

METHANOL SAFE HANDLING TECHNICAL BULLETIN

PART 2: USING PHYSICAL AND CHEMICAL PROPERTIES TO MANAGE FLAMMABLE LIQUID HAZARDS¹

INTRODUCTION

This is part two of the three-part Technical Bulletin, which provides guidance for using physical, chemical, thermal, and electrical properties to identify and control hazards of flammable liquids. Properties and characteristic parameters of eight fuels [hydrogen, compressed natural gas (CNG), propane, methanol, ethanol, gasoline, No. 2 diesel, and biodiesel] are listed in part 1B of the Technical Bulletin². This bulletin compares various properties for gasoline and methanol.

Chemical and physical properties data may be difficult to locate and even more difficult to interpret and verify. Flame speed is an example of this difficulty. Some sources indicate the flame speed of methanol is greater than that for unleaded gasoline; others sources state the reverse. Still others report that small additions of methanol increase the flame speed of gasoline. All may be correct, depending on the temperature, pressure, mixing, and stoichiometry at which combustion occurs and how flame temperature is determined.

Flame speeds of methanol and gasoline have similar values (1.12 and 1.41 feet per second [ft/s] for gasoline and methanol, respectively). Therefore, there may be overlap of flame speed parameters depending on whether measurements were made at lean, rich, or stoichiometric fuel/air ratios. Flame speed data used in this three-part bulletin series are characteristic of stoichiometric combustion of a vapor at NTP (Normal Temperature = 68oF and Normal Pressure = 14.7 psia or 760 mmHg).

Differences between the published values of flame speed for methanol and gasoline do not have a large effect on first order estimates for explosive overpressure and fire radiant heat flux, and are not of major concern. The approximately tenfold difference between the flame speed of hydrogen (≈ 12 ft/s)³ and those of gasoline and methanol have a very large difference on overpressure and heat flux.

The purpose of collecting and comparing data for different fuels is to determine and compare the severity of potential consequences: fires, explosions, and toxic plumes for particular circumstances. Consequence analysis⁴ has been in widespread use for about 25 years, but remains an inexact mixture of science and art borne of experience. Results of modeling may be generally correct, but are typically inexact and non-specific. Nevertheless, modeling results are highly useful in estimating order-of-magnitude consequence severity⁵.

¹ This three-part Technical Bulletin was written by Mr. Robert R. Roberts of Roberts & Roberts Risk & Reliability Engineering and edited by Alliance Consulting International, San Diego, California under contract to the Methanol Institute.

² Information and data are collected from a variety of published and internet sources, though different sources may contain conflicting data regarding the same information. Effort has been made to use reliable sources; however, no responsibility is taken for correctness, accuracy, or errors in information.

³ Refer to Part 1B of Methanol Institute Technical Bulletin on Using Physical and Chemical Properties to Manage Flammable Liquid Hazards.

⁴ Center for Chemical Process Safety: *Guidelines for Chemical Process Quantitative Risk Analysis*, 2nd edition, © 2000, American Institute of Chemical Engineers, ISBN 0-8169-0720-X

⁵ A.J. Roos, The Director-General of Labour, Committee for the Prevention of Disasters caused by Dangerous Substances, and The Netherlands Organisation of Applied Scientific Research (TNO): *The Green Book, CPR 16E, Methods for the Determination of Possible Damage to People and objects Resulting from Releases of Hazardous Materials*, December 1989, 1st edition 1992, ISBN 90 5307 052 4.

Gasoline and methanol are NFPA class IB flammable liquids. Both are known to BLEVE in non-bulk and bulk transport containers, in pressure vessels, and storage tanks in 'roll-over' situations. Vapors of both fuels form plumes and may accumulate in unventilated areas, and both are considered to present an explosion hazard in confined spaces. Beyond this point, the behavior of gasoline and methanol begin to diverge.

The vapor density and equilibrium of gasoline and methanol vapors show marked differences. Gasoline vapor is heavier than air, while methanol vapor is near neutral in buoyancy. Gasoline has an equilibrium true vapor pressure (TVP) two to three times greater than that of methanol. The flammability range of gasoline is 1.4 to 7.6 v/v % versus 7.3 to 36 v/v % for methanol; flash point temperature of gasoline is minus (-) 45 oF versus 52 oF for methanol. Finally, the lower heating value of gasoline is over twice that of methanol; the mass burn rate of gasoline is over three times that of methanol; minimum ignition energy and stoichiometric flame velocity are approximately the same for both.

