Investigation of Hazards Associated with Using
Hydrogen as a Military Fuel

Report 4541

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NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

Bethesda, Md. 20084

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INVESTIGATION OF HAZARDS ASSOCIATED WITH USING HYDROGEN AS A MILITARY FUEL

by
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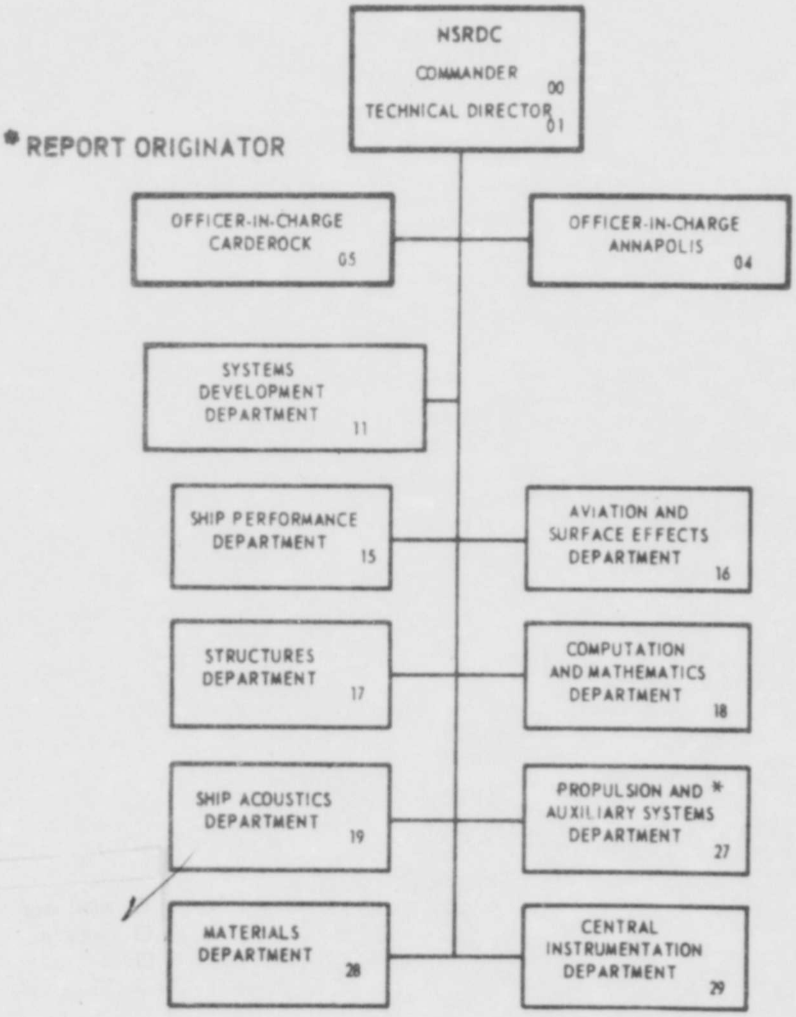

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This hazards investigation was undertaken as part of an overall exploratory Navy program intended to examine the logistic implications, the engineering problems, and the potential hazards associated with hydrogen as a military fuel. Existing literature which is relevent to the hazards

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associated with hydrogen was surveyed and summarized. The hazards of certain alternative fuels including hydrogen, ammonia, hydrazine, ethyl and methyl alcohol, and representative conventional fuels including diesel fuel marine, gasoline, JP-5, and methane, were compared. The comparison covered leakage, volatility, dissipation, ignition, flammability, deflagration, radiation, detonation, and health hazards. On the basis of the findings of this study, further investigation is recommended to determine whether hydrogen is too hazardous to be used as a military fuel. As a result of an extensive literature search, a bibliography containing nearly 200 documents was compiled.

(Author)

ADMINISTRATIVE INFORMATION

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LIST OF ABBREVIATIONS

ACGIH	- American Conference of Government Industrial Hygienists
atm	- atmosphere
Btu/lb	- British thermal units per pound
cal/cm^2	- calories per square centimeter
° C	- degrees Centigrade
cm	- centimeters
cm^2/sec	- square centimeters per second
DFM	- diesel fuel marine
° F	- degrees Fahrenheit
ft^2	- square feet
ft^3/lb	- cubic feet per pound
ft/sec	- feet per second
gal	- gallon
gm	- gram
in/min	- inch per minute
° K	- degrees Kelvin
Kcal	- thousand calories
lb/ft	- pounds per foot
lb/gal	- pounds per gallon
LNG	- liquified natural gas
mg/m^3	- milligram/cubic meter
min	- minute
mJ	- millijoules
ml	- milliliters
mm	- millimeters
mole	- absolute weight of a substance which contains Avogadro's number of molecules
NBP	- normal boiling point
NTP	- normal temperature and pressure
psi	- pounds per square inch
psia	- pounds per square inch absolute
ppm	- parts per million
RT	- room temperature
sec	- second
Sr.	- senior
TLV	- threshold limit value

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LIST OF SYMBOLS

C_p = Heat capacity, cal/mole ° K

H_c = Net heat of combustion, Btu/lb

ΔH_f = Standard heat of formation, K_{cal}/mole

H_{max} = Maximum height of hydrogen fireball, ft

ΔH_r = Heat of reaction, K_{cal}

H_v = Heat of vaporization, Btu/lb

I = Radiant energy intensity, Btu/hr ft^2

I_o = Radiant energy intensity at the source, Btu/hr ft^2

M = Mass of liquid hydrogen spilled, lb

n = Moles of a substance

r = Distance from the source of radiation, ft

T_b = Adiabatic flame temperature, ° K

T_i = Initial temperature of surroundings, ° K

ΔT = Temperature difference, ° K

$V_{f_{max}}$ = Maximum flame volume of hydrogen fireball, ft^3

V_ℓ = Volume of liquid hydrogen spilled, liters

w = Percent water vapor in the atmosphere

W_{max} = Maximum width of hydrogen fireball, ft

INTRODUCTION

Fossil fuels have been the nation's prime energy source for the past century, but we have come to realize that our fossil fuel resources are finite. At some time in the future, coal, petroleum, and natural gas must be replaced by nuclear energy, solar energy, wind and tidal energy, geothermal energy, and ocean thermal energy. Several groups in DOD, NASA, and other government and private agencies are studying hydrogen and its derivative compounds as potential alternative fuels for chemical propulsion systems. Apparently, progress toward a hydrogen economy faces economic rather than technological barriers. Most people will agree that a major shift to hydrogen is beyond the year 2000, when the cost of recovering and producing conventional fuels exceeds the cost of producing hydrogen fuel.

This investigation was undertaken as part of an exploratory Navy program intended to examine the logistic implications, the engineering problems, and the potential hazards associated with hydrogen as a military fuel. Hydrogen-based synthetic fuels such as ammonia, hydrazine, and methyl and ethyl alcohols have been included since these fuels may provide a more viable means for handling, storage, and transporation of hydrogen. Briefly, the purposes of this investigation were to catalog documentation related to hydrogen safety, to summarize the hazards associated with hydrogen, to compare the hazards of certain alternative fuels with representative conventional fuels, and to recommend any further investigation required to determine whether hydrogen is too hazardous to be used as a military fuel.

Much is already known about the inherent hazards of using hydrogen in research and development, industrial, and aerospace applications. Safe practices and precautions for using liquid hydrogen have evolved during the past 20 years through its large scale use as a rocket propellant. However, significant differences in environment and missions exist between space flight and military operations. This investigation is an initial step in the assessment of the hazards associated with using hydrogen fuel in a military environment.

HAZARDS ASSOCIATED WITH HYDROGEN

A usual criticism leveled at the enthusiasts of the hydrogen economy concept involves the hazards associated with hydrogen. During the early 1900's, several disasters involving hydrogen-filled airships cultivated a universal fear of hydrogen, but most of the illusion evolved from the spectacular fire which destroyed the Hindenburg at Lakehurst Naval Air Station, New Jersey. The Hindenburg, built in 1936, was the largest airship ever built. During that year the airship had successfully completed 10 round trips to the United States from Europe. On 6 May 1937, the Hindenburg was to make its first landing of the 1937 schedule at Lakehurst. The airship was designed to operate using helium for lift. Unable to obtain helium from the United States, the Germans had to fill the Hindenburg with hydrogen. Initially, sabotage was suspected as the cause of the fire that, in less than 1 minute, consumed the more than 7 million cubic feet of hydrogen (figures 1 and 2). Immediately before landing, heavy rain and thunderstorms had lasted for more than an hour at Lakehurst. Thus, ignition of the hydrogen vented during mooring operations by electrostatic charge in the atmosphere is the likely cause of the fire. Fatalities included 13 passengers and 22 crew members; however, 65 people on board survived. Since that event the magnitude of the disaster and the hazards associated with hydrogen have been highly dramatized.

Despite the bad reputation acquired during the airship era, hydrogen came into large-scale use as a liquid rocket propellant during the 1960's. The high specific impulse achieveable with hydrogen meant advantages in the performance of propulsion systems for missiles and space vehicles. Relatively small quantities of liquid hydrogen had been used previously in laboratory experiments. Many unique properties of hydrogen - ease of leakage, wide flammability limits when mixed with air, low ignition energy requirements, reactivity with strong oxidizers, and detonation effects under confined conditions - made handling and storage hazards appear great.

Research on the hazards associated with the large-scale use of liquid hydrogen began circa 1958 with the early programs of Arthur D. Little, Incorporated, and the Bureau of Mines. Many investigations into the aspects of hydrogen safety followed, and their results were well documented. From the existing information of these past research programs, a review of the hazards associated with hydrogen follows. The review is organized into several subtopics: leakage, gross spillage, ignition, flammability, deflagration, radiation, detonation, TNT equivalence, contamination by solidified atmospheric gases, quenching distance, physiological hazards, and compatability of materials. The important physical constants of parahydrogen are summarized in table 1. (Gaseous hydrogen at room temperature consists of a mixture of 25% parahydrogen and 75% orthohydrogen, while at the normal boiling point of liquid hydrogen the equilibrium mixture contains 99.8% parahydrogen.)

TABLE 1
PHYSICAL CONSTANTS OF PARAHYDROGEN(1)

Chemical symbol	H_2
Molecular weight	2.016
Specific volume of gas at NTP(2)	192.3 ft^3/lb
Density of gas at NTP	0.0052 lb/ft^3
Density of saturated gas at NBP(3)	0.0836 lb/ft^3
Density of liquid at NBP	4.419 lb/ft^3 0.591 lb/gal
Boiling point at 1 atm	-423.188° F
Freezing point at 1 atm	-434.825° F
Critical temperature	-400.313° F
Critical pressure	187.5 psia
Triple point at 1.021 psia	-434.825° F
Latent heat of vaporization at NBP	191.7 Btu/lb
Sensible heat (gas to 70° F)	1654 Btu/lb
Specific heat, C_p, at 70° F	3.558 Btu/lb ° F
Specific heat, C_v, at 70° F	2.572 Btu/lb ° F
Heat of combustion	
Gross(4)	60,958 Btu/lb
Net(5)	51,571 Btu/lb

(1) Values are taken from reference 1 except heat of combustion which is taken from reference 2.

(2) Normal temperature and pressure is 70° F and 1 atm.

(3) Normal boiling point of the liquid at 1 atm pressure.

(4) Heat evolved from the complete combustion of a fuel under constant pressure at a temperature of 25° C when all water initially present and formed is condensed to a liquid.

(5) Obtained by subtracting the latent heat of vaporization of the water formed and vaporized in the combustion of a fuel from the gross heat of combustion.

LEAKAGE

Certain properties of liquid hydrogen, make it unusually liable to leakage.[3] The small size of the hydrogen molecule permits it to leak through nominally airtight seals and escape from systems that appear leak-free when tested with other fluids. Liquid hydrogen is stored at an extremely low temperature (-423° F).* The large difference between liquid hydrogen and ambient temperatures causes variant contraction of dissimilar confining materials, which may create leaks and allow hydrogen to escape. Equipment most likely to develop leaks are flanges, connections, or joints of transfer lines through which liquid hydrogen flows intermittently, resulting in numerous temperature cycles from ambient down to the normal boiling point of hydrogen. Stresses resulting from the thermal contraction of materials can cause catastrophic failure of confining equipment. Failures of this type are minimized through the use of materials suitable for liquid hydrogen service. Suitable materials include aluminum, copper, Monel, Inconel, titanium, austenitic stainless steels, brass, and bronze, because these metals remain ductile at cryogenic temperatures, and their coefficients of thermal expansion and thermal conductivity are relatively low. Nonmetals reported to be suitable for liquid hydrogen service include Dacron, Teflon, Kel-F, asbestos impregnated with Teflon, Mylar films, and Nylon. Leakage is inversely proportional to viscosity; therefore, the low viscosity of liquid and gaseous hydrogen contributes to the leakage problem. The viscosity of hydrogen at its normal boiling point is lower than that of most cryogenic fluids (table 2); leakage of liquid hydrogen is approximately 12 times that of liquid nitrogen and 14 times that of liquid oxygen. At room temperatures, the viscosity of hydrogen is lowest of the significant industrial gases (table 3); leakage of gaseous hydrogen is approximately twice that of air or nitrogen.

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*Abbreviations used in this text are identified on page i.

[3] Superscripts refer to similarly numbered entries in the Technical References.

TABLE 2 - VISCOSITY OF CRYOGENIC LIQUIDS

Cryogenic Liquid	Viscosity lb/ft-sec	NBP ° F
Fluorine	172×10^{-6}	-307
Oxygen	127×10^{-6}	-297
Nitrogen	111×10^{-6}	-320
Air	89×10^{-6}	-318
Methane	78×10^{-6}	-259
Hydrogen	9.1×10^{-6}	-423
Helium	2.4×10^{-6}	-452

TABLE 3 - VISCOSITY OF INDUSTRIAL GASES

Industrial Gas	Viscosity lb/ft-sec	Temperature ° F
Oxygen	13.9×10^{-6}	77
Helium	13.3×10^{-6}	77.4
Air	12.4×10^{-6}	80
Nitrogen	12.0×10^{-6}	80
Carbon dioxide	10.1×10^{-6}	80
Methane	7.5×10^{-6}	80
Hydrogen	6.0×10^{-6}	77

GROSS SPILLAGE

The effects of gross spillage of liquid hydrogen on land have been investigated. Hydrogen's low heat of vaporization, 194 Btu/lb and the great difference between liquid hydrogen and ambient temperatures cause rapid evaporation of liquid hydrogen spills. The quantity of liquid hydrogen spilled, the nature of the contacting surface, and the rate at which heat is transferred from the surface to the liquid hydrogen affect the rate of evaporation significantly. A theoretical prediction of the liquid-level regression rate has been reported for liquid hydrogen following spillage onto a dry sandy soil, a moist sandy soil, and an average soil.[4] The curves, predicting the decrease in liquid hydrogen level versus elapsed time (figure 3), approach constant slopes or evaporation rates of 0.7, 1.2, and 1.7 in/min for the three soils, respectively. Tests performed by Arthur D. Little, Incorporated, produced similar experimental results, summarized in plots of liquid depth versus evaporation time (figure 4) and evaporation rate versus time (figure 5). These and similar experiments have revealed that the evaporation rate in a spill area is affected significantly by the specific surface area. The use of a pebble bed or crushed rock in a spill area increases the evaporation rate, while use of smooth diked areas decreases it. Liquid hydrogen spills of 50 gallons under similar test conditions required evaporation times of approximately 1 minute on a crushed rock surface and 8 to 14 minutes on a sand or gravel surface. On the basis of these tests, observations as to the mechanism governing the evaporation of liquid hydrogen spills include:

- The initial evaporation rate is high.

- The evaporation rate decreases rapidly in the first few minutes to a lower, constant, evaporation rate.

- Initially, all heat for evaporation is supplied by the ground.

- Condensation of air into the liquid hydrogen is a major heat source contributing to later stages of evaporation.

The effects of gross spillage of liquid hydrogen on water are <u>not</u> precisely known, although several water-boiling liquid systems have been studied to determine the explosive boiling mechanism associated with spillage of liquefied natural gas on water.[6-9] Among the boiling liquids studied were methane, ethane, propane, propylene, isobutane, LNG, Freon 22, and nitrogen. The chemical and physical properties of these liquefied gases are very different from those of liquid hydrogen. To accurately assess the hazards of liquid hydrogen spillage on water, further investigation will be required.

Rapid evaporation of liquid hydrogen spills and subsequent mixing with the surrounding air forms hazardous, flammable vapors. The formation, movement, and dissipation of unconfined vapors are influenced by density, diffusivity, and prevailing weather conditions. The low molecular weight of hydrogen gas produces a high diffussion coefficient; hydrogen diffuses approximately 3.8 times faster than air.[10] The density of hydrogen vapor at the normal boiling point is approximately equal to the density of air at normal temperature and pressure.

At normal temperatures, hydrogen has the lowest density of all the gases; its density is 1/14 that of ambient air. Therefore, the diffusivity and buoyancy of hydrogen may be advantageous in some accident situations, since both facilitate the rapid dissipation of hazardous hydrogen-air mixtures. For example, a 500-gallon spill of liquid hydrogen in an unconfined area has been observed to diffuse to a nonflammable mixture in about 1 minute.[10]

Utilization of reliable containment and transfer equipment, ventilation systems, and leak detection devices in hydrogen areas is the first step in preventing serious accidents.

IGNITION

The autoignition temperature of hydrogen (1075° F) is higher than that of most hydrocarbons (400° to 700° F), which misleads some into thinking that the combustion of hydrogen is more difficult. However, the low initiation energy requirements and its wide flammability limits make ignition of hydrogen-air mixtures more likely. The minimum spark ignition energy required for various concentrations of hydrogen in air is lowest near the stoichiometric composition and increases as the flammability limits are approached (figure 6).[11] The minimum spark ignition energy at stoichiometric compositions is an order of magnitude lower for hydrogen than for the hydrocarbons. Flammable mixtures of hydrogen and air can be ignited by several ignition sources including friction or impact sparks, electrical sparks, static electricity, explosive charges, hot solid objects, open flames, hot gases, or smoking.[12] An electrostatic discharge from a person could ignite a hydrogen-air mixture even though the amount of static electricity could not readily be felt on discharge.[11] Using an electrostatic voltmeter, it was determined that a charge several times the minimum spark ignition energy could be developed by the action of removing a coat made of synthetic material. Since hydrogen is a non-conductive material, electrostatic charges accumulate when liquid or gaseous hydrogen flows through conducting lines.[12] Although no ignition source may be apparent, hydrogen leaks and unflared hydrogen vent stacks often ignite. The ignition source is usually assumed to be a small discharge of static electricity. Turbulence in liquid hydrogen transfer and storage equipment should be avoided as much as possible to minimize the accumulation of static charge. Hazardous static charges may also be induced during electrical storms.

