

Methanol

Safe Handling, Loading / Unloading,
Transportation / Storage

WHAT IS METHANOL?

- o Methanol is a colorless alcohol, hygroscopic and completely miscible with water, but much lighter.
- o Methanol, also known as methyl or wood alcohol, is a colorless organic liquid at normal temperature and pressure.
- o The particular hazards of methanol that matter most to your facility depend in large part on how methanol is received and stored, how it is used, where it is used, and how much is stored and used at any given time.

FIVE OVERRIDING CONSIDERATIONS ARE IMPORTANT WHEN HANDLING METHANOL:

- o Methanol is a flammable, easily ignited liquid that burns and sometimes explodes in air.
- o The molecular weight of methanol vapor is marginally greater (denser) than that of air (32 versus 28 grams per mole).
- o In certain specific circumstances, methanol vapor may explode rather than burn on ignition.
- o Methanol is a toxin;
- o Methanol is totally miscible in water and retains its flammability even at very high concentrations of water.

TRANSPORTATION AND STORAGE OF METHANOL

Ocean-Going Transport

- o Methanol is pumped from dockside storage tanks into sealed cargo holds of tanker ships. Delivery to dockside storage may be by pipeline, barge, rail, or truck.
- o Double-hulled vessels are commonly used by shippers.
- o Accidental releases into open ocean are to be avoided, but are considered to pose less of a threat to the environment than crude oil, bunker fuel, gasoline, or diesel fuels. Solubilisation of pure (100%) methanol in water is rapid and complete.

TRANSPORTATION AND STORAGE OF METHANOL, Cont.

Rail Transport

- o Precautions for rail transport are much the same as those for ethanol, gasoline, MTBE, jet fuel (kerosene), and distillate. This includes grounding for protection against static discharge.
- o Specially designed tanker cars are equipped with provisions for pressure relief in order to accommodate thermal expansion during transit and short-term (less than 30 days) side-lining during switching and temporary holding. Rail transport is considered to be safe, as long as methanol is contained within an upright tanker car.
- o In the event of derailment, first responders should treat methanol as highly flammable and highly toxic.

TRANSPORTATION AND STORAGE OF METHANOL, Cont.

Tanker Truck Transport

- Comments relating to rail tank cars apply equally for tankers attached to tractor haul trucks and for tank trailers towed by tractor haul trucks. Methanol transport by truck haulage is subject to substantially the same precautions as are routinely exercised for gasoline transport.

METHANOL STORAGE

- Storage of methanol is subject to substantially the same provisions as those used for gasoline storage.
- Because methanol is commonly stored with other solvents and feed stocks, all piping and valves subject to carrying methanol should be consistently labeled, and direction of flow should be indicated.
- Methanol burns with a non-luminescent flame, which may be invisible in bright sunlight.

METHANOL STORAGE, Cont.

Docks and Marine Terminals

- Storage facilities at docks and marine terminals are typically floating roof tanks, dedicated to methanol handling. Internal floating roofs are preferred to avoid contamination.

Tank Farms

- Tank farms at facilities such as refineries and chemical plants likely have dedicated methanol storage and handling systems.

METHANOL HANDLING

Certain aspects of methanol handling require special provisions and protective measures. These include the following:

- o As much as possible, methanol should be stored and used in a dedicated area that is specifically marked off and appropriately labeled.
- o The area designated for methanol handling should be equipped with an effective audible alarm, which will summon assistance in a timely manner.
- o Use positive materials identification for gaskets, filters, hose material, and similar supplies.
- o Replace gaskets, hoses, and “O” rings periodically, *before* they are expected to degrade or fail.
- o Ensure that procedures are in place to:
 - o ground, and periodically verify grounding.
 - o protect from water uptake and accumulation.
- o Ensure that provisions and procedures are in place to/for:
 - o prevent spilled methanol from entering drains, manholes, and confined spaces.
 - o preventing methanol entry into the water table or aquifers.
 - o personnel protection and exposure mitigation. This should include eye wash and shower stations.
- o Ensure that procedures and equipment are in place for:
 - o leak detection and alarm.
 - o onsite emergency response.
- o Ensure that procedures and possibly specialized equipment are in place for offsite emergency responders.

