Atmospheric Above Ground Tank Storage Of Methanol -

1.1 INTRODUCTION

Guidelines for designing, fabricating, constructing, repairing, and safeguarding above-ground methanol storage tanks are essentially the same as those for liquid transportation fuels such as ethanol and gasoline, and flammable liquid feed stocks such as benzene, acetone, and toluene. However, physical and chemical properties of methanol are unique to methanol and are not the same as those of other bulk-stored flammable liquids. Some considerations of tank storage are unique to methanol.

One important consideration is flammability range. Because the upper flammability limit of methanol is 36 percent by volume (vol%) compared to that of gasoline which is 6-7 vol%, methanol vapor can ignite and burn inside tank vapor space.

Corrosion is another consideration. Methanol is a conductive polar solvent; gasoline is a non-conductive, non-polar solvent. Galvanic and dissimilar metal corrosion in methanol service may be high if incompatible materials are placed in electrical contact with one another. Cathodic protection, and regulator inspection of methanol storage tanks and trim hardware is vitally important to avoid corrosion failure.

Principal considerations of tank storage of methanol are siting, liquid and vapor containment, electrical grounding, cathodic protection, protection from stray currents, in-tank vapor control, vapor space fire suppression, and management of inhalation, ingestion, and dermal contact.

Methanol Institute recommends that users familiarize themselves with relevant codes and standards, and devise and implement a disciplined layers of protection program to prevent spills, accidental release, over pressure, ignition, and fire suppression. It is essential that fire detection, alarm, response, and suppression be rapid and effective.

Guidance for design, fabrication, construction, and tank safety are available in American Petroleum Institute (API) publications:

- API Standard 620, *Design and Construction of Large, Welded, Low-Pressure Storage Tanks*
- API Standard 653, *Tank Inspection, Repair, Alteration, and Reconstruction.*

Provisions for siting, electrical grounding, berming, and safeguarding above ground storage tanks containing flammable liquids are given by the International Code Council (ICC) and the National Fire Protection Agency (NFPA). Guidelines are available in:

- NFPA 1, *Uniform Fire Code*
- NFPA 30, *Flammable and Combustible Liquids Code.*

Considerations not addressed in the above-sited references are specific to methanol storage, namely:

- Materials selection
- Purity and cathodic protection
- Fire prevention, suppression and spill containment.

1.2 TANK MATERIALS OF CONSTRUCTION & TRIM MATERIALS COMPATIBILITY

Methanol is classified by the International Code Council and the National Fire Protection Agency as a class IB flammable liquid. Other IB liquids are ethanol, hydrocarbon fuels such as gasoline and kerosene, and reactants such as benzene, acetone, and toluene. No. 1 diesel, No. 2 diesel, and biodiesel are classified as combustible motor fuels, and are also handled and stored in above ground atmospheric storage tanks.

Methanol gasoline fuel blends are subject to phase separation in the presence of water. Methanol and water, two polar compounds, form a mixture which separates from gasoline, a non-polar mixture of C4 thru C12 hydrocarbons. Methanol boils at 149 °F; gasoline boils over a range of temperatures extending from 95°F to 390 °F.

Methanol tanks can be constructed of either carbon steel or 300 series austenitic stainless steel. Carbon steel has the advantage of lower capital cost, but the disadvantage of higher life cycle cost due to increased maintenance and costs associated with corrosion protection. Because methanol is a polar solvent, galvanic corrosion is more prevalent with methanol than with other commonly-used motor fuels.

Because of its very high affinity to form mixtures with water, methanol is hygroscopic and extracts moisture from ambient air that enters tank vapor space during normal liquid level cycling. In the presence of neat or technical grade methanol, the small amount of water added by desiccation of atmospheric air does not substantially increase the rate of general corrosion. Never-the-less, because of the relatively high conductivity of liquid methanol, corrosion induced failures of carbon steel tanks have been reported. Efforts to coat interior tank surfaces with epoxy resin have met with limited success. Typical coating life is less than seven years, and the coatings tend to form an electrically non-conductive barrier between the methanol and the tank thereby complicating bonding and grounding. Recent reports indicate progress is being made in developing more suitable electrically conductive spray-on tank liner coatings.

