driver starts the car. This eliminates this failure mode (or, more correctly, puts another "and" element in the fault tree -- the driver has to forget to shut off the ignition switch after parking the vehicle *and* the door interlock circuit has to fail, which will significantly lower the probability of such a leak). The shut-off valve failure rate cited by Hatch Associates, 0.1/year, is undoubtedly based on a faulty design. Hansel's study uncovered other manual shut off valves with failure rates in the range from 0.013/year to 1.8×10^{-14}/year. Furthermore, Ford has recommended eliminating these valves, based on their NGV experience -- the solenoid valves internal to the high pressure tank are sufficient for normal operation and maintenance.

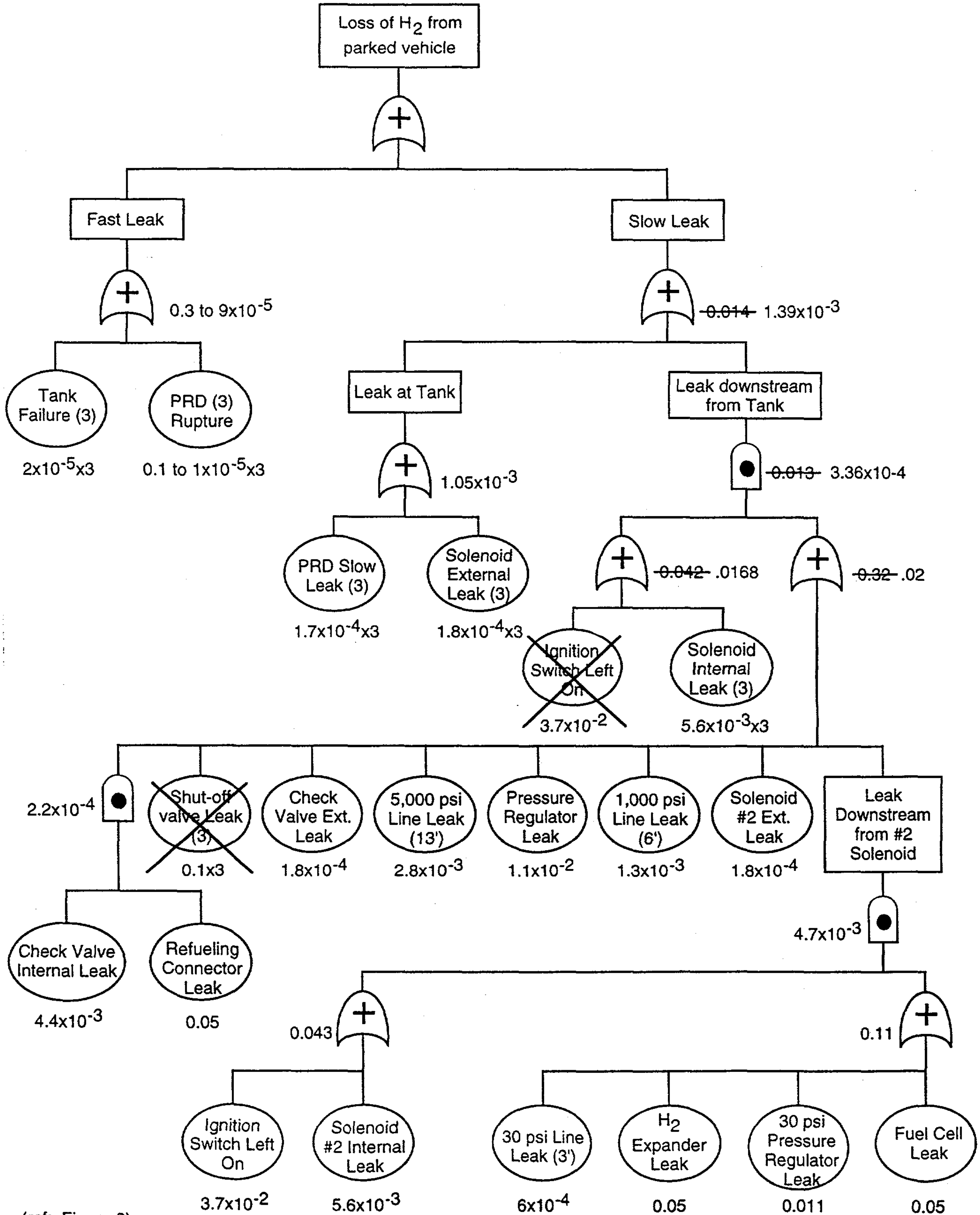
With these two changes, the fault tree predicts a slow leak failure rate of 1.39×10^{-3}/year, as shown in Figure 12. A single vehicle could expect to have a leak once every 700 years. But, with one million FCVs on the road, even this failure rate would predict 1,400 garage leaks per year, which *might* be too high. Once again, though, these failure rates are based on old data, mostly from large nuclear plumbing systems, and may not be appropriate for the hydrogen vehicle system. Much more work is needed before these projections have significant quantitative merit. They should be used now to indicate trends and identify likely methods of improving safety, not for quantitative assessment.

For our comparative risk assessment, we would like to obtain similar data on existing gasoline vehicle garage leaks. Jim Hansel did conduct a literature search on gasoline line failures, and was not able to locate any relevant data. The NFPA reports a gasoline vehicle fire rate of about

[65]"Site Assessment of NGV Bus Operations at the HSR Mountain Garage," by Hatch Associates, Toronto, Canada, 1993.

[66]James G. Hansel, "Hydrogen Powered Vehicles Hazard Review and Fault Tree on Leakage/Garage Explosion: Discussion of Piping Component Failure Rate Data, Air Products & Chemicals, Inc., January 1996.

Figure 12. Modified Fault Tree Analysis, Assuming No Shut-Off Valves and Door Interlocks to Shut Off Ignition Switch



(ref: Figure 6)

6.6 x 10^{-4}/year. (See Table 10-1). But these include all (non-collision) vehicle fires fueled by gasoline. Many more gasoline leaks may have occurred but did not ignite. Hence we do not at this time have a comparable gasoline vehicle fault tree analysis.

In one sense the gasoline ICE vehicle may be more prone to leaks, since it does not have the equivalent of the internal solenoid cut-off valve. The hydrogen FCV has two lines of defense against leakage. Any gasoline leak that develops in the fuel line system will continue to drip after the ICE vehicle is parked and the engine is shut off until the gasoline fuel line was emptied, when the leakage would cease. The only other major leak source would be due to a small puncture of the gasoline tank, or if the driver left the engine (and hence the fuel pump) on when the car was parked. If we assumed that the gasoline fuel system had the same propensity to leak as the hydrogen fuel line system (0.02/year in the modified fault tree), then the hydrogen FCV would be less likely to leak by the solenoid failure rate, or 0.0168/year for three solenoid valves (three hydrogen tanks) -- the FCV would be 70 times less likely to leak. This would be offset, however, by the 34.5 MPa (5,000 psi) driving force behind any hydrogen leak, compared to atmospheric pressure for gasoline. Higher tank pressures are possible for a vehicle parked in the hot sun, but not inside a home garage.

We are therefore left with comparing the probability of a small puncture of a gasoline tank with the probability of a high pressure hydrogen leak combined with a solenoid valve failure. Even a small puncture hole, on the order of 2 mm, could empty a 19-gallon gasoline tank in less than an hour, posing a significant risk (although the odor of gasoline would alert any person in the vicinity of the leak). The situation is further complicated by the automobile industry shift to high density polyethylene fuel tanks. The old steel tanks were prone to punctures by stones and other debris, and the tanks eventually corrode. The polyethylene tanks are much more durable. At this time 75% of gasoline tanks in Europe are plastic, but only 30% are plastic in the U.S. One producer of plastic tanks predicts, however, that 70% of all fuel tanks will be plastic in the U.S. market by 2000.[67] It may be difficult to collect meaningful statistics on plastic tank leakage rates given their relative youth and durability. Until we determine the probability of fuel tank leakage, we cannot make a reasonable estimate of the relative risks of hydrogen vs. gasoline garage leaks.

> Key issue: what is the probability of a gasoline tank leak for steel tanks? For polyethylene tanks?

B.4.2 *Probability of ignition in garage*. Mike Swain at the University of Miami has simulated gaseous leaks in a home kitchen.[68] He compared small leaks of hydrogen with those of natural gas and propane. The leak rate was similar to those from faulty natural gas lines removed from service. A ceiling vent and an opening under the kitchen door were included in his model, but no forced convection. The hydrogen leak rate was larger than those of propane and methane to simulate equal energy transfer.

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[67]Private communication with BASF engineers, April 10, 1996.

[68]M.R. Swain and M.N. Swain, "A Comparison of H_2, CH_4, and C_3H_8 Fuel Leakage in Residential Settings," Int. J. Hydrogen Energy, Vol. 17, No. 10, pp. 807-815, 1992.

Some of Swain's results are shown in Figures 13 through 15. Figure 13 shows the flammable clouds four minutes after the leaks began. Hydrogen has produced no flammable cloud, natural gas has a very small flammable area near the leak, and the propane flammable cloud has spilled onto the floor, since propane is heavier than air. After 12 minutes (Figure 14, propane has filled the bottom of the kitchen with a flammable mixture, while hydrogen and natural gas are unchanged. Finally, Figure 15 shows the 0.3% contour for hydrogen and the 2.1% contour for natural gas at 12 minutes, both well below their flammability limits, just to show that the computer program is working and hydrogen and natural gas are flowing from the leak to the ceiling vent. These data show that propane is the most dangerous and hydrogen the least dangerous of these three fuels.

Based on these simulations, the probability of hydrogen igniting would seem very small compared to propane, and equal to or smaller than natural gas. However, the leak rates were low, and the kitchen had a vent opening. We need to investigate the effects of higher flow rates and determine if the kitchen results can be translated to a typical home garage which may not have a passive vent opening. In addition, we need to estimate the probability of a gasoline ignition under similar leak scenarios for our comparative risk assessment.

The comparative risks between hydrogen and the other fuels will undoubtedly depend on air ventilation rates inside the garage. Gasoline and propane vapors will accumulate at the garage floor level, and will be susceptible to static electricity ignition. Further simulation will be needed to determine if gasoline or propane flammable mixtures would reach as high as wall switches. Hydrogen and natural gas will congregate at the ceiling, near possible electrical ignition sources such as lights and garage door openers. Risks should diminish with the gaseous fuels as air circulation rates increase, but higher air flow may generate more gasoline vapor, assuming that the gasoline leak produces liquid gasoline on the garage floor. Thus gasoline vapors will have a race between increased vaporization and increased dilution. As discussed in Section 12, we have contracted with Dr. Swain at the University of Miami to run a set of computer simulations to predict the relative risks of gasoline, natural gas, propane and hydrogen in the residential garage.

Figure 13. Flammable Gas Clouds in a Residential Kitchen:
Comparison of Hydrogen, Natural Gas and Propane Leaks after 4 Minutes

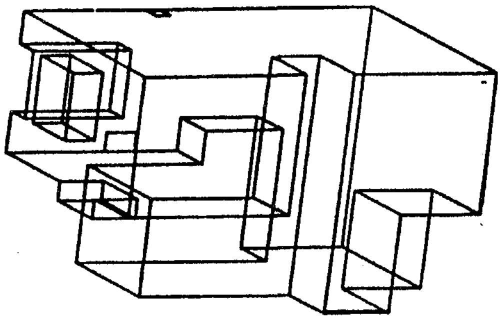

Fig. 14. After 4 min, hydrogen lean limit 4.1%.

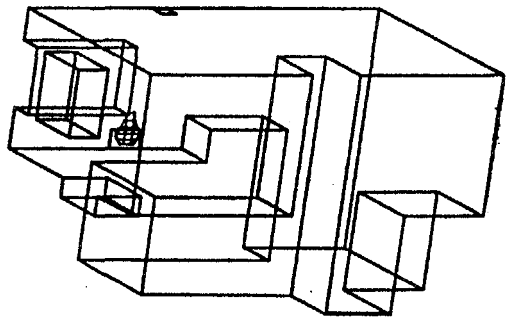

Fig. 15. After 4 min, methane lean limit 5.3%.