Elimination of all potential ignition sources in hydrogen storage or operations areas is the second step in preventing serious accidents.

FLAMMABILITY

Hydrogen's wide flammability limits when mixed with air are exceeded only by acetylene and hydrazine. The lower and upper limits are usually recognized as 4% and 75% hydrogen by volume at room temperature and pressure.[13] The flammability limits are affected by changes in pressure and temperature.[14] In general, the limits are narrowed with increasing pressure from 1 to 5 atmospheres, but higher pressures cause the limits to steadily widen. As pressure is lowered below atmospheric, the limits narrow. Increasing the temperature of the gas widens the flammability limits (figure 7). Addition of diluent gases to hydrogen-air mixtures narrows the flammable range by decreasing the upper limit, but has little effect on the lower limit until the dilution approaches the point of total suppression of flammability (figure 8). Nitrogen and carbon dioxide are less effective than certain halogenated hydrocarbons, such as Halon 1301, in reducing the flammability of hydrogen in air. A combination of inerting and chemical inhibition accounts for the increased effectiveness of the halogenated hydrocarbons. The compounds interrupt the combustion chain reaction by inhibiting the reaction of hydrogen atoms with hydroxyl ions or oxygen.

DEFLAGRATION

Once initiated, flames propagate rapidly through flammable hydrogen-air mixtures. Burning velocity, defined as the flame velocity relative to the unburned gas velocity, ranges from a few inches to 11 ft/sec depending on the composition of the mixture.[17] The maximum velocity occurs at about 40% hydrogen by volume in air (figure 9). Flame speeds, defined as the flame velocity relative to a stationary reference, are of the order of several tens of feet per second. At one atmosphere pressure, complete combustion of one volume of liquid hydrogen produces about 20,000 volumes of uncooled gaseous products. In constant volume deflagration, pressure increases to approximately seven times the initial pressure. The flame temperature of premixed, stoichiometric hydrogen-air mixtures is approximately 3700° F, while diffusion flames such as those occurring at a spill or leak, burn at about 3000° F.

Early investigation into the hazards associated with liquid hydrogen included experiments designed to determine the effects of unconfined combustion of spills. The tests simulated accidental spillage and ignition, and the resulting fires were observed. The dimensions of the fireballs were found to be dependent on the volume of hydrogen spilled, the rate at which it is spilled, the nature of the surface on which spillage occurs, the location of the ignition source, and the time delay before ignition. Spill tests conducted by the Bureau of Mines[4] ranged from a few liters to 90-liter quantities (approximately 24 gallons), and the ignition delay was varied from 1 to 16 seconds. General equations for estimating the maximum dimensions and maximum volume of the resulting fireball were derived. For the maximum height and width:

$$H_{max} = W_{max} = 7\sqrt{V_{\ell}} = 17.8\sqrt{M} \text{ ft},$$

And for maximum flame volume,

$$V_{f_{max}} = 750\cdot(V_{\ell}) \text{ ft}^3,$$

where V_{ℓ} is the volume in liters and M is the mass in pounds of the liquid hydrogen spilled. The maximum flame volume is approximately equal to the lower limit mixture volume at 81° F.

Typical spills anticipated during Navy use of liquid hydrogen could conceivably involve quantities much larger than those used in the spill tests conducted by the Bureau of Mines. It is questionable whether the above equations can be extrapolated to characterize fires resulting from larger spills of liquid hydrogen. This belief is reinforced by the differing results reported by Arthur D. Little, Incorporated, when fires from liquid hydrogen spills as larage as 5000 gallons were studied.

Spill tests conducted by Arthur D. Little, Incorporated,[5] involved 1 1/4-, 32-, 500-, and 5000-gallon quantities of liquid hydrogen. Fires from 1 1/4-gallon quantities were observed during 48 spill tests. Spark height was varied from 4 inches to 10 feet above ground level, and time delay between spillage and ignition was varied from 0 to 10 seconds. The results revealed that an optimum spark height and time delay produced fireballs of maximum size. Optimum conditions allowed the greatest quantity of hydrogen to take part in the reaction. Maximum fireball dimensions were 15 feet in diameter and 25 feet high, which occurred with spark heights of 6 to 8 feet and delay times of 3 to 5 seconds. Further tests were made with 32-gallon quantities. The maximum size of the combustible cloud was 30 to 35 feet in diameter and 15 to 21 feet high; the duration of the fire ranged from 0.3 to 0.7 seconds. The fireball produced in a 500-gallon test was estimated as 100 by 50 feet, and the maximum flame height in the 500-gallon tests was 150 feet. In general, the dimensions of the flames were roughly the size of the liquid hydrogen pool with a height-to-diameter ratio of less than 5 to 1. The two 5000-gallon spills demonstrated the short duration of liquid hydrogen fires, since flames consumed the entire 5000 gallons in 2 1/2 minutes during the first test and 3 minutes during the second test. The fireball dimension data reported by A. D. Little, Incorporated, does not correlate with the Bureau of Mines equation. Probable reasons for the disagreement are variations in test conditions and the larger quantities used by A. D. Little, Incorporated.

Studies of liquid fires in circular or square pools[21] indicate that the regression rate, or rate of fuel consumption measured by decrease in pool depth in in/min, is directly proportional to the ratio of heats of combustion and vaporization in Btu/lb.

$$\text{Regression rate} = 0.003 \frac{H_c}{H_v} \text{ in/min.}$$

The equation is valid for pools having a surface area greater than 10 square feet. For this size pool a turbulent flame regime occurs and consumption rate is insensitive to pool diameter. Substituting the values for heat of combustion and heat of vaporization of hydrogen in the above equation gives a regression rate of 0.8 in/min.

RADIATION

Invisible flames and a low level of thermal radiation to surroundings characterizes the electromagnetic radiation from hydrogen fires. The spectral distribution, or the amount of radiation emitted in the various wavelength regions of the electromagnetic spectrum, accounts for the invisibility of hydrogen flames, while emissivity influences the total heat radiated.

The optical radiation from pure hydrogen-air flames is emitted principally by OH^- and H_2O molecules formed in the combustion reactions:

$$H_2 \longrightarrow 2H^+$$

$$H^+ + O_2 \longrightarrow OH^- + O^-$$

$$H_2 + O^- \longrightarrow OH^- + H^+$$

$$OH^- + H_2 \longrightarrow H_2O + H^+.$$

These molecules emit radiation in the ultraviolet and infrared regions, but little visible light.[3] Any appreciable visible light from hydrogen fires must come from impurities which color the flame. Therefore, locating a hydrogen fire is difficult; even if the location is known, the envelope of the flame is not easily distinquishable.

The hydroxyl radical, OH^-, is a short-lived intermediate product in the combustion process shown above. OH^- radiation appears in the near ultraviolet region in the form of bands---collections of spectral lines. There are seven principle OH^- bands with peaks at wavelengths of 0.3428, 0.3124, 0.3064, 0.2875, 0.2811, 0.2677, and 0.2608 microns (1 micron = 10^{-6} meters). The most intense bands are located at 0.3064 and 0.2811 microns. In hydrogen flames, this radiation appears to arise mainly from thermal excitation, and is much weaker than OH^- radiation from hydrocarbon flames. This radiation comes principally from the reaction zone and disappears almost immediately when the flame is extinquished, although hot gases still remain. Measurements of ultraviolet radiant intensity from hydrogen-air diffusion flames over the spectral range from 0.22 to 0.40 microns have been reported. The ultraviolet emission also has been studied as a function of ambient pressure.[22]

Ultraviolet radiant intensity increases, over three times its value at atmospheric pressure, as pressure is lowered to 60-mm Hg. The radiant intensity then drops rapidly between 60- and 15-mm Hg.

Water, H_2O, is the final combustion product of hydrogen and air. Almost all of its radiation is emitted in the infrared region with some very faint bands in the deep red part of the visible region.[3] The H_2O radiation bands are located at 0.65, 0.72, 0.8, 0.9, 1.1, 1.4, 1.9, 2.7, and 6.3 microns. The bands are wide with peaks not as well defined as the OH^- bands, so the wavelengths above are only approximate. Intensity of the bands increases up to the 2.7-micron band which is by far the strongest band in the water spectrum. Cooler water vapor in the atmosphere absorbs part of the radiation in these bands. The infrared radiant intensity in the 2.2- to 2.7-micron range is fairly constant from atmospheric pressure down to about 100-mm Hg, then decreases steadily as the pressure is lowered further.[22]

Thus the invisible nature of hydrogen fires is understood by examining its optical radiation characteristics. Information of the spectral distribution has been useful for fire detection, since it shows the distribution of radiated energy and can serve as a guide to the necessary spectral response of the sensor or sensor-filter combination.

The apparent, or average, emissivity of the flame is a more significant factor, when considering thermal radiation damage from fires, than flame temperature.[11] Flame emissivity is the ratio of the energy radiated per unit area of the flame envelope to the energy per unit area radiated by a blackbody surface at the same temperature. The emissivity of hydrogen flames ranges from 0.01 to 0.10; the variation in emissivity values reported probably results from differences in time delay before ignition, the assumed flame temperature, quantity of liquid spilled, and to the absorption of radiation by atmospheric water vapor. The hydrocarbon fuels have flame emissivities approaching 1.0. Based on relative emissivities, the radiation from a hydrogen flame is 1% to 10% of the radiation from a hydrocarbon flame of equal size. It is important to note the effect of differences in heats of combustion, burning rates, and flame sizes. The radiation from a pool of burning liquid, per unit area of pool surface, is approximately the same for liquid hydrogen as for liquefied natural gas. The rapid burning rate of hydrogen, however, reduces the total energy radiated for equal volumes of liquid.

Depending on the basis of comparison, the radiation hazard of hydrogen fires could be less or more severe than hydrocarbon fires.[17] For equal volumes of liquid, hydrogen emits about 1/5 the radiation of burning gasoline. For equal pool diameters, hydrogen emits about 1/2 the radiation of burning gasoline. For equal weight of liquid, hydrogen emits about twice the radiation of burning gasoline. Radiation hazard is directly proportional to exposure time, burning rate of the liquid, flame emissivity, size of burning surface, heat of combustion, and percent heat of combustion immediately appearing as radiant heat that can reach the receiver and be absorbed by it. Radiation hazard is inversely proportional to the square of the distance between emitter and receiver, and the absorptivity of the media within the path traversed by the radiation beam.

As noted above, a considerable amount of the radiation emitted from a hydrogen flame is absorbed by water vapor in the surrounding air. The intensity of the collimated radiation is given by the equation:

$$I = I_o e^{-0.015wr},$$

where w is the percent water vapor, and r is the distance from the radiation source in feet.[17] The radiation flux decreases rapidly with distance if the air contains as much as 2% water vapor (figure 10); 2% is less than the saturation value at temperatures above 70° F at sea level.[4] Air at 77° F and 65% relative humidity absorbs about 1/3 of the total radiation within a distance of 12 feet from the source.

Radiation from hydrogen and from hydrocarbon fires differs because hydrocarbon flames approximate gray body emitters while hydrogen flames, by virtue of their discrete band emissions, do not approximate gray body emitters. Tests performed by A. D. Little, Incorporated,[5] compared the thermal radiation effects of propane, JP-4, gasoline, and liquid hydrogen fires. Equal volumes of these fuels, 32 gallons, were spilled into a 10-square-foot diked area and ignited. The propane flame was brilliant orange, with an emissivity of approximately 1, and burned for a period of 4 minutes. Gasoline flames produced a high level of thermal radiation and dense clouds of black smoke. The time required to consume the gasoline was approximately 5 minutes. JP-4 burned like the gasoline, but it required 7 minutes to burn the 32 gallons. The hot radiant JP-4 flame equalled or exceeded the radiation from the propane and gasoline flames. The typical liquid hydrogen fire produced a low level of thermal radiation and burned for approximately 30 seconds. Hydrogen fires from the 500- and 5000-gallon tests exhibited the same radiation characteristics as in the small-scale tests. The JP-4 and gasoline flames showed a thermal flux density 12 times that of the liquid hydrogen. Radiation measurements, from propane and from hydrogen flames, versus time were compared (figure 11). The maximum radiation flux from hydrogen flames was measured at 12.7 Btu/ft^2-sec, which corresponds to an emissivity of 0.085 based on the adiabatic flame temperature of 3720° F. Based on the results of these tests, it was concluded that the radiation effects from hydrogen fires are much less than those of conventional fuels and for the same volume of spillage would be of much shorter duration.

DETONATION

Flames can propagate through a flammable hydrogen atmosphere as a deflagration or detonation.[23] Deflagration is a self-sustained reaction in which the energy is transmitted from the burning to the unburnt layers of the fuel by means of transport properties. Deflagration velocities are subsonic. In detonation, the energy liberated in the chemical reaction is transmitted to the unburnt layers of fuel by means of shock waves. Detonation velocities are supersonic. Under certain conditions, a detonation may build up from an ordinary deflagration that has been ignited in a confined or partially confined mixture. The flame propagation mechanism is affected by composition of the gas mixture, geometry of surroundings, degree of confinement, ignition source, and ignition energy.

Detonation limits of hydrogen-air mixtures range from 18% to 59% hydrogen by volume. Therefore, not all flammable mixtures will detonate. Flame speeds in a detonation are of the order of several thousand feet per second, compared to several tens of feet per second in a deflagration.[17] In constant volume deflagration, the pressure rise ratio is approximately 7, while in a detonation the pressure increases to as much as 20 times the initial pressure. When the pressure wave strikes an obstacle, the reflected pressure is multiplied 2 to 3 times the incident pressure (40 to 60 times the initial pressure). Even larger pressure ratios occur locally in the region where a deflagration transforms to a detonation.[12] Detonation is not simply deflagration proceeding under pressure, but it has its own distinct mechanism of propagation. Hydrogen-air detonations are likely with near stoichiometric mixtures, high energy ignition sources, confining surroundings, and long flame paths.

Studies have revealed that unconfined hydrogen-air mixtures do not detonate unless the ignition source delivers considerable initiation energy in the form of a shock wave. In the liquid hydrogen spill tests and pipeline rupture tests performed by A. D. Little, Incorporated,[5] no detonation or tendency to detonate was observed when the unconfined vapor clouds were ignited by spark or flame sources. To provide conclusive evidence that liquid hydrogen vapor mixed with air would not detonate, spill tests with explosive initiators were carried out. Even when 2- or 4-gram pentolite charges were used as the initiator, no detonation wave or measureable pressures were observed. In another series of tests, 5- and 8-foot-diameter latex balloons were filled with stoichiometric mixtures of hydrogen and air, and ignited at the center with explosive and flame sources, hot wires, or sparks. With the 5-foot-diameter balloons filled with 32% hydrogen by volume, a minimum initiation energy to produce full explosive yield was supplied by a 2-gram charge of pentolite. Ignition by a blasting cap, which is approximately 1/2 gram of explosive, reduced the yield by 95%. Ignition by flame sources, sparks, and hot wires produced only combustion of the gases with no measureable pressures. Tests with the 8-foot-diameter balloons produced similar results. It was concluded that the probability of detonating unconfined hydrogen-air mixtures resulting from the accidental release of liquid hydrogen is extremely low, since explosive initiators and ideal mixtures are required.

Ignition of confined or partially confined hydrogen-air mixtures may cause a detonation. Confinement increases the pressure developed by combustion and provides a mechanism for the transition from deflagration to detonation. The Bureau of Mines conducted a series of experiments in which the combustible vapors from liquid hydrogen spills in a 21- x 13.3- x 13.5-foot blockhouse were ignited. Relatively weak (an electric match) and strong (M-36 military detonator) ignition sources were used and both deflagration and detonation occurred with both ignition sources. Spills of 10 to 30 liters of liquid hydrogen produced deflagration, while spills of 30 to 40 liters produced detonation. The worst detonation resulted when a quantity of 40 liters was ignited by an electric match 30 seconds after spillage. The blast pressures pushed the enclosures's heavy blocks apart, shattered the one masonite wall designed to relieve the internal pressure, and damaged equipment in the enclosure. Noise from the blast was reportedly head 15 miles away.

TNT EQUIVALENCE

The common practice of comparing explosive effects, on the basis of blast waves generated by TNT, led to the expression of blast yields of propellant explosions in equivalent "pounds of TNT." Several methods for estimating the TNT equivalent of hydrogen have been reported, but most apply to situations in which liquid hydrogen and liquid oxygen are simultaneously involved. One method estimates the explosive yield of ideal hydrogen-air mixtures based on theoretical heats of explosion. Heat of explosion is "the heat evolved from an explosive mixture at ambient temperature and atmospheric pressure going to the products of the explosion at room temperature and atmospheric pressure, but with the composition which is in equilibrium at the temperature and pressure of the explosion."[5] It is intended to represent the amount of energy developed in a perfect detonation which is available to heat the detonation products. The theoretical heat of explosion serves as the extreme upper limit of energy per unit mass which could contribute to the formation of shock waves. In estimating the explosive yield, it was assumed that hydrogen-air mixtures would have yields equivalent to those of conventional explosives with the same heat of explosion. Since the heats of explosion for hydrogen-air mixtures were somewhat lower than those for conventional explosives, it was necessary to extrapolate the explosive yield curve. The calculated heats of explosion for hydrogen-air mixtures (figure 12), and the TNT equivalent of conventional explosives having various heats of explosion (figure 13) was used to estimate the maximum explosive yield of hydrogen-air mixtures. Results of these estimates indicated that an ideal 32% hydrogen by volume in air mixture produces the maximum yield equivalent to 12 pounds of TNT for each gallon of liquid hydrogen vaporized. An increase in the percentage of either hydrogen or air in the mixture would cause a rapid decrease in the explosive potential (figure 14).

Many people contend that liquid propellant explosions differ from TNT explosions in a number of ways, so that the concept of "TNT equivalence" quoted in pounds of TNT is far from exact.[26] The specific energies of liquid propellants in stoichiometric mixtures are much greater than for TNT. Although the potential yield is very high, the actual yield is much lower because fuel and oxidizer are never ideally mixed in proper proportions before ignition. Confinement of propellant and oxidizer, and the subsequent effect on explosive yield, are very different for liquid propellants and TNT. Degree of confinement can seriously affect explosive yield of liquid propellants, but it has only a secondary effect on detonation of TNT or any other solid explosive. The geometry of the liquid propellant mixture at time of ignition can be quite different from that of the spherical or hemispherical geometry of TNT charges usually used for generating controlled blast waves. The sources of compiled data for blast waves from TNT rely on measurements of blasts from spheres or hemispheres of explosive, whereas liquid propellants may be in a large shallow pool or a large volume of gases at the time of ignition and detonation. These differences are evident in the results of many blast experiments conducted in Project Pyro.[27]

Experiments have proven that near the source of the explosion, blast waves from liquid propellant explosions differ from the classical TNT blast waves.[28] Typical differences in peak pressure and impulse of these explosions versus distance is illustrated in figure 15. The triangles represent the comparative change in impulse with distance from TNT and propellant explosions. The curves represent the equivalent TNT yield based on the blast wave characteristics. Near the source of the explosion, impulse is generally larger, and peak pressure is generally smaller than an "equivalent terminal yield." As distance increases, the curves converge to a point where the characteristics of propellant and TNT explosions are the same. The term "equivalent terminal yield" applies beyond this point.

