

Special Project

Fire, Explosion, Compatibility, and Safety Hazards of Hypergols - Monomethylhydrazine

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Special Project Report

Fire, Explosion, Compatibility, and Safety Hazards of Hypergols - Monomethylhydrazine

Sponsored by

American Institute of Aeronautics and Astronautics

Approved

Abstract

This Special Project report presents information that designers, builders, and users of monomethylhydrazine systems can use to avoid or resolve monomethylhydrazine hazards. Pertinent research is summarized, and the data are presented in a quick-reference form. Further information can be found in the extensive bibliography.

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Contents

Foreword.....vi

Acronyms.....vii

Glossary viii

Trademarks.....xii

1 Introduction..... 1

1.1 About this special report..... 1

1.2 Hazard assessment 2

2 Fire hazards 4

2.1 Assessing MMH fire hazards 4

2.2 Criteria 4

2.2.1 Vapor flammability limits..... 4

2.2.2 Liquid flash and fire points..... 6

2.2.3 Ignition sources..... 6

2.3 Effects..... 8

2.3.1 MMH reaction products 9

2.3.2 Vapor flame speed..... 10

2.3.3 Liquid burning rate 13

2.4 Data 14

2.4.1 Vapor 14

2.4.2 Liquid 17

2.4.3 Ignition 18

2.5 Assessment example 22

3 Explosion hazards..... 23

3.1 MMH deflagration 24

3.1.1 MMH deflagration assessment 24

3.1.2 MMH deflagration criteria 25

3.1.3 MMH deflagration effects 26

3.1.4 MMH deflagration data..... 27

3.2 Exothermic reaction 28

3.2.1 Exothermic reaction assessment 28

3.2.2 Exothermic reaction criteria 29

3.2.3	Exothermic reaction effects	29
3.2.4	Exothermic reaction data.....	31
3.3	Detonation	31
3.3.1	Detonation assessment.....	31
3.3.2	Detonation criteria.....	33
3.3.3	Detonation effects	36
3.3.4	Detonation data	37
3.4	Assessment examples	38
3.4.1	Deflagration assessment example	38
3.4.2	Detonation assessment example	40
4	MMH and material compatibility	40
4.1	Material degradation	41
4.1.1	Material degradation assessment	41
4.1.2	Material degradation criteria	41
4.1.3	Material degradation effects	41
4.1.4	Material degradation data.....	42
4.2	MMH degradation	42
4.2.1	MMH degradation assessment	42
4.2.2	MMH degradation criteria	43
4.2.3	MMH degradation effects	44
4.2.4	MMH degradation data.....	46
4.3	Assessment example	58
5	Safety.....	60
5.1	MMH toxicity.....	61
5.1.1	Results of MMH exposure	62
5.1.2	Inhalation.....	63
5.1.3	Dermal exposure.....	64
5.1.4	Ingestion.....	65
5.1.5	Developmental toxicity	65
5.1.6	Carcinogenicity	65
5.1.7	Relative toxicity of MMH to other hydrazines.....	66
5.2	MMH exposure guidelines	66

5.2.1	Threshold limit values of the American Council of Governmental Industrial Hygienists.....	66
5.2.2	Guidelines of the Occupational Safety and Health Administration	67
5.2.3	Guidelines of the National Institute of Occupational Safety and Health.....	68
5.2.4	Emergency planning requirements	68
5.2.5	Spacecraft maximum acceptable concentrations.....	68
5.3	MMH exposure remediation and control.....	69
5.3.1	First aid	69
5.3.2	Personnel protection	71
5.3.3	Fire fighting.....	73
5.3.4	Spill cleanup	73
5.4	MMH handling	74
5.4.1	Engineering design	74
5.4.2	Storage containers.....	75
5.4.3	Storage areas	75
5.4.4	Shipping	76
5.4.5	Monitoring equipment.....	76
5.4.6	Waste disposal	80
5.4.7	Regulatory requirements	80
5.4.8	Additional information.....	81
5.5	Assessment example	81
	Annex A: Hazard assessment example	85
	Annex B: Chemical and physical properties of monomethylhydrazine	94
	Annex C: Rapid compression experimental measurements.....	99
	Annex D: References.....	101

Foreword

Monomethylhydrazine (MMH) is a colorless, corrosive, strongly reducing liquid compound. It is used chiefly in aerospace propulsion and power systems. It is currently used in the Space Shuttle as a fuel for the orbital maneuvering system and reaction control system. Although MMH is immensely useful in aerospace applications, there are also drawbacks. For example, MMH vapor in air is flammable and detonable; both liquid and vapor MMH are corrosive, react with many materials, and are susceptible to catalytic decomposition; and MMH is highly toxic. The users and designers of MMH systems must be aware of these hazards and safeguard against them. The goal of this document is to summarize the existing hazards data into one document. The subjects addressed in this document are fire, explosion, compatibility hazards, and overall safety considerations.

Although a substantial amount of information has been compiled, testing in several areas is still being conducted and will continue for several years. In the interest of safety, the need for such a document is immediate. Therefore, this document will be released with the currently compiled information and will be periodically updated as new data are obtained.

The authors of the NASA manual, dated May 3, 1993 were Stephen S. Woods, Radel L. Bunker, Nathalie B. Martin, Donald B. Wilson, and David L. Baker.

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Acronyms

A, E _a	Arrhenius parameters
ACGIH	American Conference of Governmental and Industrial Hygienists
AIT	Autoignition temperature
AHJ	Authority Having Jurisdiction
ASME	American Society of Mechanical Engineers
ASTM	American Society of Testing and Materials
C-J	Chapman-Jouguet
CPIA	Chemical Propulsion Information Agency
DDT	Deflagration to detonation transition
DOT	Department of Transportation
EPA	Environmental Protection Agency
GI	Gastrointestinal
HAZMAT	Hazardous Materials
HZ	Hydrazine
IDLH	Immediately Dangerous To Life or Health
LEPC	Local Emergency Planning Committee
LFL and UFL	Lower and Upper Flammability Limit
MIE	Minimum Ignition Energy
MMH	Monomethylhydrazine
MSDS	Material Safety Data Sheet
NIOSH	National Institute of Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limits
RCRA	Resource Conservation and Recovery Act
REL	Recommended Exposure Limit
SARA	Superfund Amendments and Reauthorization Act
SERC	State Emergency Response Commission
SI	International System units
SMAC	Spacecraft Maximum Acceptable Concentration
STEL	Short Term Exposure Limit
TLD-1	Toxic Level Detector 1
TLV	Threshold Limit Value
TLV-TWA	Threshold Limit Value - Time Weighted Average
TOMES	Toxicology, Occupational Medicine, and Environmental Series
TRACE	Toxic Release Analysis of Chemical Emissions
TSCA	Toxic Substances Control Act

Glossary

Activation Energy (or Apparent Activation Energy): In absolute-rate theory, the energy associated with the formation of an activated complex intermediate between the reactant(s) and product(s) of an elementary reaction. An “apparent” activation energy is used as the parameter E_a in an Arrhenius function when the exact kinetic mechanism is unknown.

Adiabatic: A process in which the system changes state without thermal energy exchange between the system and the surroundings.

Adiabatic Compression: Mechanical work transferred to a system under conditions where there is an increase in the internal energy of the material for a static system or an increase in the enthalpy for a dynamic system. If the process is also reversible (in the thermodynamic definition), this change is also isentropic.

Adiabatic Factor: The temperature change that occurs when all the limiting reactant is completely consumed (normalized extent of reaction equals 1, when the reaction system is operated adiabatically). This factor is useful for comparing exothermicity or endothermicity of several reactions.

Adiabatic Flame Temperature: The temperature of thermodynamic equilibrium in a reaction or in a set of reactions that occurs in a process operating adiabatically.

Arrhenius Function: A mathematical model for defining the temperature dependency of an observed macroscopic kinetic reaction rate—the rate is proportional to $\exp(-E_a/RT)$, where E_a is the apparent activation energy, R is the ideal gas law constant, and T is the absolute temperature.

Authority Having Jurisdiction (AHJ). The AHJ is the organization, office, or individual responsible for “approving” equipment, an installation, or a procedure. The designation is used in a broad manner because jurisdiction and “approval” agencies vary as do their responsibilities. Where public safety is primary, the AHJ may be a federal, state, local, or other regional department or individual such as a fire chief, fire marshal, chief of a fire prevention bureau, labor department, health department, building official, electrical inspector, or others having statutory authority. For insurance purposes, the AHJ may be an insurance inspection department, rating bureau, or other insurance company representative. In many circumstances the AHJ is the property owner or his designated agent. At government installations, the AHJ may be the commanding officer or a designated departmental official.

Autoignition Temperature: The lowest temperature at which a material will spontaneously ignite. No additional ignition energy (ignition source) is required.

Burning Rate: The rate of liquid mass consumption per unit area ($\text{kg}/(\text{m}^2\cdot\text{s})$).

Burning Velocity: The velocity at which the liquid level decreases. It is the burning rate/density of the liquid (m/s).

Catalyst: A chemical compound or chemical species that alters the rate of a chemical reaction. The catalyst is not altered by the reaction.

Cell Size: Refers to the width of the characteristic fish scale-shaped cell pattern etched on a smoked foil during a gas-phase detonation. The cell pattern is produced by a detonation (the path of the triple-point intersection of the primary shock wave, the transverse shock wave, and the Mach stem wave. The cell width is used as a parameter for characterizing detonations.

Chapman-Jouguet (C-J) Detonation: Describes a stable detonation state that is consistent with most experimental measurement. The steady-state solution of the conservation equations at which the Rankine line is tangent to the Hugoniot curve.

Compatibility with MMH: Materials should not corrode, deform, or lose strength when in prolonged contact with MMH.

Critical Diameter: The tube diameter necessary for a gaseous detonation to propagate from the tube to an unconfined environment (Equation 3.6, $d_c = 13\lambda$).

Critical Energy: The minimum energy required to initiate an unconfined detonation in a specified mixture.

Deflagration: A flame moving through a flammable mixture in the form of a subsonic wave (with respect to the unburned mixture).

Dermal Exposure: The penetration of a toxic chemical through skin and into the blood stream. Such exposure can be rapid and difficult for the body to eliminate.

Detonable Mixture: The state of a specified mixture that, upon application of the critical energy for the mixture, will initiate and sustain a detonation. This mixture is also flammable.