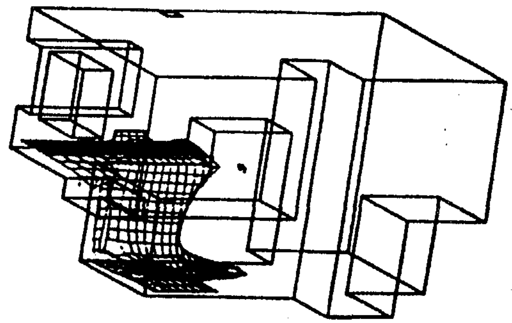

Fig. 16. After 4 min, propane lean limit 2.1%.

Ref: International Journal of Hydrogen Energy, Vol. 17, No. 10, pp. 807-815, 1992.

Figure 14. Kitchen Leaks after 12 Minutes

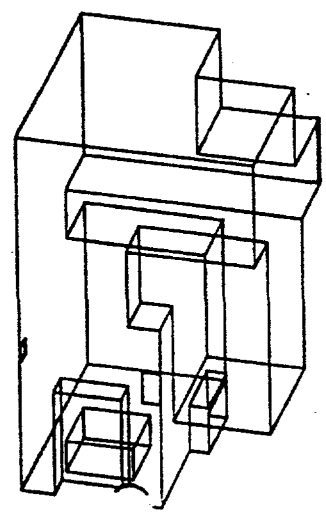

Fig. 17. After 12 min, hydrogen lean limit 4.1%.

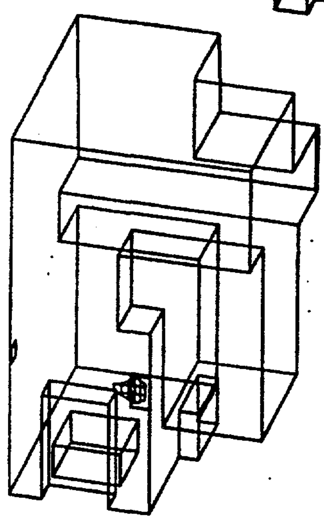

Fig. 18. After 12 min, methane lean limit 5.3%.

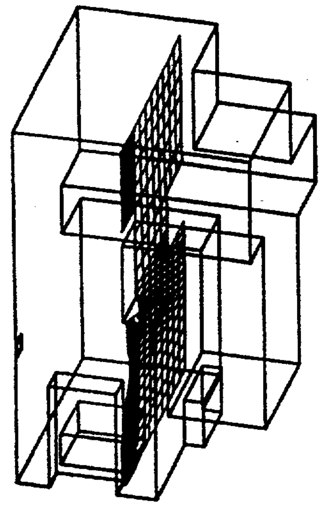

Fig. 19. After 12 min, propane lean limit 2.1%.

Figure 15. Kitchen Leaks after 12 Minutes at Concentrations Below the Flammable Limit for Hydrogen and Natural Gas.

Hydrogen at **0.3%** (vs. 4.1% LFL)

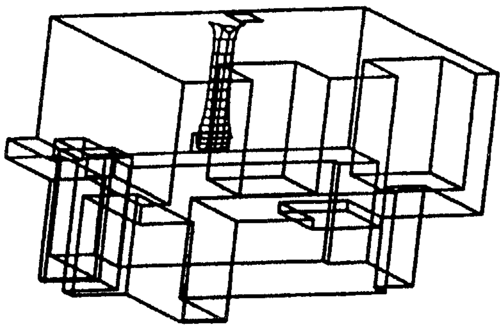

Fig. 23. After 12 min, hydrogen boundary at 0.3%.

Methane at **2.1%** (vs. 5.3% LFL)

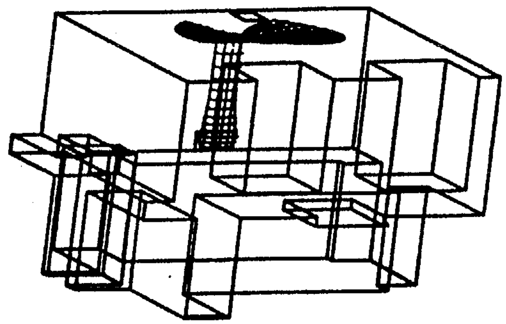

Fig. 24. After 12 min, methane boundary at 2.1%.

Propane at LFL of 2.1%

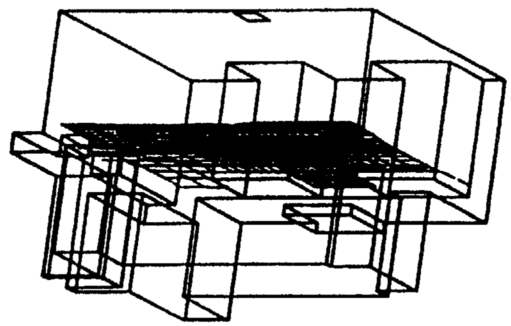

Fig. 22. After 12 min, propane lean limit 2.1%.

Appendix C - Hydrogen Accident History Assessment

C-1 Accident History Assessment Introduction

We reviewed the primary hydrogen safety literature including all past issues of the International Journal of Hydrogen Energy and the meeting records of the National Hydrogen Association. Based on these inputs, we contacted key individuals within NASA and industry that have extensive experience in hydrogen safety issues, asking them for other sources for hydrogen accident histories. We have collected copies of what we believe to be most relevant hydrogen safety reports, as described in more detail in the bibliography.

Although we have reviewed several dozen major hydrogen safety reports, there are only two previous studies of hydrogen accidents: one by Paul Ordin of NASA[69] (1974) and one by Robert Zalosh and Thomas Short related to industrial hydrogen accidents[70] (1978). More recently, James Ringland of Sandia National Laboratory has updated these studies with the help of Jim Hansel of Air Products and Chemicals, including some industrial accidents between 1970 and 1993.[71] To the best of our knowledge, no one has compiled a comprehensive hydrogen accident history report since 1978.

C-2 NASA Hydrogen Accident Experience

Liquid hydrogen has been a major fuel for the space program because it carries the most energy per unit weight. For a given unit of energy, hydrogen is 2.7 times lighter than gasoline, 2.4 times lighter than natural gas, and 7.1 times lighter than hydrazine, another common rocket fuel. The second and third stages of the Saturn launch vehicle and the Space Shuttle main engines use a combination of liquid hydrogen and liquid oxygen. The liquid hydrogen is routinely transported by tanker trailers (up to 16,000 gallons), railroad tank cars (34,000 gallons) and by barge (250,000 gallons).

The safety record handling hydrogen for NASA has been excellent. Ordin lists 96 mishaps in the hydrogen program prior to 1974. Of these 96 mishaps, 83 resulted in some type of hydrogen release, including 4 explosions caused by hydrogen generated from recharging or outgassing of batteries. Ordin reported no deaths, but several workers were injured, including frost-bite and burns from spilled liquid hydrogen. He listed these as the primary causes of the mishaps:[72]

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[69] Paul M. Ordin, "Review of Hydrogen Accidents and Incidents in NASA Operations," NASA Lewis Research Center #749036, p. 442 (1974).

[70] Ibid., Zalosh and Short.

[71] James T. Ringland, "Safety Issues for Hydrogen-Powered Vehicles," Sandia National Laboratories, SAND94-8226, March, 1994.

[72] More than one cause is listed for some mishaps.

Valve malfunctions/valve leaks	20
Leaking connections	16
Safety disc failures	10
Unsatisfactory materials, embrittlement	10
High venting rates	10
Cryopumping	10
Air in system	5
Bellows failure	4
Battery-restricted ventilation	4
Tank rupture	3
Highway-traffic accidents	3
Vacuum loss	2
Line rupture	2

Of the 96 mishaps, Ordin estimated that 87 percent were traceable to some sort of deficiency: deficiency in the work area (27%), procedural deficiencies (25%), design deficiencies (22%), and planning deficiencies (14%). Only 11% were due to component malfunctions (8%) or material incompatibility (3%). We contend that material incompatabilty should be considered a design deficiency, which would increase the total potentially avoidable mishaps to nearly 90%. That is, if we learn from past mistakes and design hydrogen systems to avoid the dominant failure modes such as leaky valves and connections and faulty safety discs, then accident rates should be less in the future.

Eighty-three of the 96 mishaps released any hydrogen. Of these 83 cases, 61 or 73% were ignited, indicating that we must generally expect hydrogen to be ignited if it is released. However, most of these mishaps involved very large volumes of liquid hydrogen, including tanker trucks with up to 16,000 gallons, and the high ignition rate may not apply to the hydrogen vehicle case or even to a small refueling station. Thus a small hydrogen leak from a vehicle may not reach a flammable mixture, or the flammable mixture may extend only an inch or so from the leak, significantly reducing the chances of ignition.

The sources of ignition identified by Ordin include:

Unknown	36.2%
Electric shorts, sparks	24.1%
Static charge	17.2%
Flare stack	6.9%
Cutting torch	5.2%
Metal fracture	5.2%
Impact	5.2%

One striking lesson from the NASA hydrogen accident record is the lack of a dramatic event, similar to the Hindenburg fire of 1937. In one case, a liquid hydrogen tanker returning from a delivery nearly empty was hit head-on by another truck at 50-55 mph. The tractor was demolished, but the liquid hydrogen tank did not even lose pressure after the crash.

In August of 1972, a NASA tanker truck with 16,000 gallons of liquid hydrogen on its way to the Kennedy Spaceflight Center was struck by an auto that ran a red light in Tallahasse, Florida. The rig jackknifed and the tanker landed on its right side in a ditch. The crushing of the side diesel tank on the cab and sparks from the sliding on the pavement ignited the diesel fuel, which flowed down the embankment toward the hydrogen trailer. The vaccum seal was broken and hydrogen gradually vaporized and escaped out the vent, which was by then horizontal, pointed away from the highway toward some trees. The hydrogen caught fire from the diesel fire, and over 2 million cubic feet burned like a blowtorch without further damage. There was no explosion or even large fireball that would certainly have erupted had the tanker carried gasoline.[73]

Despite the 61 fires or explosions experienced by NASA, some involving large quantities of hydrogen, no one was killed. This excellent safety record is due in part, no doubt, to the safety training of NASA personnel and their contractors. All hydrogen is handled by trained professionals in a closed environment, and this safety record may or may not translate over to a fuel used by thousands or millions of ordinary citizens without extensive training.

C-3 The Hindenburg

The most infamous hydrogen accident, and the one most often linked in the public's mind with the hazards of hydrogen, is the Hindenburg airship (See analysis of this accident on page 17.)

C-4 Industrial Hydrogen Accident Experience

The Factory Mutual Research study from 1978 analyzed 409 hydrogen accidents, including 88 of the NASA accidents. These 409 hydrogen accidents caused 22 deaths and 101 injuries. No details of individual accidents are provided, but the authors of the report have summarized the leading causes and ignition sources for these accidents.

Most hydrogen is produced (or recovered as by-product in the case of oil refineries or electrolytic chlorine production) and consumed within the plant gates of oil refineries or chemical industries. About 90% of all hydrogen is consumed between ammonia production for fertilizers (30%) and oil refining (60%). Methanol production (often collocated with ammonia plants) accounts for another 5% of hydrogen use, with all other uses consuming less than a percent of the total hydrogen production. Total merchant hydrogen sales account for at most two percent of total hydrogen production, and most of this is delivered by pipeline.[74] Dave Nahmias estimates that only 0.5% of hydrogen is delivered as a liquid, and 0.08% is delivered by truck as a gas to outside

[73]Private communication, Addison Bain, April 18, 1997.

