

Methanol Gasoline Blends

**Alternative Fuel For Today's
Automobiles and Cleaner Burning
Octane For Today's Oil Refinery**

Methanol Blending Technical Product Bulletin

methanol.org

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I. INTRODUCTION

Methanol is a clean burning, high octane blending component made from alternative non-petroleum energy sources such as natural gas, coal and biomass. It has been commercially blended into gasoline at various times and locations since 1980. Although methanol has been widely manufactured for use in chemical production, methanol has also been successfully used for extending gasoline supplies in many gasoline markets around the world. Unlike some other alcohols, methanol blending in gasoline has been economical without government subsidies or fuel blending mandates.

Besides providing non-petroleum alternative energy into gasoline supplies, blending methanol also delivers a clean burning high octane to the oil refiner's gasoline supplies that can be used reduce the refiner's energy consumption as well as improve gasoline yields from the crude oil. Methanol's high octane and oxygen content produce a cleaner burning gasoline which significantly lowers vehicle exhaust emissions. When produced from natural gas or biomass, methanol fuel has a lower carbon intensity (or carbon footprint) than gasoline produced from petroleum.

Following the crude oil price shocks of the 1970's, methanol blending in gasoline was first introduced commercially in the early 1980's. Because carburetted fuel systems were most prevalent in the vehicle fleets on the road at that time, and because those vehicles had limited ability to handle high oxygen levels in the fuel, methanol blends were generally limited to 3 to 5 volume percent of the gasoline blend. However, with today's modern pressurised fuel injector systems with computerised feedback control loops, current experience shows that methanol blends as high as 15 volume percent (M15) of the gasoline can now be successfully used in the more modern vehicles that are on the road today.

Methanol has many fuel properties that make it cleaner burning in gasoline engines. Besides containing oxygen for improved fuel combustion, methanol also has a high blending octane value for smoother burning, a lower boiling temperature for better fuel vapourisation in cold engines, the highest hydrogen-to-carbon ratio for a lower carbon intensity fuel, and no sulphur contamination which poisons catalytic converter operation. These unique blending properties allow oil refiners to produce cleaner burning gasoline that reduces vehicle emissions, which are precursors to ozone and particulate matter (PM) in the atmosphere. Blending high octane methanol also replaces aromatic compounds normally used for adding octane in gasoline, but which also contribute to toxic emissions from vehicles. In addition, blending methanol also allows oil refiners to expand gasoline production, upgrade regular gasoline production to higher premium grade gasoline, and meet new environmental specifications as well as minimise refinery capital investments to achieve these goals.

For the oil refinery, using methanol blends is one of the lowest cost means to expand gasoline supplies to meet the growing gasoline demand and new environmental regulations, and thereby delay capital investment in refinery processing capacity. For developing economies around the globe, the blending of methanol in gasoline is one of the quickest and lowest cost means for both displacing high cost petroleum energy consumed in the existing vehicle fleet, and also for reducing vehicle emissions that lead to air pollution such as ozone, carbon monoxide (CO), PM and air toxics.



II. PHYSICAL PROPERTIES

Methanol is a clear, low viscosity liquid with a faintly sweet alcohol odour at low concentrations in air. Chemically, methanol is an aliphatic alcohol containing about 50 wt% oxygen with physical properties consistent with other alcohols used as gasoline blending components (see Table 1).

As is common for most alcohols blended in gasoline, methanol is fully soluble in water and also miscible with gasoline-type hydrocarbons (HC). The addition of some cosolvent alcohols (ethanol, propanols, or butanols) are generally required in methanolgasoline blends to provide adequate water tolerance (solubility) or phase stability under colder temperature conditions. As with most gasolines and alcohol fuel blends, inhibitors or additives are generally recommended with methanol blends to provide added protection against metal corrosion. Properly blended gasoline with methanol is typically compatible with materials commonly used in gasoline distribution systems as well as vehicle fuel systems. Neat fuel methanol (premixed with co-solvents and corrosion inhibitors) is handled in a similar manner as gasoline or other gasoline blending components with the exception of certain materials of construction and added precaution to keep the fuel methanol dry. Methanol-gasoline blends have been successfully shipped commercially in barges, pipelines, and tanker trucks similar to those used to transport gasoline. As discussed later, because of methanol's affinity for water, some precautions are necessary when shipping and storing methanol-blended gasolines, such as mitigating water addition and using fire extinguishing foam approved for alcohol fires.