Detonation: Exothermic chemical reaction coupled to a shock wave that propagates through a detonable mixture. The velocity of the shock wave is supersonic with respect to the unburned gases. After initiation, the thermal energy of the reaction sustains the shock wave, and the shock wave compresses the unreacted material to sustain the reaction. Initiation of a detonation can occur with a deflagration to detonation transition (DDT).

Diluent: In a mixture, an inert material that reduces the concentration of the remaining materials.

Dynamic Parameters: Four parameters (detonability limits, initiation energy, cell size, and critical tube diameter) used to describe the dynamic characteristics of a detonation. They are in contrast to the static C-J detonation parameters: velocity, detonation temperature, detonation pressure, and detonation density.

Equivalence Ratio: The ratio of the actual fuel-oxidizer ratio to the stoichiometric fuel-oxidizer ratio.

Exothermic: The production of thermal energy by a chemical reaction.

Explosion: The rapid equilibration of pressure between the system and the surroundings, such that a shockwave is produced. Explosions may occur through mechanical failure of vessels containing high-pressure fluids or through rapid chemical reactions producing large volumes of hot gases.

Explosion Potential: A parameter that is useful for comparing an unknown system (reaction) to well-known reactions. It is the product of system volume (constant), adiabatic flame temperature, total moles per unit of mass in the system at equilibrium, and the ideal gas law constant.

Fire: Sustained burning, as manifested by any or all of the following: light, flame, heat, and smoke (ASTM E 176-90).*

Fire Point: The lowest temperature at which a flame continuously exists over a liquid surface upon ignition by an open flame.

*ASTM Fire Test Standards, 3rd Ed. 1990, ASTM, 1916 Race St., Philadelphia, PA 19103.

Flame: A hot, usually luminous zone of gas, or particulate matter in gaseous suspension, or both, that is undergoing exothermic chemical reaction. A flame may be stationary with the flammable mixture fed into the reaction zone, or a flame may propagate through the flammable mixture, as in a deflagration.

Flame Speed or Flame Velocity: Refers to the velocity of propagation of the reaction zone through the flammable mixture, as measured by a stationary observer. Usually measured at the front of the flame.

Flammability Limits: The lower (LFL) and upper (UFL) vapor concentrations (usually reported as volume percent) of fuel in a flammable mixture that will ignite and propagate a flame. These limits are functions of temperature, pressure, diluents, and ignition energy.

Flash Point: The lowest temperature, corrected to 101.3 kPa (14.7 psia) of pressure, of a material at which application of an ignition source causes the vapor of the material to ignite momentarily under specified conditions.

Froth: The froth is a medium in which gas bubbles are surrounded by a thin film of liquid hydrazine, maximizing the surface area between the ullage gas and the liquid hydrazine.

Halocarbons: Organic compounds containing one or more of the elements fluorine, chlorine, bromine, and iodine.

Hazard: Existing or potential condition that can result in or contribute to a mishap.

Heat Generation Potential: The product of the temperature sensitivity and the adiabatic factor. A useful dimensionless group for characterizing and comparing reactions.

Heat of Reaction: For a given temperature and pressure, the enthalpy of the products of a reaction minus the enthalpy of the reactants.

Hypergolic: Spontaneous ignition upon contact of two materials upon contact (no additional ignition energy is required).

Ignition: Introduction of sufficient energy into a flammable mixture or material to produce a flame.

Ingestion: The introduction of a toxic material into the body through the mouth or by breathing.

Material Compatibility: Materials are considered compatible with each other if their rate of degradation when in contact is insignificant for the application.

Minimum Ignition Energy: The minimum energy required to ignite a flammable mixture under given conditions (temperature, pressure, diluents).

Monopropellant: A liquid propellant that decomposes exothermically to produce hot gases; e.g., hydrogen peroxide, hydrazine.

Order of Reaction: A parameter used to define the concentration (or pressure) dependency of the kinetic rate of reaction. For elementary reactions, the order coincides with the molecularity (for $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ the forward reaction rate is second order, the $R_{\text{forward}} \propto \{\text{Conc. H}_2\}^m \times \{\text{Conc. I}_2\}^k$ where $m=1$ and $k=1$. The overall order of reaction $n = m + k = 2$ for this example.

Oxidizer: Primarily air, oxygen, halogens, the hypergolics (N_2O_4 or fuming nitric acid) or any material that undergoes a reduction in chemical terms (will readily accept electrons from the fuel).

Permissible Exposure Limit (PEL): The degree of exposure of workers to hazardous gases and vapors is regulated by the Occupational Safety and Health Administration (OSHA). The regulation specifies permissible exposure limits (PELs) that for MMH includes a ceiling limit (employee exposure not to be exceeded during any part of the work day) of 0.2 ppm (0.35 mg/m³) and a skin designation that requires the use of protective clothing and equipment. For more information, see Section 5.2.2.

Pool Fire: Used to describe the sustained burning of a pool of liquid fuel. The rate of burning, called burn rate, is measured in terms of depth change/time or mass loss/time.

Shock: A violent collision or impact and the subsequent transmission of energy through the system. The energy moves as a wave at velocities greater than the speed of sound relative to the undisturbed material.

Spacecraft Maximum Acceptable Concentration (SMAC): The maximum allowable concentration for spacecraft applications, typically based on standards and requirements for ground applications. For specific SMACs see Section 5.2.5.

Temperature Sensitivity: A measure of the response of reaction rate to temperature, E_a/RT^2 (E_a = activation energy; R = gas constant; T = temperature).

Thermal Runaway: Operation of a system that contains material which reacts exothermically, in a manner that the rate of thermal energy generation exceeds the rate at which thermal energy is transferred to the surroundings. The system temperature increase can lead to an increase in this imbalance and then lead to autoignition of the reaction.

Threshold Limiting Value: The average concentration of toxic gas to which most workers can be exposed during working hours (8 hours per day, 5 days per week) for prolonged periods without adversely affecting their health.

Toxic: Poisonous. A material that causes physiological damage to the body.

Ullage: The vapor space above the liquid surface within the system.

Vapor: A component in the gas phase that is in equilibrium with its corresponding liquid phase. The temperature of the system must be below the critical temperature of the component so it can exist as a liquid phase.

Trademarks

The following commercial products that require trademark designation are mentioned in this document. This information is given for the convenience of users of this special report and does not constitute an endorsement. Equivalent products may be used if they can be shown to lead to the same results.

Apiezon
Autospot
Cabot Alloy
Chemglaze
Chemturion
Ecolyzer
Freon
GASBADGE
Grafoil
Graphitar
Hastelloy
Haynes
Inconel
Inconel X-750
Interscan
Kalrez
Kel-F
Koropon
Krytox
Kynar
MACOR
Microseal
Mobil Jet Oil II
Monitox
Mykroy/Mycalex
Mylar
Permendur
Pyrex
Pyromet
Ryton
SCAPE
SCAN Kit
Splash Suit
Stoody 6
Stycast
Teflon
Tefzel
Vacomax
VYDAX
Waspaloy

1. Introduction

Monomethylhydrazine (MMH, $\text{CH}_3\text{N}_2\text{H}_3$) is used as an aerospace fuel and an antioxidant in industrial processes and is used in the production of pesticides and pharmaceuticals. MMH is a strong reducing agent, weakly alkaline, and very hygroscopic. MMH readily reacts with a variety of organic, inorganic, and metallic compounds. The principal MMH reactions of interest include decomposition reactions, reaction with dinitrogen tetroxide, reaction with carbon dioxide, and reaction with oxygen. Its chemical characteristics are such that it presents fire, explosion, material compatibility and safety hazards for the user to evaluate. For example, Table 1 gives relative values for the explosion potential (Rase 1977) for several materials and MMH. Clearly MMH needs to be treated as a hazardous material.

Table 1 — Typical explosion potentials^a

System	Initial conditions	Adiabatic flame temp K	Explosion potential, EP atm/g/cm ³
Acetylene + Stoichiometric O ₂	Gases, 298 K, 1 atm	3979	13800
Propane + Stoichiometric O ₂	Gases, 298 K, 1 atm	3633	13150
High Ammonium Nitrate Explosive	Room temp, 1 atm	2325	28600
60% Gelatine Dynamite	Room temp, 1 atm	3186	38900
MMH (decomposition)	Vapor, 361 K, 1 atm	951	6300
MMH + Stoichiometric Air	Vapor, 301 K, 1 atm	2328	11580
MMH + Stoichiometric O ₂	Liquid, 361 K, 1 atm	3058	41820
^a Rase 1977			

1.1 About this special report

This special report presents available information for hazard assessment in applications of MMH. All literature sources are referenced so the user can verify original sources as deemed necessary. As research provides new data on the hazards of MMH, this special report will incorporate the information. Revisions will be published to maintain a complete, up-to-date source for MMH hazard assessment.

Readers are cautioned that, although every reasonable effort has been made to present accurate information in this special report, the authors and publishers make no warranty nor do they assume legal responsibility for its accuracy. Readers are urged to assess each situation carefully and to choose data that appear most appropriate.

The Glossary contains definitions for some of the technical terms used in this special report.