[74]Barbara Heydorn, "Hydrogen Industry and Markets," Proceedings: Transition Strategies to Hydrogen as an Energy Carrier, First Annual Meeting of the National Hydrogen Association, March 1991.

customers[75]. Small users include the electronics industry, hydrogenation of fats and oils in the food industry, float glass production, cooling of large electrical generators, metal fabricators,

The Factory Mutual data show that explosions are nearly twice as likely as fires after an industrial hydrogen leak, and explosions are much more likely to lead to fatalities than hydrogen fires. Hydrogen was ignited in 80% of these accidents, again showing that hydrogen is almost always ignited in industrial class accidents.

Summary of Industrial Hydrogen Accidents

Type of Incident	No. of Hydrogen Incidents	No. of Fatalities	No. of Injuries
Fire	117	1	15
Explosion	211	14	76
Pressure Rupture	25	1	0
Unignited Release	39	2	3
Other	17	4	7
Totals:	409	22	101

The primary causes leading to a combustible mixture were:

External leak	17.4%
Vessel or pipe rupture	16.9%
Venting incident	13.2%
Operator Negligence	8.6%
Intentional operation	8.1%
Internal leak	7.3%
Inadequate ventilation	7.1%
Inadequate purging	6.4%
Electrolysis malfunction	4.4%
Other	1.7%
Collision or puncture	1.2%
Battery charging	1.2%
Exposure to fire	1.0%
Excessive vacuum	0.7%

[75]Private communication, Dave Nahmias, June 19, 1995.

One key finding is that undetected hydrogen leaks accounted for at least 40 percent of the incidents. Hydrogen detection should be an important element of any safety program. Hydrogen can be detected using human senses, either by adding odorants or illuminants to the gas, or by installing hydrogen detectors in vehicles or garages.

The ignition sources for the 409 incidents were listed as:

Unknown	153	37.4%
High Temperature	60	14.7%
Electrical spark	53	13.0%
Static discharge	35	8.6%
Hot Object	26	6.4%
Open flame	18	4.4%
Heat from fuel equipment	14	3.4%
Welding	12	2.9%
Runaway chemical reaction	6	1.5%
Catalyst	5	1.2%
Lightning	4	1.0%

The large number of unknown ignition sources again amplifies the conclusion that large hydrogen leaks will find an ignition source, even if it is not apparent to the observer, or at least the post accident investigator. Almost all hydrogen used by industry is consumed as a gas, unlike NASA which uses primarily liquid hydrogen for rocket propulsion.

C-5 Hydrogen vs. Natural Gas Safety Record

The Factory Mutual study also attempted to compare the safety of hydrogen with that of natural gas, but noted that there are very little data for comparable situations. Natural gas is used almost exclusively as a fuel, while hydrogen is used almost exclusively as a chemical agent in an industrial process. With these fundamentally different applications, comparing safety records may not be valid. The study did conclude, however, that "*Based on the limited data currently available, the comparisons do not reveal any conclusive, statistically significant differences that would preclude future widespread use of hydrogen with a safety record comparable to that of natural gas today.*"

The Factory Mutual report also referred to a 1977 UK study that compared natural gas with town gas, a 50/50 mixture of carbon monoxide and hydrogen. This analysis may be more relevant, since both fuels were used for the same application: home heating. This application is also more analogous to the safety risks associated with parking a hydrogen vehicle in a home garage, since it involves a smaller amount of gas than the industrial cases. This study concluded that there is "*no significant evidence of difference between the frequency and severity of structurally damaging explosions due to natural gas and town gas.*"

While these tentative conclusions are reassuring for the widespread use of hydrogen, at least two findings within the Factory Mutual report are disturbing. First, they report that the hydrogen incident rate at ferrous metal plants was 21 times higher than the rate for natural gas, per unit energy delivered. Similarly, petroleum refineries reported that energy-normalized incidence rates for hydrogen were 4.5 times higher than for natural gas and 2.4 times higher than for propane. The authors of the report state that these results are tentative due to the small data base combined with the fact that hydrogen is used as a process chemical, while natural gas is used as a fuel, but they suggest that the poor relative performance of hydrogen may be due to its lower ignition energy relative to natural gas and propane.

Again, this assessment may be valid in the industrial setting with a large leak of hydrogen that reaches 20 to 30% hydrogen mixed with air, where hydrogen does have an extraordinarily low ignition energy (0.02 millijoules). For a slower leak that may be more representative of the safety risk in a hydrogen vehicle parked inside a residential garage, the system would be designed to minimize the chances of any hydrogen leak accumulating to the 4% lower flammability limit for hydrogen. At the 4% level, the ignition energy for hydrogen is in the range of 1 to 5 mJ, only slightly lower than the ignition energy for natural gas at these concentration levels(See Figure 3 in the main body of the report). To the extent that hydrogen safety systems would sense leaks above 1% to 2% and either sound an alarm or start active ventilation, then hydrogen should be no more of a threat than natural gas.

The Factory Mutual report also compared hydrogen and natural gas transportation accidents over the 1971-1975 time period. The comparison is not really valid, however, since natural gas is transported by pipeline, while most hydrogen is delivered by truck. Despite the obviously more dangerous transportation mode, hydrogen fared reasonably well, showing an injury rate of 25.6 per 10^{15} BTU delivered (3 injuries per 23.4 $\times 10^{12}$ BTU/year) compared to 22.1 per 10^{15} BTU for natural gas (1,642 injuries per 14,860 $\times 10^{12}$ BTU/year). The hydrogen fatality rate was much larger, 8.5 per 10^{15} BTU compared to 2.0 per 10^{15} for natural gas (152 fatalities). The hydrogen rate was based on just one fatality, however, so the data are clearly not statistically significant.

While there are only a handful of experimental hydrogen powered vehicles on the road today, natural gas powered vehicles have been used since the 1930's in Italy. Natural gas has safety attributes similar to those of hydrogen: both are lighter than air (gasoline and propane fumes are heavier than air), both have greater lower flammability limits (LFLs) than gasoline or propane, and both are usually stored as high pressure gases. The accident history for NGVs should therefore have some bearing on the safety record for hydrogen vehicles.

Indeed, the history of NGVs could be much more relevant than the history of hydrogen usage in large chemical factories. For example, Italy has about 250,000 NGVs today. Almost all of the NGVs are operated by private citizens, whereas most of the 40,000 NGVs in the U.S. are operated by fleet owners, and could have better maintenance records than the average U.S. vehicle. Not only are the Italian NGV's owner-operated, most of them have been converted to operate on compressed natural gas by the owner or a small garage shop. Italy has had few commercial NGV suppliers over the last 60 years of NGV experience.

Despite the home-made flavor of these NGVs, and despite the fact that these NGVs have been operating since the late 1930's, the safety record appears to have been excellent. Some early natural gas steel cylinders did fail in Italy. In 1974, for example, there were 6 reported tank failures out of 408,000 tanks in use, or one failure for every 68,000 tanks. By 1980, the failure rate had dropped to one per every 460,000 tanks, with no failures reported after 1980.[76] Since Italy does not require a pressure relief device on all tanks[77] -- a DOT requirement in the U.S. -- even these few failures might have been avoided with U.S. standards. Apparently no deaths or injuries were reported as a result of these early tank failures.

One study in Sweden by the Co-Nordic Natural Gas Project[78] reports that "*there has never been a recorded accident resulting from a faulty CNG system*" and "*CNG components rarely failed and never caused a death or injury*"[in Italy]. If we use U.S. statistics of one gasoline fire fatality per 4.6 billion miles traveled, and if natural gas was as hazardous in a collision as gasoline, then we would expect to witness one fatality every 2 years, assuming that Italy's 200,000 NGVs travel 12,000 miles per year. The fact that they have not recorded any fatalities in 40 to 50 years might indicate that natural gas has less risk than gasoline, but the numbers are far too small to be statistically significant, particularly since Italian authorities might easily miss recording one natural gas caused fire fatality every 2 years. In any case, the NGV history shows that compressed gas storage on-board a vehicle is not a major risk, even if the vehicles are converted to run on compressed gas by inexperienced owners or local garage mechanics.

C-6 Hydrogen Transportation Safety History

Some of the NASA and industrial hydrogen safety data came from transportation incidents prior to the mid 1970's. Jim Hansel of Air Products has updated the more recent history of hydrogen accidents, as reported by Ringland, including some accidents through 1993. Air Products is the largest supplier of liquid hydrogen, with an average of 70 trailer trucks on the road every day, making 14,000 deliveries per year and traveling 48 million miles. These trucks deliver about 9 billion SCF of hydrogen each year, with 92% or 70 million gallons delivered as a liquid.

Despite all of this activity, Hansel reports that Air Products has never lost any liquid hydrogen in 25 years of operation. Hydrogen gas has vented from an average of 12 accidents per year, but no liquid hydrogen has been released despite some very severe accidents including hitting a bridge abutment that sheared the wheels from the trailer, a trailer that rolled over on its side, and another that rolled over 360 degrees.

Hansel reported five accidents during loading or unloading of liquid hydrogen trailers between 1987 and 1993. Of these, only one could be associated with the properties of hydrogen, when a weld failed on the trailer tank as it was being unloaded. The other four were due to mechanical or procedural failures, including the driver pulling away with the filling hose still

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[76]International Association for Natural Gas Vehicles, A Position Paper on Natural Gas Vehicles, Auckland, New Zealand, 1993, Chapter 6, p.4.

[77]Thomas J. Grant et. al., Safety Analysis of Natural Gas Vehicles Transiting Highway Tunnels, Ebasco Services, Inc., New York, August 1989, p. 6-3.

[78]Mats Ekelund et. al., NGVs and Safety, Co-Nordic Natural Gas Bus Project, 1993.

attached. These accidents and all of the road accidents would have occurred no matter what gas the truck was carrying.

Ringland did report one serious accident on August 25, 1987, when a Linde truck trailer carrying liquid hydrogen overturned on an interstate highway in Columbus, Ohio. The hydrogen escaped after the tank lost vacuum, removing its primary thermal insulation. But the hydrogen did not ignite. The potential danger did disrupt the local residents as the highway was closed and near-by homes were evacuated.

Put in perspective, this hydrogen transportation safety record is impressive. A liquid hydrogen tanker truck carries up to 16,000 gallons with an energy content of 486 million BTUs (LHV). One hydrogen powered fuel cell vehicle (FCV) would carry approximately 15 pounds of hydrogen, or 0.77 MBTUs, which would be sufficient to travel 342 miles on the Federal Urban Driving Schedule (FUDS). Each liquid hydrogen tanker truck carries up to 630 times more hydrogen energy than a FCV, and Air Products has logged 1.2 billion miles over 25 years without a serious accident. Had all this hydrogen transported by Air Products (70 million gallons per year) been used in FCVs, they could have traveled 950 million miles each year.

C-7 Natural Gas Vehicle Tank Failures

There are about 750,000 natural gas vehicles operating world wide, with about 40,000 in the U.S. Recent NGV's use very light but extraordinarily strong tanks made by wrapping aluminum or even plastic liners with layers of glass or carbon fibers. Three of these composite tanks have failed in service.