Extensive product research, as well as years of commercial experience, indicate that properly blended methanol in gasoline has no adverse effect on vehicle performance. In fact, methanol-gasoline blends have cleaner burning properties that generally reduce CO, HC, PM and air toxics from most gasoline engine vehicles.



Table 1: Methanol

Table 1: Methanol	
Typical Composition -	Wt. %
Methanol purity	> 99.7
Water	< 0.1
	PPM
Chlorides as Cl ion	< 0.5
Sulfphur	< 0.5
Typical properties -	
Specific Gravity (20/20°C)	0.792
Reid Vapour Pressure @ 38°C, kpa (PSI)	32 (4.6)
Melting Point °C	- 97.6
Flash Point (TCC) °C	12
Auto Ignition Temperature °C	470
Boiling Point, °C	64.6
Distillation Range, °C	< 1.0
Heat of Combustion, Net kj / g	19.93
Latent Heat of Vapourisation, kj/g @ 25°C	1.16
Index of Refraction 20°C	1.37840
Solubility @20C (wt %)	miscible
Octanol Partition Coefficient, Kow	- 0.82
Flammability Range in Air (Volume %)	
Higher Flammability Limit	36.5
Lower Flammability Limit	6.0
Viscosity, Ns/m ² x10 ^{**3} @20 °C (cP)	0.544
Kinematic Viscosity, m ² /sec @20 °C	7.37x10 ⁻⁷
Appearance	clear
Odour (neat)	faintly sweet
Odour threshold in air (mean ppm)	160
CAS No.	67-56-1

III. OCTANE IMPROVEMENT

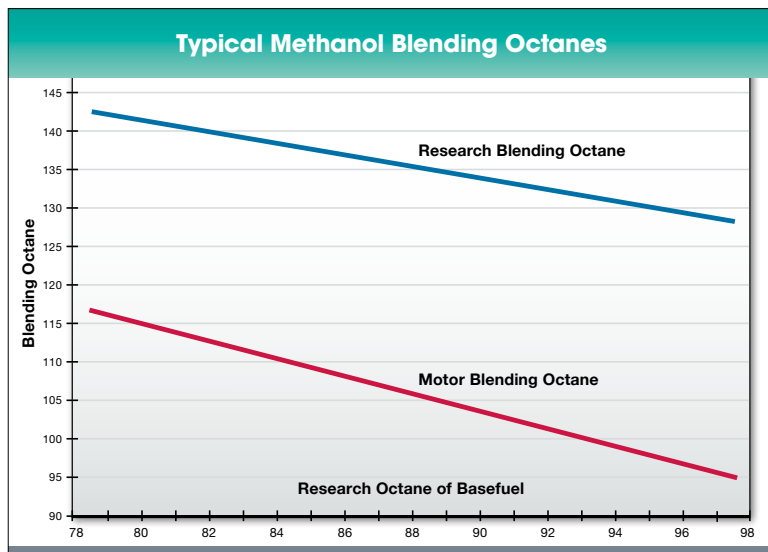
Methanol’s blending octane values (BOV)⁽¹⁾ are nominally 129-134 research octane number (RON) and 97-104 motor octane number (MON). Methanol’s actual BOV will vary depending on the octane of the gasoline base fuel and its composition. Using the RON of the base fuel, the BOV can be estimated as shown in the nearby figure. In general, the BOV of methanol in unleaded gasoline will increase with a decreasing octane rating of the base fuel.

The high octane of methanol provides a convenient and cost effective way to upgrade low octane gasoline components, such as low octane raffinate streams from BTX aromatic production units. For a refinery that is limited by octane capacity, each barrel of methanol added to the gasoline supplies can yield as much as 2.4 additional barrels of gasoline.