Throughout this special report, the following conventions are used:

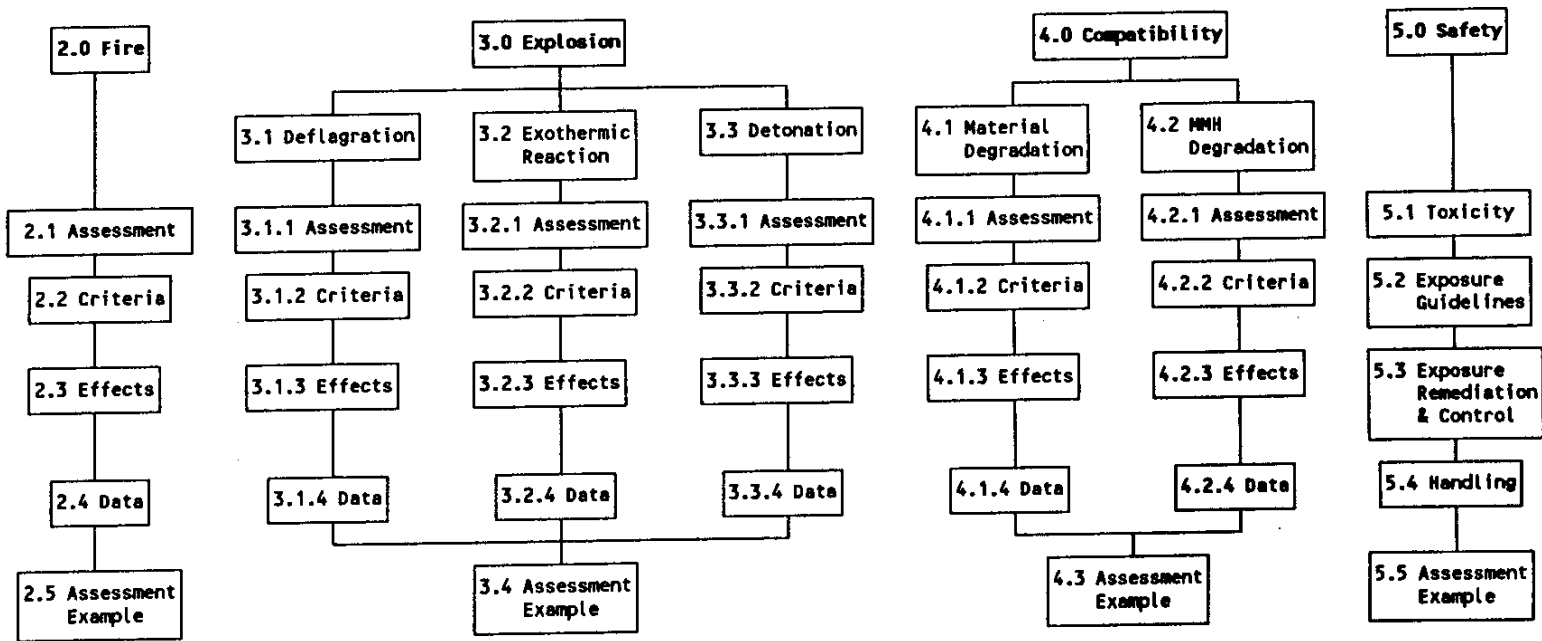
1. ambient pressure and temperature refer to a pressure of 101.3 kPa (14.7 psia) and a temperature of 298 K (77 °F),
2. neat MMH is free from contamination (considered 100-percent-by-weight MMH),
3. high-purity MMH contains a minimum of 99.0-percent-by-weight MMH and less than or equal to 0.005-percent-by-weight aniline,
4. propellant-grade MMH contains a minimum of 98.5-percent-by-weight MMH,
5. data are given in SI (International System) units with US customary units in parentheses,
6. unless otherwise specified, pressures given are total pressures.

1.2 Hazard assessment

Each design and potential application of MMH is a unique system for hazard assessment. Yet it is essential that the hazards associated with a process be known and quantified as much as possible. Only in this manner can sound decisions result. While many potential MMH applications may be covered by mandatory codes, e.g., National Electric Code, the fire codes of the National Fire Protection Association, the Occupational Safety and Health Act, and the regulations and standards of the Environmental Protection Agency, the decision maker has the responsibility for assuring accurate hazard assessment. It is to meet this responsibility that the material of this special report has been assembled.

The available information on MMH is presented under four categories: Fire, Explosion, Material Compatibility, and Safety. Each category of hazard has both “theory” and available “data” sections. The theory material is to help evaluate and assess whether the criteria for the hazard exist. The available data is to assist in determining the potential effects. The material presented includes thermodynamic calculations, experimental data, and literature values. No specific methodology for hazard assessment is presented, although each section provides appropriate examples. Risk assessment methodology is available from Rase (1977).

Figure 1 is a schematic representation of the topical sections of the special report for quick referencing.



2. Fire hazards

The precondition for a fire (a chemical reaction that releases heat and light (Lapedes 1974)) is the existence within a system* of a flammable material and an ignition source. MMH is a flammable material. MMH fires can occur when the MMH is a liquid, vapor, mist, droplet, or spray. As seen in Table 1, the adiabatic flame temperature of MMH decomposition (951 K (1252 °F)) is sufficient to ignite surrounding materials and produce a hazardous event, although it is much less than the corresponding temperature when MMH combusts with air (2328 K (3731 °F)). MMH also reacts on contact with dinitrogen tetroxide without an ignition source (a hypergolic mixture).

2.1 Assessing MMH fire hazards

The fire hazard assessment in this special report is divided into three steps:

- 1) Identify the system and the initial conditions.
- 2) Determine whether the criteria for a fire exist.
- 3) Evaluate the effects of fire.

To identify the system and the initial conditions, the user must determine the concentration (and phase) of MMH, the concentrations of all other chemicals, temperature, pressure, material components, materials of construction, and operating characteristics of process (its interaction with the surroundings). This step will not be discussed in further detail in this special report.

The criteria for a fire are met when an appropriate ignition source is present and either the gaseous and vapor mixtures are within their flammability limits or the liquids are above their fire points.

Flammability limits, fire points, and ignition energy are functions of concentration, temperature, pressure, vessel configuration, and flow rates (if applicable). Details of these criteria are discussed in Section 2.2.

When the conditions for a fire exist, the effect of a fire must be assessed by calculating the heat generation rate, potential rate of fire spread (flame speed), maximum system temperature, maximum system pressure, and potential effect, (whether it affects mechanical, electrical, instrumentation, or control components of the system and surroundings). The effects of MMH fires are discussed in Section 2.3.

Section 2.5 presents an example of assessing the MMH fire hazard in a typical system using of the material in the previous sections.

2.2 Criteria

A fire can occur with MMH vapor or liquid, and a fire can occur if MMH liquid is dispersed as a droplet, mist, or spray. This section presents a discussion of flammability limits, flash- and fire-points, and ignition sources.

2.2.1 Vapor flammability limits

Flammability limits are defined as the range of concentrations between a *Lower Flammability Limit* (LFL) and an *Upper Flammability Limit* (UFL), for a given temperature, pressure, diluent, and catalyst. Normally expressed as percentages by volume, the LFL and UFL refer to the most dilute and the most concentrated MMH vapor mixtures that will support a flame at given system conditions.

*For the purposes of this special report, a system is that portion of the universe under consideration, usually defined in terms of a piece of equipment or portion of a process, its contents, and conditions.

2.2.1.1 Temperature dependency

Generally, for gases and vapors, the flammability range increases as temperature increases (Glassman 1987). The increased range may result from a decrease in the LFL (Benz, Bishop, and Pedley 1988), or an increase in the UFL (Allison and Faeth 1972), or both.

2.2.1.2 Pressure dependency

Pressure below ambient narrows the flammability range (Coward and Jones 1952). As the pressure decreases, the two flammability limits approach each other until they become identical. When the LFL and UFL reach the same value, the flammability limits are said to have reached the *low pressure limit*. This limit refers to the minimum pressure for ignition. The low pressure limit, however, varies inversely with ignition energy; as ignition energy increases, this limit decreases (Benz, Bishop, and Pedley 1988).

2.2.1.3 Direction of flame propagation

The direction of flame propagation (upward or downward) has a significant effect upon flammability limits. Flame cannot propagate when opposing convection currents exceed the flame speed. The flammability range is narrower for downward propagation (Coward and Jones 1952) and are intermediate for lateral propagation. The flammability limits reported in this text assume upward propagation.

2.2.1.4 Vessel configuration dependency

Flammability limits vary with the shape of the confining container. One study involving tubes showed that the flammability range increased as the tube diameter increased (Coward and Jones 1952). This result was attributed to reducing the quenching effect of the tube walls. In another study with both open and closed tubes, the flammability range in closed tubes decreased as the tube length increased, but no change was observed in open tubes (Mullins and Penner 1959). The general effect that can be extrapolated from observations is that the quenching effect of vessel surfaces increases with a reduction in the surface-to-volume ratio.

2.2.1.5 Diluent dependency

Diluents such as nitrogen and helium generally reduce the flammability of MMH vapor. The ability of a diluent to quench MMH flames depends on its heat capacity and thermal conductivity. Diluents with large heat capacities generally have greater quenching ability than those with low heat capacities, and high thermal conductivity dissipates energy to the surroundings at a greater rate (Coward and Jones 1952). The flammability limits of the vapor above an MMH-water mixture are narrower than the LFL and UFL of the vapor above neat MMH liquid.

2.2.1.6 Mixture dependency

The composite flammability limits of MMH blended with a fuel* can be estimated by using the simple rule proposed by Le Chatelier and later modified by Coward and Jones (1952) (Equation 1):

$$\text{Composite } L = \frac{100}{c_1 / L_1 + c_2 / L_2 + c_3 / L_3 + \dots c_n / L_n} \text{ Percent} \quad (1)$$

*Flammability data for other hydrazine-type fuels are given in *Ignition and Thermal Hazards of Selected Aerospace Fluids* (Benz, Bishop, and Pedley 1988)

where

<i>Composite L</i>	= Composite value of the flammability limit (LFL or UFL)
$C_1, C_2, C_3, \dots, C_n$	= Concentration of each combustible (percent weight/volume) ($C_1 + C_2 + C_3 + \dots + C_n = 100$)
$L_1, L_2, L_3, \dots, L_n$	= Flammability limit for each combustible (percent volume/volume)

Le Chatelier's Rule gives only approximate limits; the flammability range for upward propagation may be underestimated significantly. Small amounts of one component can inhibit ignition of the major component, and the LFL can be lowered when the major component has a low LFL.

2.2.1.7 Material dependency

Many materials considered for use in construction of engineering systems are known to catalyze the decomposition of MMH or have been shown to catalyze the oxidation of MMH (Martin et al. 1989). The presence of this type of material changes flammability limits. Specific discussion is in Section 4.

2.2.2 Liquid flash and fire points

MMH liquid flash and fire points vary depending on whether the MMH vapor above the liquid surface is mixed with air, an inert gas, or other oxidizing atmosphere. The flash point of a liquid is the lowest temperature at which the liquid gives off enough vapor to form an ignitable mixture at or near its surface (Sax 1975). The American Society for Testing and Materials (ASTM) defines flash point as the lowest temperature at which a liquid gives off sufficient vapor to ignite in air at 101.3 kPa (14.7 psia) (Tag Closed-Cup (ASTM 1986b); Cleveland Open-Cup (ASTM 1986c)). A flame is usually used as the igniter. The flash point obtained with the closed-cup test almost corresponds to the LFL vapor concentration.

The fire point of a liquid is the lowest temperature at which fire continuously burns, in still air, over a liquid surface upon exposure to an ignition source (Scott, Burns, and Lewis 1949). A sustained fire may not occur at the flash point but will occur at the fire point.