When comparing the hazardous characteristics of these vapors, it is apparent that gasoline vapor accumulates in low-lying areas and is capable of traveling long distances. Gasoline is also more easily ignited, ignites at lower concentrations, burns faster, and releases more radiant heat than methanol. As a result, gasoline vapor is more likely to concentrate and explode. Gasoline fires produce a much greater radiant heat flux hazard, and as much or more shock wave over pressure. The sum of these characteristics has caused gasoline to be replaced with methanol in high performance race cars where collision, tank rupture, fuel spillage, ignition, fire and explosion are expected to occur.

If consequence severity must be determined beyond a first order level, then users should verify that data contained in the Technical Bulletin's Part 1-B Physical and Chemical Properties tables is appropriate for the desired level of precision in determining the radius of overpressure and radiant heat flux hazard zones. Second order consequences can be readily determined using proprietary consequence modeling software (a variety of software packages can either be purchased or leased). Each software package uses parameter values and calculation techniques, which are judged by the software providers to be appropriate for the algorithms used in their particular model. Therefore, parameter values in the Physical and Chemical Properties tables in Part 1-B of this Technical Bulletin may not correspond to the values used by third-party software.

In order to establish whether the software is appropriate for your specific needs, it is recommended to compare software modeling results to results of actual fire and explosion incidents. Additionally, it is good practice to confirm software modeling results with hand calculations to verify that results provided by the software are reasonable.^{6,7,8,9}

A word of caution regarding the use of chemical and physical properties parameters is appropriate. Values of parameters presented in the Physical and Chemical Properties tables are determined in a laboratory environment, and therefore characterize a narrow range of standardized, controlled, and repeatable conditions. Test results for pure materials are not representative of fuel blends, contaminated materials, complications associated with switch loading, and substance property parameters at elevated temperature and pressure. Values presented in the Physical and Chemical Properties tables may or may not typify your conditions of usage or process environments.

⁶ Institution of Chemical Engineers: *Explosions in the Process Industries*, 2nd edition, © 1994 by Institution of Chemical Engineers, pp. 74, ISBN 0 85295 315 1

⁷ Institution of Chemical Engineers: *Calculation of the Intensity of Thermal Radiation from Large Fires, Thermal Radiation Monograph, First Report of the Major Hazards Assessment Panel – Thermal Radiation Working Group*, © 1989 by The Institution of Chemical Engineers, 22pp., ISBN 0 85295 236 8

⁸ Institution of Chemical Engineers: *The Effects of Explosions in the Process Industries, Overpressure Monograph, First Paper of the Major Hazards Assessment Panel – Overpressure working party*, © 1989 by The institution of Chemical Engineers, 26 pp., ISBN 0 85295 235 X

⁹ Sdu Uitgevers, and Committee for the Prevention of Disasters: *Yellow Book, CPR 14E Parts 1 & 2, Methods for the Calculation of Physical Effects*,

FLAMMABLE LIQUIDS

ICC, NFPA, and OSHA classify liquids as flammable or combustible. Each of these designations is divided into sub-classes based on values of selected physical and chemical parameters. These parameters indicate conditions at which vaporization, piloted ignition, and combustion are likely to occur. Liquids are assigned to classes based on the values of identifiable and measurable properties (boiling point temperature and flash point temperature); each flammability class contains materials whose properties fall within a specified range of values. For example, class IA flammable liquids have flash point temperatures below 73oF and boiling point temperatures below 100oF (e.g., n-pentane). Class IA substances have substantial equilibrium vapor pressure at NTP, and are known to ignite in air at temperatures below normal ambient temperature in the presence of a sufficiently energetic ignition source. Class IB flammable liquids are defined as having flash point temperatures less than 73oF and boiling point temperatures at or above 100oF (e.g., methanol, ethanol, and unleaded gasoline). Class IC flammable liquids have flash point temperatures at or above 73 oF, and boiling point temperatures below 100oF (e.g., turpentine). Guidance provided in this Technical Bulletin series focuses on IB flammable liquids. This flammability class contains three widely-used motor fuels which are transported, handled, and stored in large volumes by persons and organizations highly experienced in safe handling, as well as in small volumes by users who are less familiar with and practiced in safe handling requirements and procedures.