The first two failures occurred during refueling of two GM Sierra natural gas-powered trucks. The installer molded shields over the bottoms of the fiberglass tanks to provide protection from road debris. Unfortunately no leak holes were added to these shields. The trucks were used to carry batteries, and acid leaked out, collecting in the shields. Over time, the acid etched the glass (not the epoxy resin) on at least one tank. Another tank may also have been mechanically abraided due to improper installation One tank on one truck (there were two per truck installed parallel to the drive train) ruptured when it was filled to 24.8 MPa (3,600 psi). The man loading the NGV was thrown backwards, but not hurt. In the second case, the man filled the tanks, drove away when the tanks ruptured. He was not hurt, although the truck was reportedly thrown into the air. Neither tank ignited, and there were no injuries, even though there was no special protection from shrapnel from the tanks. Note at least one of these tanks would not have failed had they been carbon fiber tanks, since battery acid does not dissolve carbon.[79]

The third accident occurred on August 21, 1996, when an EDO carbon fiber composite tank ruptured during refueling of a natural gas-powered bus at a Los Angeles Metropolitan Transit Authority garage. The MTA maintenance worker had connected the natural gas line to the bus for a 5- to 10-minute fast fill to 24.8 MPa. The worker then connected a large vacuum suction to the front of the bus in preparation for interior cleaning while the bus was refueling, the standard procedure at the time. She was standing within four or five feet of the rear end of the bus when one of the 12 EDO tanks ruptured. Two tanks are located above the engine, and ten are located longitudinally below the bus. The tank that ruptured was on the bottom, outboard on the street side at the rear of the bus. One end dome came loose. The tank was propelled back, shearing the other end dome. The remains of this first tank crashed into a second tank, which also ruptured. The gas release from both tanks and the resulting projectiles caused significant damage to the bus, but the woman was not injured.

At least one of the ruptured tank fragments penetrated through the plywood bus floor and severely damaged the interior of the bus. About "2/3" of the windows on the bus were shattered from the concussion, although the laminated safety glass constrained most of the glass fragments from becoming shrapnel. One witness reported that some of the stainless steel seat frames looked like "tin foil" after the incident.[80]

Exterior damage was less but still significant. The MTA engineering manager said that there were about 50 "coffee can" sized objects scattered about the garage at distances up to 100 feet from

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[79]Private communication, Rex Haddock, EDO Fiber Sciences, April 7, 1995.

[80]Private communication, Mike Morley, November 25, 1996.

the bus. One projectile broke the windshield of another bus in the garage that was 50 to 75 feet from the ruptured tank.[81]

The cause of the tank rupture is still under investigation. The local gas company and MTA officials seem to be in general agreement that the most likely cause was mishandling of the tank during assembly and/or routine inspections, most likely a dropped tank. The NGV-2 requires inspections of every tank every 3 years. They all agreed that road damage was possible, but not likely, even though there was no shield between the tanks and the road surface. Given the extensive tank testing, none believed that there were any manufacturing flaws.

One MTA research representative explained that carbon fiber composite tanks are virtually impervious to low mass, high velocity projectiles such as rocks or other road debris. But they are susceptible to high mass, low velocity impacts. In particular, they can be damaged by being dropped on their dome ends. After the accident, MTA personnel dropped a tank from four feet on the dome, and observed visible cracks in the dome. A tank could also have been damaged by a severe impact during bus operation, such as running over a curb or possibly a heavy object such as a dislodged steel road plate hitting the tank.[82]

The Los Angeles MTA has made several physical and operational modifications to their fleet of approximately 120 natural gas buses, which are back on the road. First, 14-gauge aluminum sheets have been placed between the road and the tanks. These do *not* provide serious protection from road debris -- the carbon tanks are far stronger than 14-gauge aluminum. Rather, these shields are simply detection or early warning devices. If the maintenance crew sees a damaged shield, then the tank is inspected for damage. Second, MTA is considering replacing the plywood bus floors with tougher composite material which would solve two other bus problems: dry rot and cock roaches!

The MTA also modified fueling procedures, and no longer permit cleaning crew on the bus during refueling. Inspectors have been trained to look for damaged tanks. In one sense this failure may have been due in part to the reputation these tanks had acquired of being virtually indestructible. As a result, maintenance crews may have been too lax in their handling procedures.

Fiber tank testing procedures were already being modified before the L. A. bus accident. The 1992 edition of NGV-2, the natural gas tank test procedure, included a 10-foot drop qualification test, but only with the tank in a horizontal position. After the 10-foot drop, if the tank had no visible damage, it was cycled 5,000 times from 10 percent service pressure to 125 percent of service pressure, and then 13,000 times from 10% to 100% of service pressure. Thus the EDO tanks on the MTA buses did not have to pass any drop tests on the end dome.

The proposed 1996 revisions (pre-dating this accident) to NGV-2 include two new drop tests as part of the tank qualification procedure: one tank is dropped on each end from at least 6 feet or 360 ft-lbs of impact energy. The second tank is dropped from six feet at a 45 degree angle, and

[81]Private communication, Jeff Johnson, November 25, 1996.

[82]Private communication, Mike Eaves, November 25, 1996.

allowed to bounce without restraint after the first impact. After the drop tests, the tanks are cycled 15,000 times from 10% to 125% of service pressure. These new testing procedures should help to detect potential tank dome weak spots in the future.

EDO has already decided to put more physical protection on their end domes. Lincoln Composites has always included glass fibers in their tanks specifically to improve toughness. Including glass will increase weight slightly (lower tank figure of merit), but the increase in safety should be worth the sacrifice in weight.

The two GM truck tank failures and the more recent L. A. MTA bus failure illustrate two different failure modes, and point out potential weaknesses of glass and carbon fibers. Glass fibers are susceptible to acid etching and also experience "static creep." That is, a glass fiber tank that is loaded to just 30% of its ultimate strength will eventually fail over a 15 year period as the glass fibers gradually elongate (strain). This is not statistical failure -- all glass fiber tanks would eventually fail. All glass fiber tanks would also fail within minutes if loaded to 90% of their ultimate strength. This is the reason for a four times safety factor for glass fiber tanks. Carbon fibers, on the other hand, have been tested at 90% of their ultimate strength and did not fail after six months. From a scientific viewpoint, a carbon fiber tank could therefore have a safety factor of only 1.2, compared to the current requirement of 2.25 to one, since carbon does not elongate under stress. But pure carbon fiber tanks are susceptible to impact damage. The best solution seems to be a combination of both fibers: carbon for strength and light weight, and some glass or other high impact strength fibers such as aramid (Kevlar™) or Spectra™ for toughness and impact resistance.

C-8 Conclusions from the Hydrogen Accident History Assessment

Since only a few vehicles are currently fueled by hydrogen, there is no accident data base to directly judge the safety of hydrogen compared to other common motor vehicle fuels. Any conclusions based on accident records are necessarily inferred from related hydrogen uses or from accident histories of similar fuels such as natural gas.

Based on accident history data, we conclude that:

* Hydrogen has been used safety as a home heating fuel since the early 1800's in the form of "town gas," a mixture of hydrogen and carbon monoxide. One UK study found "*no significant evidence of difference between the frequency and severity of structurally damaging explosions due to natural gas and town gas.*"

* Liquid hydrogen has been carried safely on the nation's highways at the rate of 70 million gallons per year, without a major incident.

* Hydrogen has been handled with relative safety within the gates of major oil and chemical plants, but hydrogen does have 21 times higher incidence rate than natural gas in the ferrous metal industry, and 4.5 times higher incidence rate in the petroleum industry.

* Most industrial hydrogen leaks are ignited (80%), indicating that system designs should strive to keep hydrogen below the lower flammability limit.

* Undetected leaks were involved in 40% of industrial hydrogen incidents, indicating that hydrogen detection coupled with warning or active ventilation may be required.

* Natural gas vehicles have a good safety record, with one Swedish study of 250,000 NGV's that have been operating in Italy since the late 1930's concluding that "*there has never been a recorded accident resulting from a faulty CNG system*" and "*CNG components rarely failed and never caused a death or injury.*"

In short, we find that there is no evidence of unusual safety risk associated with the use of hydrogen, based on the accident history assessment, that would preclude its use as a motor vehicle fuel. There is no indication that a properly designed hydrogen vehicle and hydrogen refueling infrastructure would pose any more risk than conventional motor vehicle fuels.

Appendix D - Hydrogen Vehicle Safety Analysis[83]

By T.G. Halvorson, C. E. Terbot, and M. W. Wisz of Praxair

D.1 Background and Scope of Work

A safe hydrogen fueling infrastructure must complement onboard vehicle safety to achieve overall consumer confidence and acceptance. Each part must provide the highest level of safety for the "motoring public" if this new, clean fuel is to emerge successfully for general use. It won't matter how the economics of supply stack up against today's fuels if the system is not safe, or perceived to not be safe.

We all have experience refueling our own gasoline-powered vehicles at today's myriad of self-serve gas stations. We generally judge that brief operation as "safe" and seldom give it second thought. If we want to maintain that "safety transparency" while transferring hydrogen at 34.5 MPa (5000 psig), considerable effort will be required to design, evaluate, refine, redesign, and re-evaluate the equipment and procedures that we all will routinely use at these future fuel dispensing stations.

A start in that process might be to step back from the design details and cost estimates that have been presented and review some of the known hazards associated with operation and use of this equipment. To that end, preliminary hazard reviews have been made of the systems devised to produce and deliver fuel to the consumer's vehicle. The work here is not meant to be quantitative risk assessment. There is not enough detail in system design nor component selection to accurately determine levels of risk. A quantitative risk assessment needs to be performed when more detailed designs are developed.

The approach has been to systematically review major equipment items and evaluate what hazards may result from possible deviations in operating conditions. The consequences of these deviations may result in hazardous situations unless the system has built-in safeguards to respond in ways that mitigate the hazards.

Three subsystems have been examined in this fashion and will be discussed below:

- On-site Gaseous Hydrogen Production by Steam Methane Reforming
- Gaseous Hydrogen-Based Vehicle Fueling System, and
- Liquid Hydrogen-Based Vehicle Fueling System.

Each of these systems can impact the safety of people refueling their vehicles at commercial dispensing stations. Hydrogen production units present risks that could affect the safety of the fuel consumer because of the proximity to the fueling operation. The vehicle fueling systems directly interface with consumers at the dispenser.

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[83]This appendix is copied (with permission) from Section 5 of the Praxair report entitled "Hydrogen Production and Fueling System Infrastructure for PEM Fuel Cell-Powered Vehicles," prepared under Ford Subcontract No. 47-2-R31157, April 12, 1996, pg 35 ff.

From these reviews, insight may be gleaned from areas of the systems that may be weak or deficient in providing adequate protective measures from potential hazards. These provide a basis for extension, modification, or alternative design to reduce perceived hazards to acceptable levels.

D.2 Safety Review of On-site Production Systems

A preliminary hazard review has been completed on a generic steam methane reforming production plant. The size of this on-site plant is not an issue in the review. The SMR process has been selected over methanol reforming because natural gas is widely available and likely to result in preferred economics under most situations.

The review is based on examining a typical commercial offering available in today's market and installed for industrial customers. Future commercialized processes that may convert natural gas into hydrogen more efficiently and cheaply may also alter the hazard landscape from this system.

Table D-1 presents the completed worksheets for this review. Figure D-1, the process flow diagram for the SMR plant, provides reference for the equipment items listed.

D.3 Safety Review of Vehicle Fueling Systems

D.3.1 Gaseous Hydrogen-Based Vehicle Fueling System

A hazard review of a gaseous hydrogen-based vehicle fueling system has been completed. This fueling system would be matched with either the on-site SMR or methanol reforming production process. Low pressure hydrogen gas is compressed, stored, and dispensed on demand by an automatic, unattended supply system.

Table D-2 presents the completed worksheets for this review. Figure D-2 provides reference for the equipment items included here.

D.3.2 Liquid Hydrogen-Based Vehicle Fueling System

Similarly, a review of the hazards associated with a liquid hydrogen-based fueling system has been prepared. In this case, liquid hydrogen is delivered to a local dispensing site, stored in vacuum insulated tanks, pumped to high pressure, vaporized, stored as high pressure gas, and dispensed on demand to onboard vehicle fuel tanks. Table D-3 presents the completed worksheets, and Figure D-3 provides a schematic reference for the equipment involved.