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.

BEST PRACTICE

- o 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;
 - 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 to a radial distance of 50 feet.

BEST PRACTICE, Cont.

OR

- 3) Prevent contact with air (oxygen) by padding free board in vessels tanks and containers with inert gas (e.g., nitrogen). 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.

BEST PRACTICE, Cont.

Electrical Classification

- o Electrical equipment within the proximity of methanol storage and handling must be explosion proof to meet National Electrical Code requirements.

Grounding and Bonding

- o Grounding is especially important in protecting methanol from accidental ignition resulting from static discharge
- o Grounding is required for lighting systems, pipe racks, pumps, vessel, filters, and all other equipment near and potentially within range of methanol vapor.
- o Hoses must be grounded.
- o Methanol transfer operations should be bonded and grounded.
- o Metal containers (drums or totes) and the associated fill equipment pump should be bonded together and grounded during methanol transfer operations. Fill pipes or hoses should be conductive and should be bonded to the filling system

HEALTH AND SAFETY

- o Methanol should always be kept within closed systems and not left open to the atmosphere.
- o The building ventilation system should provide fresh air for normal operation and should take into consideration the possibility of a leak.

HEALTH AND SAFETY, Cont.

Personal Protective Equipment

- Exposure to methanol can occur via inhalation, skin absorption, contact with the eyes, or ingestion, whenever methanol is used or handled.

Respiratory Protection

- Respiratory protection should be selected based on hazards present and the likelihood of potential exposure.

HEALTH AND SAFETY, Cont.

- o The following table is a guide for whether respiratory protection is required or not, when the air concentration of methanol is known.

Respiratory Protection Guide

Air Concentration of Methanol	Respiratory Protection
<200 ppm	No protection required. Skin and eye protection may still be needed.
200 ppm or greater	Protection required if the daily time-weighted-average (TWA) exposure is exceeded or if there are additional routes of exposure (skin, eyes, ingestion). A supplied air system must be used if protection is needed.
>200 ppm sustained	A supplied air breathing apparatus (SCBA) system must be used (i.e., positive-pressure SCBA).

HEALTH AND SAFETY, Cont.

Chemical-Resistant Clothing/Materials

- o Chemical-resistant clothing/materials should be worn if repeated or prolonged skin contact with methanol is expected. These may include rubber boots, resistant gloves, and other impervious and resistant clothing. Chemical-resistant materials include butyl rubber and nitrile rubber. Use chemical goggles when there is a potential for eye contact with methanol, including vapor. A full face-shield may be worn over goggles for additional protection, but not as a substitute for goggles.

Personal Protective Equipment Selection

Low risk of vapor/low risk of volume splash	High risk of vapor/low risk of volume splash	High risk of vapor/high risk of volume splash
Fire retardant clothing	Full chemical resistant suit	Full chemical resistant, impermeable suit
Gloves (Silvershield or disposable nitrile)	Chemical-resistant rubber gloves	Chemical-resistant rubber gloves
Safety glasses with side shields	Full face supplied air respirator	SCBA or compressed air breathing apparatus (CABA)
Full boot cover	Chemical-resistant rubber boots	Chemical-resistant rubber boots

FIRST AID MEASURES

A Safety Data Sheet (SDS) for methanol or materials containing methanol should be carefully reviewed for information on first aid measures.

Inhalation

- In case of inhalation of methanol vapors, first remove the individual to fresh air if it is safe for you to do so, and keep him or her warm and at rest. Monitor for respiratory distress. If difficulty in breathing develops or if breathing has stopped, administer artificial respiration or cardiopulmonary resuscitation (CPR) immediately and seek medical attention. If trained to do so, administer supplemental oxygen with assisted ventilation, as required.