Galvanic corrosion of dissimilar trim materials may be accelerated in methanol service, particularly trim mate- rials of aluminum, lead, magnesium, copper, zinc and platinum alloys. An example of this resulted in a methanol tank fire when the aluminum alloy flame arrester corroded to the point of being non-functional. "The Chemical Safety Board concluded that the flame arrester did not prevent the fire outside the tank from igniting the tank contents. Routine inspections would have detected the corrosion in the flame arrester that occurred over 12 years. The use of an aluminum flame arrester in methanol service coupled with the lack of inspection and maintenance allowed the flame arrester to corrode to the point that it no longer functioned."

Galvanized steel is not suitable for methanol service.

If the methanol-water mixture forms within a gasoline-methanol blend and separates from the gasoline as a separate phase, then localized corrosion may be accelerated. If the water phase accumulates chloride salts due to proximity to a coastal environment, then under-deposit corrosion, localized pitting corrosion, and crevice corrosion may be accelerated. In extreme cases, stress corrosion cracking (SCC) of high carbon, non-molybdenum stabilized austenitic stainless steel weld heat- affected zones may result due to localized exposure to water containing high concentrations of chlorides.

Methanol is one of the few specialized environments, which may cause SCC in titanium alloys. SCC failures have occurred in dry methanol, methanol/acid and methanol/halide mixtures. Water is an effective inhibitor and will maintain the passivity of titanium alloys in some environments.

Titanium Alloy Grade	%water- Intermittent exposure[1]	% water - Sustained exposure
1,2,7,11,16,17	1.5	2.0
9, 12	2.0	2.0
28	2.5	3.0
5,23	3.0	3.0
19, 29, 6-2-4-6	5.0	10.0

1 Intermittent exposure is short term non-continuous contact; sustained exposure is long term continuous contact.

Where-as, SCC has been observed in ethanol tanks, this phenomenon has not been reported for methanol service. Never-the-less, good practice for analysis of failed components should include consideration of phe- nomena observed in ethanol service.

Plastics are generally not recommended for storage purposes due to long-term deterioration of plasticizers, loss of mechanical integrity, and risk of methanol contamination. Many resins, nylons and rubbers, particularly nitrile (Buna-N), ethylene-propylene, Teflon and neoprene are used satisfactorily as components of equipment in methanol service.

1.3 METHANOL PURITY PROTECTION

Carbon steel is more likely to corrode and cause methanol contamination than stainless steel, particularly in the presence of moist air and/or water in coastal environments. This can be mitigated by padding tank free- board space with dry inert gas such as nitrogen.

Stainless steel has higher capital cost than carbon steel, but offers the advantage of lower life cycle maintenance cost, and reduced likelihood of methanol contamination. Three-hundred series stainless steel alloys are recommended. Alloy selection and welding procedures should avoid sensitization of weld heat-affected zones. The American Welding Society (AWS) and the American Society of Metals (ASM) offer guidelines for preventing heat-affected zone sensitization.

The National Association of Corrosion Engineers (NACE) offers guidance for cathodic protection of above ground storage tanks. Internal cathodes are not required or recommended to achieve adequate protection in methanol service, particularly in floating roof tanks.

Methanol absorbs moisture from air. If tank liquid level cycles through large volumes on frequent intervals, then moisture-laden ambient air may be pulled into the tank. This may be particularly harmful in a coastal en- vironment where moisture laden air carries dissolved chloride salts. If the facility is in a region that has char- acteristically high relative humidity, then methanol will dry the air in the vapor space of the tank and thereby self-contaminate the contained methanol.

If purity is an important consideration, then inert gas padding and stainless steel tanks may be economically justified as product quality and risk reduction measures. Be certain to pay equal attention to selecting compatible trim materials.

Water absorption can be eliminated by padding tank vapor space with an inert gas such as argon or nitrogen, or by padding the vapor space with dry natural gas. If natural gas is used, then measures to eliminate ignition must be thorough, consistent, and rigorously enforced. Methane is a lighter-than-air gas and is expected to float up and away from the tank vent when expelled. Never-the-less, precaution should be taken to avoid accidental ignition of expelled methane by controlling potential ignition sources near and above the tank. Hot work above unpadded and methane-padded methanol tanks must be managed and controlled.