CONTAMINATION BY SOLIDIFIED AIR

As noted earlier, condensation of air into liquid hydrogen is a major heat source contributing to later stages of evaporation of liquid hydrogen spills. Therefore liquid hydrogen is subject to contamination with air condensed and solidified from the atmosphere, or by accumulation of traces introduced in manufacturing. Such a mixture is ustable and may detonate with effects similar to high explosives. Since oxygen has a higher boiling point than nitrogen, oxygen-enriched solid air is likely to form through preferential condensation of oxygen from the atmosphere. Tests made to determine the explosive potential of solid air in liquid hydrogen showed that these mixtures would not detonate unless the percent of oxygen in the air was increased to 40% or greater.[5]

QUENCHING DISTANCE

When the dimensions of a passage or enclosure containing a flammable gas become small, the heat transfer and/or active particle loss can become great enough to prevent propagation of a flame.[3] Quenching distance is the distance between surfaces that will just permit a flame to pass without being cooled to extinction.[11] This distance depends on the gas composition, temperature, pressure, and the geometry of the passage. The nature of the passage's surface apparently has no affect on quenching distance. Most laboratory measurements are for flames progagating between parallel plates. Increasing temperature or pressure results in a decrease in quenching distance. Quenching distance between parallel plates have been reported for hydrogen-air mixtures at atmospheric pressure (figure 16). Due to the high velocity of flame propagation, quenching distances for hydrogen are quite small compared to hydrocarbons. At atmospheric pressure, the minimum quenching distance for hydrogen in air is 0.06 centimeter, while for propane in air it is 0.2 centimeter. Quenching distance measurements are applicable to design of flame arrestors or flame traps to stop a flame from passing from one place to another. In practice, workable flame arrestors must have openings even smaller than the minimum quenching distance, because there may be a large pressure gradient driving the flame and hot gas toward the arrester.

PHYSIOLOGICAL HAZARDS

The physiological hazards of hydrogen, including toxicity, effects of short-term exposure, thermal radiation, and blast pressures, are considered with respect to personnel safety.

Hydrogen gas is a nontoxic gas, but it can act as a simple asphyxiant by excluding oxygen from the lungs. Nontoxic gases such as nitrogen, argon, and methane act similarly. The effect of these asphyxiant gases is proportional to the extent to which they diminish the amount of oxygen in the air that is breathed.[29] The oxygen may be reduced to 2/3 of its normal percentage in air before appreciable symptoms develop. This requires the concentration of asphyxiant gas to be at least 33% by volume. When a composition of 50% asphyxiant is reached, marked symptoms are evident. A concentration of 75% is fatal in a matter of minutes. The first symptoms produced by simple asphyxiant gases are rapid respirations and air hunger; mental alertness is diminished and muscular coordination is impaired.

Later, judgement becomes faulty, and all sensations are depressed. Emotional instability often results and fatigue occurs rapidly. As the asphyxia progresses, there may be nausea and vomiting, prostration and loss of consciousness, and finally convulsion, deep coma, and death. Asphyxiation can result from the rapid vaporization of liquid hydrogen spills in enclosed and inhabited areas. The concentration of oxygen in a blockhouse 21 x 13.3 x 13.5-feet was reduced to a dangerous level in less than 5 seconds by the vaporization of 65 liters (17.2 gallons) of liquid hydrogen spilled on the blockhouse floor.[24] Hydrogen concentrations in the blockhouse varied from 50% to 80% by volume.

Tissue damage in the form of frostbite or "cold burn" results when skin comes into contact with cryogenic fluids, surfaces cooled by such fluids, or their cold vapors.[30] The temperature of the skin may be decreased to 32° F without causing permanent damage, but below 32° F the local circulation of blood is arrested, and tissue damage may result. Apparently the damage occurs when the tissue is thawed, as abnormal accumulation of blood usually follows. A blood clot may form and body fluids may accumulate, and thus decrease the local circulation of blood. If the localized deficiency of fresh blood is extreme, gangrene may result. The severity of cryogenic frostbite depends on the period of exposure and the heat flux to the low temperature vapor, fluid, or solid. If skin is splashed with a cryogen, cooling does not take place immediately because the blood supply to the tissue acts as a heat source, and a gas film between the cryogen and the warm tissue forms.[31] Touching cold metal surfaces can result in damage to tissue more rapidly. Tissue damage may be virtually unknown with such cryogens as helium and hydrogen. It is more frequently seen among the cryogenic fluids with higher heat capacity, such as oxygen or nitrogen. Rapid thawing of frozen tissue in a 105° to 115° F water bath is the recommended treatment and, in most cases, an anticoagulant is administered by a physician.[32]

Although the thermal radiation from hydrogen fires is less than that from hydrocarbons fires, unprotected personnel may suffer serious radiation burns. Such burns are basically restricted to the eyes and exposed skin areas. Based on radiation and flame measurements during hydrogen fires, and several medical studies of thermal injury, A. D. Little, Incorporated, estimated the distance from various fires in which second-degree burns would be suffered by unprotected personnel (figure 17) and recommended safe distances from hydrogen fires[5] (figure 18). The authors noted that if similar assumptions had been used on equivalent-sized hydrocarbon fires, safe distances would have been four times greater than those calculated for hydrogen fires. The Bureau of Mines used as a basis for its recommended quantity-distance criteria the distance at which a radiant flux of approximately 2 cal/cm^2 is received through an atmosphere containing 1% water vapor (table 4).[4] This is roughly the radiant flux required to produce flesh burns and ignite combustible materials in short exposure times.

TABLE 4 - BUREAU OF MINES
PROPOSED QUANTITY-DISTANCE CRITERIA

Distance to Inhabited Buildings			Distance Between Storage Tanks		
Pounds		Distance ft	Pounds		Distance ft
Over	Not Over		Over	Not Over	
0	200	100	0	2,000	50
200	1,000	150	2,000	10,000	100
1,000	5,000	200	10,000	20,000	150
5,000	20,000	250	20,000	40,000	200
20,000	40,000	300	40,000	60,000	250
40,000	100,000	350	60,000	100,000	300

Blast pressures resulting from hydrogen-air detonations present a hazard to personnel. The degree of injury sustained by an individual depends on the maximum overpressure experienced during the detonation. Threshold criteria for human casualties from blast pressures are summarized in table 5. Injury may be sustained from missiles generated during the explosion or from personnel thrown against other objects.

TABLE 5
PHYSIOLOGICAL EFFECTS OF BLAST PRESSURES[39]

Maximum Overpressure, psi	Effect on Personnel
1	Knock personnel down
5	Eardrum damage
15	Lung damage
35	Threshold for fatalities
50	50% fatalities
65	99% fatalities

COMPATABILITY OF MATERIALS

Compatibility of materials with cryogenic and gaseous hydrogen environments determines which materials should be used in hydrogen service. Suitable materials of construction for liquid hydrogen systems include aluminum, copper, Monel, Inconel, titanium, austenitic stainless steels (types 304, 304L, 308, 316, and 321), brass, and bronze. These metals remain ductile at cryogenic temperatures, and their coefficients of thermal conductivity are relatively low. Nonmetals reported to be suitable for liquid hydrogen service include Dacron, Teflon, Kel-F, asbestos impregnated with Teflon, Mylar films, and Nylon. Lubricants are generally not practical in the presence of liquid hydrogen, as they solidify and become brittle at the liquid's temperature. Actual selection of materials will depend on the specific application and the weight, strength, performance, and cost constraints. High-strength materials such as HY steels, nickel steels, and titanium minimize the weight penalty associated with high-pressure storage of gaseous hydrogen. Many of these materials are susceptible to the damaging effects of hydrogen embrittlement. Further investigation is needed to determine the long-term, cyclic-pressure effects of gaseous hydrogen on these materials.

SUMMARY

To conclude this section, the important points of discussion are summarized in the following list.

- Some unique properties of liquid hydrogen make it unusually liable to leakage.

- Liquid hydrogen is extremely volatile; its low heat of vaporization and the large difference between liquid hydrogen and ambient temperatures cause rapid evaporation of liquid hydrogen spills.

- Rapid evaporation of liquid hydrogen spills and subsequent mixing with the surrounding air forms hazards, flammable vapors.

- The diffusivity and buoyancy of hydrogen may be advantegeous in some accident situations, since each facilitates the rapid dissipation of hazardous hydrogen-air mixtures.

- Low initiation energy requirements and wide flammability limits make ignition of hydrogen-air mixtures likely.

- Hydrogen's wide flammability limits are usually recognized as 4% and 75% hydrogen by volume at room temperature and pressure.

- Addition of diluent gases, such as nitrogen, carbon dioxide, and certain halogenated hydrocarbons, to hydrogen-air mixtures, narrows the flammable range by decreasing the upper limit, but has little effect on the lower limit until dilution approaches the point of total suppression of flammability.

- Experimental studies of liquid hydrogen fires have yielded methods for estimating the maximum fireball size and duration, and the rate of fuel consumption measured by decrease in pool depth.

- Depending on the basis of comparison, the radiation hazard from hydrogen fires could be less or more severe than hydrocarbon fires. For equal volumes of liquid, hydrogen emits about one-fifth the radiation of burning gasoline. For equal pool diameters, hydrogen emits about one-half the radiation of burning gasoline. For equal weight of liquid, hydrogen emits about two times the radiation of burning gasoline.

- Atmospheric water vapor absorbs a significant amount of the radiation emitted from a hydrogen flame.

- Experimental studies have shown that unconfined hydrogen-air mixtures do not detonate unless the ignition source delivers considerable initiation energy in the form of a shock wave.

- Ignition of confined or partially confined hydrogen-air mixtures may cause a detonation.

- Estimated values for the TNT equivalent of various hydrogen-air mixtures are given in the literature. However, liquid propellant explosions differ from TNT explosions in several ways, so that the concept of TNT equivalence is not accurate.

- Liquid hydrogen, when contaminated by air condensed and solidified from the atmosphere, is unstable and may detonate with effects similar to high explosives.

- Due to high flame velocities, quenching distances for hydrogen are quite small compared to hydrocarbons.

- Hydrogen is a nontoxic gas, but it can act as a simple asphyxiant by diminishing the amount of oxygen in the air that is breathed.

- Tissue damage in the form of frostbite or "cold burn" may result from skin contacting liquid hydrogen, surfaces cooled by liquid hydrogen, or cold hydrogen vapors.

- Although the thermal radiation from hydrogen fires is less than that from hydrocarbon fires, unprotected personnel may suffer serious radiation burns.

- Personnel may sustain injury from blast pressures experienced during a hydrogen-air detonation, from missiles generated during the explosion, or from being thrown against other objects.

- Materials compatible with cryogenic and gaseous hydrogen environments must be used to prevent catastrophic failures of equipment.

COMPARISON OF ALTERNATIVE AND CONVENTIONAL FUEL HAZARDS

In this section, the chemical and physical properties, combustion characteristics, and health hazards of certain alternative fuels are compared to those of conventional fuels. The alternative fuels considered include hydrogen, ammonia, hydrazine, and methyl and ethyl alcohols. The fuels selected as representative conventional fuels include diesel fuel marine, motor gasoline, JP-5, and natural gas (methane). Categories used in evaluating the relative hazards of each fuel include leakage, volatility, dissipation, ignition, flammability, deflagration, radiation, detonation, and physiological effects. Within each category, the nine alternative and conventional fuels are ranked, 1 through 9, from the least to the most hazardous fuel.

The comparison begins with an examination of two important properties of a fuel - density and calorific value. Table 6 lists the liquid density and the net heat of combustion, on a mass and volume basis, for each fuel. Although hydrogen has 2.8 times the heating value of JP-5 on a mass basis, it has less than one-fourth the heating value of JP-5 on a volume basis. The other alternative fuels have about 50% or less of the heating value of JP-5 on a mass or volume basis. This reduced energy density of the alternative fuels has a significant impact on the design and range of a given vehicle.[20]

TABLE 6
FUEL DENSITY AND CALORIFIC VALUE

Fuel	Liquid Density		Net Heat of Combustion	
	Lb/Ft^3	Lb/Gal	Btu/Lb	Btu/Gal
Ammonia	42.6	5.70	8,000	45,600
DFM	53.0	7.08	18,500	131,000
Ethyl alcohol	49.7	6.64	11,600	77,000
Gasoline	43.8	5.86	19,100	111,900
Hydrazine	62.5	8.36	7,200	60,200
Hydrogen	4.4	0.59	51,600	30,400
JP-5	50.9	6.80	18,300	124,400
Methane	25.9	3.46	21,500	74,400
Methyl alcohol	49.7	6.64	8,600	57,100

The following paragraphs describe the approach used and the results obtained in ranking the relative hazards of the alternative and conventional fuels.

LEAKAGE

Evaluation of relative leakage was based on the viscosity of each fuel under normal storage conditions. The physical characteristics, including cross-sectional area, length, and driving force, of the leak are assumed to be the same in each case. The dimensions of the leak are assumed to be large enough for viscous flow; otherwise, molecular flow results and leakage becomes a function of molecular size. Since the leak rate is inversely proportional to viscosity, the reciprocals of viscosity were compared, using the viscosity of water at 80° F as a basis. In table 7, leakage rates of the nine fuels stored as liquids are ranked, 1 through 9, from the lowest to the highest relative leakage rate.

TABLE 7 - RELATIVE LEAKAGE

Fuel	Storage Conditions		Leakage Rate Relative to Water	Rank
	Temperature ° F	Viscosity lb/ft-sec		
Ammonia	-28	1.8×10^{-4}	3.2	7
DFM	80	1.3×10^{-3}(1)	0.4	1
Ethyl alcohol	80	7.4×10^{-4}	0.8	3
Gasoline	77	3.5×10^{-4}(1)	1.7	6
Hydrazine	68	6.5×10^{-4}	0.9	4
Hydrogen	-423	9.1×10^{-6}	64	9
JP-5	80	9.1×10^{-4}(1)	0.6	2
Methane	-259	7.8×10^{-5}	7.4	8
Methyl alcohol	80	3.7×10^{-4}	1.6	5
Water	80	5.8×10^{-4}	1.0	

(1) Typical value; viscosity varies over a range.
Note: Physical state for all fuels is liquid.

The fuels stored at subnormal temperatures were found more liable to leakage. Liquid hydrogen, with a relative leakage rate an order of magnitude greater than any other fuel, was ranked 9. Liquid methane and liquid ammonia were ranked 8 and 7, respectively. The relative leakage rates of the six fuels stored at ambient temperatures ranged from 0.4 to 1.7. Diesel fuel marine, ethyl alcohol, hydrazine, and JP-5 have relative leakage rates less than that of water, while gasoline and methyl alcohol have relative leakage rates greater than that of water. At a given temperature, the viscosity of pure substances such as ethyl alcohol, hydrazine, and methyl alcohol, is constant. Diesel fuel marine, gasoline, and JP-5 are blends of several pure hydrocarbons, the composition of which may vary. At a given temperature the viscosity of the conventional fuels varies over some range. Therefore, the order of fuels ranked 1 through 6 could change depending on the values chosen to represent the viscosities of the conventional fuels. The values used in this evaluation are considered typical values for the viscosity of diesel fuel marine, gasoline, and JP-5. Perhaps the most accurate conclusion regarding leakage is that the fuels stored at subnormal temperatures, particularly liquid hydrogen, are more liable to leakage, and the rates of leakage of fuels stored at ambient temperatures are roughly similar.

VOLATILITY

Volatility is the tendency of a substance to evaporate under given conditions. If the given conditions of interest are those at or near normal atmospheric pressure and temperature, then the properties which indicate the volatility of a substance include normal boiling point or boiling range, flash point, and vapor pressure. Table 8 lists the normal boiling point or boiling range, latent heat of vaporization, and the flash point of each fuel. The normal boiling points of diesel fuel marine, gasoline, and JP-5 are given as ranges, because these fuels contain several fractions with varying boiling points. The conventional fuels and hydrogen have relatively low heats of vaporization (100 to 220 Btu/lb) compared to the other fuels (386 to 590 Btu/lb) The flash point of a liquid is the minimum temperature at which it gives off sufficient vapor to form an ignitable mixture with the air near the surface of the liquid or within the vessel used.[33] Some evaporation takes place below the flash point but not in sufficient quantity to form an ignitable mixture. The fuels having low boiling points, including ammonia, hydrogen, and methane, also have low flash points. Gasoline has a low flash point, -45° F.

TABLE 8 - RELATIVE VOLATILITY

Fuel	Normal Boiling Point, ° F	Latent Heat of Vaporization Btu/lb	Flash Point, ° F	Rank
Ammonia	-28	590	(3)	7
DFM	400 to 725(1)	~100(2)	140 minimum	1
Ethyl alcohol	173	386	55	4
Gasoline	100 to 400(1)	140	-45	6
Hydrazine	236	540	100	3
Hydrogen	-423	194	(3)	9
JP-5	390 to 555(1)	100 to 120	140 minimum	2
Methane	-259	220	-306	8
Methyl alcohol	147	474	52	5

(1) Boiling point range of the fuel's several hydrocarbon fractions.

(2) Estimated from boiling point range.

(3) Flash points for these normal temperature gases are not reported in the literature.

Some of the alternative fuels such as ethyl alcohol, hydrazine, and methyl alcohol have much higher flash points than gasoline. Diesel fuel marine and JP-5 have the highest flash points, 140° F minimum. Vapor pressure versus temperature data are given for all of the fuels except diesel fuel marine and gasoline (figure 19). Vapor pressure versus temperature data will vary with the composition of diesel fuel marine, gasoline, and JP-5.

In table 8 the fuels are ranked 1 through 9, from the least to the most volatile fuel.