To an extent, fire hazards that characterize a particular flammability class are common to all of the materials within that class. Class IB flammable liquids include motor fuels, solvents, reactants, and feed stocks. Benzene, toluene, acetone and alcohols are examples of class IB solvents and feed stocks. Notice from the “General Information, Section 1,” of the Physical and Chemical Properties tables that NFPA uses a different classification system than that used by the United Nations (UN) and the United States Department of Transportation (DOT). The latter do not distinguish between Class IA, IB, and IC flammable liquids, and class 2 combustible liquids. Substances in all four of these classifications are grouped together as class 3 flammable liquids by the UN and DOT.

Knowing that a liquid is labeled by UN and DOT as flammable for purposes of transportation and shipping, or falls within a particular NFPA flammability class for storage and handling is useful. However, it is insufficient information to adequately control material hazards and implement effective safe handling programs, though NFPA has published guidance specific to handling each class of flammable and combustible liquids.¹⁰

In order to implement an effective program, it is necessary to recognize and appreciate differences in the hazards posed by specific hydrocarbons¹¹ and chemical compounds within each flammability class. Hazards of one material may be different from hazards of another material even though both materials are categorized within the same NFPA flammability class.

Hazard severity is assessed within the context of the properties of the liquid, the circumstances in which the liquid is being used, and the manner in which the chemical is packaged, transported, stored, and handled (blended and processed).

Generalized statements such as “handle and store methanol in a manner similar to the way in which gasoline is handled and stored” are useful only to the extent they establish general expectations of what sorts of safety issues must be addressed. However, guidance based solely on flammability class seldom goes far enough or is specific enough to allow selection of a suite of overlapping safety measures which provide multiple independent layers of protection. Depending on the circumstances between three and eight levels of protection should be established for each hazard. Some levels of protection will safeguard multiple hazards while additional provisions may be necessary to adequately control and protect against a particular hazard in a particular set of circumstances.

¹⁰ NFPA 30, 2008 edition

¹¹ Hydrocarbons are understood to be liquids that boil over a range of temperatures; chemical compounds are understood to boil at a single characteristic boiling temperature.

Electrical conductivity is an example. ‘Specific electrical conductance,’ or the electrical conductivity of gasoline is so low that gasoline and other similar hydrocarbons such as kerosene, jet, diesel, and fuel oil are considered to be dielectrics (non-conductors or insulators). By comparison, specific conductance of methanol is several orders of magnitude greater than that of gasoline. Depending on the circumstances, precautions for bonding and grounding may be the same for gasoline and methanol. However, precautions for methanol may necessarily exceed those for gasoline if, for example, methanol containers are coated with a non-conducting spray-on material for corrosion protection. Because of its high conductivity, containers holding methanol are more susceptible to galvanic corrosion than containers holding gasoline. Additionally, methanol is a solvent, and is compatible with only selected plastics and rubbers. Plastic containers commonly used for gasoline may lose structural integrity when used to hold methanol.¹²

No two hydrocarbons, fuels, or chemicals have identical properties. It is essential that users implement safeguards based on properties specific to their materials, to their specific circumstances, and to their particular use. Guidance provided by NFPA, ASME, API, NEC, NACE, ISA, IEEE, and other groups are ‘generally-accepted good engineering practices.’ Protective measures provided by these organizations stipulate a minimum standard of care. Depending on users’ circumstances and aversion to the consequences of fire and explosion, additional measures beyond those indicated in codes, standards, recommended practices, and regulations may be deemed appropriate, necessary, and cost effective over the long term.

Despite the existence of commercial and industrial guidance, it must be emphasized that little or no specific guidance has been published for the personal use of methanol for ‘backyard’ batch-type manufacture of biodiesel. Guidance must be extracted from more generalized information published by organizations such as NFPA. First time or relatively inexperienced methanol users are advised to thoroughly research and become familiar with the hazards associated with the material and the use of that material prior to bringing it home. This is true for those manufacturing fuel for personal consumption or making a fuel blend.