Skin Contact

- In case of contact with skin, immediately use an emergency eyewash or safety shower, and flush the exposed area with copious amounts of tepid water for at least 15 minutes. Contaminated clothing and shoes should be removed under the shower. Wash the area thoroughly with soap and water. Seek medical attention if irritation or pain persists or if symptoms of toxicity develop. Wash contaminated clothing and shoes before reuse.

Eye Contact

- In case of contact with eyes, immediately irrigate the eyes with copious amounts of tepid water for at least 15 minutes. The eyelid should be held apart during the flushing to ensure all accessible tissue of the eyes and the lids are in contact with water. Obtain medical attention.

Accidental Ingestion

- Ingestion of methanol may be life threatening. Onset of symptoms may be delayed for 18 to 24 hours after ingestion. Do not induce vomiting. Get medical attention immediately. The individual should remain under close medical care and observation for several days.

SPILL RESPONSE

Steps if a Spill Occurs

The first steps to take if a spill occurs are:

- Stop or reduce methanol release rate at the point of release, if it can be done safely.
- If there are noxious vapors, evacuate, sound a vapor release alarm, and notify supervisor or emergency coordinator.
- Eliminate all sources of ignition to a safe standoff distance from the point of release and nearby methanol pooling.
- Evacuate all persons not wearing protective equipment from the area of the spill or leak until cleanup is complete (this requires that cleanup levels be pre-determined).
- Do not walk through spilled product. Avoid skin contact and inhalation.
- Stay upwind and keep out of low-lying areas that might accumulate vapor.
- For large spills and fires, immediately call the fire department.

SPILL NOTIFICATION AND REPORTING

- o Federal, State and Local government agencies may have notification and reporting requirements following a hazardous materials spill.
 - o Methanol's Reportable Quantity in the United States is 5000 pounds (2.2 tonnes), which is equivalent to 755 gallons (2858 liters).
 - o In Canada, reporting requirements are triggered for spilled amounts as low as 53 U.S. gallons (200 liters).
 - o In the European Union (EU), the public will be able to access an electronic database on pollutant releases through Regulation Number 166/2006 (European Pollutant Release and Transfer Register).
- o Spill notification may trigger requirements to remediate the spill area and restore any damage to the environment, in addition to penalties and fines.

WASTE MANAGEMENT

- o Methanol is a commonly used solvent in many organic reactions, and the resulting spent methanol is considered a hazardous waste.
- o Waste methanol, or water contaminated with methanol, is considered a hazardous waste and must never be discharged directly into sewers or surface waters. It may only be disposed of at a licensed facility permitted to handle Hazardous Waste.



Nariné Demirchian

Director Regulatory Affairs and Quality Compliance
Unipex Solutions Canada Inc.
Tel: 450-449-2007
e-mail: narine.demirchian@unipex.com

Normand Brisson

Business Manager, Chemical Division
Unipex Solutions Canada Inc.
Tel: 514-235-1792
e-mail: normand.brisson@unipex.com

APPENDIX(s)

COMPATIBILITY OF GASKET AND O-RING MATERIALS IN METHANOL-FUELED TRUCK SERVICE

Compatibility of Gasket and O-Ring Materials with Methanol⁷		
Gasket/O-Ring Material	Rating⁸ (Compatibility with Methanol Fuel in Truck Service)	Recommended^{9, 10}
Natural Rubber	Good	No Recommendation Given
EPDM (ethylene-propylene)	Good	Yes, Recommended
Neoprene	Good	Yes, Recommended
Silicone	Good	Yes, Recommended
Kalrez	Good	Yes, Recommended
Teflon	Good	No Recommendation Given
Fluorosilicone	Good	No Recommendation Given
Buna-N	Fair	Not Recommended
Nitrile	Fair	Not Recommended
Polyurethane	Sometimes OK	No Recommendation Given
Butyl Rubber	Poor	No Recommendation Given
Butadiene	No Data	No Recommendation Given
Fluorocarbon	No Data	No Recommendation Given
VITON (most types)	No Ranking Given	Not Recommended