DISSIPATION

The diffusivity coefficient of fuel vapor in air, vapor density, and buoyancy in air were compared to determine the relative dissipation rates of hazardous fuel vapors into the atmosphere. Experimentally determined values of diffusivity for some gases and vapors in air are given in the literature. When experimental values are not available, several prediction methods, based on the kinetic theory of gases, can be used to estimate diffusivity coefficients. Accurate estimates for ammonia, ethyl alcohol, hydrazine, hydrogen, methane, and methyl alcohol were calculated by using the Wilke and Lee modification of the equation by Hirschfelder, Bird, and Spotz.[2] Vapors from diesel fuel marine, gasoline, and JP-5 are mixtures of several hydrocarbons, each having a different diffusivity coefficient. For multicomponent systems, diffusivity may be a strong function of composition. Diffusivities reported for napthalene, straight-chained hydrocarbons having 6 to 12 carbon atoms, and cyclic hydrocarbons range from approximately 0.05 to 0.08 cm^2/sec at 0° C. Since diesel fuel marine, gasoline, and JP-5 are mixtures containing some of these and similar hydrocarbon fractions, it is likely that their diffusivity falls in this range. At room temperature, the diffusivities should range from 0.06 to 0.09 cm^2/sec, which is lower than the other diffusivities shown in table 9. The equation used to predict diffusivity indicates that an increase in molecular size and weight causes a decrease in diffusivity. Therefore, diffusivity of gasoline should be greater than JP-5 and diesel fuel marine, and diffusivity of JP-5 should be greater than diesel fuel marine.

Diffusivity coefficients characterize molecular diffusion between gases in a stagnant environment; but dissipation is also affected by mass flow and turbulence of the atmosphere above a fuel spill. The prevailing weather conditions, especially wind velocity and direction, will greatly influence the dissipation of hazardous fuel vapors. However, it is assumed that under given weather conditions the vapor dissipation rates will be proportional to those under controlled conditions.

TABLE 9 - RELATIVE DISSIPATION

Fuel	Diffusivity Coefficient at RT cm^2/sec	Vapor Density at RT lb/ft^3	Buoyancy in Air at RT(1)	Vapor Density at NBP lb/ft^3	Buoyancy in Air at RT(1)	Rank	
						Unconfined Dissipation	Confined Dissipation
Ammonia	0.282	0.0442	Positive	0.056	Positive	2	8
DFM	<0.1	-	-	-	-	9	1
Ethyl alcohol	0.128	0.117	Negative	0.0996	Negative	6	4
Gasoline	<0.1	-	-	-	-	7	3
Hydrazine	0.146	0.0817	Negative	0.063	Positive	5	5
Hydrogen	0.752	0.0051	Positive	0.084	Negative	1	9
JP-5	<0.1	-	-	-	-	8	2
Methane	0.231	0.0410	Positive	0.109	Negative	3	7
Methyl alcohol	0.151	0.0818	Negative	0.072	Positive	4	6

(1)Density of air at room temperature is taken to be 0.07493 lb/ft^3.

Densities of ammonia, ethyl alcohol, hydrazine, hydrogen, methane, and methyl alcohol were determined from information in the literature. Values for the density of diesel fuel marine, gasoline, and JP-5 were not available. The vapor density data were compared to the density of air at room temperature to determine whether the fuel vapors have positive or negative buoyancy. Depending upon the circumstances, buoyancy may or may not be important when ranking relative dissipation. In a confined area, such as in a room where the ascent of fuel vapors is restricted, comparative buoyancy is not important.

Whether rapid dissipation of fuel vapors is considered desirable or undesirable will determine the ranking order for relative dissipation. Rapid dissipation would be desirable following fuel spills in unconfined areas, since the concentration and duration of flammable fuel-air mixtures would be reduced. Rapid dissipation would be undesirable following fuel spills in confined areas, such as the hull of a ship. Ideally mixed, flammable fuel-air mixtures may rapidly accumulate under these circumstances. Ranks are shown in table 9 for both situations - unconfined and confined dissipation.

IGNITION

Autoignition temperature and spark ignition energy of each fuel are compared in table 10. The autoignition temperature of a substance is the minimum temperature required to initiate or cause self-sustained combustion independent of the heating or heated element.[33] Autoignition temperatures observed under one set of conditions may be changed significantly by a change of conditions. Therefore, ignition temperatures should be regarded only as approximations. Spark ignition energy is the minimum energy which will ignite a flammable gas mixture when applied instantaneously. An electrical capacitance spark is commonly used for ignition studies of this type. The values shown in table 10 are for stoichiometric fuel-air mixtures at a pressure of 1 atmosphere. Calcote et al,[38] have reported minimum spark ignition energy data for several fuels including ammonia, hydrogen, methane, and methyl alcohol. The relative ranks of the remaining fuels considered in this study were determined from the principles reported by Calcote, et al, concerning the effect of molecular structure on spark ignition energy.

TABLE 10 - RELATIVE IGNITION

Fuel	Autoignition Temperature ° F	Reference	Rank	Spark Ignition Energy(1) mJ	Rank
Ammonia	1204	2,29,33	1	(2)	1
DFM	494	29,33	7	>JP-5	2
Ethyl alcohol	689	13,33	5	<Methane	6
Gasoline	536-853	33	6	>Methane	4
Hydrazine	(3)	33	9	-	-
Hydrogen	1075	2,29	2	0.02	8
JP-5	473	29,33	8	>Gasoline	3
Methane	1004	13,33	3	0.48	5
Methyl alcohol	725	13,33,37	4	0.22	7

(1) Minimum energy for spark ignition of stoichiometric mixtures at 1-atm pressure.
(2) No ignition at spark energy of 1000 millijoules.
(3) Varies from 75° to 518° F depending on the type of surface contacted.

Fuels which are ignited easily will have a low autoignition temperature or small spark ignition energy. Results of ranking the relative ease of ignition of the nine fuels based on autoignition temperature are different from results based on spark ignition energy. Hydrogen with a high autoignition temperature of 1075° F ranks second, but with a low spark ignition energy of 0.02 millijoules ranks eighth. Thus, two separate ranks were necessary to indicate ease of ignition. The results are shown in table 10.

FLAMMABILITY

Relative flammability was determined by comparing the flammable range of each fuel in air. The lower and upper flammability limits at normal atmospheric temperatures and pressures are shown in table 11. There may be significant variation in flammable limits at pressures or temperatures above or below normal. The general effect of an increase in temperature or pressure is to lower the lower limit and raise the upper limit. Decrease in temperature or pressure has the opposite effect.[33] Flammable range is the difference between the upper and lower flammability limits (figure 20). The fuels were ranked, 1 through 9, from the narrowest to the widest flammable range. The conventional hydrocarbon fuels have narrow flammable ranges compared to the alternative fuels.

TABLE 11 - RELATIVE FLAMMABILITY

Fuel	Flammable Limits in Air(1)		Flammable Range	Reference	Rank
	Lower	Upper			
Ammonia	15	28	13	13,33	5
DFM	0.5	4.1	3.6	36	1
Ethyl alcohol	3.3	19	15.7	13,33	6
Gasoline	1.4	7.6	6.2	29,33	3
Hydrazine	4.7	100	95.3	13,29,33	9
Hydrogen	4.0	75	71	13,33	8
JP-5	0.6	4.5	3.9	36	2
Methane	5.0	15	10	13,33	4
Methyl alcohol	6.7	36	29.3	13,33	7

(1) Percent by volume of fuel vapor in air.

DEFLAGRATION

Evaluation of deflagration hazards was based on stoichiometric fuel-air ratio, stoichiometric composition, adiabatic flame temperature, burning liquid regression rate, and maximum burning velocity. These data appear in table 12. The stoichiometric fuel-air ratio and stoichiometric composition were taken from Perry's Chemical Engineers' Handbook.[2] The adiabatic flame temperature was estimated using a short hand method.[39] An example of this method is given below using ammonia as the source of the flame.

Step 1: Write the combustion reaction.

$$NH_3 + 0.75\ O_2 + 2.82\ N_2 \rightarrow 1.5\ H_2O + 3.32\ N_2.$$

Step 2: Assign standard heats of formation to products and reactants.

$$\Delta H_f \begin{cases} NH_3 = -11.0 \text{ Kcal/mole} \\ H_2O = -57.8 \text{ Kcal/mole.} \end{cases}$$

Step 3: Calculate heat of reaction.

$$\Delta H_r = \sum n\Delta H_f(\text{products}) - \sum n\Delta H_f(\text{reactants})$$

$$\Delta H_r = 1.5\ (-57.8) - 1\ (-11) = -75.7 \text{ Kcal.}$$

Step 4: Calculate heat capacity of product gases.

$$\bar{C}_p \begin{cases} H_2O = 10.2 \text{ cal/mole } ^\circ K \\ N_2 = 7.9 \text{ cal/mole } ^\circ K \end{cases}$$

$$C_p = 1.5\ (10.2) + 3.32\ (7.9) = 41.5 \text{ cal/}^\circ K.$$

Step 5: Calculate adiabatic flame temperature.

$$T_b = T_i + \Delta T$$

$$\Delta T = \frac{\Delta H_r}{C_p} \quad \frac{75{,}700 \text{ cal}}{41.5 \text{ cal/}^\circ K} = 1{,}824\ ^\circ K$$

$$T_b = 300^\circ K + 1{,}820^\circ K = 2{,}124^\circ K$$

$$T_b = 1{,}851^\circ C = 3{,}364^\circ F$$ Answer.

The burning liquid regression rate, or rate of fuel consumption measured by decrease in pool depth in inches per minute, was calculated from the equation:

$$\text{regression rate} = 0.003 \frac{H_c}{H_v} \text{ in/min,}$$

where H_c and H_v are the fuel's heats of combustion and vaporization in Btu/lb, respectively.[21] Maximum burning velocity data were taken from a recent study by Berkowitz, *et al.*[20]

TABLE 12 - RELATIVE DEFLAGRATION

Fuel	Combustion Properties at Stoichiometric Conditions Moles of Air/ Mole of Fuel	 Lbs of Air/ Lbs of Fuel	 Fuel Concentration Volume %	 Adiabatic Flame Temperature °F	Burning Liquid Regression Rate in/min	Maximum Burning Velocity ft/sec	Rank
Ammonia	3.57	6.10	21.81	3364	0.041	0.034	1
DFM	-	~12	~1	~4000	0.555	1.1	8
Ethyl alcohol	14.29	9.02	6.52	3918	0.090	-	4
Gasoline	-	~15	~1	~4000	0.409	~1	6
Hydrazine	4.76	4.28	17.4	4040	0.040	-	3
Hydrogen	2.38	34.34	29.50	4242	0.798	8.8	9
JP-5	-	~12	1.1	~4000	0.499	1.1	7
Methane	9.53	17.27	9.47	3811	0.293	1.2	5
Methyl alcohol	7.15	6.48	12.24	3825	0.054	1.6	2

Hydrogen is ranked 9, the most hazardous, because hydrogen has the highest flame temperature, regression rate and burning velocity. Ammonia is ranked 1, the least hazardous, because ammonia has the lowest flame temperature, regression rate, and burning velocity. Methyl alcohol, hydrazine and ethyl alcohol have low regression rates and low flame temperatures; therefore, these fuels have low ranks. The conventional fuels have much greater regression rates and were assigned high ranks.

RADIATION

The heat release rate, the percentage of the heat of combustion radiated, and the flame emissivity were used to rank the relative thermal radiation hazard of each fuel. The heat release rate from a pool of burning liquid is given by the equation.

$$\text{Release rate} = 0.01456 \times (\text{specific gravity}) \times \frac{H_c^2}{H_v} \quad \text{Btu/ft}^2\text{sec},$$

where H_c and H_v are the heats of combustion and vaporization, respectively.[21] This equation is valid for pools having a surface area greater than 10 square feet. The heat release rate for each fuel was calculated and is listed in table 13.

TABLE 13 - RELATIVE RADIATION

Fuel	Heat Release Rate Btu/ft^{2}sec	Percent Radiated	Flame Emmissivity	Rank
Ammonia	1,078	-	-	1
DFM	42,325	-	~1.0	9
Ethyl alcohol	4,043	-	-	4
Gasoline	26,631	-	~1.0	7
Hydrazine	1,400	-	-	2
Hydrogen	14,098	25	0.01 to 0.10	5
JP-5	39,774	-	~1.0	8
Methane	12,698	23	~1.0	6
Methyl alcohol	1,809	20	-	3

The approximate percentage of the total thermal output (heat release rate) of fires is determined experimentally. Values for hydrogen, methane, and methyl alcohol were extrapolated from small-scale tests under windless conditions.[17] Emissivity of hydrogen flames range from 0.01 to 0.10, while hydrocarbon fuels have flame emissivities approaching 1.0.[3]

Based on the information shown in table 13, the fuels were ranked, 1 through 9, from the least to the most hazardous. The alternative fuels ranked lower in hazards from thermal radiation than the conventional fuels.

DETONATION

In evaluating the relative detonation hazards of each fuel, several characteristics should be considered, including detonability limits in air, detonation velocities, minimum initiation energy for direct detonation, and maximum explosive potential. Detonation limits of hydrogen-air mixtures range from 18% to 59% hydrogen by volume. Detonation velocities of hydrogen-air mixtures range from approximately 4300 to 7200 ft/sec.[19] A. D. Little, Incorporated, has reported that a minimum initiation energy to produce full explosive yield from a stoichiometric mixture was supplied by a 2-gram charge of pentolite. A maximum explosive potential of 12 pounds of TNT for each gallon of liquid hydrogen vaporized was calculated.[5]

Unfortunately, comparative values of these properties were not available for the other fuels. Therefore, the relative detonation hazards of each fuel could not be ranked.

HEALTH HAZARDS

The physiological hazards of fuels are important when considering the safety of personnel. Toxicity of the fuel is determined from its threshold limit value, and the principal effects of inhalation exposures above the threshold limit value. Skin contact with fuel liquids and vapors may also have significant detrimental physiological effects. Health hazards relating to liquid and vapor exposures resulting from skin contact, eye contact, ingestion, and inhalation of vapors as well as detrimental effects of ultraviolet and infrared radiation exposures should be carefully evaluated. Protective clothing, equipment, and respiratory protection may be required to preclude over-exposures to fuel liquids and vapors, blast overpressure, as well as adverse effects to the skin and eyes due to ultraviolet and infrared radiation.

Ammonia has caustic properties in either liquid or vapor form.[40] The liquid is cold (-28° F) and highly volatile. Liquid ammonia when contacting the skin will produce severe burns, and the freezing effect due to rapid evaporation from the skin surface can cause frostbite. Ammonia vapors are irritating to the eyes and mucous membranes of the respiratory tract.[41] Irritation of the skin may be experienced at high concentrations, especially if the skin is moist. When exposed to heat, ammonia emits toxic vapors. The American Conference of Governmental Industrial Hygienists has recommended a threshold limit value of 25 ppm (parts of vapor per million parts of air by volume) at room temperature and atmospheric pressure. Men exposed to ammonia each workday over long periods develop a higher and higher tolerance for the irritant effect of ammonia gas. Consequently, the odor of ammonia should not be relied upon as an indicator of potential personnel over-exposures. Symptoms of exposure are irritation of the eyes, conjunctivitis, swelling of the eye lids, irritation of the nose and throat, coughing, dyspnoea, and vomiting.[29] Corneal ulcers have been reported following splashing of ammonia in the eye.

Ethyl alcohol is an irritant to sensitive tissue, a fat solvent, and when absorbed into the body it causes depression of the higher brain centers.[40] The ACGIH recommended threshold limit value for ethyl alcohol is 1000 ppm; this concentration will rarely be achieved except in enclosed spaces. If pure ethyl alcohol is swallowed, alcoholic intoxication results from depression of the higher brain centers. Consumption of denatured alcohol must be avoided because of the poisonous compounds used to denature it. Ethyl alcohol is oxidized in the body, forming carbon dioxide and water, with no cumulative effects.[29] Exposure to concentrations above the threshold limit may cause headache and irritation of the eyes and mucous membranes of the upper respiratory tract. If continued for an hour or more, stupor, drowsiness, lassitude, loss of appetite, and inability to concentrate result.

Hydrazine, a clear, hygroscopic liquid at normal temperatures, is caustic to human tissue.[40] If spilled on the skin or in the eyes, liquid hydrazine can cause severe local damage, dermatitis, or chemical burns. It can penetrate the skin to cause systemic effects similar to those produced when the compound is swallowed or inhaled. If inhaled, hydrazine vapor causes irritation of the eyes and respiratory tract. Systemic effects involve the central nervous system. The ACGIH recommended threshold limit value for hydrazine is 1 ppm. On short-term exposure, resultant symptoms include tremors; on exposure to high concentrations, convulsions and possibly death follow.[29] Repeated exposures may cause toxic damage to the liver, interstitial nephritis, and destruction of red blood corpuscles (anemia). When heated to decomposition, hydrazine emits highly toxic vapors of nitrogen compounds.

Hydrogen, as already discussed, is a nontoxic gas, but it can act as a simple asphyxiant by excluding oxygen from the lungs. Tissue damage in the form of frostbite or "cold burn" may result when skin comes into contact with liquid hydrogen, surfaces cooled by liquid hydrogen, or cold hydrogen vapors.

Methane has no specific toxic effect, but it can act as a simple asphyxiant. Low temperatures are associated with liquid methane; therefore, frostbite or "cold burn" may result.

Methyl alcohol is irritating to the eyes and mucous membranes and, if inhaled in sufficient quantity, to the lungs.[40] Its main toxic effect is exerted on the central nervous system, particularly the optic nerve. The ACGIH recommended threshold limit value for methyl alcohol is 200 ppm. Toxic concentrations of vapor can readily build up in enclosed spaces. Effects of concentrated short-term exposure include blurring of vision, photophobia, conjunctivitis, development of definite eye lesions, irritation of the mucous membranes of the throat and respiratory tract, headache, gastrointestinal disturbances, dizziness, and a feeling of intoxication.[29] The visual symptoms may clear temporarily, only to recur later and progress to actual blindness. Severe exposures may cause dizziness, unconsciousness, sighing respiration, cardiac depression, and eventually death. Ingestion of methyl alcohol causes abdominal pain, with nausea and vomiting, dizziness, and headache. There may be muscle twitching, progressing to convulsive spasms and cramps. Some people may suffer blindness for several hours or days after drinking as little as 1/3 ounce (10 ml), but individual susceptibility varies.[40] Severe poisoning may cause a coma lasting for several days and terminated by death. Methyl alcohol can also penetrate the skin to produce poisoning. Once absorbed by the body, methyl alcohol is very slowly eliminated.[29] The products formed by its oxidation are formaldehyde and formic acid, both of which are toxic. Because of the slowness with which it is eliminated, methyl alcohol should be considered a cumulative poison. Though single exposures to fumes may cause no harmful effect, daily exposure may result in the accumulation of sufficient methyl alcohol in the body to cause illness.