Within the context of hazardous materials transport, storage and use, it is important to consider what might happen in addition to what one expects to happen. For example, there are very good reasons why transporting five-gallon cans of methanol in the trunk of a car or even in the bed of a pickup truck, is considered a dangerous activity.

- What if the can leaks?
- What if you are rear-ended by another vehicle?
- What if you suffer a seizure or heart attack while driving from the supplier to your home?

Not all of these events are likely, but all do have a chance of occurring. Guidance and regulations such as those for vehicular transport and storage of five and 55 gallon containers of methanol, ethanol, gasoline, diesel, and biodiesel may be obtained from local fire authorities. Be certain that you have assessed the potential consequences of actions which may jeopardize your safety and the safety of those around you.

The necessity of using material-specific parameters to assess and control hazards is illustrated by three examples. The examples are selected to characterize the range of methanol users from private individuals making biodiesel in 25- to 50-gallon batches to those who transport, store and use large quantities of methanol (e.g., oil refineries, chemical manufacturers, shipping companies, terminal operators, and transport companies).

¹² Refer to Methanol Institute Technical Bulletins “Above Ground Tank Storage of Methanol,” and “Methanol Drum Transport, Storage and Handling.”

1. BOUTIQUE-USERS: HANDLING AND TRANSFER OF GASOLINE/METHANOL IN NON-BULK CONTAINERS:

Gasoline is classified as an irritant; methanol is classified as a toxic material. The consequences of inhaling gasoline vapor when mouth-siphoning liquid from one container to another are unpleasant and may cause acute health effects; however, these are mild compared to consequences of swallowing liquid methanol or inhaling methanol vapor.

Methanol may be toxic to some individuals in tea-spoon-sized amounts. Toxic effects of methanol vapor are cumulative within the body. An exposure that does not result in a health effect after the first instance may cause serious health effects on the second or third occasion. Avoid ingesting, inhaling, and contacting methanol and methanol containing fuel blends. If siphoning transfer of methanol is warranted, then use a siphon pump constructed of a methanol compatible material, wear personal protection equipment (PPE), bond and ground the siphon, and provide containment in the event of a spill. NEVER transfer methanol by sucking on an improvised siphon hose to start liquid flow.

Static accumulation is another situation to consider when siphoning, pouring, and performing other forms of container-to-container transfer of flammable liquids. The electrical conductivity of gasoline is 25 pS/m (pico Siemens per meter), and that of low sulfur diesel fuel is 5 pS/m.¹³ Conductivity of gasoline and diesel is so low that these fuels can accumulate static charge during pumping, filtering, and splash transfer operations. Grounding and bonding during liquid transfer is a necessary protection against static discharge when handling all flammable liquids. This is especially true for liquids that have conductivities less than 50 pS/m, and for practical purposes, 100 pS/m. Liquids with conductivity less than 50 pS/m accumulate static charge.¹⁴ Low conductivity hydrocarbon fuels such as gasoline, kerosene, and low sulfur No. 2 diesel are liquid dielectrics (i.e., insulators).^{15,16} Transfer rate must be carefully controlled,¹⁷ and containers, hoses, and piping must be bonded and grounded so that electrical resistance of the connection to ground is no greater than 106 ohm for static dissipation and 1-2 ohms for lightning and stray current protection.¹⁸

¹³ Refer to the Physical and Chemical Properties Tables of this Technical Bulletin

¹⁴ http://www.nts.gov/recs/letters/1987/M87_23_25.pdf; Marine Accident Report "Explosion Aboard Tank Barge TTT 103, Pascagoula, Mississippi, July 31, 1986" (NTSB/MAR-87/06)

¹⁵ Fuel oils (kerosene, diesel, fuel oil, and residual fuel oil in the USA; fuel oil and residual fuel oil in Europe) and gasoline are dielectric liquids. Dielectric liquids are defined as having electrical conductivity < 10⁻⁶ S/m or 1 μS/m. [http://www.mbhes.com/conductivity_measurement.htm; <http://www.dispersion.com/non-aqueous-conductivity.html>]

¹⁶ A.I. Belousov, I.V. Rozhkov, and E.M. Bushueva: *Measurement of Bulk Conductivity of Hydrocarbon Liquids*, © 1983 Plenum Publishing Corporation, UDC 665.7:543, p. 474.