2.2.2.1 Pool fires

In general, MMH liquid pool fires are influenced by temperature and wind. As the temperature exceeds the fire point, the vaporization rate increases, and the fire spreads rapidly. At temperatures well above the fire point, the effects of the vaporization rate on the spread rate are less dramatic (Botteri et al. 1966; Kuchta 1973). A strong wind can extinguish a burning pool, but larger pool diameters require greater wind velocity to extinguish the fire (Atkinson and Eklund 1971).

2.2.2.2 MMH and water

The flash and fire points of MMH-water mixtures increase with the percentage of water.

2.2.3 Ignition sources

Ignition of MMH vapor or MMH mixtures can occur through the system reaching the autoignition temperature (AIT) or through the introduction of energy greater than a specific minimum ignition energy (MIE). AIT ignition is characterized by an accelerating rate-of-temperature increase. MMH vapor or MMH mixtures could be reacting at a very slow rate. If this energy is retained in the system (adiabatic), the temperature could reach the AIT and ignition would occur. The AIT is very dependent on the system; for example, MMH and dinitrogen tetroxide are hypergolic (ignite at ambient temperature) while MMH and air have an AIT of approximately 470 K (386 °F), which is 170 K (306 °F) above ambient (Section 2.4.3).

In contrast, the very rapid addition of energy from external sources to a small region of the system increases the temperature in this region to a value that is sufficiently high to start a chemical reaction that supplies thermal energy to sustain the reaction. This energy is the MIE.

The criteria in assessing ignition of an MMH fire are as follows:

Can the system exceed its AIT?

or

Do the ignition sources available exceed the MIE for the system?

2.2.3.1 Autoignition temperature

The AIT is affected by fluid composition, concentrations (flammable mixture), pressure, vessel configuration (interaction with surroundings), catalytic activity of materials, droplet and mist formation, homogeneity of system, and gravity (Benz, Bishop, and Pedley 1988).

The standard methods for determining AIT are detailed in ASTM E 659-78 (ASTM 1986a) and other publications (Mullins 1955; Setchkin 1954). Although ASTM E 659-78 is not specifically designed for materials that undergo exothermic decomposition, it can be used if the results are evaluated carefully (Benz, Bishop, and Pedley 1988).

Pressure Dependency: In general, increased pressure leads to a decreased AIT (Benz and Phippen 1980; Bodurtha 1980; Furno, Imhof, and Kuchta 1968). Pressure dependency; however, can be a complex function depending on the system (hydrogen-oxygen system) (Benz, Bishop, and Pedley 1988).

Vessel Configuration: Increased vessel size leads to a decreased AIT, which is attributed to diminished wall-quenching effects (Setchkin 1954).

Concentration Dependency: Mixtures with excessively high or low MMH-to-air ratios have higher AITs than those with intermediate ratios. MMH-oxygen mixtures have slightly lower AITs than MMH-air mixtures (Bodurtha 1980). In general, for fuels in the range of concentrations corresponding to flammability, the AIT is independent of composition except near the LFL and UFL (Furno, Imhof, and Kuchta 1968). MMH data do not show this behavior.

Diluent Dependency: Mixing inert gases with MMH increases the AIT (Mullins and Penner 1959). Because ignition is an unsteady-state event, any property change of the mixture (thermal conductivity, specific heat, diffusivity, reaction rate) that changes the thermal energy balance can change the AIT.

Catalytic Surfaces: Studies have shown catalysts decreasing the AIT (Scott, Burns, and Lewis 1949; Stevens and Benz 1978, 1980), while other studies have shown catalysts increasing the AIT (Lewis and von Elbe 1961; Benz, Bishop, and Pedley 1988). Section 4 details material compatibility with MMH. These latter studies were either limited by the amount of fuel available or by excessive heat loss to the surroundings.

2.2.3.2 Minimum ignition energy

In general, the MIE decreases with 1) increasing oxygen concentration (Lewis and von Elbe 1961); 2) increasing temperature (Mullins and Penner 1959); and 3) increasing pressure (Benz, Bishop, and Pedley 1988). The standard method for determining MIE is ASTM E 582-76 (ASTM 1986d).

A variety of ignition sources (flames, electric sparks, heated wires, incendiaries, hot surfaces, rapid compression, etc.) must be considered in evaluating the fire hazards of MMH (Benz, Bishop, and Pedley 1988).

2.3 Effects

The severity of a fire is determined by the amount, rate, and duration of the heat release. A useful factor for estimating the exothermicity and endothermicity of a reaction is the adiabatic factor (Rase 1977) (Equation 2):

$$\text{Adiabatic factor} = \frac{(-D_R H)(N_A^0)}{\sum n_i C_{pi}} \quad (2)$$

where

$$\begin{aligned} (-D_R H) &= \text{standard enthalpy of reaction (kJ/mol)} \\ N_A^0 &= \text{initial moles of reactant (mol)} \\ \sum n_i C_{pi} &= \text{total mixture heat capacity over the sum of the products } n_i \text{ (kJ/K)} \end{aligned}$$

The adiabatic factor is defined as the adiabatic temperature change assuming complete consumption of the reactant, although most actual systems reach an equilibrium so the adiabatic factor is a maximum value. Table 2 gives values for MMH systems and several well-known reactions for comparison.

The effect of temperature on rate of heat generation can be evaluated by calculating the temperature sensitivity, E_a/RT . This is a useful concept and is fundamental for combustion (Zeldovich et al. 1985). The product of the adiabatic factor and the temperature sensitivity produces a dimensionless group for characterizing and comparing reactions—the heat generation potential (qp) (Equation 3):

$$qp = (\text{Adiabatic Factor}) \left(\frac{E_a}{RT_o^2} \right) \quad (3)$$

where

$$\begin{aligned} E_a &= \text{apparent activation energy (kJ/mol)} \\ R &= \text{gas law constant (kJ/mol K)} \\ T_o &= \text{initial temperature (K)} \end{aligned}$$

The heat generation potential values are given in Table 2.

Table 2 — Adiabatic factors and heat generation potential^a

Reaction	Adiabatic factor K	Heat generation potential
$1/2 \text{ N}_2 + 3/2 \text{ H}_2 \rightarrow \text{NH}_3$	633	26.52
$\text{MMH} \rightarrow \text{C} + 3\text{H}_2 + \text{N}_2$	1128 ^b	19.94 ^c
$\text{MMH} + 5/2 \text{ O}_2 \rightarrow \text{CO}_2 + 3\text{H}_2\text{O} + \text{N}_2$	3681	ND ^d
$\text{N}_2\text{H}_4 \rightarrow 1/3 \text{ N}_2 + 4/3 \text{ NH}_3$	2650	192.5
$\text{N}_2\text{H}_4 + \text{O}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$	7212	541.2
$\text{H}_2 + 1/2 \text{ O}_2 \rightarrow \text{H}_2\text{O} \text{ (in air)}$	3883	147.0
^a Rase 1977 ^b Value estimated assuming reaction temperature of 1100 K (1520 °F) and an average heat capacity (C_p) from 298 to 1100 K (77 to 1520 °F), 32.3 cal/K (Data obtained from Chase et al. 1985) ^c Value of E_a used = 22.93 kcal/mol (Internal communication with N. B. Martin, WSTF 1991); $T_0 = 808.0 \text{ K}$ where $T_0 \equiv 0.85 \times T_{\text{adiabatic}}$ (Zeldovich et al. 1985) ^d ND = not determined; E_a not available to determine the heat generation potential		

The adiabatic factor can always be calculated from thermodynamic data. The temperature sensitivity requires an experimental activation energy for the specific reaction.

A high value of the adiabatic factor if metals are present or a low value if soft goods are present indicates a potential ignition source for adjacent materials and a potential for fire spread. A high value of the heat generation potential indicates the system will heat very fast and will quickly reach adiabatic-limit temperatures. Further, the high value of heat generation potential is an indication that self-quenching is not likely.

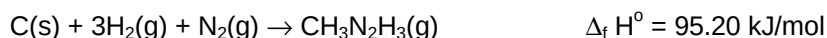
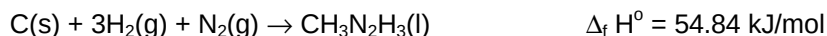
To determine the rate that the fire spreads and the duration of the fire, the flame speed (vapor fire), burning rate (liquid fire), and the amount of reactants available must be known. While there are formulas for calculating flame speed and burn rates, these values are very system-dependent and the calculated values should be used cautiously.

2.3.1 MMH reaction products

MMH is a strong reducing agent, weakly alkaline, and very hygroscopic. MMH readily reacts with a variety of organic and inorganic compounds and metallic materials. The principal MMH reactions of interest include decomposition reactions, reactions with dinitrogen tetroxide, reactions with carbon dioxide, and reactions with oxygen.

2.3.1.1 Heat of formation

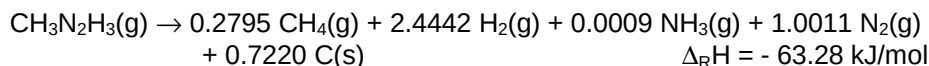
At 298 K (77 °F), the heat of formation ($\Delta_f H^\circ$) for MMH gas and liquid are as follows:



2.3.1.2 Decomposition

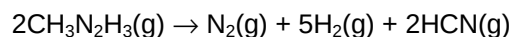
The main products of MMH decomposition are ammonia, methylamine, and azomethane. Additional products include nitrogen, methane, hydrogen, and carbon. The nature of the products is highly dependent upon temperature and the presence of heterogenous catalysts and dissolved impurities (Ross, Hendry, and Kirshen 1971). The heat of decomposition would depend on the specific set of

decomposition products selected. For example, the adiabatic equilibrium computation (Gordon and McBride 1976) at 950.7 K (1252 °F) and 101.3 kPa (14.7 psia) gives the following:

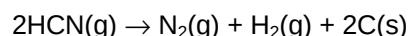


The possibility exists that MMH decomposition can produce hydrogen cyanide (HCN) (Schmidt 1984):

between 800 K (980 °F) and 900 K (1160 °F)



above 900 K (1160 °F)

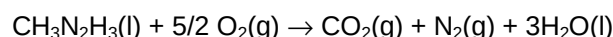


The titanium surface-catalyzed decomposition of MMH was studied using an accelerating rate calorimeter (Davis and Wedlich 1988). The products were complex and included nitrogen, ammonia, methylamine, methane, ethane, dimethyldiazene, and traces of several other compounds. Additional information on the interaction of MMH and materials is given in Section 4.