Figure D-1. On-Site Steam Methane Reformer and Service Station

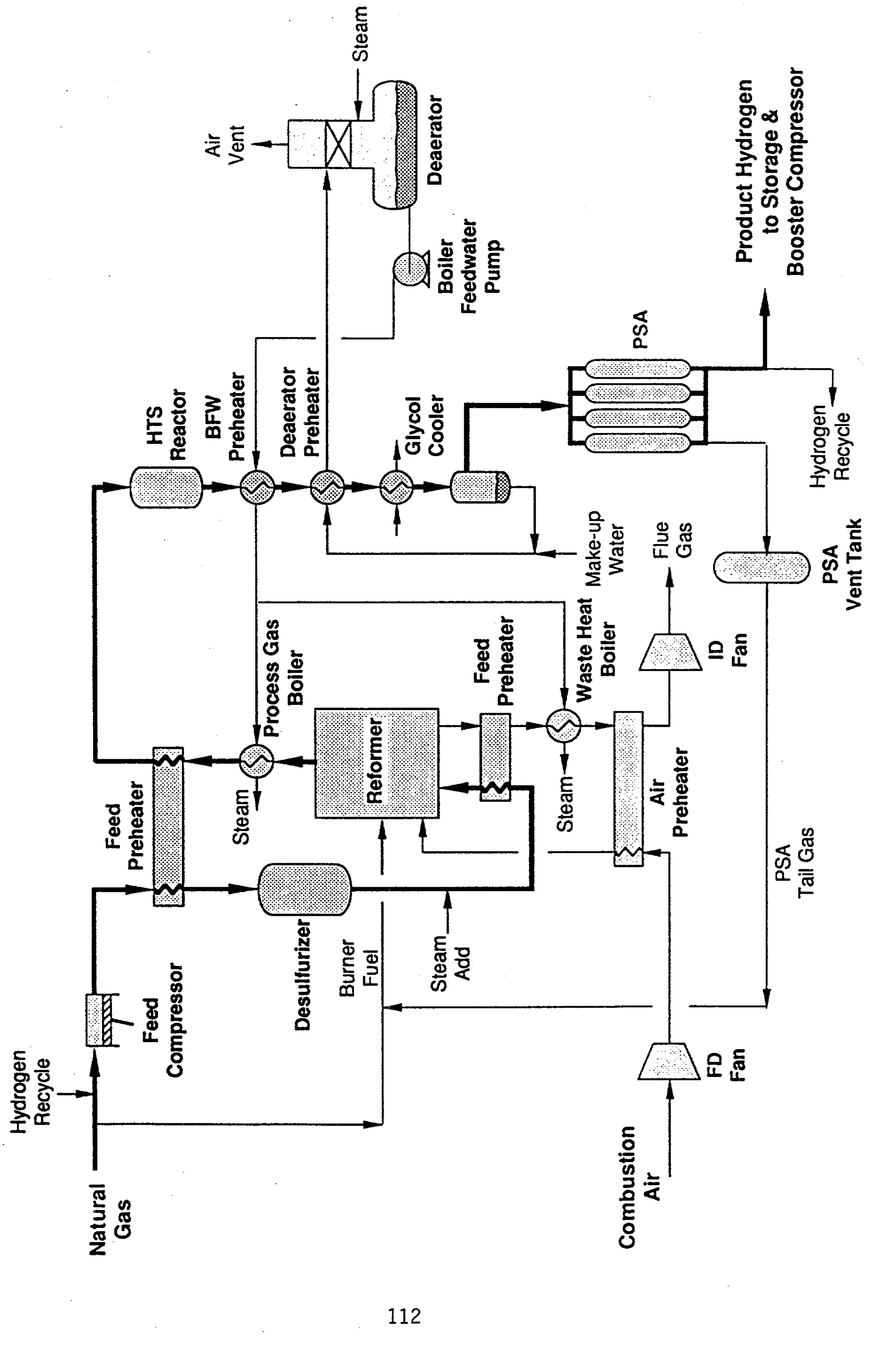

Table D-1. Hazard Review of On-Site Gaseous Hydrogen Production by Steam Methane Reforming

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Natural Gas Feed Compressor	High pressure on discharge line	Failure of high pressure limit switch.	Discharge line safety relief valve opens.	High pressure gas is vented safely to the vent stack system for safe dispersal into the atmosphere. A flow switch should probably be installed in the discharge line to detect this event and shut down the compressor.
	High flow in discharge line	None identified.	None identified.	Flow rate is automatically limited by positive displacement reciprocating compressor.
	Loss of discharge pressure or low flow rate while operating	Excessive blowby past rings due to damage or wear	Inability to maintain gas storage pressure above minimum levels	Need to perform preventative maintenance on regular schedule to maintain compressor operations within specification.
	Leakage of natural gas to the surrounding atmosphere	Rod seal packing failure	Potential for flammable mixture formation.	Distance piece is purged continuously with nitrogen and vented to the vent stack system. Packing is vented between the first and second ring to the vent system.
	Loss of nitrogen purge to distance piece and crankcase.	Primary nitrogen supply disrupted.	Likely migration of natural gas into crankcase forming flammable gas mixture with potential for explosion or fire.	Plant is shut down.
	Loss of lubricating oil pressure (for lubricated machines)	Lube pump failure	High piston/cylinder wall friction with excessive temperatures.	Lube oil system has low pressure switch to prevent operation without sufficient supply pressure.
	High lubricating oil temperature	Oil cooler failure	High piston/cylinder wall friction with excessive temperatures.	Lube oil system has high temperature switch to prevent operation.
	Low oil level in reservoir	Oil system leakage, excessive consumption, or failure to refill reservoir	Potential for oil vapor explosion if heater becomes exposed.	Oil reservoir should have a low level switch to prevent operation of the oil heater and activate an alarm/shutdown.
	High cylinder discharge temperature (any stage)	Inadequate cylinder cooling	Potential for accelerated ring wear and damage.	RTDs should be installed to monitor the discharge temperature of each cylinder and activate an alarm in the monitoring system.

Table D-1. Hazard Review of On-Site Gaseous Hydrogen Production by Steam Methane Reforming

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Natural Gas Feed Compressor (continued)	Excessive vibration in compressor drive frame.	Not specifically defined.	Potential for destruction of machine with catastrophic failure and natural gas leakage.	Vibration monitor ("earthquake" device) is mounted directly to the frame to monitor for excessively large displacements. If detected, the compressor system is immediately shut down.
	High interstage pressure	Blocked discharge line or valve damage.	Potential for destructive failure of compressor.	Safety relief valves are installed on the discharge of each stage to release excess gas pressure to the vent stack system if activated. Valves are sized appropriately to accommodate the maximum flow rate at the relieving pressure per the ASME code.
	Failure of tube in an intercooler heat exchanger.	Weak weld	Potential for destructive failure of heat exchanger shell with release of high pressure natural gas to the surroundings forming a flammable mixture.	Heat exchanger shell is protected by relief valves set to relieve at the shell-side design pressure per ASME code.
	Failure of process gas piping on compressor skid.	Weak weld	Release of high pressure natural gas to the surroundings forming a flammable mixture.	Not likely to occur since process gas piping is designed according to ANSI B31.3 piping code for materials, flexibility and supports.
Feed Preheater	High pressure on tube side	Failure of high pressure limit switch on feed compressor discharge line.	Potential for destructive failure of heat exchanger shell with release of high pressure gas to the surroundings forming a flammable mixture.	Safety relief valves are installed on the shell and tube side supply lines to release excess gas pressure to the vent stack system if activated. Valves are sized appropriately to accommodate the maximum flow rate at the relieving pressure per the ASME code.
	High temperature on the process gas side inlet	Process Boiler bypass valve failure	Potential for destructive failure of heat exchanger with release of high pressure gas to the surroundings forming a flammable mixture.	A downstream, high temperature shutdown device should be installed to shutdown the reformer system in the event of a bypass valve failure.

Table D-1. Hazard Review of On-Site Gaseous Hydrogen Production by Steam Methane Reforming

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Hydrotreater and Desulfurizer	High pressure	Failure of high pressure limit switch on feed compressor discharge line.	Potential for destructive failure of vessel with release of high pressure gas to the surroundings forming a flammable mixture.	A safety relief valve is installed on the feed compressor discharge line to release excess gas pressure to the vent stack system. Valves are sized appropriately to accommodate the maximum flow rate at the relieving pressure per the ASME code.
Reformer Burners and Furnace	Loss of burner flame.	Fuel flow disruption, draft fan failure	Potential for accumulation of unburned fuel and subsequent reignition with destructive force	Flame out is sensed by "fire eye" burner sensor. Reformer is automatically shut down, and burner fuel supply is isolated.
	Burner sensor failure	Not specifically defined.	Burner flame is not photo optically sensed.	Reformer is automatically shut down, and burner fuel supply is isolated. Two sensors are normally installed to prevent nuisance shutdowns.
	High natural gas pressure	Sample tap isolated during operation, or a regulator has failed.	Gas velocities could blow out burner flames, or hot spots in the furnace could develop. Either case has the potential for destructive failure.	Pressure switch activates and burner fuel is isolated from reformer (block and bleed to vent). System is shut down.
	High reformer burner draft pressure	High burner fuel flow, ID fan problem, or isolated sample tap	Potential for destructive failure of reformer with release of high temperature and combustible gas to the surroundings.	Draft pressure transmitter senses high pressure and burner fuel is isolated from reformer (block and bleed to vent). System is shut down.
	High Reformer furnace temperature	Low process gas flow rate through catalyst tubes	Potential destructive failure of reformer with flammable gas release to surroundings	Furnace high temperature switch activates and burner fuel is isolated from reformer (block and bleed to vent). System is shut down.
	Low burner fuel pressure	Loss of gas supply or a control problem	Hot spots could develop in the reformer or air could blow back into the burner causing the flame to sputter. Potential destructive failure exists	Low pressure switch automatically shuts down the reformer and isolates the fuel lines.

Table D-1. Hazard Review of On-Site Gaseous Hydrogen Production by Steam Methane Reforming

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Reformer Catalyst Tubes	High reformer catalyst tube temperature	Low steam-to-carbon ratio	Will cause higher than normal operating temperatures and lead to premature tube failure. Potential destruction of reformer tubes	Catalyst tube temperature switch activates and burner fuel is isolated.from reformer (block and bleed to vent). System is shut down. A low steam-to-carbon ratio in the reformer will allow the formation of coke on the tubes. This retards heat transfer and catalytic activity.
High Temperature Shift Reactor	High reactor temperature	Feed preheater fouling	Potential destruction of vessel resulting in high temperature flammable gas release to surroundings	System is shut down by reactor temperature switch activation.
	High pressure	Failure of high pressure limit switch	Line safety relief valve opens.	A safety relief valve is installed on the feed compressor discharge line to release excess gas pressure to the vent stack system. Valves are sized appropriately to accommodate the maximum flow rate at the relieving pressure per the ASME code.
Process Gas Coolers and Condensate Separators	High pressure	Failure of high pressure limit switch	Line safety relief valve opens.	A safety relief valve is installed in the downstream piping to release excess gas pressure to the vent stack system. Valves are sized appropriately to accommodate the maximum flow rate at the relieving pressure per the ASME code.
PSA Skid	Impurities in product hydrogen	Upstream equipment failure or PSA operating problems	Off spec. product to customer. This could imply a potential hazard to the customer.	Product supply to customer is isolated and system either shut down, or gas is vented to stack until the problem is corrected.
	Low discharge pressure	Inadequate flow or pressure	Low pressure product could result in a potential operating hazard within the customers operations	Product supply to customer is isolated and system either shut down, or gas is vented to stack until the problem is corrected.