¹⁷ Pipe maximum velocity = 23 ft/s and maximum air drop velocity = 3 ft/s until fill pipe is submerged at which time velocity may be increased to between 15 and 20 ft/s. [American Petroleum Institute: "Precautions Against Electrostatic Ignition During Loading of Tank Motor Vehicles," 1975, NFPA 70, and http://resource.invensys.com/instrumentation/documentation/eib/ti/ti_027-072.pdf]

¹⁸ API Recommended Practice 2003, 6th edition, September 1998, "Protection Against Ignitions Arising Out of Static, Lightning, and Stray Currents"

By comparison, the electrical conductivity of neat methanol is 44×10^6 pS/m¹⁹ (44 μ S/m) and that of industrial grade methanol is 30 μ S/m²⁰. The specification for electrical conductance of fuel grade methanol varies by manufacturer, but it is given by PCC Morava Chemicals as less than 1000 μ S/m.²¹

Like water, methanol is a polar material and has a relatively high conductivity compared to non-polar hydrocarbon dielectrics such as gasoline and diesel fuel (conductivities less than 1×10^4 pS/m). Liquid fuels which have specific conductivity greater than 50 pS/m are not exempt from the necessity of bonding and grounding. The relatively high conductivity of methanol indicates that accumulation of static charge within the liquid is less likely and is not expected under normal circumstances. However, static accumulation, static discharge, and vapor ignition are known to occur in abnormal circumstances more often than might be supposed. The risk of not taking appropriate bonding and grounding measures is that an abnormal circumstance may exist, but can go unrecognized.

Two examples of the consequences of failing to adequately bond and ground when unrecognized abnormal circumstances existed during methanol transfer are described below.

- 2006, California. Green Star Products, Inc., of Bakersfield, California reported a serious “fire incident” late last month at the site of ABF’s biodiesel plant. According to GSPI, the accident occurred outside of the plant building when, during a transfer of methanol, a small spill ignited. While the ignition source remains unknown, GSPI expects it was likely caused by static electricity. ABF suffered a total loss of the building and equipment. No plant personnel were injured during the blaze.²²
- 2008, Canada. During abnormal transfer of methanol from one tanker truck to a second tanker truck, the methanol ignited causing one fatality, destroying the trucks, and damaging a load out facility. Investigators suggested the source of ignition was static discharge resulting from a damaged transfer hose which interfered with grounding and bonding.²³

Never transport methanol or gasoline in the trunk of a car, even if the trunk lid is open. Vehicular transport must be placarded, and transport within the US must comply with other DOT requirements including provisions for manifest papers, driver emergency response training, emergency response equipment, and emergency notification capability. Always store gasoline and methanol outside, under cover, and in a well ventilated location. It is not normal practice to store and use 55-gallon quantities or even five-gallon quantities of methanol in urban and suburban housing environments. Contact your local fire marshal before bringing 55-gallon and even five-gallon quantities of flammable liquid to your residence. DO NOT store flammable liquids of any kind, including gasoline and methanol, in your house, garage, patio, or basement, or immediately adjacent to your house, garage, or car port.

¹⁹ Laurence G. Britton: *Avoiding Static Ignition Hazards in Chemical Operations*. © 1999 by American Institute of Chemical Engineers, ISBN 0-8169-0800-1, pp. 282

²⁰ <http://baltchemtrade.com/site/files/metanol-en.pdf> and http://n-azot.ru/download/product/product_337.pdf

²¹ http://www.pccmorava-chem.cz/tw/mch.nsf/id/EN_Methanol

²² Joseph LaStella, GSPI: “Methanol Spill at CA Biodiesel Plant Ignites Devastating Fire,” *Alternate Transportation Fuels Today*, March 3, 2006; <http://www.allbusiness.com/operations/shipping/870584-1.html> as of March 2011.

²³ Fires & Explosions in the Canadian Upstream Oil & Gas Industry: Incident #23-Methanol Spill Ignited While Preparing to Repair Tank Truck Leak; http://www.firesandexplosions.ca/case_studies/case_details.php?id=27.