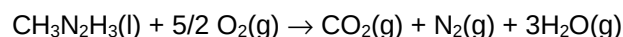
2.3.1.3 Combustion

The heat of combustion for MMH with oxygen is given as a higher heating value and a lower heating value.

Higher Heating Value: $\Delta_{\text{c}}H^0 = -1305.9 \text{ kJ/mol}$



Lower Heating Value: $\Delta_{\text{c}}H^0 = -1261.0 \text{ kJ/mol}$



2.3.1.4 MMH and air

With air as the oxidizer, the adiabatic temperature depends on the MMH:air ratio. Table B.1 in Annex B, gives values for several different MMH:air ratios. The specific product distribution also changes with the MMH:air ratio. Table 3 shows two examples of MMH:air ratios.

When air (oxygen) is present, MMH will react with many different surfaces both catalytically and non-catalytically (Section 4). With carbon dioxide present, MMH will react and produce a carbamate ($\text{C}_2\text{O}_2\text{N}_2\text{H}_6$).*

2.3.1.5 MMH and dinitrogen tetroxide

MMH and dinitrogen tetroxide are hypergolic. For a stoichiometric mixture at 101.3 kPa (14.7 psia), the adiabatic equilibrium temperature is 2956.8 K (4863 F) with a heat of reaction of -63.19 kJ/mol .

2.3.2 Vapor flame speed

The vapor flame speed (burning velocity) is defined relative to a specific coordinate system. For coordinates centered in the flame, it is the velocity at which unburned gases move through the combustion zone in the direction normal to the flame front. For laboratory coordinates, it is the velocity of

*WSTF internal communication by N. Martin, 1991

the flame through the unburned gases. The flame speed is dependent on whether the flow is laminar or turbulent. It is important to consider flame speed for determining the rate that a fire can move through the flammable mixture and subsequently distribute the fire throughout the system.

In evaluating the rate that heat is being generated throughout the system, the flame speed is used to calculate the mass rate of consumption of the fuel.

Table 3 — MMH-air at equilibrium (101.3 kPa (14.7 psia))^a

MMH: air ratio	Adia- batic temp ^b K	Products distribution moles with $N^{\circ}_{\text{MMH}} = 1.0$													
		CH ₄	CO	CO ₂	H	H ₂	H ₂ O	HCN	NH ₃	N ₂	NO	O	OH	O ₂	C
1:1	2370	NSQ ^c	0.1770	0.8229	0.0171	0.1062	2.8436	NSQ	NSQ	10.3796	0.0470	0.0088	0.0824	0.0974	NSQ
6.4:1	1260	0.0150	0.7737	0.0008	NSQ	2.9654	0.0051	0.0004	0.0002	2.4681	NSQ	NSQ	NSQ	NSQ	0.2104

^aCalculated using Gordon and McBride code (Gordon and McBride 1976) for conditions shown in Table B.1

^bCalculated equilibrium temperature.

^cNSQ = No significant quantity calculated

2.3.2.1 Flame speed in laminar flow

The elementary combustion theory of Mallard and Le Chatelier (Glassman 1987) predicts that the laminar-flow flame speed is (Equation 4):

$$S_L \propto \sqrt{(a \times RR)} \quad (4)$$

where

S_L = laminar-flow flame speed, (m/s)
 a = thermal diffusivity (m^2/s)
 RR = reaction rate (s^{-1})

A minimal amount of appropriate reaction rate data are available on MMH, and no flame speed measurements have been reported.

Typical hydrocarbon laminar flames have speeds on the order of 0.40 m/s (1.3 ft/s) (Glassman 1987). Hydrazine was measured to have a decomposition flame speed of 1.10 m/s (3.61 ft/s) and a flame speed in oxygen of 2.8 m/s (9.2 ft/s) at a total pressure of 5.33 kPa (0.77 psia) (Gray and Lee 1959).

2.3.2.2 Effect of temperature

The laminar flame speed varies with temperature through a change in unburned gas mixture properties (heat capacity, thermal conductivity, density), a change in reaction rate with temperature, and the initial temperature of the unburned gases, although the latter effect is small (Glassman 1987).

2.3.2.3 Effect of pressure

The reaction rate is a function of pressure, which translates to the following pressure dependency for flame speed (Equation 5):

$$S_L \propto (p^{n-2})^{1/2} \quad (5)$$

where

S_L = laminar-flow flame speed, (m/s)
 n = overall order of the reaction (Kanury 1976)
 p = pressure of the unburned gases

Many combustion reactions have $n=2$, which would mean that the flame speed would be approximately independent of pressure.

2.3.3 Liquid burning rate

The burning rate for MMH liquid is the mass of fuel consumed per unit surface area per unit time for the burning pool. A burning velocity can be defined as the rate that the level of the liquid pool decreases.

After ignition (temperature exceeds the fire point, Section 2.2.2), the MMH liquid will continue to burn only if the rate of vaporization is at least as great as the rate of consumption of the vapor. In general, the burning rate will increase with an increase in surface area of the liquid pool. Pool depth has little effect on burning rate.

2.4 Data

2.4.1 Vapor

This section summarizes MMH vapor flammability data available in the literature.

2.4.1.1 Flammability limits

Neat MMH: Below ambient pressure a 1 J (9.48×10^{-4} Btu) electric spark did not ignite neat vapor MMH (Benz, Guerrasio, and Rollins 1983). Since the normal boiling point of MMH is 360.8 K (189.8 °F), this non-flammable vapor region corresponds to temperatures below 360.8 K (189.8 °F).

MMH and Air: Table 4 summarizes the flammability limits reported for MMH and air at ambient pressure. The highest reported UFL is 98 percent (USAF 1973). The lowest reported LFL is 2.5 percent (NFPA 1977; USAF 1973).

As shown in Figure 2, temperature has a small effect on the LFL of MMH-air mixtures at ambient pressure. One data point for UFL is also shown. At pressures below ambient, the flammability limits for MMH vary with temperature in a way similar to the variation of the MMH vapor pressure. Figure 3 shows these limits. Figure 4 and Table 5 (Benz, Bishop, and Pedley 1988) summarize the effects of reduced pressure and temperature on the flammability range of MMH-air. The lowest pressure for flammability was 3.10 kPa (0.45 psia), with 7.7-percent MMH. The temperatures were 311 K (100 °F) and 366 K (200 °F). These tests were conducted with a 1 J (9.48×10^{-4} Btu) electric spark as an ignition source.

Table 4 — MMH and air flammability limits at ambient pressure^a

MMH concentration (% v/v)		Reference
LFL	UFL	
2.8 (366 K)	95.7 (366 K)	Benz, Bishop, and Pedley (1988)
2.5	92.0	NFPA (1977)
2.5	98.0	USAF (1973)
2.5	97.0	Clayton and Clayton (1979)
4.0 (298 K)		Van Dolah, Zabetakis, and Scott (1962)
^a Temperature provided when known.		

MMH and Oxygen: The LFL and UFL of MMH and oxygen have been reported as 3.6 percent and 99.8 percent, respectively (Benz, Bishop, and Pedley 1988). These measurements involved a 1 J (9.48×10^{-4} Btu) electric spark and were conducted in a 2-L (122-in³), hemispherical, stainless steel chamber at 366 K (200 °F) and 101.3 kPa (14.7 psia). (Effects of vessel materials are discussed in Section 4.)

MMH as a Hypergol: MMH is hypergolic with dinitrogen tetroxide at ambient temperature and pressure. No low-temperature, low-pressure limits have been reported for these reactions.

MMH and Inert Gas: No data on the flammability effects of diluents or inert gases are available.

MMH and Hydrocarbons: No data are available on the flammability effects of hydrocarbons; however, MMH vapor flammability may be reduced by the same hydrocarbons that reduce the flammability of hydrazine (isopropylbenzene, cumene, toluene, xylene, butane, and hexane) (Pedley et al. 1990).

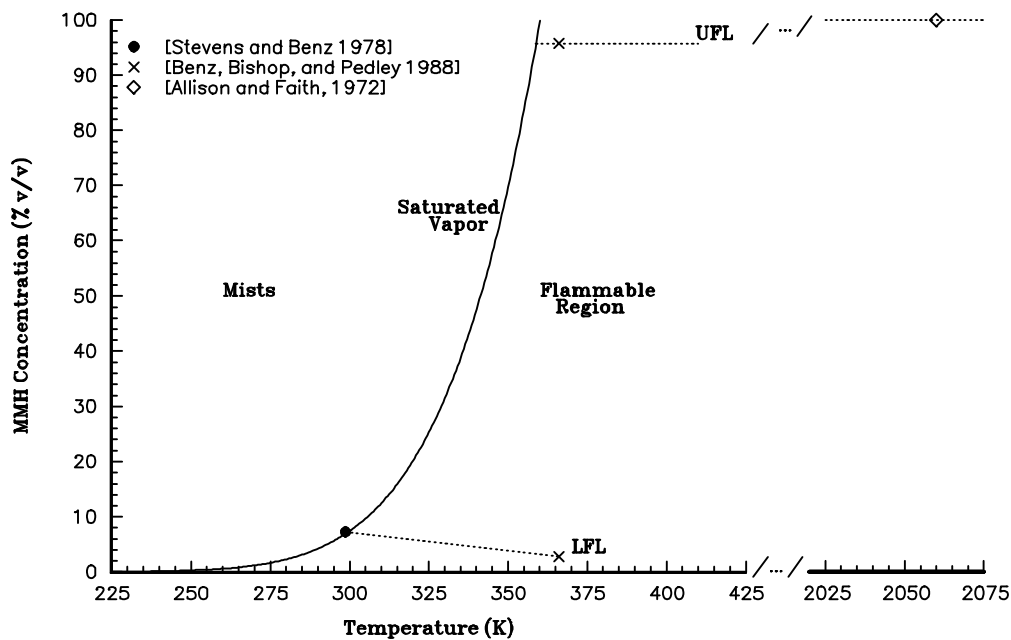


Figure 2 — Flammability limits for MMH-air as functions of temperature and composition at 101.3 kPa (14.7 psia)

