METHANOL INSTITUTE

METHANOL SAFE HANDLING TECHNICAL BULLETIN

PRECAUTIONS FOR LOADING, UNLOADING, TRANSPORT AND STORAGE OF METHANOL

Methanol requires that handlers pay particular attention to two specific hazards in order to avoid accidental release and ignition of methanol and methanol mixtures: 1) accidental combustion hazard, and 2) accelerated corrosion of common containment alloys.

Hazards associated with loading, unloading, rail and road transport, and tank storage of methanol are essentially the same regardless of intended use. The severity of the hazards varies depending on circumstances and ambient conditions. For example, accidental release of methanol from pressurized piping causes immediate liquid flashing and vapor generation. Accidental release of methanol from a gravity transfer system results in liquid pooling and substantially less vapor generation. Combustion and corrosion hazards are always present to a greater or lesser extent when handling methanol.

COMBUSTION

Combustion is the most widely recognized hazard associated with methanol. Ignition and sustained combustion occur in the vapor phase immediately above a liquid surface: vapors burn; liquids do not. Conditions capable of supporting combustion are determined by the partial pressure of methanol vapor above a liquid, and the relative molar concentration of methanol vapor in surrounding air. Methanol vapor/air mixtures with concentrations between the flammability limits will burn in a sustained manner if ignited. Ignition energy of methanol is similar to that for gasoline boiling-range fuels.

A uniform mixture of methanol and air at ambient temperature and pressure, and above the upper flammability limit is too rich to burn because there is insufficient oxygen to support combustion. Similarly, if the methanol vapor in air is below the lower flammability limit, then combustion cannot be sustained because there is insufficient fuel. In this case the mixture is too lean to burn. If the concentration of methanol vapor in air is within the flammability range, then ignition and sustained combustion are expected to occur in the presence of a sufficiently energetic ignition source.

It is particularly important to understand the principles of hazard control for methanol because methanol, a weakly polar flammable chemical, is 100% miscible in water. The attraction between water vapor and methanol liquid is so great that methanol is an effective desiccant for removing moisture from air.

The affinity between water and methanol requires special fire fighting techniques when responding to methanol fires. Because the partial pressure of methanol vapor is high compared to that of water vapor in methanol/water solutions , these solutions will burn at concentrations which are 70% water. Water may or may not act as an effective extinguishing medium for methanol fires, depending on circumstances. For example, a mist or fine spray generated by a loading rack spray curtain may knock methanol molecules out of the air above a pool fire, reducing the further spread of flames. Application of water as a pressurized stream from a nozzle or water cannon may create “running fires” in methanol gasoline blends, which may be doubly hazardous because methanol flames are difficult to see in bright sunlight, and because uncontrolled addition of water may cause a fire to spread rapidly and unpredictably.

CORROSION

Corrosion is a second hazard resulting from the affinity between methanol and water. Air-absorbed moisture in the presence of inorganic salts causes methanol to be unexpectedly corrosive to carbon steel alloys which are commonly used for containment. Methanol containment systems require special provisions for corrosion monitoring, crack detection around high stress welded joints, and nondestructive inspection of anomalous conditions which are subject to crevice and pitting-types of corrosion. This is true for storage, transport and piping systems. Pipelines may also be subject to accelerated localized corrosion if used to transport methanol or methanol/gasoline blends.

BEST PRACTICE

Best practice for loading, unloading, transporting, and storing methanol is determined by inherent hazards of methanol, and by circumstances associated with blending and handling, and by considerations which accompany potential accidental release. In order to prevent fire, practices for loading, unloading, transporting, and storing methanol should consider taking the following precautions:

1. Avoid accumulation and subsequent discharge of static electricity within low methanol concentration blends which may result from turbulence:
   - A. Control flow rate into and out of containers to minimize turbulence and avoid accumulation of static electricity within the flowing liquid[1];
   - B. Discharge through a liquid seal dip leg pipe rather by free-falling through air to prevent air entrainment, absorption of moisture, and accumulation of static electricity in the falling liquid;, Bond and ground tanks, vessels, containers, and associated piping,
   - C. Avoid switch loading with gasoline, diesel, and other petroleum products that have bulk electrical conductivities less than 50 picosiemens per meter.

2. Isolate liquid and vapors from recognizable ignition sources (electrically-caused sparking, electrically-generated hot spots, welding, brazing, grinding, oxy-acetylene cutting, air-arc gouging, internal combustion engines, space heaters, etc.) to a radial distance of 50 feet.

OR

3. Prevent contact with air (oxygen) by padding free board in vessels tanks and containers with inert gas (e.g., nitrogen). International Maritime Organization (IMO) regulations make padding a requirement for individual vessel tanks 3000 m3 or larger. Consider using a combination of gravity and pressure transfer using nitrogen rather than pump transfer.

4. Cordon the area surrounding transfer to a radial distance of 50 feet and use caution tape and signage indicating presence of a flammable hazard.

5. Seal drains and sewers to a distance of 50 feet or more as appropriate. Methanol spills may create flammable mixtures of vapor in air as they run down hill and pool.

6. Use appropriate personal protection equipment.

Methanol is not a static accumulator. This is recognized by the American Petroleum Institute (API) in recommended Practice 2003 (API-RP-2003) Protection Against Ignitions Arising out of Static, Lightning and Stray [1]Currents which states in part that in most situations when water-soluble liquids (such as alcohols) are handled in grounded conductive equipment they "do not accumulate electrostatic charges because of their relatively high electrical conductivity (greater than 50 picosiemens per meter)". API-RP-2003 also states that the necessary precautions for prevent build-up of static charge "do not apply to the loading of … water-soluble products such as alcohols. These materials do not accumulate hazardous static charge." The APRP-2003 stipulates that the accumulation of electric charge is likely if the electrical conductivity of the liquid is below 50 picosiemens per meter. However, the electrical conductivity of methanol is considerably greater than 50 picosiemens per meter. A value for pure methanol has been reported as 150,000 picosiemens per meter (Commercial Solvents Corporation). Values measured for commercial grade methanol have been in the range of 2 X 106 to 2 X 107 picosiemens per meter (Methanex).

Physical properties of methanol are available in Appendix B of the Methanol Institute's *Methanol Safe Handling Manual.*