GENERAL INFORMATION	
Property/Information	
DOT Number	UN 1230
DOT Hazard Class or Division	3.6.1 flammable liquid
DOT Guide Number	28
CAS Number	65-56-1
STCC Number	4909230
ICC, OSHA, NFPA Liquid Flammability Class	IB flammable liquid
DOT Packing Group	PG II
DOT Packaging (non-bulk/bulk)	202/242
Types of Shipping Containers	NON-BULK: 1-119 gal DOT PG-II performance oriented containers BULK: tank cars, tank trucks
Shipping Container Hazards	rupture, BLEVE: containers may fragment & rocket in fire
Special Fire Hazards	blue flame invisible in daylight; flame flashes back from ignition source to leak point; accumulated vapor may explode if ignited in confined area or deflagrate as a near- neutral-buoyancy radiant fire ball in unconfined poorly ventilated area
Other Information	liquid floats & mixes with water; near neutral vapor buoyancy
Molecular Weight	32.04
Chemical Composition	
Carbon (w/w %)	37.5
Hydrogen (w/w %)	12.6
Oxygen (w/w %)	49.9
LIQUID PROPERTIES	
Freezing Point Temp. (°F)	-143.5
Specific Gravity (@ 60 °F/60 °F)	0.796
Density (lb/gal @ 60 °F)	6.63
Viscosity	
@ -4 °F (centipoises / mm ² /s)	1.15 1.345
@ 68 °F (centipoises / mm ² /s)	0.59 0.74
@ 104 °F (centipoises / mm ² /s)	- -
Specific Heat (Cp, Btu/lb-°F)	0.60
Thermal Conductivity (Btu/hr-ft-°F)	0.12
Coefficient of Thermal Volume Expansion (@ 60 °F & 1 atm)	0.00067
Electrical Conductivity	
Neat or without additives	4.4 x 10 ⁷ pS/m
Industrial use	30 μS/m
Fuel specification	< 1000 μS/m
Latent Heat of Vaporization	
(Btu/gal @ 60 °F)	3,340
(Btu/lb @ 60 °F)	506

Heating Value	
Lower [liquid fuel combusted to water as vapor] (Btu/gal @ 60 °F)	56800
	57250
Lower [liquid fuel combusted to water as vapor] (Btu/lb)	8570
	8637
Higher [liquid fuel combusted to liquid water] (Btu/gal)	65200
Higher [liquid fuel combusted to liquid water] (Btu/lb)	9750
	9837
Heat of Combustion [ΔH_c^0] [liquid fuel combusted to liquid water] (Btu/lb)	9900
	9378
Equilibrium Vapor Pressure	
Reid [RVP] (psi @ 100 °F)	4.6
True Vapor Pressure [TVP] (mm Hg @ 68 °F)	92
	104
Boiling Pt. Temperature (°F)	149
Water Solubility @ 70 °F	
Fuel in Water (v/v %)	100
Water in Fuel (v/v %)	100
Vapor Specific Heat (Btu/lb/ °F)	0.38
Equilibrium Vapor Pressure	
Reid (psi @ 100 °F)	4.6
True Vapor Pressure (mm Hg @ 68 °F)	92
	104
Vapor Density (air=1)	1.1
Vapor Heat of Combustion	
Lower [gaseous fuel combusted to water as vapor] (Btu/lb @ 60 °F)	9080
FLAMMABILITY PROPERTIES	
Flash Point Temperature	
Closed Cup (°F)	52
Open Cup (°F)	-
Autoignition Temperature (°F)	867
Flammability Limits	
Lower (v/v %)	7.3
Upper (v/v %)	36.0
Flammability Range (v/v %)	28.7
Stoichiometric air/fuel ratio (w/w)	6.45
Fuel in Vaporized Stoichiometric Mixture (v/v %)	12.3
Stoichiometric Flame Speed (ft/s)	1.41
Minimum Ignition Energy (mJ)	0.14
Adiabatic Flame Temperature (°F)	3470
Flame Temperature (°F)	3,398
Mass Burning Rate (lb/ft ²)	0.083