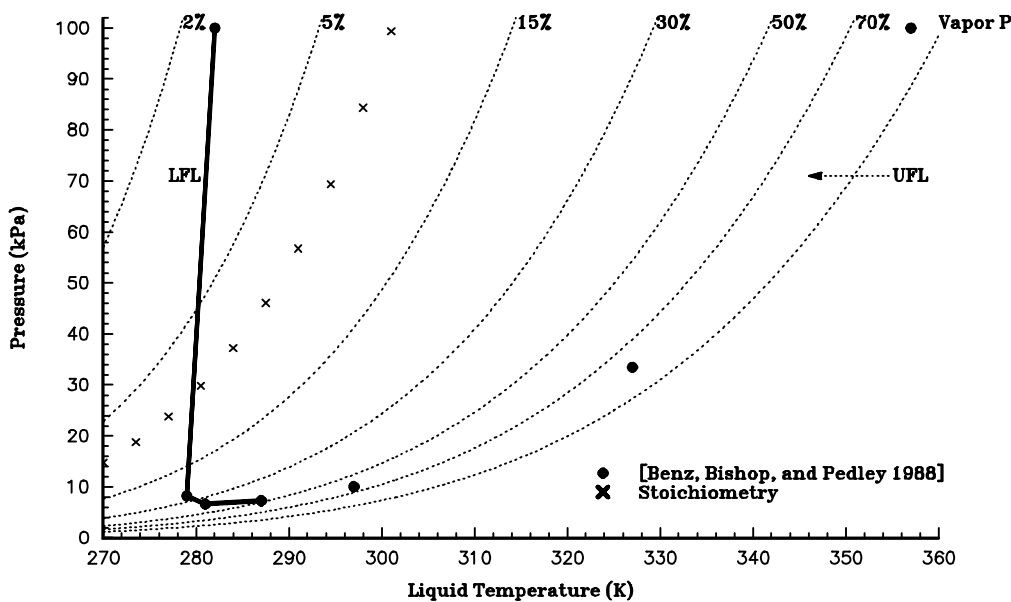


Figure 3 — Flammability limits above liquid MMH in air as functions of temperature and pressure

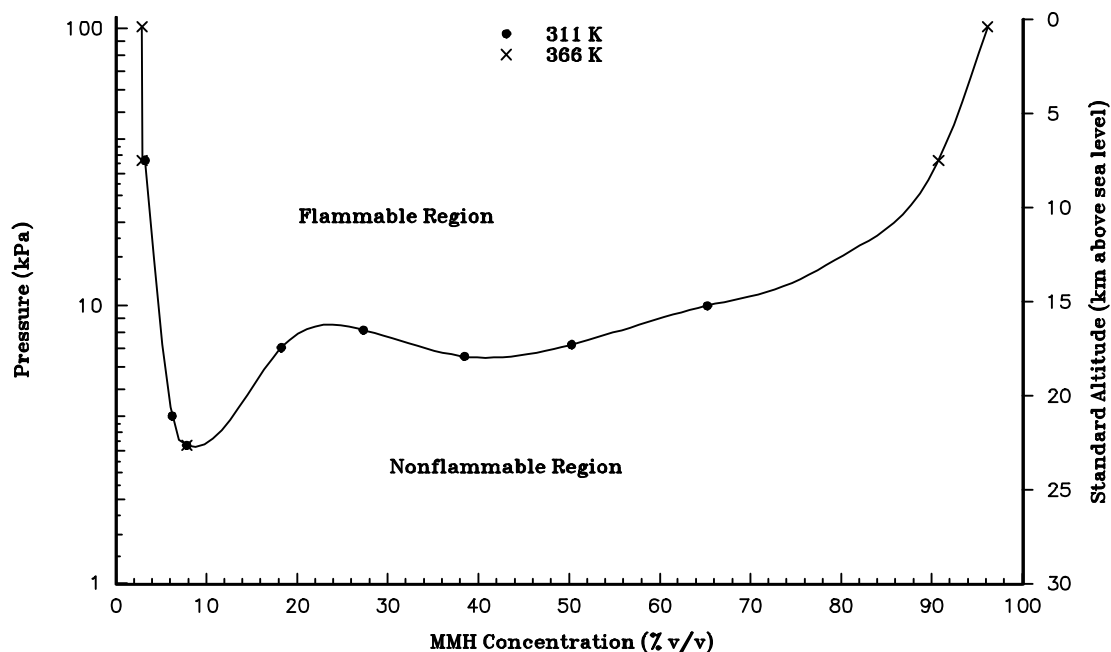


Figure 4 — The effect of pressure on the flammability of mmh-air (Benz, Bishop, and Pedley 1988)

Table 5 — MMH flammability in air at reduced pressures and temperatures of 311 K (100 °F) and 366 K (200 °F)^a

MMH concentration % v/v	Pressure		Temperature	
	kPa	psia	K	°F
3.1	33.4	4.85	311	100
6.1	4.0	0.58	311	100
7.7	3.10	0.45	311	100
18.1	7.10	1.03	311	100
27.1	8.17	1.19	311	100
38.2	6.59	0.96	311	100
50.0	7.24	1.05	311	100
64.9	10.0	1.45	311	100
2.8	101.3	14.7	366	200
2.8	33.4	4.85	366	200
7.7	3.10	0.45	366	200
90.3	33.4	4.85	366	200
95.7	101.3	14.7	366	200

^a Benz, Bishop, and Pedley 1988

NOTE: The extension of reactivity data, based on homologous compounds, should be considered carefully.

MMH and Halocarbons: The effect of bromotrifluoromethane (Halon 1301) is discussed in Section 2.4.2.

2.4.1.2 Flame speed

Very little appropriate reaction rate data on MMH are available, and no flame speed measurements have been reported.

Typical hydrocarbon laminar flames have speeds on the order of 0.40 m/s (1.31 ft/s) (Glassman 1987). Hydrazine was measured to have a flame speed of 2.8 m/s (9.2 ft/s) at a total pressure of 5.33 kPa (0.77 psia) (Gray and Lee 1959).

2.4.2 Liquid

2.4.2.1 Flammability

Flash Points: Open-Cup flash points and Tag Closed-Cup flash points reported for MMH in air at ambient pressure are given in Table 6.

Fire Point: No fire point data have been reported in the literature.

MMH-Water: MMH is hygroscopic and readily absorbs water. The vapor above a mixture containing 20 percent-by-volume water is nonflammable below 300 K (80 °F); the vapor above a mixture containing 65 percent-by-volume water is nonflammable below 339 K (150 °F) (Stevens and Benz 1980). The addition of 70 percent-by-weight water to MMH liquid prevents ignition (Burgess et al. 1969). For vapor above a liquid mixture containing 65 percent-by-weight water, Hshieh (1992) reported nonflammability below 438 K (329 °F). Additional flash and fire points of MMH-water mixtures are given in Table 7 (Hshieh 1992).

MMH-Halon: The concentration in air of bromotrifluoromethane (CF₃Br or Halon 1301) required to extinguish a 15.2-cm (6-in.) burning pool of MMH was reported to be 40 percent-by-volume (Burgess et al. 1969).

Table 6 — Flash point values reported for MMH in air at 101.3 kPa (14.7 psia)^a

Method	Flash point		References
	K	°F	
Closed Cup	265	17	NFPA 1984
Open Cup	280	44.3 ^b	Hshieh 1992
Closed Cup	290	63	Olin Corporation 1986
Open Cup	294	70	Olin Corporation 1986
^a MMH vapor flammable in air at pressures below ambient; Section 2.4.1			
^b Value determined using Tag Open-Cup tester at 85.5 kPa (12.4 psia) and corrected using ASTM Method D 1310-86 to obtain corresponding atmospheric pressure, 101.3 kPa (14.7 psia)			

Table 7 — Flash and fire points of MMH-water mixtures

MMH concentration Weight %	Flash point ^b		Fire point	
	K	°F	K	°F
99.5	280.0	44.3	280.0	44.3
90	291.0	64.1	291.0	64.1
80	292.0	65.9	292.0	65.9
70	299.0	78.5	299.0	78.5
60	316.5	110.0	316.5	110.0
50	344.0	159.5	344.0	159.5
40	359.0	186.5	368.5	203.6
35	ND ^c		ND	
30	ND		ND	

^a Hsieh 1992
^b Values determined using Tag Open-Cup tester and corrected using ASTM Method D 1310-86 to obtain corresponding values at atmospheric pressure, 101.3 kPa (14.7 psia); Original values, taken under the test conditions of 85.5 kPa (12.4 psia), obtained by subtracting 9 K (16.2 °F)
^c ND indicates no flash and fire points detected

2.4.2.2 Burning rate

Liquid: The mean burning rate of a 4.8-cm (1.9-in.) pool of MMH in stagnant air is $1.62 \times 10^{-2} \text{ kg/m}^2\cdot\text{s}$ (0.20 lb/ft²·s) (Benz, Bishop, and Pedley 1988). For a 15.2-cm (6-in.) pool of MMH, the mean burning rate is $2.44 \times 10^{-2} \text{ kg/m}^2\cdot\text{s}$ (0.30 lb/ft²·s) (Burgess et al. 1969). (These rates are significantly lower than the burn rates for hydrazine pools.)

The burning rate of MMH-water mixtures in stagnant air is reduced as the amount of water is increased. A 15.2-cm (6-in.) pool containing 20 percent-by-weight water has a burning rate of $1.2 \times 10^{-2} \text{ kg/m}^2\cdot\text{s}$ (0.15 lb/ft²·s) and a 15.2-cm (6-in.) pool containing 40 percent-by-weight water has a burning rate of $8.95 \times 10^{-3} \text{ kg/m}^2\cdot\text{s}$ ($1.83 \times 10^{-3} \text{ lb/ft}^2\cdot\text{s}$) (Burgess et al. 1969).

Liquid Droplets: The burning rate of MMH liquid droplets increases as the droplet diameter, oxygen concentration, and surrounding temperature increase (Allison and Faeth 1972). The decomposition burning rate of MMH droplets is slower than the oxidation burning rate of MMH droplets in oxygen (Figure 5).

2.4.3 Ignition

2.4.3.1 Autoignition temperature

MMH in Air: Table 8 summarizes available AIT data. Figure 6 shows the results of reduced pressure on AIT. Three different experimental systems are reported: a 2.8-L (173-in³) 304L-stainless-steel chamber (Stevens and Benz 1980); a 4.9-L (299-in³) 304L-stainless-steel chamber (Furno, Imhof, and Kuchta 1968); and a 0.5-L (30.51-in³) borosilicate glass vessel (Benz, Bishop, and Pedley 1988).