Inert gas padding reduces the need for controlling ignition sources, providing methanol vapor and/or condensed vapors do not leave the tank by way of a gravity drain that discharges alongside the tank. Inert padding protects against contamination, accidental ignition, and exposure to airborne toxic vapor. Incidentally, tank vapor space inerting may be required in order to obtain a variance regarding setback distances. Refer to International Fire Code (IFC) 2016 Sections 911.1 and 5704.2.9.5 and 5704.2.9.6 for guidelines regarding variances in setback distance.

1.4 FIRE PREVENTION

The U.S. Department of Transportation (DOT) classifies methanol as a "Primary Class" 3.2 flammable liquid and a "Secondary Class" 6.1 toxic substance. Protective safeguards should be developed for both hazards which may be present near tanks and within spill impoundment areas. This includes protection of workers during normal operation and maintenance, and safeguarding fire fighters and first responders during accidental releases.

The International Code Council (ICC) and the National Fire Protection Association (NFPA) designate methanol as a Class IB flammable liquid. Class IB liquids are characterized by flash points below 73°F and boiling points at or above 100 °F. Gasoline is another example of a commonly-used Class IB liquid, but with important differences due to the polarity of methanol, and the non-polarity of gasoline.

Practically speaking, the vapor pressure of Class IB liquids under commonly-expected conditions of outside tank storage is high during warm portions of the year. The vapor phase is the most hazardous physical state of methanol; airborne methanol vapors are mobile, and are readily ignited and readily enter the body by way of the lungs. Hazard management is especially important when the temperature of the liquid phase rises above flash point temperature. The fact that flash point temperature of methanol is low indicates substantial amounts of vapor are present immediately above the liquid surface and within the vapor space of the tank. Liquids with vapor pressure greater than 10 mm Hg are considered flammability-explosion hazards. The vapor pressure of methanol is several times this value at commonly encountered ambient storage temperatures. Ignition may occur both within and outside the tank, and may be accompanied by tank liquid contents roll-over due to external heating and subsequent Boiling Liquid Expanding Vapor Explosion (BLEVE).

Depending on liquid temperature, vapor may be capable of supporting combustion if the vapor-air composi- tion is within the flammable range, and if vapors are exposed to a sufficiently energetic ignition source. The flammable range of methanol is much broader (6 vol% to 36 vol %) than that of gasoline (1.4 v% to 7 v%). Ignition energy of methanol is 0.14 millijoules (mJ) compared to that of gasoline at 0.20 mJ. These values are essentially the same as those for most motor fuels, and therefore not a major factor in assessing ease of igni- tion. Flash point temperature, vapor pressure (or Reid vapor pressure), upper and lower flammability limits, autoignition temperature, and heat of combustion are more important parameters when assessing the relative ease of ignition and hazard severity of methanol and gasoline.

Methanol fires are more likely to occur than gasoline fires within tank freeboard space when liquid temperature is near or above the methanol flash point temperature (52 °F). The vapor pressure of methanol is 90 mm Hg at 68 °F and that of gasoline is 190 mm Hg at 68 °F. The volumetric concentration of gasoline vapor is much higher at a given temperature than that of methanol. This may cause vapor concentration of gasoline to exceed the 7 v% upper flammable limit, but not the concentration of 36 v% of the upper flammability limit of methanol. Safeguards for gasoline tank fires are no necessarily sufficient to prevent methanol tank fires. During tank filling, methanol vapor is displaced through tank vents to atmosphere thereby creating potential flammability and toxicity hazards in the ambient air which surrounds the tank. These hazards can be controlled using either of two strategies:

- Eliminating ignition sources and recognizing toxicity hazards in the proximity of the tank by classifying the area surrounding the tank as a hazardous location.
- Excluding air from tank vapor space by inerting or gas blanketing.

Tank storage of methanol requires strict and rigorously-enforced provisions to prevent over filling and tank overflow. Tank maximum allowable working volume must always allow additional volume for liquid expansion. The volumetric coefficient of thermal expansion for methanol (0.00066 /°F) is greater than that of gasoline (0.00056 /°F). A general rule of thumb is to allow 20% of tank working volume for liquid expansion.

Guidelines for sizing the volume of a methanol tank containment dike are not the same as for fuels such as gasoline and diesel. Spill containment must allow extra capacity for the substantial volume of fire water (greater than 5 parts water to 1 part methanol) necessary to dilute methanol to a non-flammable concentration. This consideration is discussed in detail under the heading of "Spill Containment."