Table D-1. Hazard Review of On-Site Gaseous Hydrogen Production by Steam Methane Reforming

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Tail Gas Tank	High pressure	Failure of high pressure limit switch	Line safety relief valve opens.	A safety relief valve is installed in the supply piping to release excess gas pressure to the vent stack system. Valves are sized appropriately to accommodate the maximum flow rate at the relieving pressure per the ASME code.
	Low pressure	I.D. Fan pulls a vacuum on the fuel supply line.	Any vacuum on the tail gas tank could allow air to leak into the tank forming a flammable gas mixture.	Sense the tank pressure and automatically block and bleed the line from the tail gas tank to the burner.
Induced Draft Fan	High reformer draft pressure	Improper function of ID fan suction valve or fan itself	Potential energy release and possible destruction of reformer furnace	Shut down reformer and isolate burner fuel upon reaching a high draft pressure setpoint.
Waste Heat Boilers	High pressure	Line is isolated while boiler is in operation, or pipe scaling occurs due to poor water quality.	Pressure relief valves open.	A safety relief valve is installed in the piping to release excess gas pressure to the vent stack system. Valves are sized appropriately to accommodate the maximum flow rate at the relieving pressure per the ASME code
	Poor water quality	Improperly functioning deaerator or water treatment system	Accelerated corrosion and scaling occurs in piping and equipment.	Periodic testing is performed on the water to determine quality. Not a safety hazard.
	Low steam drum level	Poor boiler operation	Low steam-to-carbon ratio could develop in the reformer	Coking could form on the reformer tubes.
	Process leaking	External impact or corrosion	Potential for serious burns to personnel	Precautions should be taken to avoid potential impact areas and perform regular quality inspections on the water treatment system.
Boiler Feedwater Pumps	Low suction pressure	Low water level in the deaerator	Pump does not prime which results in premature seal wear.	On/off pump control will cycle pumps. The reformer will shut down on low steam drum level if the low suction pressure persists.

Table D-1. Hazard Review of On-Site Gaseous Hydrogen Production by Steam Methane Reforming

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Deaerator	High pressure	Boiler feedwater pumps	Pressure safety valves on deaerator activate.	A safety relief valve is installed to release excess gas pressure to the vent stack system. Valves are sized appropriately to accommodate the maximum flow rate at the relieving pressure per the ASME code
	High oxygen content in boiler feed water	Loss of stripping steam	Accelerated corrosion in equipment and piping	Periodic analysis of water quality is required to prevent this event from occurring. Not a safety hazard.
	Low temperature cold condensate return	Improper cooler trim control	Hot water will be entrained and expelled via the deaerator vent. This is a potential burn hazard to personnel	Have a low temperature alarm installed with the cooler trim device.
Closed Loop Glycol Cooling System	Low coolant pressure	Cooling pump shutdown	Plant will automatically be shut down	Plant is shut down to prevent any overtemperature problems in reformer equipment.
Instrument Air Supply	Low instrument air pressure	Instrument air compressor shutdown	Plant will not run.	Proper instrument air pressure is a requirement for the plant to be started or remain in operation. Consider multiple units.
All Coded Pressure Vessels	Low oxygen sensor and LEL alarms in buildings	Leaks in flanges, weld seams or piping joints	Potential flammability hazard exists to personnel as well as the potential for carbon monoxide poisoning	Follow proper plant procedures to ensure a safe atmosphere in the work area before any maintenance activity begins.
	Loss of containment	Material defect or hydrogen embrittlement	Not applicable.	Materials used in the pressure vessels are in accordance with ASME Sec. VIII, Div.1 which requires examination to insure acceptable materials and traceability.
Entire Plant	Power failure	Ice storm, etc.	Automatic system shutdown	No problem expected
Vent Stack System	Loss of nitrogen purge	Nitrogen supply disruption	Potential flammable gas mixture formation	Low pressure switch on purge gas supply will shut down plant without adequate purge flow.

Figure D-2. Booster Compressor Dispensing Option

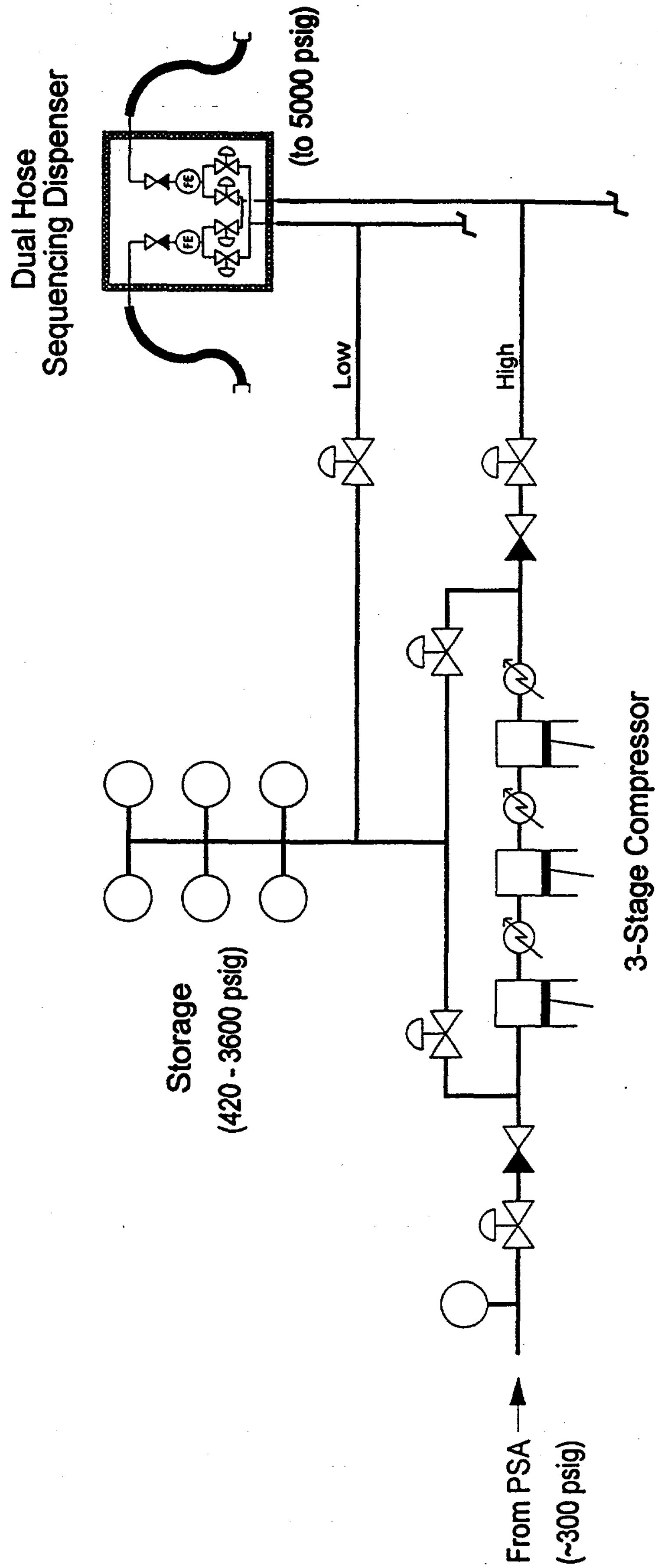

Table D-2. Hazard Review of Gaseous Hydrogen-Based Vehicle Fueling System

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Low Pressure Ballast Receivers	High pressure	Failure of master rate controller on SMR to control setpoint pressure or Failure of storage compressor or reduced flow rate due to compressor problem or Compressor operating in "Booster" mode for period of time in excess of design	Safety relief valve protecting the ballast receivers opens and discharges excess product to the vent stack.	Receivers are protected by safety valves set to open at pressures no higher than the MAWP for the receivers. Gas is vented safely to the atmosphere through the vent stack. A pressure switch should probably be used on the ballast receivers to alarm the monitoring system of this event.
	Low pressure	Failure of master rate controller on SMR to control setpoint pressure or Failure of storage compressor with leakage of hydrogen to atmosphere	Potential subatmospheric pressure on compressor suction with possible inleakage of air and formation of flammable mixture within the compressor. Possible explosion or fire within compressor.	Low pressure switch on compressor suction will activate creating an alarm and shutdown of the compressor before subatmospheric pressures are created.
	Loss of containment	External impact	Hydrogen release	Site selection identifies impact scenarios, vehicle barriers will eliminate catastrophic accidents.
	Loss of containment	Material defect or hydrogen embrittlement	Not applicable.	Materials used in the fabrication of the pressure vessels are in accordance with ASME Sec. VIII, Div.1 which requires examination to insure acceptable materials and traceability. Metal is generally SA516-70 which is acceptable for hydrogen service and does not suffer from embrittlement.
Storage/ Booster Compressor Skid	High pressure on discharge line	Failure of high pressure limit switch.	Discharge line safety relief valve opens.	High pressure gas is vented safely to the vent stack system for safe dispersal into the atmosphere. A flow switch should probably be installed in the discharge line to detect this event and shut down the compressor.

Table D-2. Hazard Review of Gaseous Hydrogen-Based Vehicle Fueling System

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Storage/ Booster Compressor Skid (continued)	High flow in discharge line	None identified.	None identified.	Flow rate is automatically limited by positive displacement reciprocating compressor.
	Loss of discharge pressure or low flow rate while operating	Excessive blowby past rings due to damage or wear	Inability to maintain gas storage pressure above minimum levels	Need to perform preventative maintenance on regular schedule to maintain compressor operations within specification.
	Leakage of hydrogen to the surrounding atmosphere	Rod seal packing failure	Potential for flammable mixture formation.	Distance piece is purged continuously with nitrogen and vented to the vent stack system. Packing is vented between the first and second ring to the vent system.
	Loss of nitrogen purge to distance piece and crankcase.	Primary nitrogen supply disrupted.	Likely migration of hydrogen into crankcase forming flammable gas mixture with potential for explosion or fire.	Fueling facility is shut down.
	Loss of lubricating oil pressure (for lubricated machines)	Lube oil pump failure.	High piston/cylinder wall friction with excessive temperatures.	Lube oil system has low pressure switch to prevent operation without sufficient supply pressure.
	High lubricating oil temperature.	Oil cooler failure	High piston/cylinder wall friction with excessive temperatures.	Lube oil system has high temperature switch to prevent operation.
	Low oil level in reservoir	Oil system leakage, excessive consumption, or failure to refill reservoir	Potential for oil vapor explosion if heater becomes exposed.	Oil reservoir should have a low level switch to prevent operation of the oil heater and activate an alarm/shutdown.
	High cylinder discharge temperature (any stage)	Inadequate cylinder cooling	Potential for accelerated ring wear and damage.	RTDs should be installed to monitor the discharge temperature of each cylinder and activate an alarm in the monitoring system.
	Excessive vibration in compressor drive frame.	Not specifically defined.	Potential for destruction of machine with catastrophic failure and hydrogen leakage.	Vibration monitor ("earthquake" device) is mounted directly to the frame to monitor for excessively large displacements. If detected, the compressor system is immediately shut down.

Table D-2. Hazard Review of Gaseous Hydrogen-Based Vehicle Fueling System

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Storage/ Booster Compressor Skid (continued)	High interstage pressure	Blocked discharge line or valve damage.	Potential for destructive failure of compressor.	Safety relief valves are installed on the discharge of each stage to release excess gas pressure to the vent stack system if activated. Valves are sized appropriately to accommodate the maximum flow rate at the relieving pressure per the ASME code.
	Failure of tube in an intercooler heat exchanger.	Weak weld	Potential for destructive failure of heat exchanger shell with release of high pressure hydrogen to the surroundings forming a flammable mixture.	Heat exchanger shell is protected by relief valves set to relieve at the shell-side design pressure per ASME code.
	Failure of process gas piping on compressor skid.	Weak weld	Release of high pressure hydrogen to the surroundings forming a flammable mixture.	Not likely to occur since process gas piping is designed according to ANSI B31.3 piping code for materials, flexibility and supports.
Medium Pressure Gas Storage Receivers	High Pressure	Failure of pressure limit switch on compressor discharge.	Safety relief on compressor discharge line opens. Gas storage receivers are also protected by adequately sized relief valves per ASME code.	High pressure gas is vented safely to the vent stack system for safe dispersal into the atmosphere. A flow switch should probably be installed in the discharge line to detect this event and shut down the compressor.
	Low Pressure	"Booster" mode operation has drawn down the storage pressure below the minimum design level.	Compression ratios for all stages will increase above design levels creating excessive heating and wear.	Not a direct safety issue, but situation needs to be monitored over time for possible corrective action and hardware upgrade.
	Low Pressure	Loss of containment, leak developed in receiver piping manifold.	Operation of the pumping system may continue to supply additional gas through leak creating flammable gas mixture around receiver area.	Pressure switch should be used to sense abnormally low pressure in receivers and prevent compressor from restarting until system can be inspected.
	Loss of containment	External impact	Hydrogen release	Site selection identifies impact scenarios, vehicle barriers will eliminate catastrophic accidents.