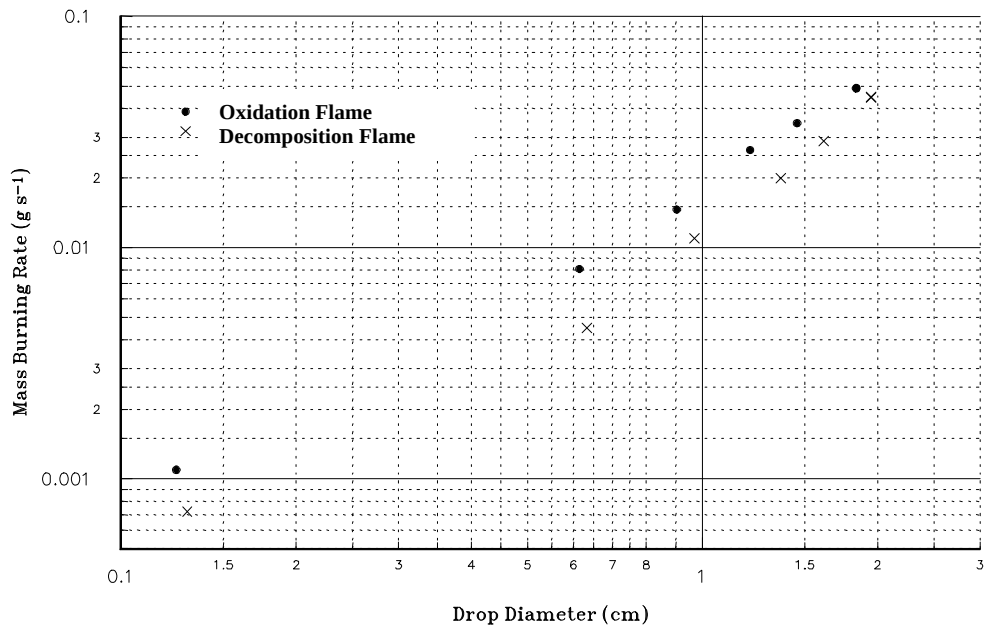


Figure 5 — MMH Burning Rates as Functions of Drop Diameter for Oxidation and Decomposition at 101.3 kPa (14.7 psia) (Allison and Faeth 1972)

MMH in Oxygen: The one reported value for AIT is 345 K (162 °F) at 98.7 kPa (14.3 psia) (Furno, Imhof, and Kuchta 1968). Figure 7 shows the results of reduced pressure on AIT (Furno, Imhof, and Kuchta 1968; Gray and Sherrington 1974). Figure 8 shows the effect of inert gases (He, Ne, N₂, Ar, Kr) on AIT for an MMH + 2O₂ mixture. These experiments were conducted at a reduced pressure of 0.93 kPa (0.135 psia).

NOTE: Extrapolation of these results to working pressures should be done cautiously.

MMH and Dinitrogen Tetroxide: Mixtures of MMH liquid and dinitrogen tetroxide (NO₂*) are hypergolic at 298 K (77 °F) (Furno, Imhof, Kuchta 1968). (NO₂* represents the equilibrium mixture of NO₂ and N₂O₄ at any temperature.)

Figure 9 shows the effect of initial liquid temperature on the AIT for MMH-NO₂*-air mixtures (Perlee, Imhof, and Zabetakis 1962).

2.4.3.2 Minimum ignition energy

Electric sparks of 1 J (9.48 x10⁻⁴ Btu) have been used as ignition sources in a hemispherical chamber for the ignition studies done in air in this test (Benz, Bishop, and Pedley 1988). No MIEs for MMH were reported in the literature reviewed for the preparation of this special report.

Table 8 — AIT for MMH in air^a

AIT		Pressure		Reference
K	F	kPa	psia	
457	363	101.3	14.7	Furno, Imhof, and Kuchta 1968
467	381	101.3	14.7	USAF 1973, NFPA 1977, Olin Corporation 1992
468	382	85.5	12.4	Benz, Guerrasio, and Rollins 1983
472	390	85.5	12.4	Benz, Bishop, and Pedley 1988
^a Compositions not reported.				

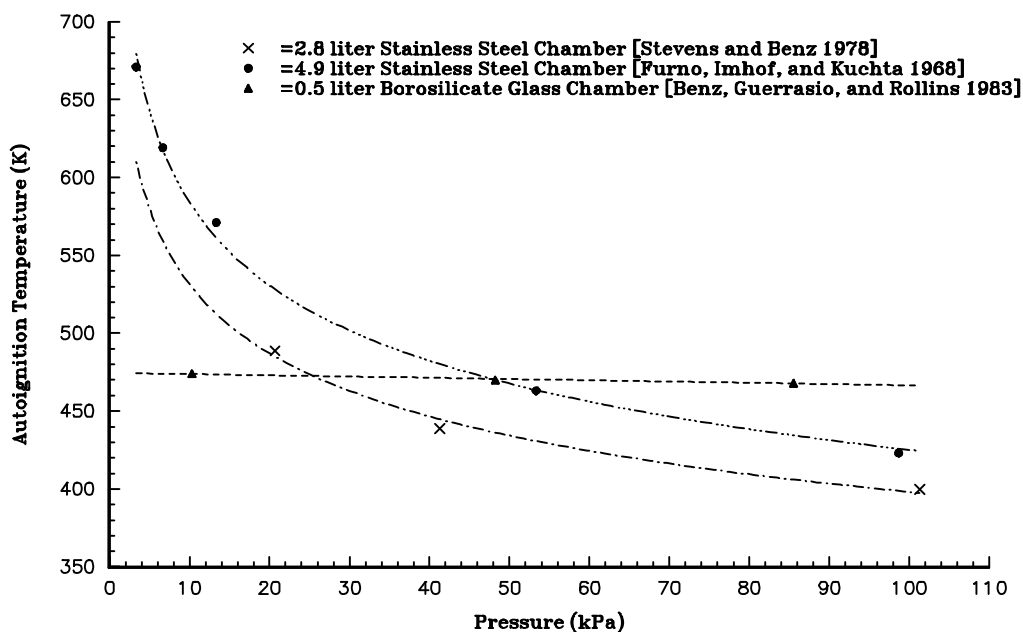


Figure 6 — The effect of reduced pressure on the AIT of MMH-air

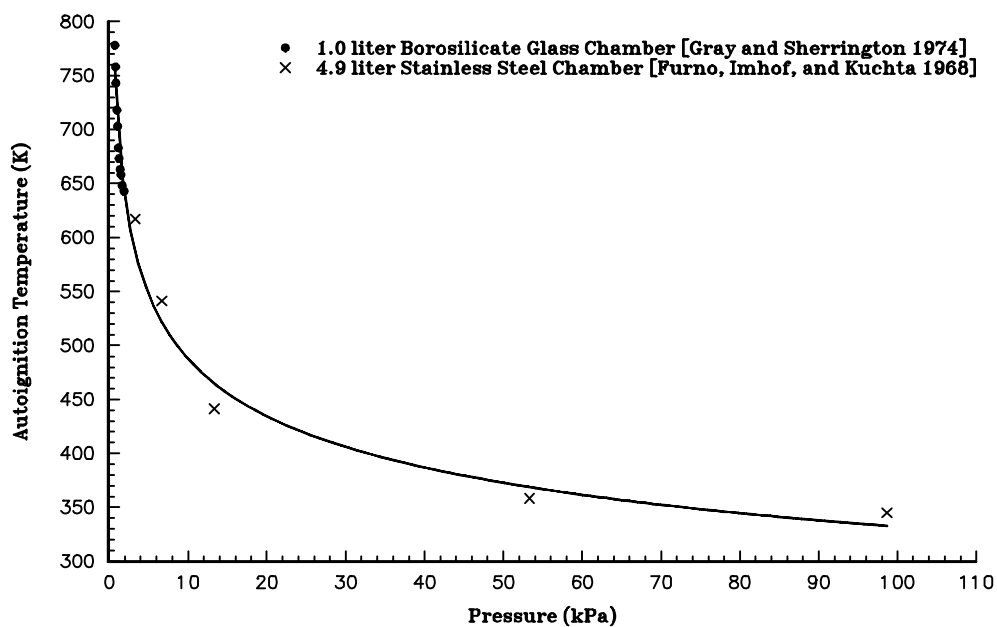


Figure 7 — The effect of reduced pressure on the AIT of MMH-oxygen

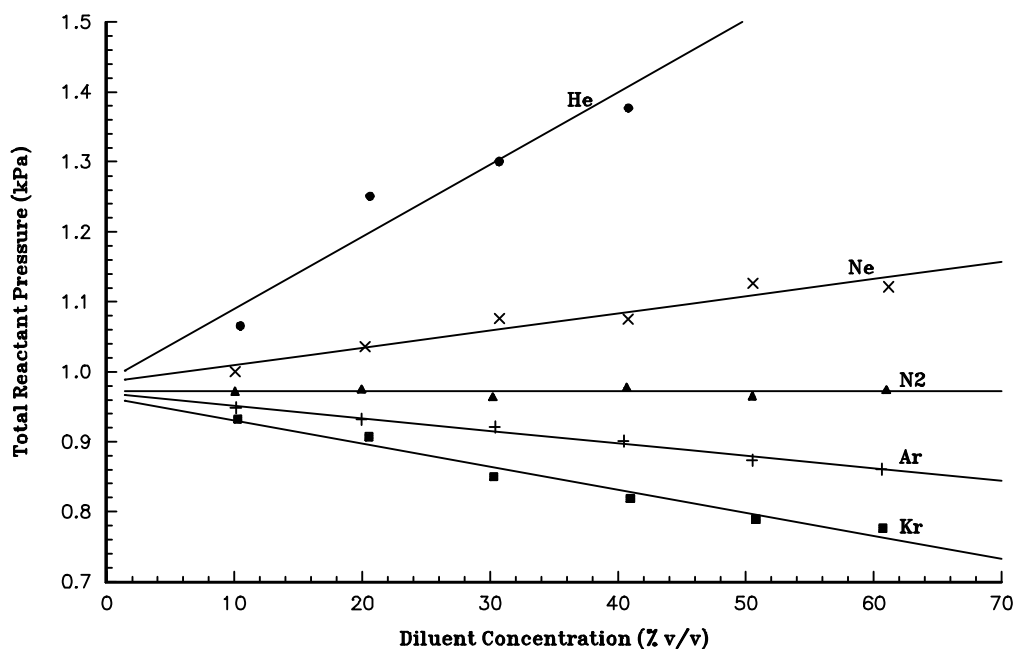


Figure 8 — The effect of diluents on the minimum reactant partial pressure for autoignition of MMH + 2O₂ mixtures at 703 K (806 °F) (Gray and Sherrington 1974)