The hydrocarbon fuels are moderately skin-irritating, and after more than momentary contact can cause scaling and fissuring of skin.[40] Inhaling the aliphatic hydrocarbons can cause narcosis; but, because of the fuels' low volatility, these effects are unlikely except in closed spaces with inadequate ventilation. The main danger comes from accidentally swallowing hydrocarbon fuels. Ingestion is not especially toxic, but gasping while swallowing or aspiration from improperly induced vomiting can introduce the liquid into the lungs, and pulmonary edema may result. TLV for each of these fuels is dependent on composition. In general, fuels high in aromatic content are the more toxic. Gasoline vapors are not considered to be very poisonous, unless the concentration in air is sufficiently high to reduce the oxygen content below that needed to maintain life.[29] Diesel fuel has moderate toxicity similar to that of kerosene. Inhalation of high concentrations of vapor can cause headache and stupor. Ingestion causes irritation of the stomach and intestines with nausea and vomiting. Aspiration of vomitus can cause serious pneumonitis. JP-5 is a high flash point, kerosene-type fuel with similar effects.

The criteria used in ranking the fuels' relative hazards to health[42] are shown in table 14. The ACGIH recommended threshold limit values are used as guides in the control of health hazards; they are not fine lines between safe and dangerous concentrations. The threshold limit values represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect. Individual susceptibility varies; thus exposure of an occasional individual at or even below the threshold limit value may result in occupational illness and disease in some workers. The letter S following the threshold limit value for hydrazine is a notation that appropriate measures must be taken to prevent cutaneous absorption; otherwise, the threshold limit is invalid. The principle effects of inhalation exposures above threshold limit values is the personal judgement of Dr. Ralph G. Smith, Wayne State University, a member of the Threshold Limit Value Committee of the ACGIH. These conclusions were based on information in "Documentation of Threshold Limit Values,"[43] which ordinarily gives a summary of the basis for the value selected. If the substance is designated "Toxic," the principal effect is damage to some essential function, usually chronic effects produced by repeated exposures in excess of threshold limit value concentrations. If the substance is designated "Irritant," the principal effect is irritation of tissue with which the substance comes into contact. This includes the entire respiratory system, or skin, or eyes.

TABLE 14 - RELATIVE HAZARDS TO HEALTH

Fuel	ACGIH 1974 TLV ppm (mg/m^3)	Principal Effects of Inhalation Exposures Above TLV	Relative Hazard from Concentrated Short-Term Exposure[1]						Rank
			Eye Contact	Inhalation	Skin Penetration	Skin Irritation	Ingestion	Supplemental Effects	
Ammonia	25 (18)	Irritant	4z	5z	-	3z	-	-	8
DFM	-	-	1	2y	3	1	1	-	4
Ethyl alcohol	1000 (1900)	Toxic Irritant	2	1	1	1	1	-	3
Gasoline	-	-	2x	3x*	3x*	1x*	2x	Chronic Toxicity	6
Hydrazine	1S (1.3 S)	Toxic	4x	4x*	3x	3x	3x	-	9
Hydrogen	-	-	-	3	-	-	-	Asphyxiant	1
JP-5	-	-	1	2y	3	1	1	-	5
Methane	-	-	-	3	-	-	-	Asphyxiant	2
Methyl alcohol	200 S (260 S)	Narcosis Toxic	2	2	2	1	1*	Permanent Injury	7

[1] Definitions of symbols given in text below.

If the designation is "Narcosis," the principal effect is depression of the central nervous system tending to produce sleep or unconsciousness. The system used for describing the relative hazard to health from concentrated, short-term exposures is based on the "Manual of Hazards to Health from Chemicals."[44] The system considers only accidental single exposures as opposed to repeated or continuous exposures. The symbols used in this system are:

(1): No residual injury is to be expected from accidental exposure, even if no treatment is applied.

(2): Minor residual injury may result from some accidental exposures if no treatment is applied.

(3): Minor residual injury may result in spite of prompt treatment.

(4): Major residual injury may result in spite of prompt treatment.

(5) Major residual injury is likely in spite of prompt treatment.

(x): Entry based on analogy with a closely similar structure, or on other estimate believed sound.

(y): Entry based on a nonstandard test (a test different from the usual test described for each type of contact).

(z): Entry based upon human experience, superceding animal data.

(*): See supplemental effects.

Statements of supplemental effects are given because the tabulated numbers do not communicate all of the pertinent judgements about the relative hazards of a substance. "Chronic Toxicity" marks those substances with which repeated contact is more hazardous. Single contact results in an unperceived effect, sufficiently persistent so that contact a day or more later adds, and eventually chronic poisoning may result. "Asphyxiant" marks those substances which have no specific toxic effect, but can cause asphyxia by excluding oxygen from the lungs. Materials labeled "Permanent Injury" have permanently disabled persons who appeared to recover, with the help of medical care, from the severe effect of a single exposure.

Based on this information, the relative hazards to health of the nine fuels are ranked, 1 through 9, from the least to the most hazardous in table 14. Hazards to health from thermal radiation and blast hazards are considered in the radiation and detonation categories.

SUMMARY

Ranks of the nine fuels in each hazard category are collectively summarized in table 15. The alternative and conventional fuels are ranked 1 through 9, from the least to the most hazardous fuel, according to leakage, volatility, dissipation, ignition, flammability, deflagration, radiation, and health hazards. Relative detonation hazards of each fuel could not be ranked because values of detonability limits in air, detonation velocities, minimum initiation energy for direct detonation, and maximum explosive potential were available only for hydrogen.

TABLE 15 - SUMMARY OF RELATIVE HAZARDS

Fuel	Leakage	Volatility	Unconfined Dissipation	Confined Dissipation	Auto-Ignition	Spark Ignition	Flammability	Deflagration	Radiation	Detonation	Health
Ammonia	7	7	2	8	1	1	5	1	1	-	8
DFM	1	1	9	1	7	2	1	8	9	-	4
Ethyl alcohol	3	4	6	4	5	6	6	4	4	-	3
Gasoline	6	6	7	3	6	4	3	6	7	-	6
Hydrazine	4	3	5	5	9	-	9	3	2	-	9
Hydrogen	9	9	1	9	2	8	8	9	5	-	1
JP-5	2	2	8	2	8	3	2	7	8	-	5
Methane	8	8	3	7	3	5	4	5	6	-	2
Methyl alcohol	5	5	4	6	4	7	7	2	3	-	7

1 2 3 4 5 6 7 8 9 →

Increasing Hazard

CONCLUSIONS

The review of hazards associated with hydrogen has shown that much is already known about the inherent hazards of hydrogen. But, some areas were identified where information is lacking or disagreement among sources exists. For example, it is not precisely known whether the rapid phase transformation resulting from the spillage of liquid hydrogen on water, as from ships at sea, will cause explosions similar to liquefied natural gas spillage on water. Further investigation in this area is required. Also experimental evidence has shown that the common practice of expressing the blast yield from liquid propellant explosions in equivalent pounds of TNT is inaccurate. Realistic scaling relationships and equations for calculating the actual explosive potential of hydrogen are needed for practical design to limit explosion damage. And, to the present time, little has been done to assess the effects of projectile or fragment impact with liquid hydrogen storage, or to develop protection for minimizing combat vulnerability. These are important areas to consider in an investigation of the hazards associated with the use of hydrogen as a military fuel.

The comparison of hazards for alternative and conventional fuels has shown that hydrogen, like the other fuels, has safety advantages and disadvantages. The unique properties of each fuel make some fuels more difficult to store, some more flammable, or some more toxic than others. Due to its low storage temperature, ease of leakage, and high volatility, liquid hydrogen will require more sophisticated fuel storage and handling systems than diesel fuel marine or JP-5. Hydrogen's low-spark ignition energy requirement and wide flammability limits imply a greater probability of fires and explosions, particularly when it is confined.

For many years, liquid hydrogen has been safely used to propel vehicles for space exploration. However, there are distinctive differences in environment and missions between space flight and military operations. War and space are hostile but dissimilar environments. Military vehicles are expected to perform their respective missions over a period of several years, while launch vehicles operate for a relatively short time. Some conclusions concerning the safe use of hydrogen as a military fuel can be inferred from the discussion up to now.

Departure from vacuum-insulated storage tanks may be necessary for safe storage of liquid hydrogen aboard military vehicles. Even a small penetration of a vacuum-insulated storage tank by a projectile or fragment would cause a loss of vacuum between the outer and inner vessels. The liquid hydrogen would vaporize and the resulting pressure build up would rupture the storage tank. Rigid foam or other nonvacuum insulations with low thermal conductivities are more desirable. When such insulation is penetrated, the heat leak to the liquid hydrogen is localized. Therefore, more time is available for corrective action such as transferring the fuel from the damaged tank to an empty reserve tank.

Protection of the liquid hydrogen storage against impact and penetration is also desirable, but heavy protective armor implies a prohibitive weight penalty. Locating the storage within the vehicle will give the most protection and minimum weight. For example, liquid hydrogen storage in the hull of a ship could use the structural members of the hull for support. A thick layer of foam insulation and a thin aluminum liner could be added to contain the liquid hydrogen.

Confining large quantities of liquid hydrogen inside the hull of a ship implies serious fire and explosion hazards. An alternate method is locating the storage tanks on the weather deck or attaching fuel modules about the sides of the ship. These free-standing storage tanks will have a greater weight penalty (per pound of liquid hydrogen stored) than storage tanks incorporated into the ship's hull. Lightweight armor could give limited protection, but damaged, leaking, or burning fuel modules could be jettisoned to a safe distance from the ship.

Regardless of the location of the storage tanks, hydrogen fuel on its way to the prime mover will be transferred through some areas of the vehicle. An automatic system of rapid-response leak detectors and fire detectors could be used to continuously monitor hazardous areas. In the event of a leak, the system could shut off the flow of hydrogen to the leak. In the event of a fire or explosion, the system could trigger the release of an appropriate fire-extinguishing or explosion-suppressing chemical.

It is apparent from the results of this investigation that the use of hydrogen as a military fuel would involve numerous serious hazards. Significant research and development will be required in the future to bring forth hydrogen-fueled military systems that are both viable and safe. The information uncovered during the course of this investigation has given an indication of the direction for further research and development.

RECOMMENDATIONS

Further investigation based on the findings of this study is recommended. The recommendations include:

- Investigate hydrogen-air deflagration and detonation to define the damage potential of probable accident situations, to generate the data required for design to limit explosion damage, and to develop realistic scaling relationships and equations for calculating the actual explosive potential of hydrogen.

- Assess the current state of the art of hydrogen leak detection and fire detection technology, and recommend further developments necessary to provide reliable hazards-detection equipment for military applications.

- Assess the current state of the art of hydrogen fire suppression and extinguishment technology, and recommend further developments necessary to provide reliable hazards-control equipment for military applications.

- Investigate liquid hydrogen-water reactions to determine the potential hazards of large-scale spills of liquid hydrogen on water, as from ships at sea.

- Investigate the effects of hydrogen embrittlement and cryogenic temperatures on containment materials when subjected to high dynamic stresses caused by projectile or fragment impact, and determine the most suitable materials for constructing impact-resistant liquid hydrogen storage tanks.

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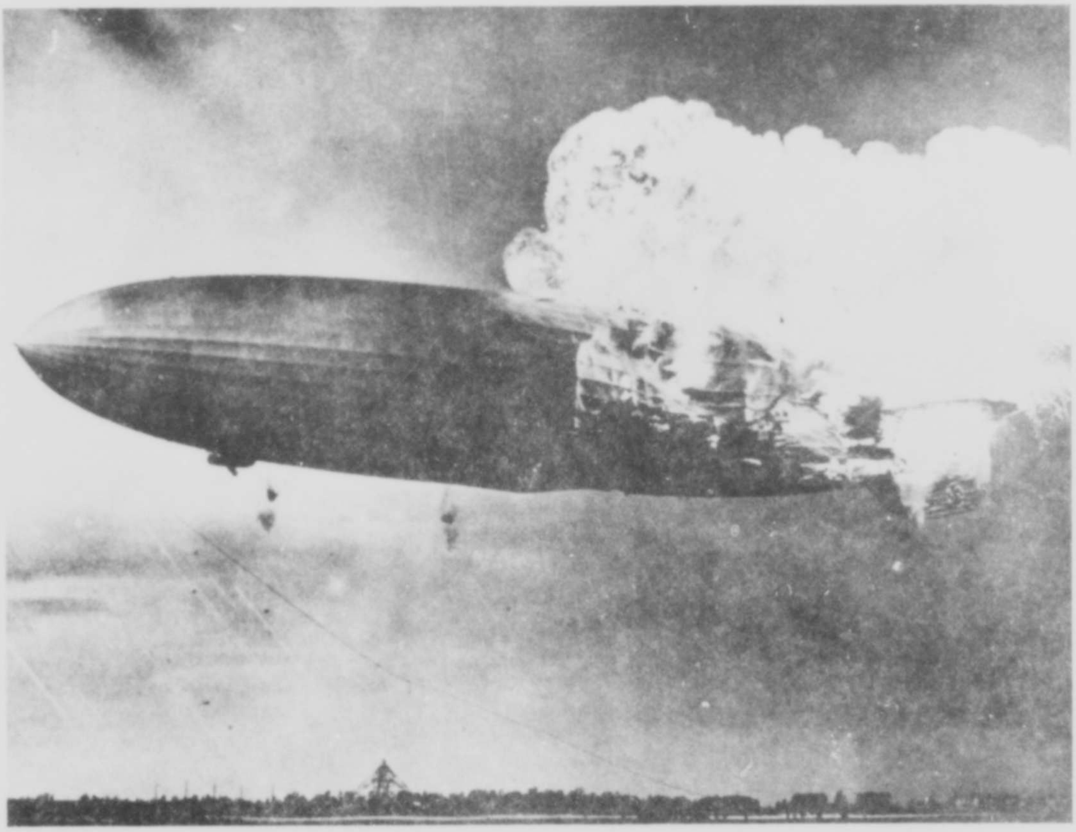

Figure 1
Hindenburg Airship Disaster of May 6, 1937

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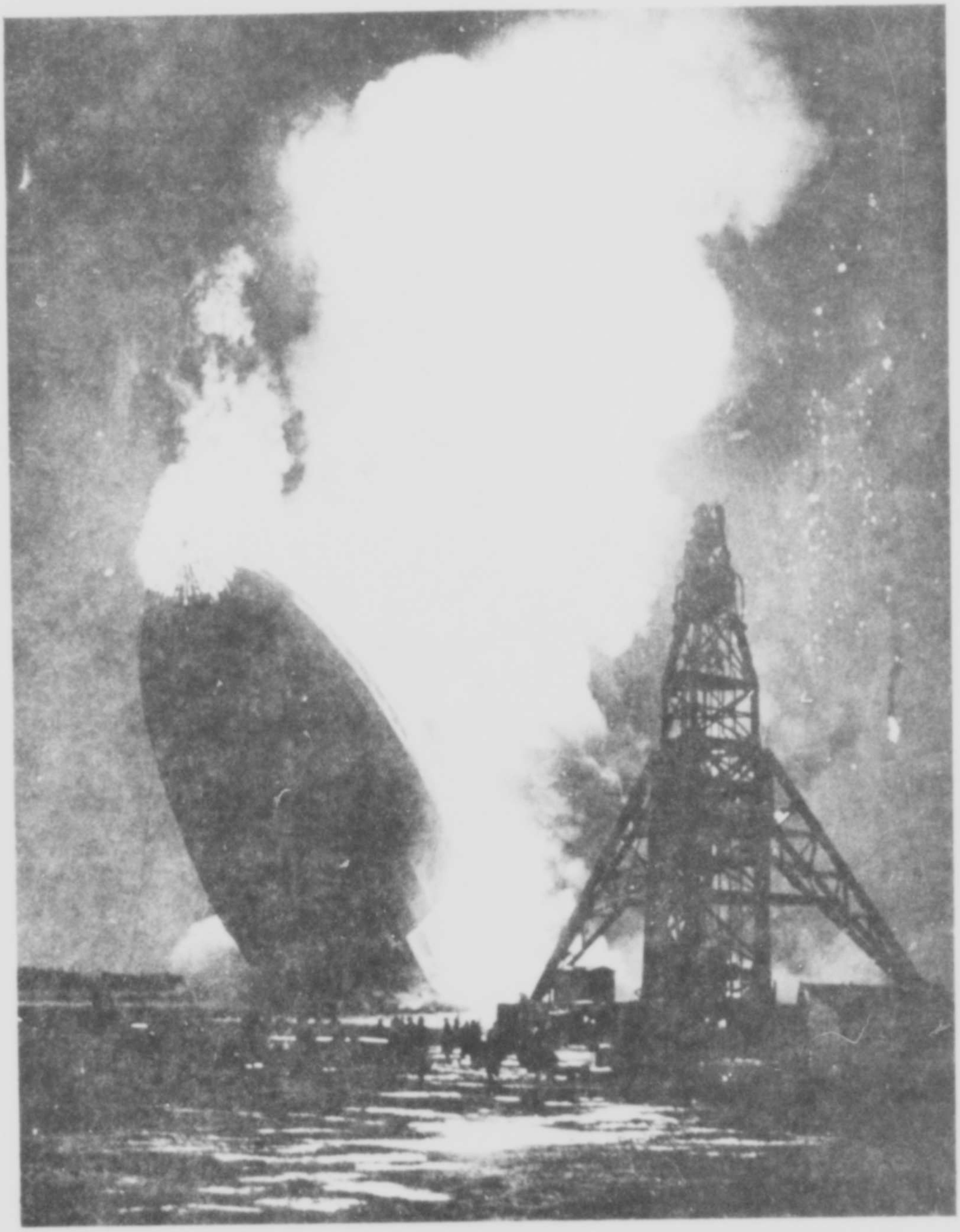

Figure 2 - Burning Hindenburg Crashes Near the Mooring Tower at Lakehurst Naval Air Station

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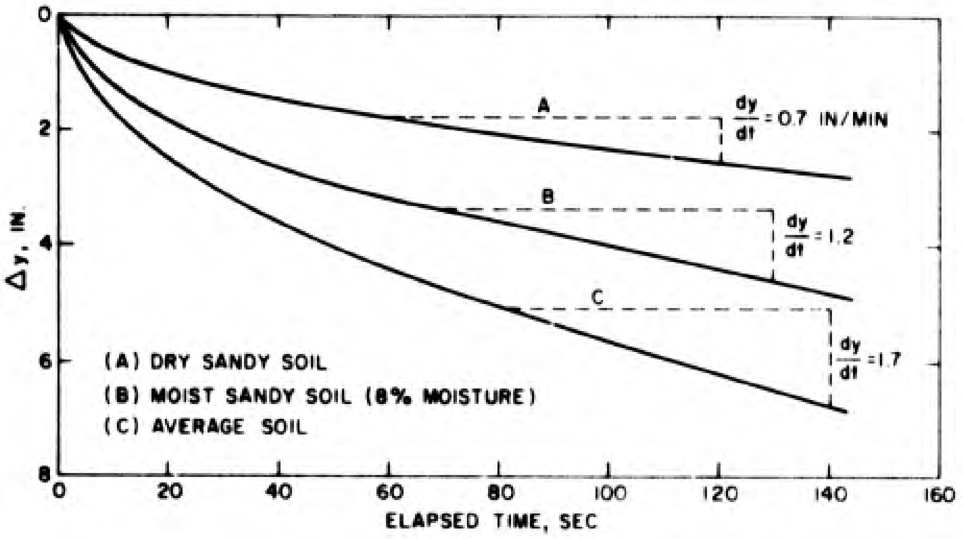