2. REFINERIES AND BIODIESEL MANUFACTURERS: HOT WORK AND FLAMMABLE LIQUID VAPOR CONTROL

Gasoline floats on water while methanol is fully miscible with water, though methanol floats during methanol-water mixing. Methanol-water mixtures burn at high water concentrations (ratios of 3:1 to 4:1 water: methanol v/v).²⁴ If floating methanol is ignited, it continues to burn as it mixes with water and the methanol-water solution burns when mixing has occurred. In this situation, addition of water may increase the volume of flammable liquid.

Gasoline TVP is 190 mmHg and the TVP of methanol is 90 mmHg. The partial pressure of gasoline vapor over liquid gasoline is twice that of methanol vapor over methanol liquid, which is to say that volume for volume gasoline emits twice as much vapor as does methanol. The amount of heat required to vaporize a pound of gasoline is about a third of that necessary to generate a pound of methanol vapor. The flammability range for gasoline is 1.4 to 7.6 v/v %, compared to 6.0 to 36.5 v/v % for methanol. Gasoline vapor is within its flammable range at 30% of the concentration of methanol under identical circumstances, but passes out of the flammability range much more quickly than methanol as liquid temperature increases.

Ignition energies of gasoline and methanol are similar (0.2 mJ and 0.14 mJ respectively). An ignition source with sufficient energy to ignite gasoline will also ignite methanol and vice versa. Gasoline vapor is heavier than air and tends to flow along the ground and accumulate in low lying areas. Methanol vapor is near neutral buoyancy and responds more readily to dilution and dissipation caused by natural convection currents and forced ventilation. Non-bulk and bulk storage of both gasoline and methanol must be grounded, bonded, and well ventilated. Storage areas should be equipped with vapor detectors. Detectors for gasoline must be positioned to detect gasoline as a dense vapor, while positioning of methanol vapor detectors may be different from that of gasoline vapor detectors because of the difference in relative density of gasoline and methanol vapors. The sensitivity of methanol detectors may need to be greater than that for gasoline.

Vapor density of methanol is 1.1 relative to that of air while the vapor density of gasoline is 3 to 4. Vapors of both gasoline and methanol may be explosive in confined spaces. It is recommended that storage areas be ventilated, that storage containers are clearly labeled, bonded and grounded, that protective restricted-access hazard zones be declared around storage areas, and that sources of ignition be eliminated within designated zones.

A shipping terminal may decide to use inert gas to pad storage tanks for both gasoline and methanol, but for different reasons. The purpose in padding gasoline storage may be for fire protection because of the relatively low concentration of the lower flammability limit. If ambient temperature of the liquid is sufficiently low that vapor pressure causes concentration within the freeboard volume of the tank to be within the flammable range, then it may be desirable to use inert gas padding to avoid piloted ignition within the tank.

The purpose of padding methanol may serve multiple purposes:

- 1.) Fire protection due to the wide flammability range of methanol
- 2.) To maintain methanol purity. Facilities which are located in areas that have characteristically high humidity, and/or which have airborne salts run the risk of contaminating neat methanol as ambient air is sucked into and out of tanks during tank level fluctuations during normal operations.

24 Methanex: *Technical Information & Safe Handling Guide for Methanol, version 3.0, September 2006.

At normal liquid storage temperatures, the concentration of gasoline vapor within the vapor space for gasoline storage quickly exceeds the upper flammability limit of 7.6 v/v %. The upper flammability limit of methanol is 36%, and methanol has a much lower equilibrium vapor pressure than gasoline. Vapor concentration within methanol storage tanks may be in the flammable range when vapor concentration in a gasoline storage tank is outside the flammable range and vice versa.

3. ALL USERS: NON-BULK AND BULK STORAGE FIRE PROTECTION AND RESPONSE:

Fire response for a methanol fire is different than that for a gasoline fire.