Table D-2. Hazard Review of Gaseous Hydrogen-Based Vehicle Fueling System

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Medium Pressure Gas Storage Receivers (continued)	Loss of containment	Material defect or hydrogen embrittlement	Hydrogen release.	Materials used in the pressure vessels are in accordance with ASME Sec. VIII, Div.1 which requires examination to insure acceptable materials and traceability. Metal is generally SA372 Gr. J CL 70 which is acceptable for hydrogen service and does not suffer from embrittlement.
Dual-Hose Sequencing Fuel Dispensers	High Pressure in fueling hose when dormant	Leaking isolation or switching valves	Fueling connector could be pressurized prematurely creating hazard for operator.	Consider using a fueling connector design that *prohibits making a connection* to the vehicle if initially pressurized (similar to ANSI/NGV-1 specification requirements).
	High Pressure in fueling hose after completion of fuel transfer	No means for pressure to be released from hose and connector	Attempts to release connector while pressurized may create situation with flying objects and potential for striking the fueling operator causing bodily injury. Release of trapped gas locally could create flammable mixture.	Consider using a fueling connector design that *prohibits making a disconnection* from the vehicle if residual pressure remains in the hose (similar to ANSI/NGV-1 specification requirements). Consider use of *automatic hose blowdown* after transfer. Residual hydrogen gas should be directed to a local vent stack for safe dispersal into the atmosphere or captured and recycled.
	High Pressure during dispensing	"Booster" fill line pressure limit switch failure.	Possible release of hydrogen from vehicle containers if safety relief devices activate with local formation of flammable mixture.	Consideration should be given to installing a *second pressure limit* switch in this line set to activate at a slightly higher setpoint to further reduce the probability of this event occurring.
	High Pressure during dispensing (>125% of service pressure of onboard containers)	System is capable of delivering gas directly in "booster" mode to 5000 psig and low pressure vehicle containers could be connected inadvertently.	Possible release of hydrogen from vehicle containers if safety relief devices activate with local formation of flammable mixture.	Provide a means to insure that no low pressure containers are ever connected through use of *listed connector components* and *certified container installations.* Provide a means to relieve dispenser pressure by venting gas to a vent stack if >125% of container pressure.

Table D-2. Hazard Review of Gaseous Hydrogen-Based Vehicle Fueling System

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Dual-Hose Sequencing Fuel Dispensers *(continued)*	Low Pressure	Isolation or switching valves are not operational, or some other supply line blockage exists.	No fuel (or only a partial fill) can be transferred from the dispenser to the vehicle.	System needs to be inspected to determine root cause of problem. Not a direct hazard.
	High flow	Leakage from downstream fueling components: hose breakaway device, hose fittings, damaged fueling connector	Creation of flammable gas mixture is imminent in area surrounding the fuel transfer point.	Investigate possible use of *excess flow check valve* in lines leaving the medium pressure receiver banks. Leak detectors should be placed in immediate vicinity of fuel transfer point.
	High flow	Vehicle drives away with fueling hose still connected.	Fueling hose is physically separated from the dispenser. High pressure hydrogen gas escapes uncontrollably to the fueling area creating flammable mixture.	*Hose breakaway device* actuates as intended to provide separation at the desired location. Fluid stream is isolated automatically on both sides of the break. Consider use of *vehicle ignition interlock* when fueling compartment door is open to preclude opportunity for event to occur.
	High flow	Fueling connector is manually disconnected during the fuel transfer operation while pressurized.	High pressure hydrogen gas escapes uncontrollably to the fueling area creating flammable mixture.	Fueling connector design should be such that the forces or torques required to separate the connector while pressurized are not possible to be generated by a human with only his hands. The connector designs should have similar requirements to those listed in the ANSI/NGV-1 specification. Automatic hose blowdown at the completion of the transfer should be considered.
	Vehicle being fueled is designed for compressed natural gas and has residual CNG in its fuel containers	Driver not aware of fuel compatibility issue or inadvertent error	Could transfer significant volume of hydrogen into the natural gas containers. Damage to internal combustion engine or onboard fueling system could occur if mixture gets too high in hydrogen content.	Insure that there is a design incompatibility between fueling connectors for hydrogen use and those for CNG such that they cannot be connected together to permit pressurization and/or product transfers.

Table D-2. Hazard Review of Gaseous Hydrogen-Based Vehicle Fueling System

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Dual-Hose Sequencing Fuel Dispensers (continued)	Air intrusion in fueling system after disconnecting fueling connector	Fueling connector remains open to the atmosphere after disconnect	Gas mixture within fueling hose may be in the flammable range; future transfer of this mixture to the next vehicle could result in combustion incident.	Consider requiring a system that retains a slight positive pressure of residual hydrogen gas within the hose after disconnect and a pressure switch interlock to disable the dispenser if this pressure is not detected.
	Fueling connector leakage	Worn seals; damaged components; extreme ambient conditions of temperature, snow, ice, etc.	Creation of flammable gas mixture is imminent in area surrounding the fuel transfer point.	Require *frequently conducted physical inspections* of connectors for damage; Provide leak detectors in the fuel transfer area (or integral with the hose and connector) to warn operators of hazardous condition and isolate the dispenser. An *emergency shutdown isolation system* should be provided such that it can also be activated manually both near the fueling dispenser as well as at a remote site away from the fueling island.
	Fueling connector leakage	Improperly-made mechanical connection	Creation of flammable gas mixture is imminent in area surrounding the fuel transfer point.	Should require use of a fueling connector similar in design to NGV-1Types 1, 2, or 3 such that no flow can occur if the nozzle and receptacle are not properly engaged.
	Transfer hose leakage	Material aging, handling abuse, etc.	Potential for flammable gas mixture formation depending on rate of leak.	Require frequently conducted physical inspections of hoses; Conduct periodic leak checks while hose is pressurized.
	Failure to ground the vehicle before commencing fuel transfer.	Design insufficiently detailed to define.	Potential for discharge of static electricity acquired on vehicle during road travel to the fueling connector when the connector is being mated. An ignition of a flammable gas mixture could occur if the connector were leaking at that moment.	Require a design of an interlock system such that the dispenser could be rendered inoperable (with warning lights, etc.) and no transfer of fuel could begin unless a positive ground has been established with the vehicle. Further design options for a cost-effective system need to be conceived and evaluated.

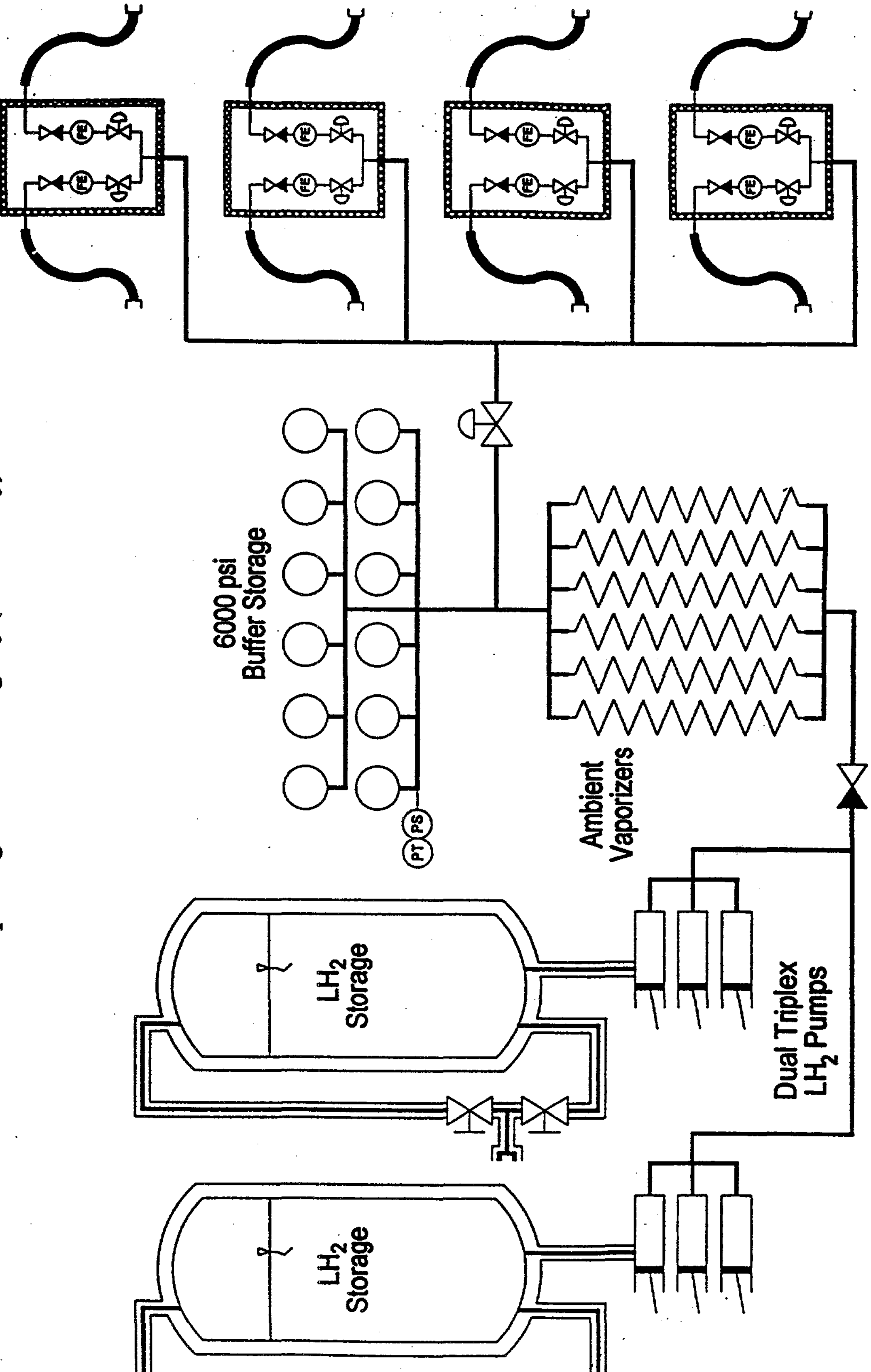

Figure D-3. Liquid Hydrogen-Based Fueling Station
for High Pressure Gas
Dispensing Rate: 2727 kg/day (6000 lb/day)

Table D-3. Hazard Review of Liquid Hydrogen-Based Vehicle Fueling System

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
LH_2 Storage Tank	High pressure in tank	No liquid withdrawn for extended period	Tank safety relief valve opens	Gas vented to vent stack safely and dispersed to air
	High pressure in tank	Tank overfilled by resupply trailer	Tank safety relief valve opens	Liquid vented into vent stack and vaporized from sensible heat of stack, problem must be detected before significant cooldown occurs and cold gas or liquid exits from stack
	High pressure in insulation space	Loss of insulation vacuum	Rapid increase in liquid boiloff, tank safety relief valve opens	Safety valve sized per CGA S-1.3 for loss of vacuum condition, product vents safely
	High pressure in insulation space	Inner container or piping leak	Tank casing pressure relief device opens at 0.5 psig	Casing relief device sized per CGA S-1.3
	Low pressure in tank	Failure of pressure building system	Low liquid flow to pumps, low pressure in suction line	Loss of prime in pump, possible pump ring damage, should use loss-of-prime detection to shut system down
	High pressure in tank piping	Liquid trapped between valves	Blocked line relief valves open to protect piping from rupture	Relief valve set no higher than MAWP of piping
	High tank liquid level	Tank overfilled by resupply trailer	Tank safety relief valve opens	Liquid vented into vent stack and vaporized from sensible heat of stack, problem must be detected before significant cooldown occurs and cold gas or liquid exits from stack
	Low tank liquid level	Delay in refilling tank, high product consumption	Low liquid flow to pumps, low pressure in suction line	Loss of prime in pump, possible pump ring damage, should use loss-of-prime detection to shut system down
	High flow in tank piping	Liquid line break external to tank	Liquid hydrogen release to atmosphere, flammable mixture formed adjacent to tank	*Excess flow check valves* are installed in all liquid lines and will activate under high flow conditions. *Remote isolation valves* are used on all major lines. The remote operating stations should be located at least 50 feet away from the valves and be easily accessible. *Leak detection system* should be required near piping.