Figure 3 - Theoretical Decrease in Liquid Hydrogen Level Following Spillage Versus Evaporation Time (Reference 4)

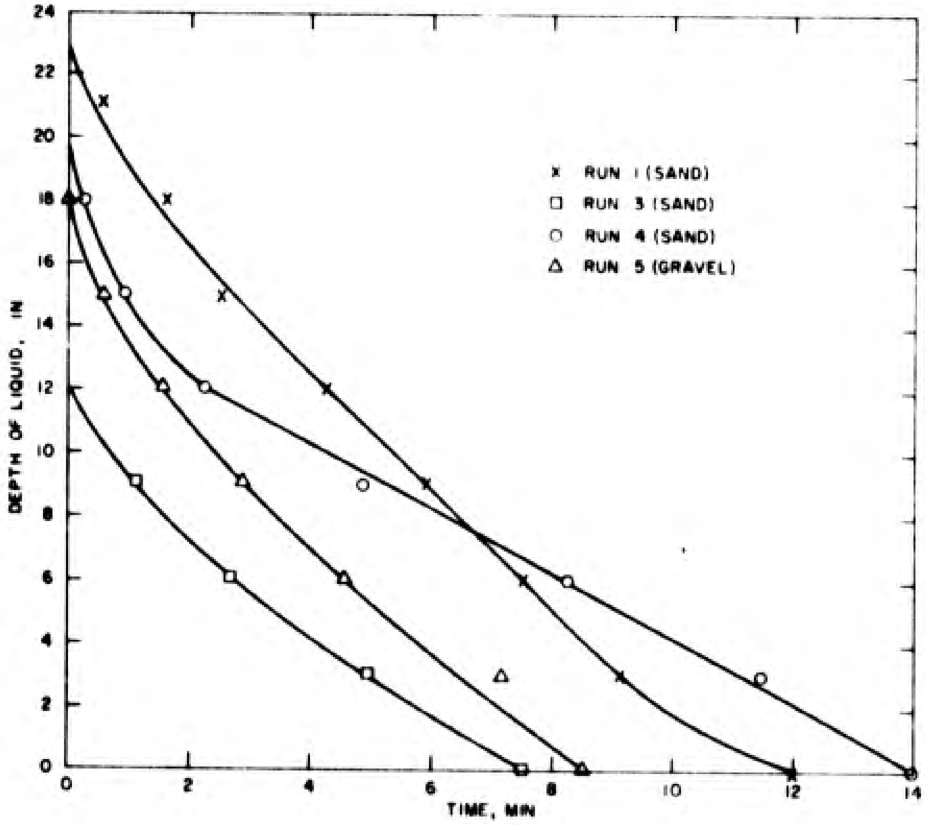


Figure 4 - Experimental Decrease in Liquid Hydrogen Level Following Spillage Versus Evaporation Time (Reference 5)

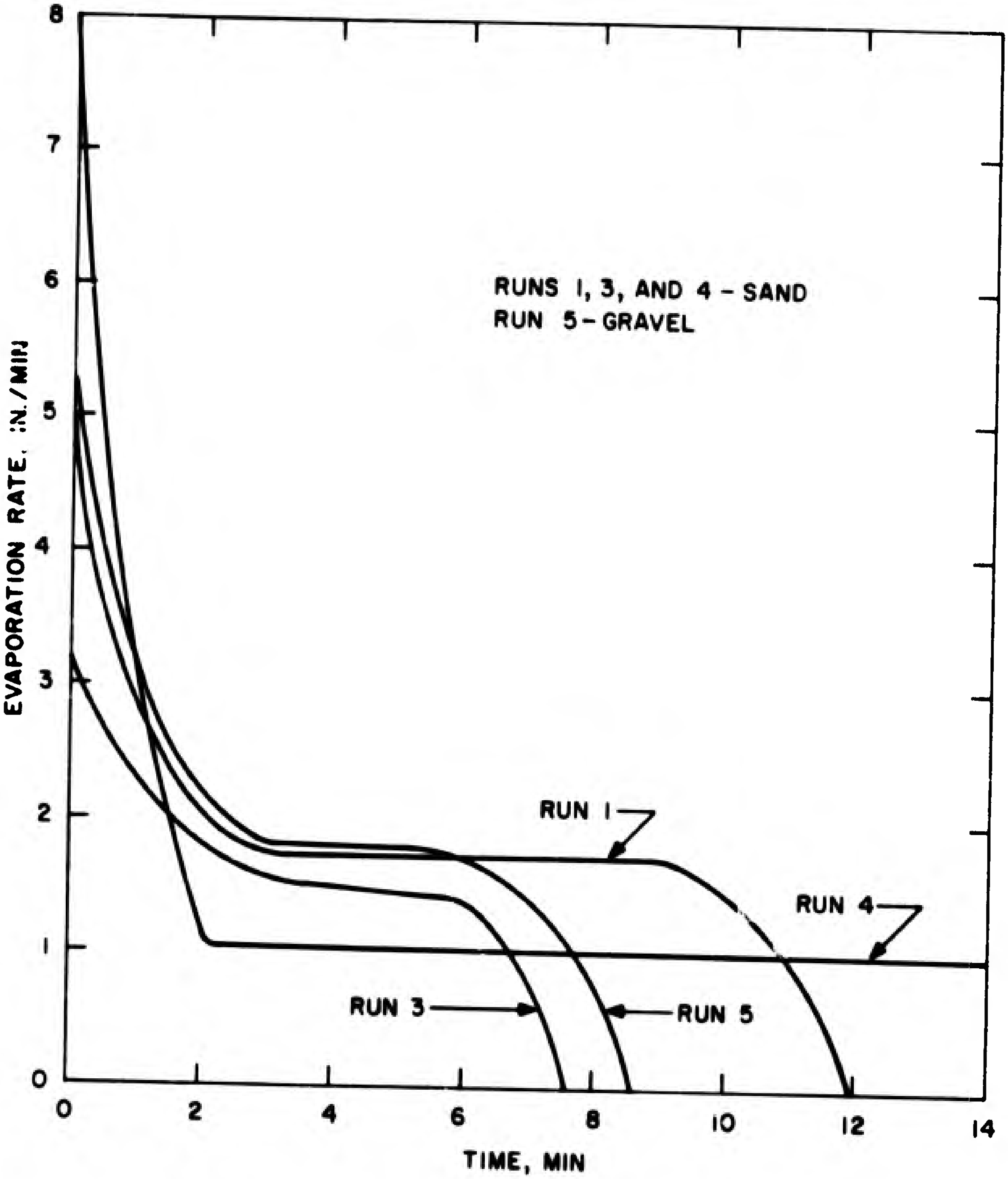


Figure 5 - Experimental Evaporation Rate of Liquid Hydrogen Following Spillage Versus Evaporation Time (Reference 5)

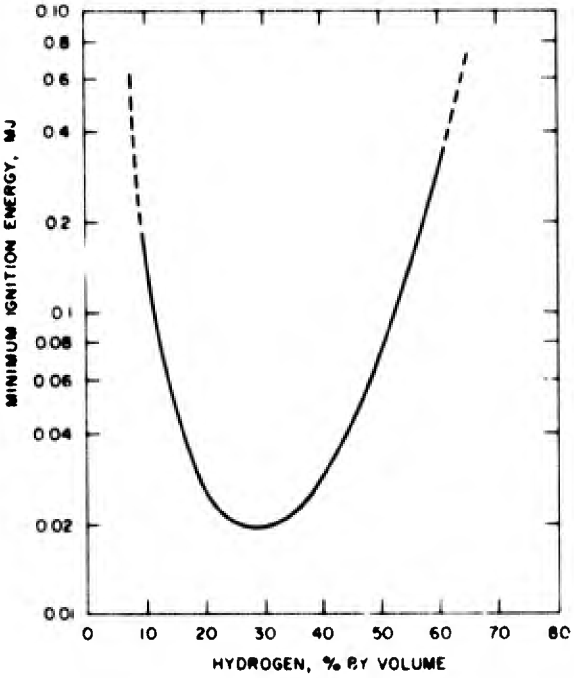


Figure 6
Minimum Spark Ignition Energy
Versus Hydrogen-Air Concentration
(References 11 and 15)

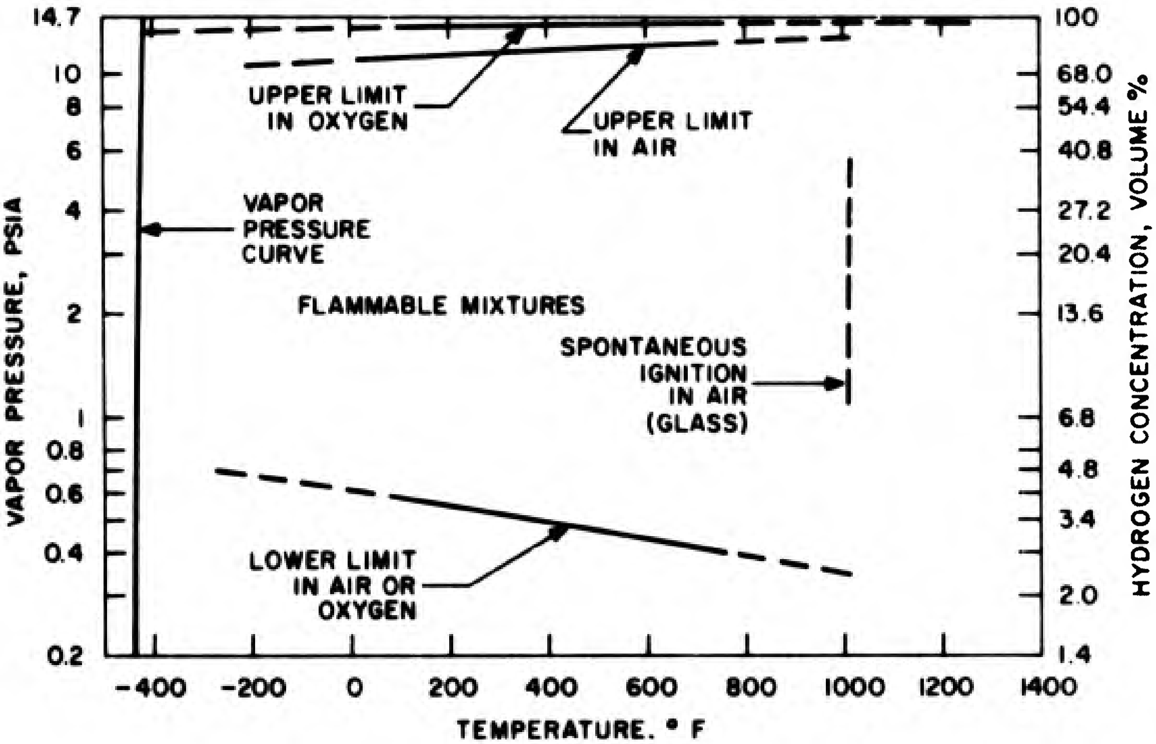


Figure 7 - Flammability Limits of Hydrogen
in Air or Oxygen as a Function of Temperature
(Reference 16)

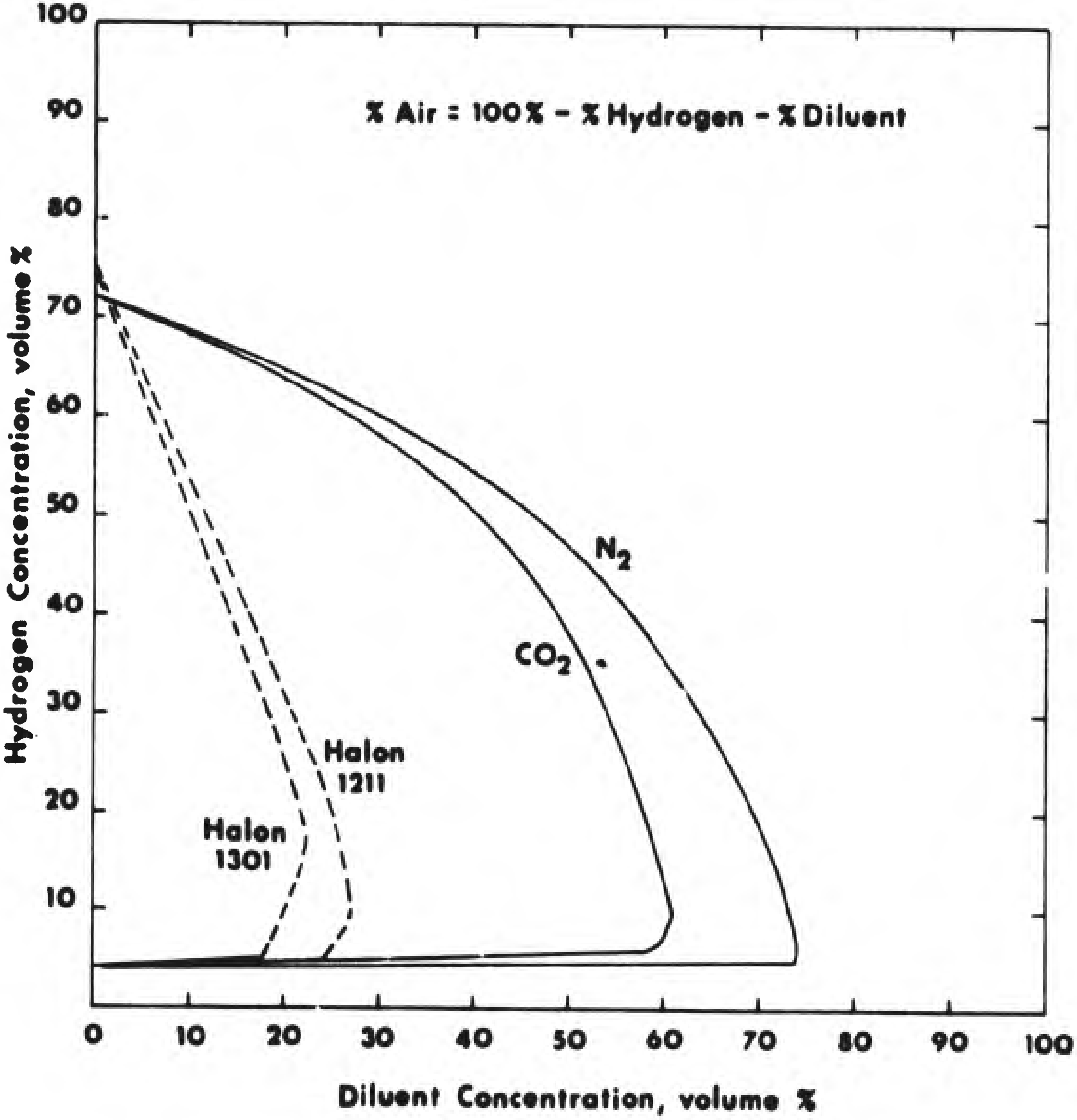
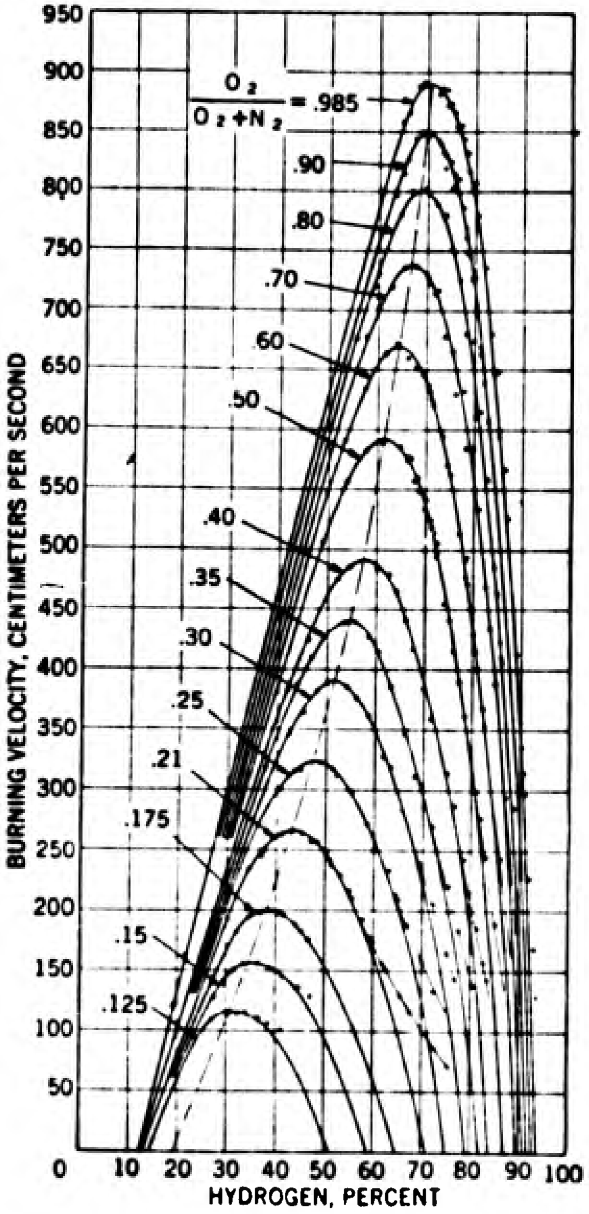


Figure 8 - Effects of Diluents on the Flammability Limits of Hydrogen in Air (References 14 and 18)



Courtesy of Academic Press,
New York

Figure 9 - Burning Velocity of Hydrogen-Oxygen-Nitrogen Mixtures (Reference 19)