Provisions for controlling potential ignition sources near methanol liquid storage tanks are more or less the same as those for gasoline. The lower flammable limit of gasoline vapor is 1.4 v% compared to 7 v% for meth- anol. The relative density of gasoline vapor is 3 to 4, compared to that of methanol which is 1.1. Gasoline vapor will travel further along the ground without being diluted below the lower flammability limit and will ignite at much lower concentration than methanol vapor.

Generally speaking, the hazard zone for ignition of methanol vapor is less restrictive than that of gasoline. The perimeter of hazard zones for methanol must con- sider both the toxicity and the flammability of methanol. Refer to the following for information on classifying, designating, and safeguarding hazardous locations:

- A.W. Cox, F.P. Lees, and M.L. Ang: *Classification of Hazardous Locations*, Published by Institution of Chemical Engineers, Davis Building, 165-171 Railway Terrace, Rugby, Warwickshire, CV21 3HQ, England, © 1990, ISBN 0 85295 258 9
- NFPA 70E, *Standard for Electrical Safety Requirements for Employee Work Places*
- NFPA 70, *National Electrical Code*

The United States Occupational Safety and Health Administration (OSHA) among others, provides guidance for permitting, testing, entering, and safeguarding employees during performance of hot work within hazardous locations and confined spaces. The applicable sections of Title 29 of the Code of Federal Regulations (CFR) are:

- 29CFR1910.106, *Flammable and Combustible Liquids*
- 29CFR1910.146, *Confined Space Entry*
- 29CFR1910.252, *Fire Protection and Prevention*
- 29CFR1910.253, *Oxygen Fuel Gas Welding and Cutting*
- 29CFR1910.254, *Arch Welding and Cutting*
- 29CFR1910.255, *Resistance Welding*
- 29CFR1917.152, *Marine Terminals Welding, Cutting, and Hot Work*
- 29CFR1910.301, *Electrical Safety*

Other applicable references include:

- API Publication 2201, *Procedures for Welding or Hot Tapping on Equipment Containing Flammables*
- NFPA 51-B, *Fire Prevention During Welding, Cutting, and Other Hot Work*
- Association of Energy Services Companies (AESC) *Hot Work*
- American National Standards Institute (ANSI) Z49.1-67, *Safety in Welding and Cutting*
- American Welding Society (AWS) Z49.1-88, *Safety in Welding and Cutting and Applied Processes*

1.5 FIRE SUPPRESSION

Fire suppression may use any of several media:

- Alcohol resistant fire-fighting, fire-extinguishing foam (AR-AFFF)
- Dry chemical extinguishers (for small fires)
- CO2
- Water mist spray

Guidelines for foam extinguishing systems with optimum application rates are provided in NFPA 11. Fixed fire monitors may be used to cool tank walls and to extinguish flames provided at least five parts water is added for every one part of methanol: i.e., methanol concentration is diluted to less than 15%. Water-methanol solutions are flammable to compositions of about ≈ 80 v% water.

Some facilities equip methanol tanks with an internal foam delivery system combined with an internal floating roof. Care must be taken to coat the internal floating roof if it is constructed of aluminum or aluminum/mag- nesium alloy. Methanol is mildly corrosive to aluminum-magnesium, aluminum-copper, and copper-zinc alloys.

1.6 TANK SPILL CONTAINMENT

General guidance for liquid hydrocarbon (gasoline, kerosene, and diesel) spill containment is to size the containment volume to at least 110% of the working volume of the largest tank within a tank battery. This volume accommodates a worst case, full tank breech when precipitated moisture is present within the containment without overflowing containment dikes. Guidelines for spill containment are provided in NFPA 1, NFPA 30, and federal regulations for spill prevention: 40CFR110 and 112.

Because methanol is highly soluble in water, and because flammability of water-methanol solutions is per- sistent to high proportions of water, it is suggested that the containment volume for methanol tank spills be enlarged accordingly if water is to be used as an extinguishing medium. The additional containment volume must be sufficient to allow responders to use water as a suppressant without overflowing the tank impoundment dike. If alcohol resistant foam is used, then less volume is required for spill containment. Provisions must insure that a sufficient amount of AR-AFFF suppressant is onsite and available to extinguish worst case fire scenarios.