Table D-3. Hazard Review of Liquid Hydrogen-Based Vehicle Fueling System

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
LH_2 Storage Tank (continued)	High flow in vent stack	Premature bursting disk failure	Cold gas vented through stack until tank pressure at 1 atm.	Vent stack designed for worst case flow, flammable gas mixture not present at ground level
	High flow in vent stack	Bursting disk failure during tank refill operation	If driver doesn't recognize problem, LH2 can be fed directly into vent stack	Drivers are trained for this occurrence and should take action to terminate transfer using emergency shutdown device.
	Low flow in piping system	Valve failure, line blockage	Low liquid flow to pumps, low pressure in suction line	Loss of prime in pump, possible pump ring damage, should use *loss-of-prime detection* to shut system down
	Reverse flow in piping system	Backflow through pump	Possible tank contamination	Not likely to backflow through check valves and discharge valves on positive displacement pumps
	Composition contamination in tank	Delivery of wrong material during tank refill operation	Possible combustible mixture, possible line blockage from solid contaminants	Special non-interchangeable fill connections and delivery procedures are used to prevent this situation from occurring.
	Power failure	Not specifically defined.	System isolation, all automatic tank valves will close.	No problem expected.
	Failure of nitrogen purge	Not specifically defined.	System isolation, all automatic tank valves will close.	No problem expected.
	Loss of containment	External impact	Hydrogen release	Site selection identifies impact scenarios, vehicle barriers will eliminate catastrophic accidents.
	Loss of containment	Material defect	Hydrogen release	Materials used in the pressure vessel are in accordance with ASME Sec. VIII, Div.1 which requires examination to insure acceptable materials and traceability.
	Loss of containment	Natural disasters	Hydrogen release	Equipment designed for Seismic Zone IV and 100 mph wind loading. Foundations designed for local conditions.
LH_2 High Pressure Pumps	High pressure in discharge line	Discharge line blockage or valve closure	Discharge line safety relief valve opens	High pressure gas is vented to the tank vent stack for safe dispersal to the atmosphere. Temperature switch to sense relief valve discharge to shutdown the pump.

Table D-3. Hazard Review of Liquid Hydrogen-Based Vehicle Fueling System

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
LH_2 High Pressure Pumps (continued)	High flow in discharge line	None identified.	None identified.	Flow rate is automatically limited by positive displacement reciprocating pump design.
	Loss of discharge pressure while pumping	Insufficient NPSH	Loss of prime	Possible pump ring damage. Should use loss-of-prime detection system to shut system down.
	Low flow through pump	Excessive blowby past rings	Inability to maintain gas storage pressure above minimum levels	Need to perform preventative maintenance on regular schedule to maintain pump operations within specification.
	Cold end seal leakage	Worn seals	Hydrogen gas leakage around pump bodies and motors, potential for flammable mixture formation	Nitrogen purge should be used for pump distance piece, seal area, and motor casing. Excessive cold gas leakage is sensed by a temperature switch which will shutdown the pump. Leak detectors should be placed adjacent to pump seals.
	Loss of nitrogen purge to seal area, motor casing	Not specifically defined.	Potential flammable gas mixture formation.	Low pressure switch on purge gas supply line provides interlock to pump motor preventing operation w/o proper purge flow.
High Pressure Vaporizer	Excessive ice formation on external fin surfaces	High flow demand for extended periods	Possible low gas temperatures	Consider adding additional vaporizer capacity.
	Low gas temperature at outlet of vaporizer	Abnormally cold ambient temperature, high humidity	Possible damage to high pressure gas receivers if metal temperature falls below -20°F	*Low temperature pipeline protection system* is required to shut system down upon detection of abnormally cold gas.
	Gas leakage from piping flanges	Seal aging	Possible flammable gas mixture formation.	Minimize use of mechanical connections, utilize all-welded construction, pressure test and leak check all piping before commissioning system, perform periodic leak detection on regularly scheduled basis
	High pressure internal to vaporizer	Liquid trapped between two valves	Vaporizer safety relief valve opens	Excessive pressure is relieved, high pressure gas is vented to atmosphere through vent stack at gas receiver manifold.

Table D-3. Hazard Review of Liquid Hydrogen-Based Vehicle Fueling System

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
High Pressure Gas Storage Receivers	High Pressure	Failure of pump control system or pressure switch to stop pump operation	Pressure continues to build in storage bank until the limit pressure switch is activated.	Entire system is shutdown by limit pressure switch and must be manually reset.
	High Pressure	Failure of limit pressure switch to stop pump	Safety relief valve(s) open on gas storage receiver manifold	Receivers are protected by safety valves set to open at pressures no higher than the MAWP for the receivers. Gas is vented safely to the atmosphere through the vent stack.
	Low Pressure	Loss of containment, leak developed in receiver piping manifold.	Operation of the pumping system may continue to supply additional gas through leak creating flammable gas mixture around receiver area.	Pressure switch should be used to sense abnormally low pressure in receivers and prevent pumps from restarting until system can be inspected.
	Loss of containment	External impact	Hydrogen release	Site selection identifies impact scenarios, vehicle barriers will eliminate catastrophic accidents.
	Loss of containment	Material defect or hydrogen embrittlement	Hydrogen release	Materials used in the pressure vessels are in accordance with ASME Sec. VIII, Div.1 which requires examination to insure acceptable materials and traceability. Metal is generally SA372 Gr. J CL 70 which is acceptable for hydrogen service and does not suffer from embrittlement.
Dual-Hose Fuel Dispensers	High Pressure in fueling hose when dormant	Leaking isolation or switching valves	Fueling connector could be pressurized prematurely creating hazard for operator.	Consider using a fueling connector design that *prohibits making a connection* to the vehicle if initially pressurized (similar to ANSI/NGV-1 specification requirements).

Table D-3. Hazard Review of Liquid Hydrogen-Based Vehicle Fueling System

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Dual-Hose Fuel Dispensers (continued)	High Pressure in fueling hose after completion of fuel transfer	No means for pressure to be released from hose and connector	Attempts to release connector while pressurized may create situation with flying objects and potential for striking the fueling operator causing bodily injury. Release of trapped gas locally could create flammable mixture.	Consider using a fueling connector design that *prohibits making a disconnection* from the vehicle if residual pressure remains in the hose (similar to ANSI/NGV-1 specification requirements). Consider use of *automatic hose blowdown* after transfer. Residual hydrogen gas should be directed to a local vent stack for safe dispersal into the atmosphere or captured and recycled.
	High Pressure during dispensing (>125% of service pressure of onboard containers)	System is capable of storing gas to 6000 psig and low pressure vehicle containers could be connected inadvertently.	Possible release of hydrogen from vehicle containers if safety relief devices activate with local formation of flammable mixture.	Provide a means to insure that no low pressure containers are ever connected through use of *listed connector components* and *certified container installations.* Provide a means to relieve dispenser pressure by venting gas to a vent stack if >125% of container pressure.
	Low Pressure	Isolation or switching valves are not operational, or some other supply line blockage exists.	No fuel (or only a partial fill) can be transferred from the dispenser to the vehicle.	System needs to be inspected to determine root cause of problem. Not a direct hazard.
	High flow	Leakage from downstream fueling components: hose breakaway device, hose fittings, damaged fueling connector	Creation of flammable gas mixture is imminent in area surrounding the fuel transfer point.	Investigate possible use of *excess flow check valve* in lines leaving the high pressure receiver banks. Leak detectors should be placed in immediate vicinity of fuel transfer point.
	High flow	Vehicle drives away with fueling hose still connected.	Fueling hose is physically separated from the dispenser. High pressure hydrogen gas escapes uncontrollably to the fueling area creating flammable mixture.	*Hose breakaway device* actuates as intended to provide separation at the desired location. Fluid stream is isolated automatically on both sides of the break. Consider use of *vehicle ignition interlock* when fueling compartment door is open to preclude opportunity for event to occur.

Table D-3. Hazard Review of Liquid Hydrogen-Based Vehicle Fueling System

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Dual-Hose Fuel Dispensers (continued)	High flow	Fueling connector is manually disconnected during the fuel transfer operation while pressurized.	High pressure hydrogen gas escapes uncontrollably to the fueling area creating flammable mixture.	Fueling connector design should be such that the forces or torques required to separate the connector while pressurized are not possible to be generated by a human with only his hands. The connector designs should have similar requirements to those listed in the ANSI/NGV-1 specification. Automatic hose blowdown at the completion of the transfer should be considered.
	Vehicle being fueled is designed for compressed natural gas and has residual CNG in its fuel containers	Driver not aware of fuel compatibility issue or inadvertent error	Could transfer significant volume of hydrogen into the natural gas containers. Damage to internal combustion engine or onboard fueling system could occur if mixture gets too high in hydrogen content.	Insure that there is a design incompatibility between fueling connectors for hydrogen use and those for CNG such that they cannot be connected together to permit pressurization and/or product transfers.
	Air intrusion in fueling system after disconnecting fueling connector	Fueling connector remains open to the atmosphere after disconnect	Gas mixture within fueling hose may be in the flammable range; future transfer of this mixture to the next vehicle could result in combustion incident.	Consider requiring a system that retains a slight positive pressure of residual hydrogen gas within the hose after disconnect and a pressure switch interlock to disable the dispenser if this pressure is not detected.
	Fueling connector leakage	Worn seals; damaged components; extreme ambient conditions of temperature, snow, ice, etc.	Creation of flammable gas mixture is imminent in area surrounding the fuel transfer point.	Require *frequently conducted physical inspections* of connectors for damage; Provide leak detectors in the fuel transfer area (or integral with the hose and connector) to warn operators of hazardous condition and isolate the dispenser. An *emergency shutdown isolation system* should be provided such that it can also be activated manually both near the fueling dispenser as well as at a remote site away from the fueling island.

Table D-3. Hazard Review of Liquid Hydrogen-Based Vehicle Fueling System

Equipment Item	Parameter or Operating Deviation	Cause	Consequences or Implications	Recommendations or Comments
Dual-Hose Fuel Dispensers (continued)	Fueling connector leakage	Improperly-made mechanical connection	Creation of flammable gas mixture is imminent in area surrounding the fuel transfer point.	Should require use of a fueling connector similar in design to NGV-1Types 1, 2, or 3 such that no flow can occur if the nozzle and receptacle are not properly engaged.
	Transfer hose leakage	Material aging, handling abuse, etc.	Potential for flammable gas mixture formation depending on rate of leak.	Require frequently conducted physical inspections of hoses; Conduct periodic leak checks while hose is pressurized.
	Failure to ground the vehicle before commencing fuel transfer.	Design insufficiently detailed to define.	Potential for discharge of static electricity acquired on vehicle during road travel to the fueling connector when the connector is being mated. An ignition of a flammable gas mixture could occur if the connector were leaking at that moment.	Require a design of an interlock system such that the dispenser could be rendered inoperable (with warning lights, etc.) and no transfer of fuel could begin unless a positive ground has been established with the vehicle. Further design options for a cost-effective system need to be conceived and evaluated.