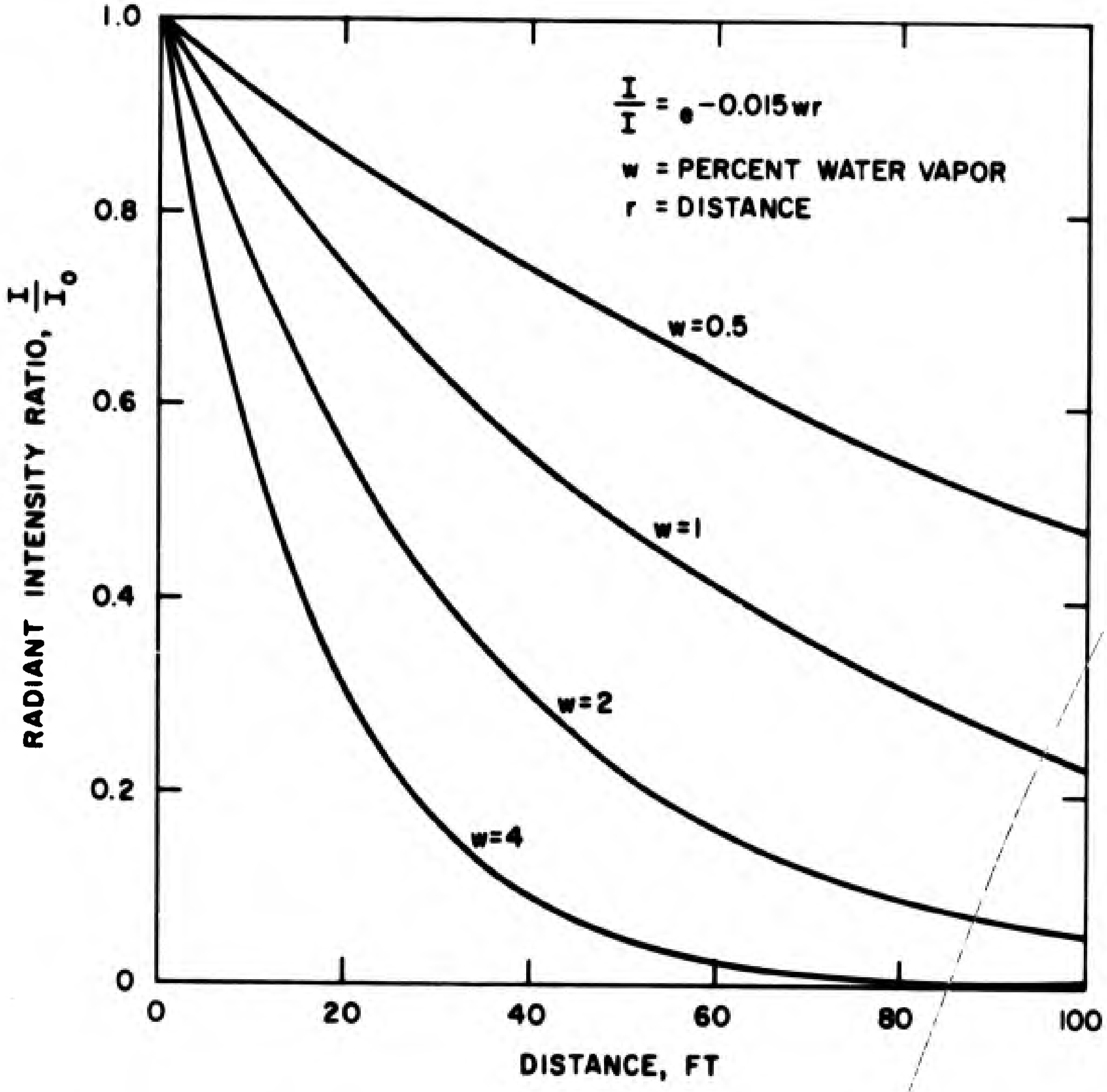


Figure 10 - Radiant Intensity Ratio Versus Distance from a Hydrogen Fire for Various Concentrations of Atmospheric Water Vapor

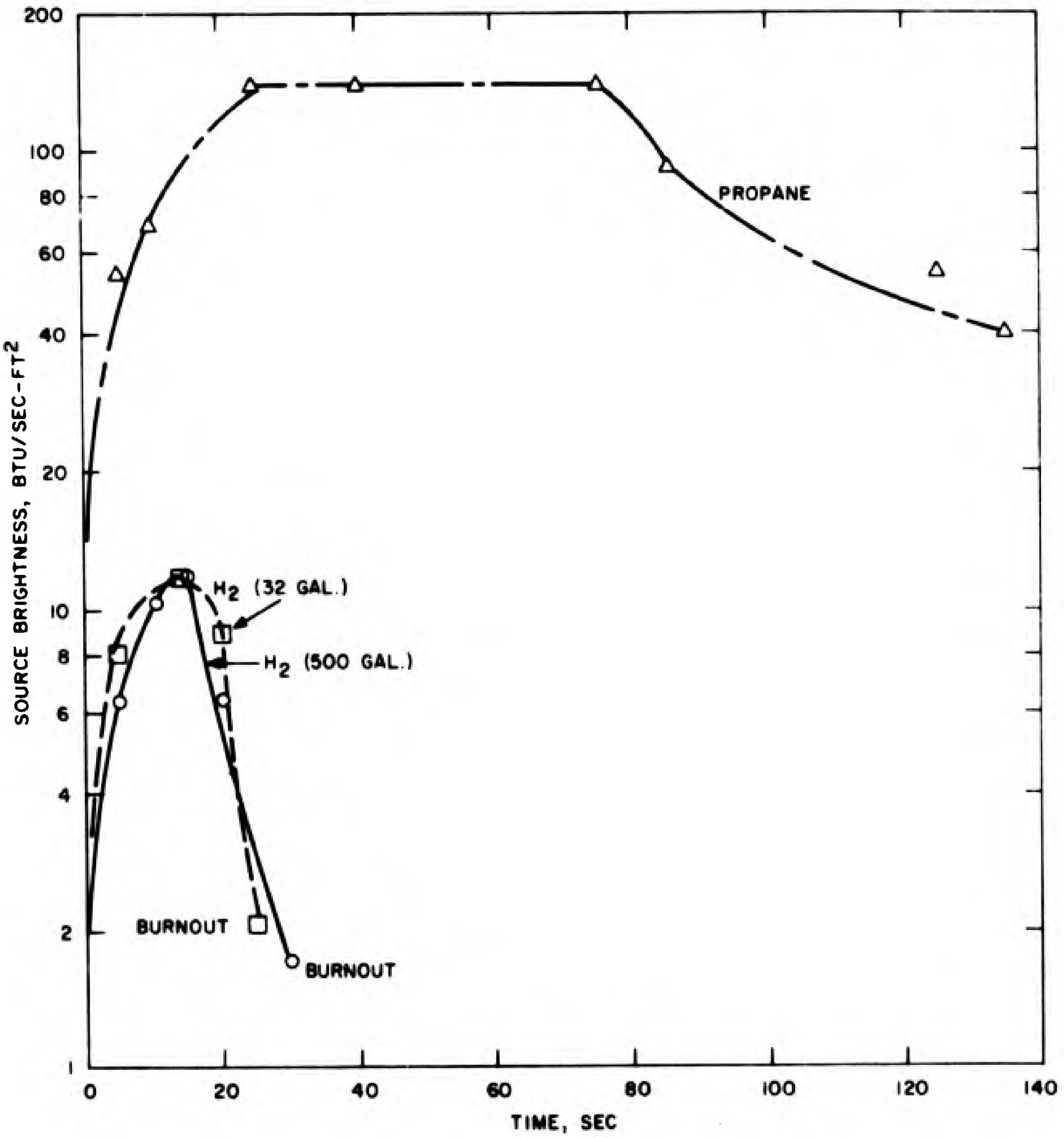


Figure 11 - Comparison of Radiation Flux from Hydrogen Flames and Propane Flames Versus Time (Reference 5)

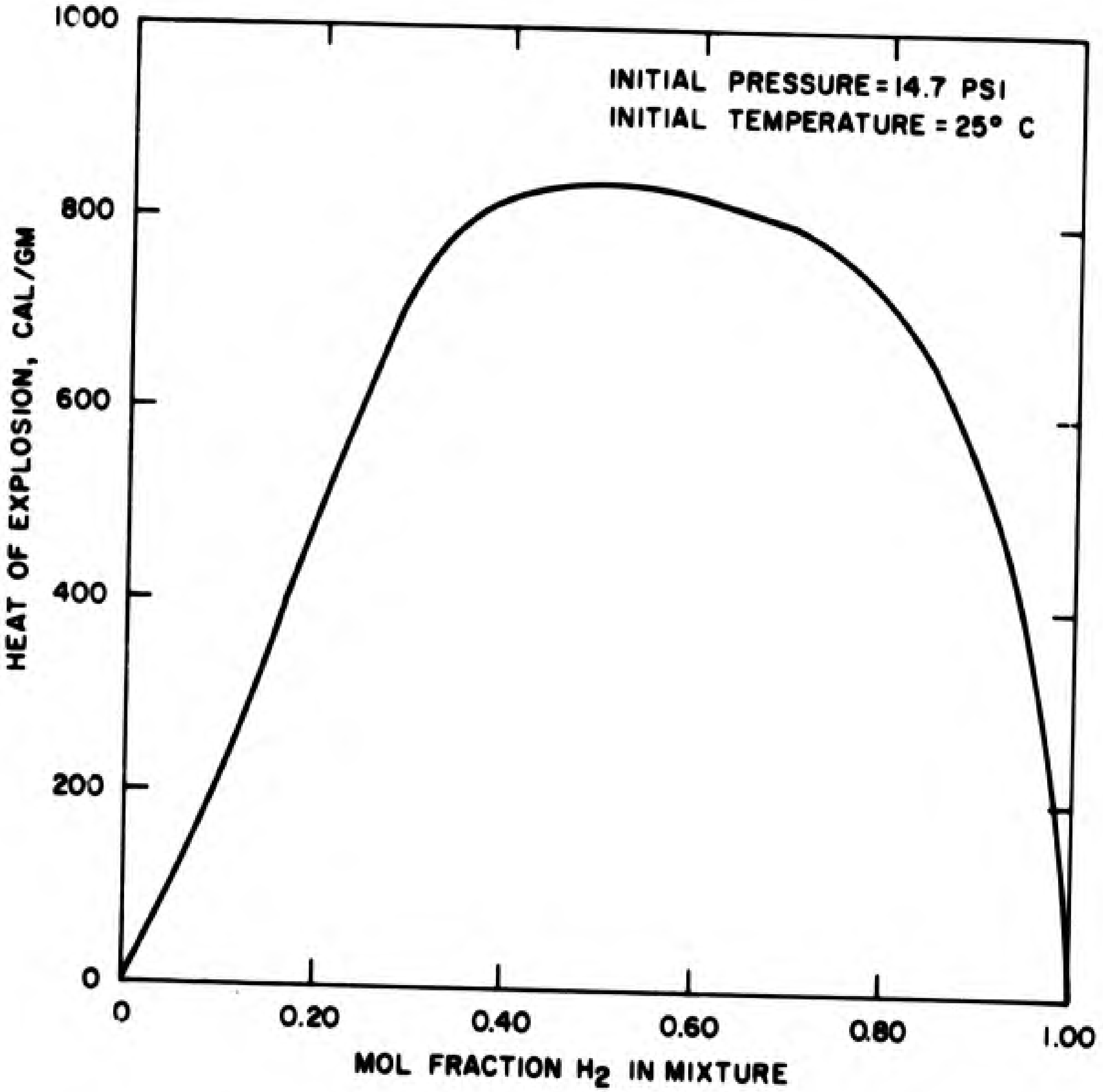


Figure 12 - Theoretical Heat of Explosion Versus Hydrogen-Air Concentration (Reference 5)

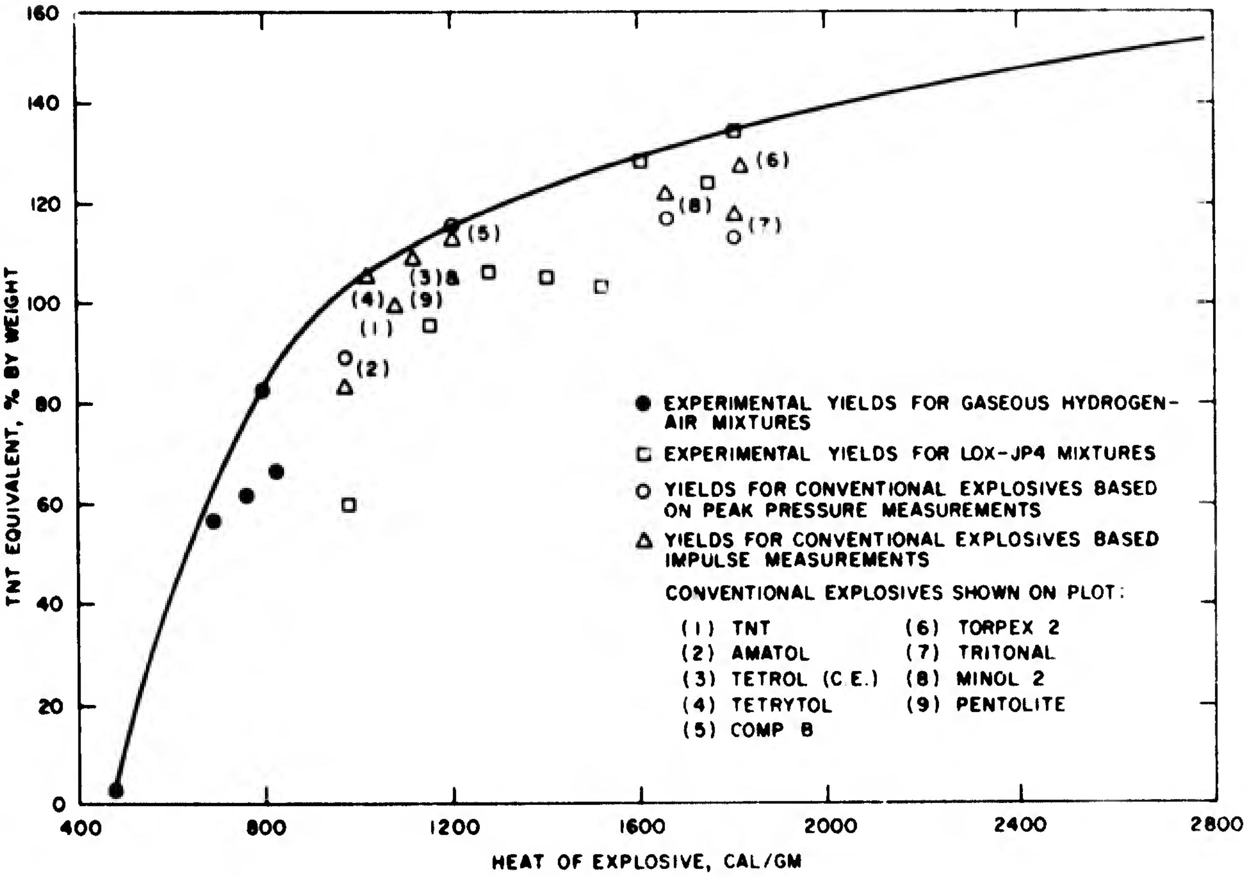


Figure 13 - Relative Yield of Explosives as a Function of Their Heats of Explosion (Reference 25)

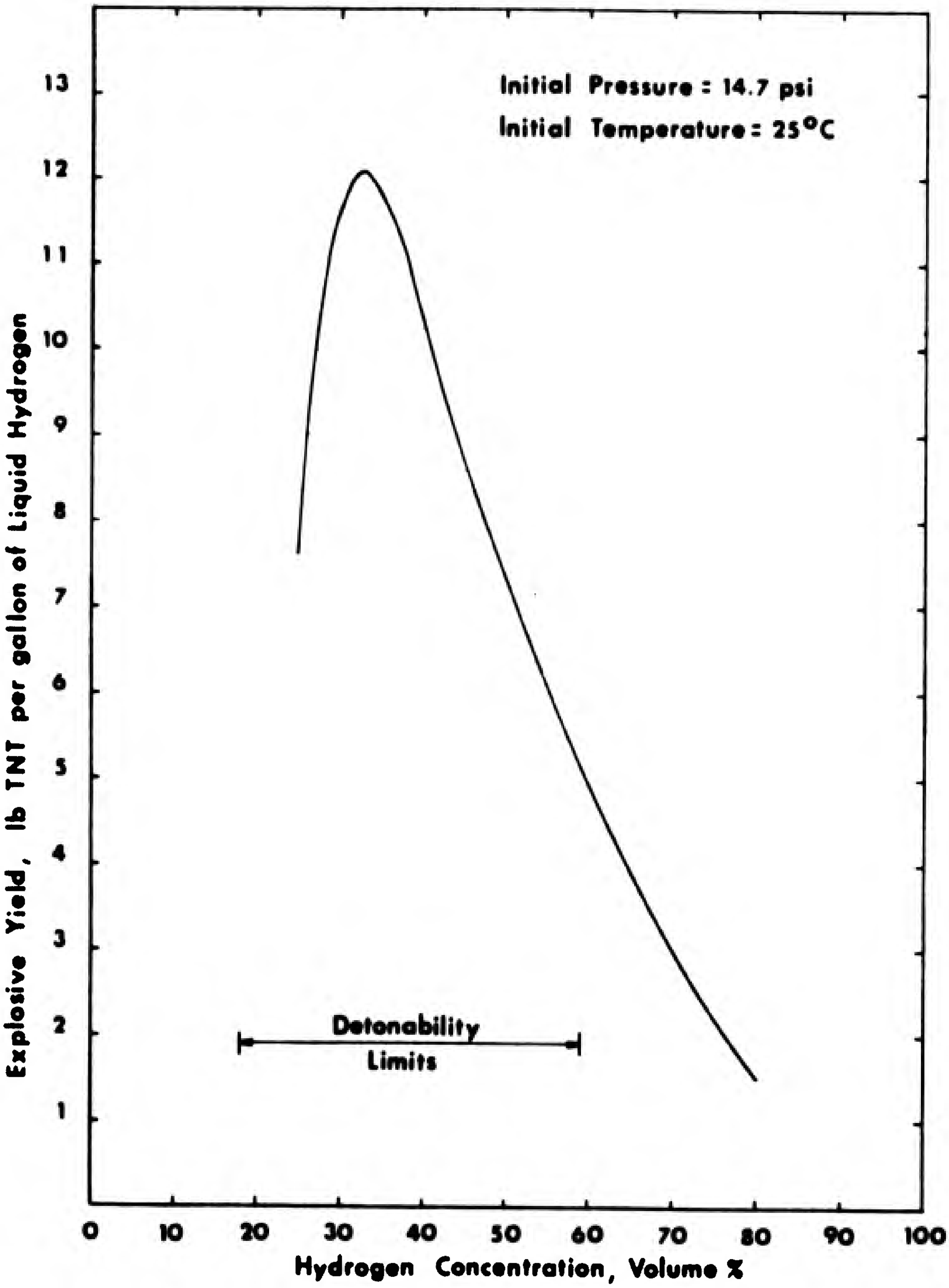
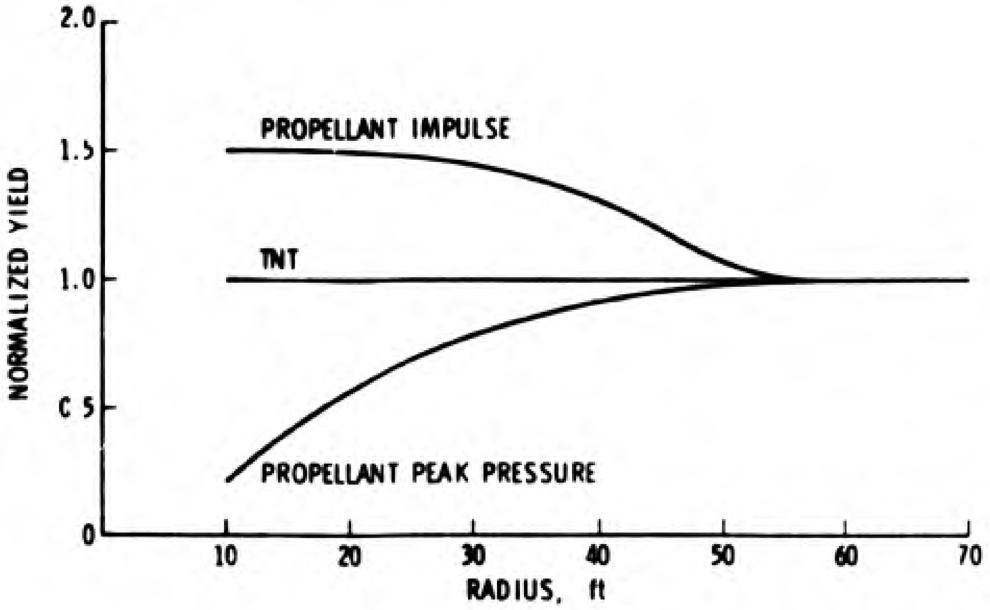