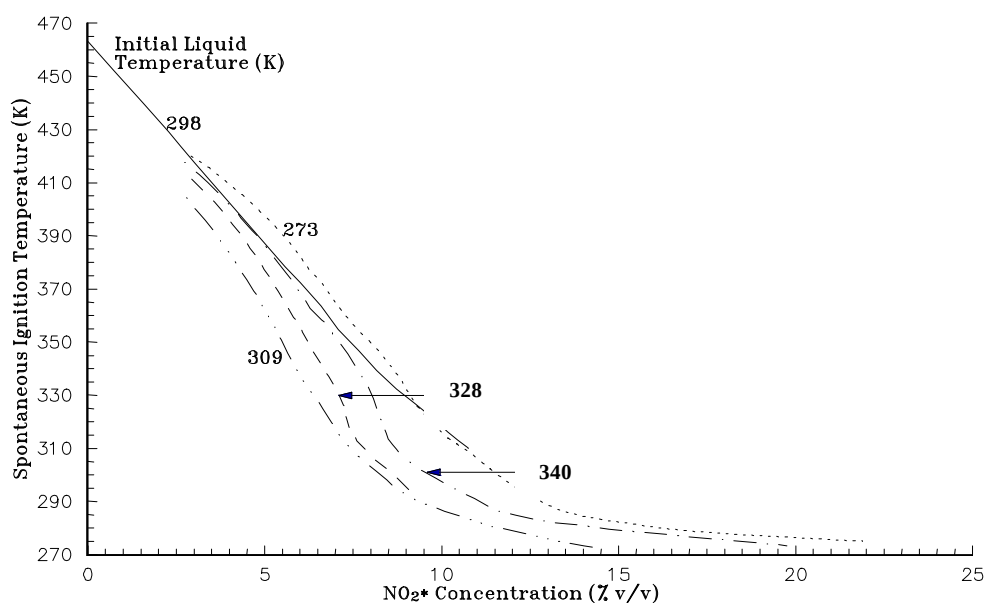


Figure 9 — Minimum spontaneous ignition temperatures for MMH liquid in contact with NO₂*-air mixtures at 97 to 100 kPa (14.1 to 14.5 psia) (Perlee, Imhof, and Zabetakis 1962)

2.5 Assessment example

Section 2.1 describes the approach to fire hazard assessment as consisting of three steps:

1. identify the system and the initial conditions,
2. determine whether the criteria for a fire are met (Is the mixture within flammability limits? Is there an ignition source?), and
3. evaluate the effects of a fire.

The following is an assessment example incorporating these steps:

1. Given: 3.06 kg (1 gallon) of MMH is spilled in a chemical storage area of volume 21.75 m³ (8 x 12 x 8 ft). There is no ventilation of the space. Temperature is 298 K (77 °F) and ambient pressure is 0.1 MPa (14.7 psia).

2. Calculation of Flammability of Mixture

Assume MMH equilibrates with air in the storage area:

Total Volume: $V_o = 21.75 \text{ m}^3$ (768 ft³)

Total Moles of air (assume ideal gas): $n_o = 0.89 \text{ mol}$

Vapor Pressure MMH (at T_o , p_o) $p^* = 6.60 \text{ kPa}$ (0.96 psia)

Total Moles MMH Vapor at Equilibrium = $n_o p^*/P_{\text{total}} = 0.058 \text{ mol}$

Total Moles MMH in Spill = 0.066 mol

Because the total moles spilled is greater than the total moles vapor MMH (at equilibrium), there will be a liquid pool remaining. The volume percent of MMH in the storage space air is 6.6 percent (vol% = 100 x p^*/P_{total}).

Table 2.3 gives the LFL at 298 K as 4.0 percent. The MMH-air mixture in the storage space is flammable.

NOTE: Flammable mixtures must always be treated as potential hazard but proper design can mitigate such hazards. For example, elimination of ignition sources from the storage space is a proper part of the design.

3. The third step in this assessment is to evaluate the effects of the fire. The first question to consider is whether there is sufficient oxygen in the storage space for complete combustion of the MMH (Section 2.3.1).

0.066 mol MMH requires 0.165 mol O₂ (Equation 6)

$$\begin{aligned} \text{moles } O_2 &= n_o \times \frac{0.21(P - p^*)}{P} = 0.89 \times \frac{0.21(94.7)}{101.3} \\ &= 0.175 \end{aligned} \quad (6)$$

Theoretically, the MMH could combust completely, releasing 83.23 kJ (based on the Lower Heating Value).

Even if the MMH-air mixture is not flammable, several questions should be considered at this point:

1. Can compositions shift during cleanup, creating a flammable mixture?
2. Can temperature changes or pressure changes cause the MMH and air mixture to become flammable?
3. What is the effect of air circulation in the storage room?
4. Will equilibration occur quickly (will rapid mixing occur)? (The hazard potential is that, while the overall average composition is outside the flammability limits, compositions at certain points could be flammable.)

The actual fuel:air ratio in the storage space corresponds to ~7.5 percent-by-volume MMH. This is almost stoichiometric, and as seen in Table B.1, the adiabatic temperature (assuming the energy from the fire heated only the air in the storage shed) would be approximately 2300 K (3680 °F). If there were other items in the shed or if the energy could leak to the walls (high thermal conductivity material), the temperature from the fire would be less. However, a very rapid spread of the flame from the fire could approach 2300 K (3680 °F) before heat is lost to the contents or surroundings.

Both the adiabatic factor (3681 K, Table 2) and the heat generation potential (greater than 20) indicate that an MMH fire can have significant effects. The maximum total energy released, 83.23 kJ as calculated above, would be released in 1.92 hours (h) if the MMH spill ignited and burned as a liquid pool fire (burn rate taken from Section 2.4.2 for mean burn-rate of a 15.2 cm diameter pool) (Equation 7).

$$\frac{3.06 \text{ kg}}{(2.44 \times 10^{-2} \text{ kg/m}^2 \cdot \text{s}) \times \left(p \cdot \left(\frac{0.0152 \text{ m}}{2} \right)^2 \right)} = 6.9112 \times 10^3 \text{ s} = 1.92 \text{ hours} \quad (7)$$

NOTE: The actual burn-time would depend on how the spilled MMH spread, the available oxidizer and vapor mixed, and how the heat from the fire was dispersed.

If ignition occurred after the MMH vapor had equilibrated with the air in the storage room, the burn time would be greatly reduced. Flame speeds will be discussed in Section 3.

3. Explosion hazards

If a flammable mixture of MMH exists in a system, there is always the potential for an explosion (Table 1). While it is possible to design pressure relief into a system, the rate of pressure increase during a detonation cannot be dissipated through such relief devices, and failure of the mechanical containment may result. Release of the energy (as a shock wave) can damage surrounding components and injure personnel.

In assessing the explosion potential of an MMH system, three separate processes must be considered: deflagration (Section 3.1), exothermic reaction (Section 3.2), and detonation (Section 3.3). A deflagration is a flame that moves through the MMH mixture. It propagates at velocities less than the sonic velocity (Figure 11) of the unburned mixture. An exothermic reaction applies to the entire system and is treated as if reaction occurs simultaneously throughout the total volume. A detonation is that condition in which

the exothermic reactions are coupled to a shock wave within the MMH mixture. This shock-wave velocity is supersonic with respect to the unburned mixture. The three processes are contrasted in Table 9. The data listed under Deflagration are calculated based on an open system, e.g., an unconfined, flammable mixture or a stationary flame with fuel and oxidizer flow. If a deflagration occurs in a closed system, the final properties would be the same as those listed under Exothermic Reaction.

Although each process involves the exothermic reaction of MMH, the three processes are described independently. However, two things should be remembered: (1) deflagrations and exothermic reactions can undergo transitions to detonations, which is potentially the most hazardous process, and (2) deflagrations and exothermic reactions in isolated systems build up pressure that can lead to explosions.

Table 9 — Detonation explosion hazard characteristic ratios for MMH^a

	Deflagration^b	Exothermic reaction^c	Detonation
Characteristic Velocity ^d	2.1 - 3.5	-	4.1 - 7.4
Products Pres./Initial Pres.	0.98 - 0.976	4.3 - 9.8	10.3 - 29.3
Products Temp./Initial Temp.	2.6 - 7.7	2.6 - 7.7	3.7 - 9.6
Products Dens./Initial Dens.	0.1 - 0.4	1.0 - 3.7	1.7 - 1.8
^a Values shown based on Gordon and McBride code calculations ^b Exothermic reaction in an <u>open</u> system (flame propagation) ^c Exothermic reaction in a <u>closed</u> system (homogeneous reaction throughout system; a system through which deflagration has propagated will approach these values) ^d Characteristic velocity: the ratio of the sonic velocity of burned gases to the sonic velocity of unburned gases for a deflagration; the ratio of the Chapman-Jouguet velocity (see Section 3.3) to the sonic velocity of the unburned gases for a detonation			

3.1 MMH deflagration

A deflagration is defined as a flame moving through a flammable mixture at subsonic velocity (Kanury 1976). The propagating flame is a zone of exothermic reaction in which heat and mass transfer sustain the reaction. In other words, the heat produced by the reaction must be transferred into the unburned fuel so that the rate of reaction is sufficiently fast to sustain the flame, and in a similar manner, the fuel mixture must be available at the flame zone to sustain the reaction. The zone may be a fraction of a millimeter to more than a centimeter thick (Zeldovich et al. 1985). When the system is filled with a flammable mixture, the usual occurrence is that ignition takes place in a small region, and the flame propagates throughout the system.

3.1.1 MMH deflagration assessment

The assessment of the potential for a deflagration is similar to that followed for fires:

1. Identify the system and its initial conditions.
2. Determine whether the criteria for a deflagration exist.
3. Evaluate the effects of the deflagration.

Identification of the system and its initial conditions is described in Section 2.1 and will not be discussed further here.

The following criteria are necessary for a deflagration to exist:

1. A flammable mixture exists.