- Gasoline fires produce copious amounts of luminous combustion products that make gasoline flames readily visible during daytime and bright sunlight. Methanol flames are non-luminous and are difficult to detect visually in daytime, particularly in bright sunlight. In order to effectively fight a liquid fire, it is necessary to identify the location of the fire. Hand held infrared sensors are available to assist fire fighters responding to methanol fires. As good practice, methanol users should have at least one sensor on site and available to first responders. Sensors should be calibrated and functional. Local fire response should also have infrared sensors.
- Gasoline floats on water and application of water spray, particularly as a cohesive stream from a fire monitor may cause the fire to spread. By comparison, methanol floats on and rapidly mixes with water. Methanol water mixtures will burn at very high water concentrations. Water is most effective as a suppressant when applied as a spray mist or as a fog. Both gasoline and methanol may form running fires if fire-suppressive water is not physically contained by dikes, berms, and curbs. Propagation of methanol fires may not be immediately noticed by responders.
- Methanol is more toxic than gasoline, even to skin contact. Responders to a methanol fire must wear PPE that protects against chemical exposure as well as exposure to radiant heat. Turnouts provide heat protection but not chemical protection. Inhalation protection is also required.
- Given identical circumstances, vapor cloud explosions may be more likely to occur from spilled gasoline than from a methanol spill. This is especially true in confined areas. The specific gravity of gasoline vapor is 3-4 times heavier than that of methanol vapor. Gasoline vapor has higher tendency to accumulate in low lying and poorly ventilated areas than does methanol vapor, and will flow along ground surface in a downhill or downwind direction over long distances. Gasoline has a lower flammability range, lower flash point temperature, and lower autoignition temperature than methanol. Ignition of vapor within a confined space may cause an explosion with either gasoline or methanol.
- Non-bulk and bulk shipping containers holding gasoline are marginally more likely to BLEVE in a fire than those containing methanol. Gasoline has higher vapor pressure, lower specific heat, and lower latent heat of vaporization than methanol (i.e., less heat is required to cause evaporation of gasoline than of methanol). Pressures within gasoline containers will increase more rapidly than within methanol containers when exposed to the same radiant heat flux. The lower heating value of methanol is 9,080 Btu/lb compared to 19,000 Btu/lb for gasoline. Radiant heat released by a gasoline BLEVE will be twice that of methanol. The stoichiometric laminar flame speed of methanol is only marginally higher than that of gasoline, so differences in overpressure due to differences in flame speed is not a consideration. Flame temperature of gasoline is marginally greater than that of methanol. Differences in flame speed and explosive overpressure are likely offset by the much higher heat release of gasoline.
- Fire suppression foam used to fight gasoline fires is not suitable for use on methanol fires, as methanol

fires require alcohol resistant foam. Good practice consists of inventorying alcohol resistant foam both on a user's property and at the location of first responders. It is also good practice to periodically perform response exercises for various scenarios. Table-top exercises may also be useful. Verify that fire suppression foam is of the correct type and that its suppression capability does not degrade as a result of time in storage, or storage temperature variability if the facility is in a hot or cold climate. Verify that fire suppression effectiveness is not compromised by freezing, or exposure to temperatures over 100oF.

In summary, gasoline may be more or less hazardous than methanol depending on the particular set of circumstances.

A tragic example of this involving a race car driver and his chief mechanic occurred in 2010. The driver and mechanic were celebrating winning an important race in the parking lot of their automobile repair shop. In their excitement they decided to ride a lighted drum of methanol across the parking lot of their garage facility. They poured four gallons of methanol racing fuel into an empty drum, tipped the drum over, positioned the bung in an easy-to-reach position, sat atop the drum like it were a horse, and lit the drum. Their expectation was that the drum would slide across the parking lot like a rocket. Instead, the drum exploded. One man died and the other was critically injured.²⁵

Methanol, which had increased their survivability in the high stakes sport of automobile racing hours earlier, caused serious injury and death under a different set of circumstances. Though it is unlikely, this may have been a near miss incident had the drum in this instance contained gasoline instead of methanol because of differences between the properties of the two materials. The high vapor pressure, heavier-than-air vapor, small flammability range, and low value of the upper flammability limit for gasoline may have created a fuel-rich atmosphere within the drum that was incapable of igniting. Had this in fact been the case, the men would have been unsuccessful at lighting the drum and the catastrophe would have been avoided. Whereas the men would have possibly recognized the hazards had they used gasoline, it is likely they did not appreciate a potentially greater hazard posed by methanol in this highly abnormal situation.

This tragic example illustrates the importance of understanding the physical and chemical properties of the specific material with which you work and how they apply to your specific circumstances, in order to be able to recognize unique hazardous conditions and establish appropriate measures to manage flammable liquids safely.

²⁵ Internet web page as of March 2011: <http://www.komonews.com/news/local/98960929.html>