Figure 14 - Theoretical Explosive Yield Versus Hydrogen-Air Concentration (Reference 5)

Item (a) - Typical Differences in Peak Pressure and Impulse Yields as a Function of Distance from the Explosion



Item (b) - Comparative Change in Impulse with Increasing Distance (a to d) from the Explosion

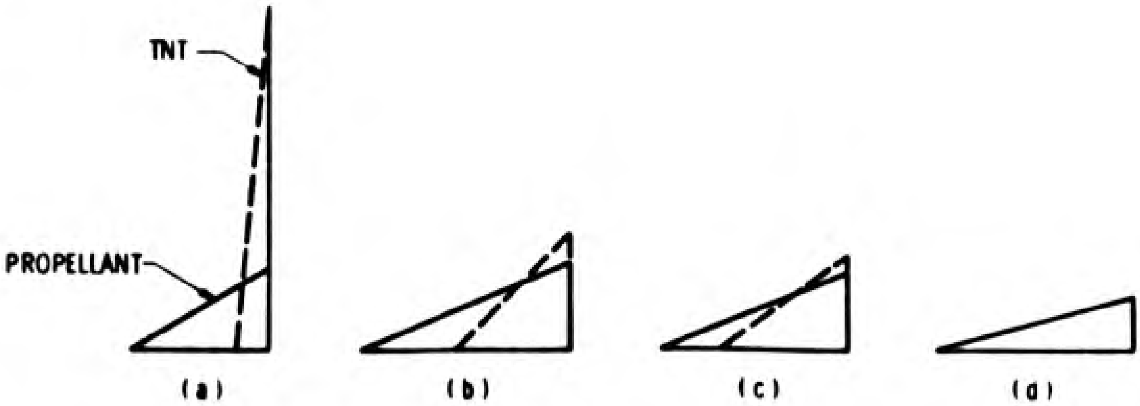


Figure 15 - Comparison of the Characteristics of Liquid Propellant and TNT Blast Waves (References 26 and 28)

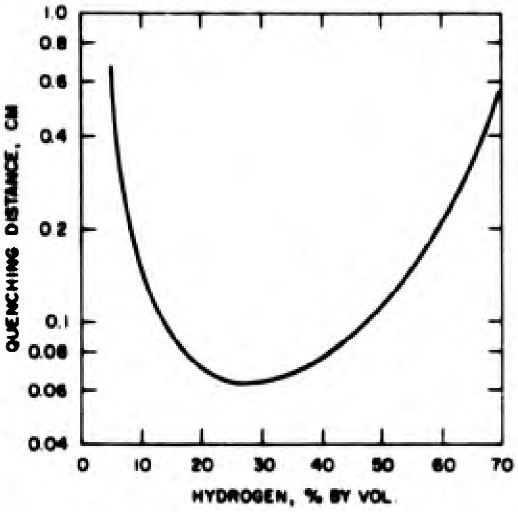


Figure 16
Quenching Distance Versus
Hydrogen-Air Concentration
(Reference 11)

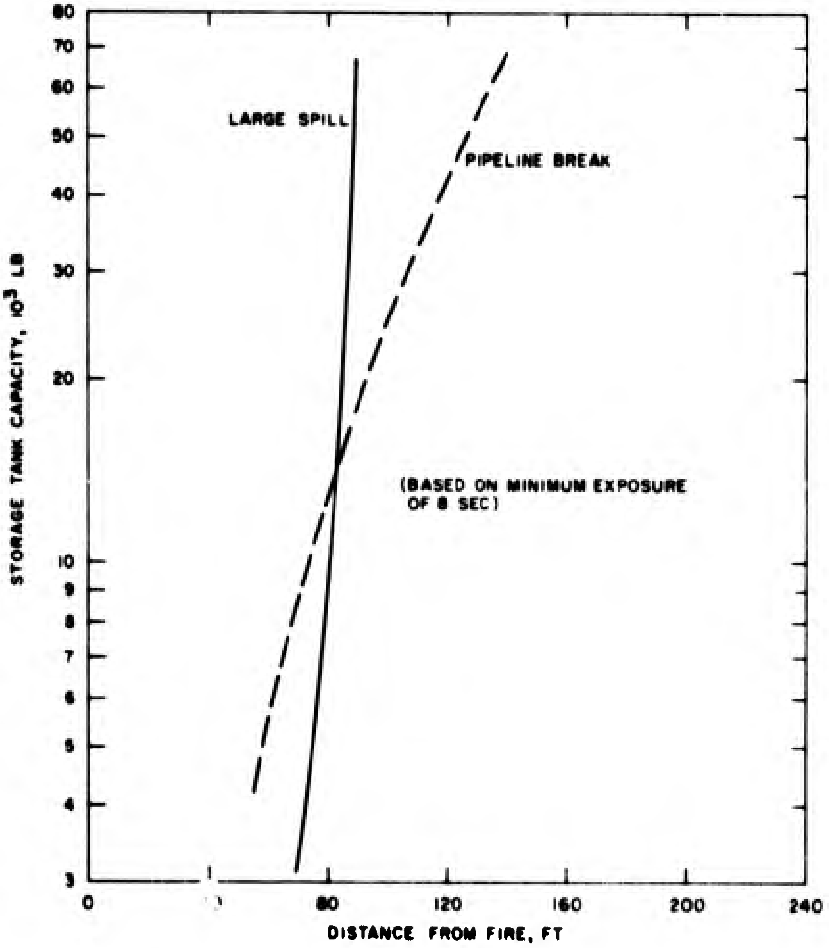


Figure 17 - Estimated Distance in Which Thermal Injury from Various Hydrogen Fires Would be Suffered by Unprotected Personnel (Reference 5)

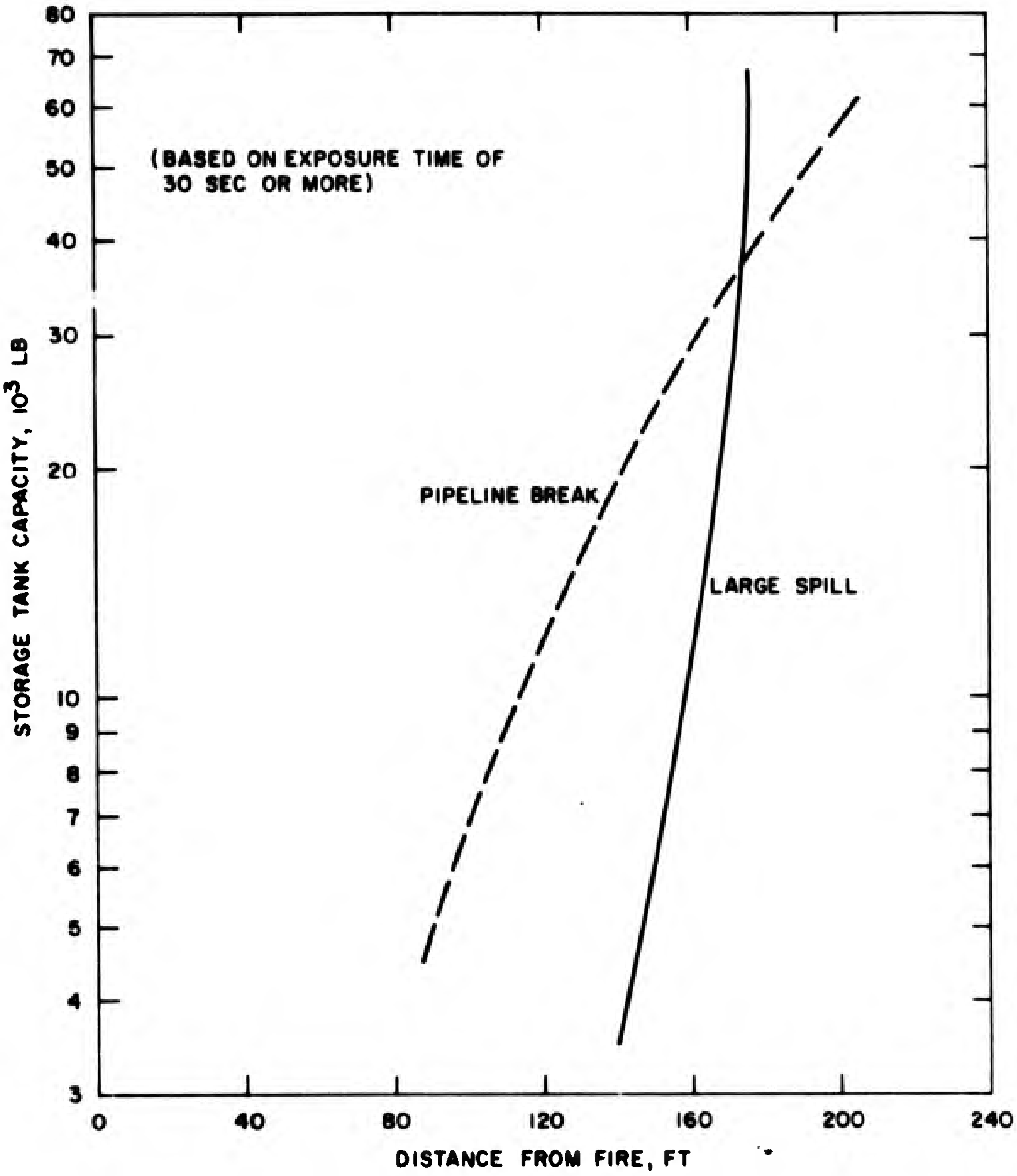


Figure 18 - Recommended Safe Distance for Unprotected Personnel During Various Hydrogen Fires (Reference 5)

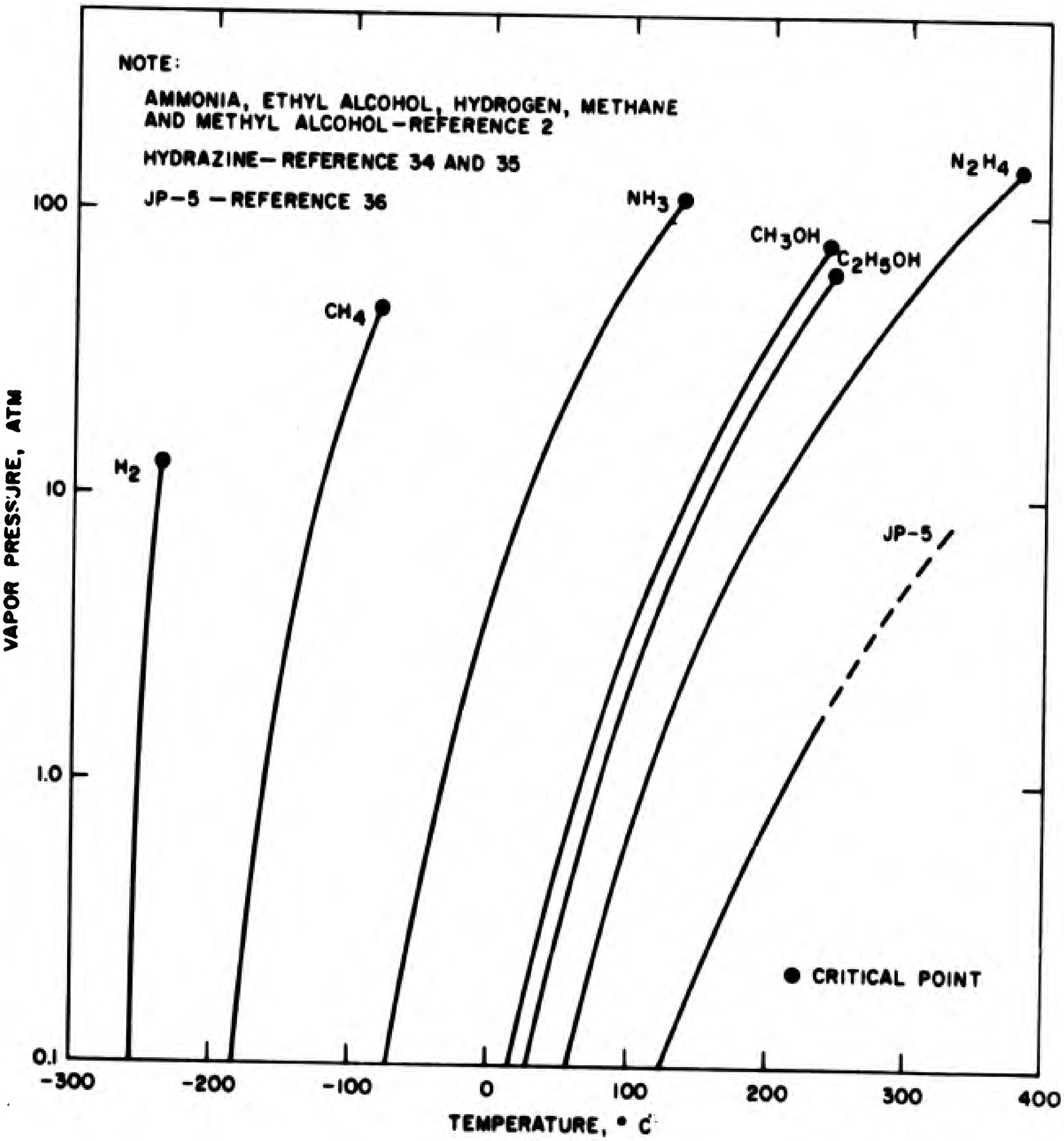


Figure 19 - Vapor Pressure of Various Fuels Versus Temperature

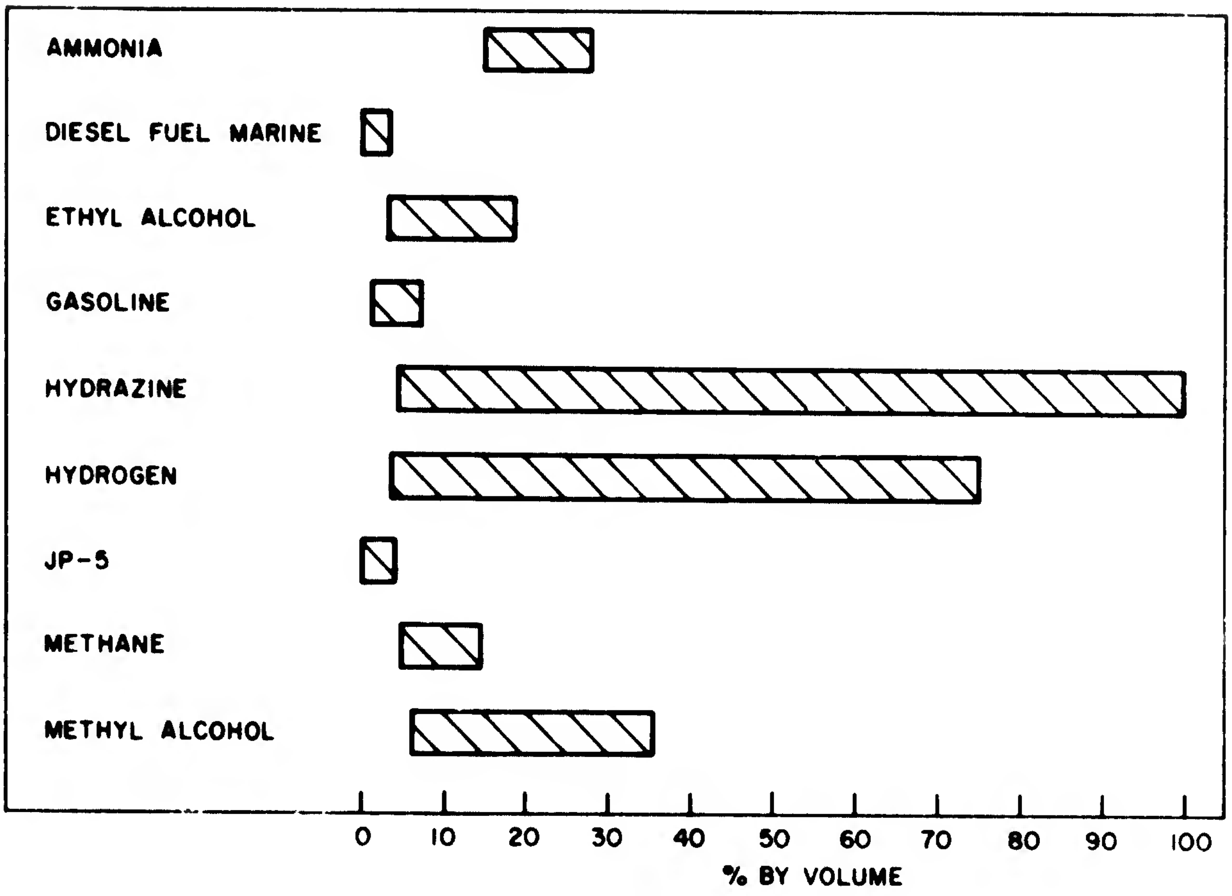


Figure 20
Flammability Limits of Various Fuels in Air

APPENDIX A
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