With one of the highest RON blending values available (higher than that of MTBE, toluene, reformat or alkylate), methanol is an excellent blending component in all grades of gasoline. A comparison of the typical RON blending values of methanol and other high octane gasoline blending components is shown in Table 2.

With its higher volatility, methanol is particularly well suited for blending in premium gasoline which tends to have most of its high octane components (aromatics) concentrated in the low volatility portion of the gasoline product blend and which can then impede cold engine operation. Methanol blending improves octane distribution in the premium gasolines for better cold engine operation.

Methanol also provides a means of improving the octane of premium gasoline without increasing its already high aromatics content, which can contribute to performance problems in some vehicles, and to higher vehicle exhaust emissions. Unlike aromatics, the use of methanol for octane in gasoline has been shown to have environmental benefits, as methanol blends reduce HC, CO, PM and air toxic emissions from most vehicles.



Methanol	129 – 134
MTBE	117 – 121
Toluene	112 – 115
Xylenes	111 – 114
Alkylate	92 – 96

(1) Blending octane values (BOV) can be calculated from the measured octane numbers of the blended fuels using the equation:

$$BOV = \{ ON - (ON_{base} \times (1-Y)) \} / Y$$

where

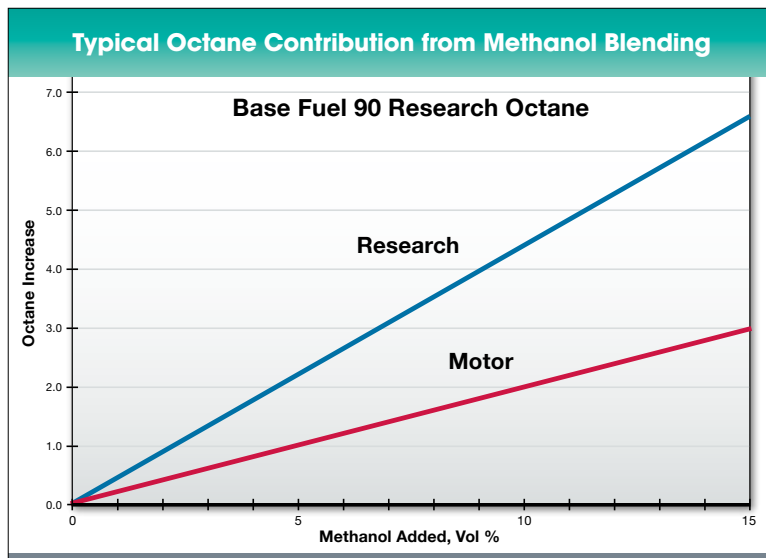
ON = RON or MON of the blended gasoline fuel

ON_{base} = RON or MON of the gasoline base fuel

and

Y = volume fraction of the blending component (e.g. methanol) in the gasoline blend

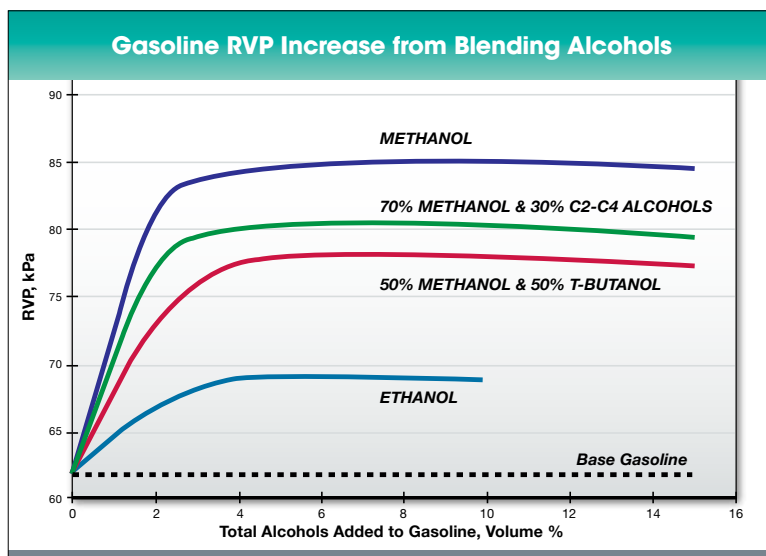
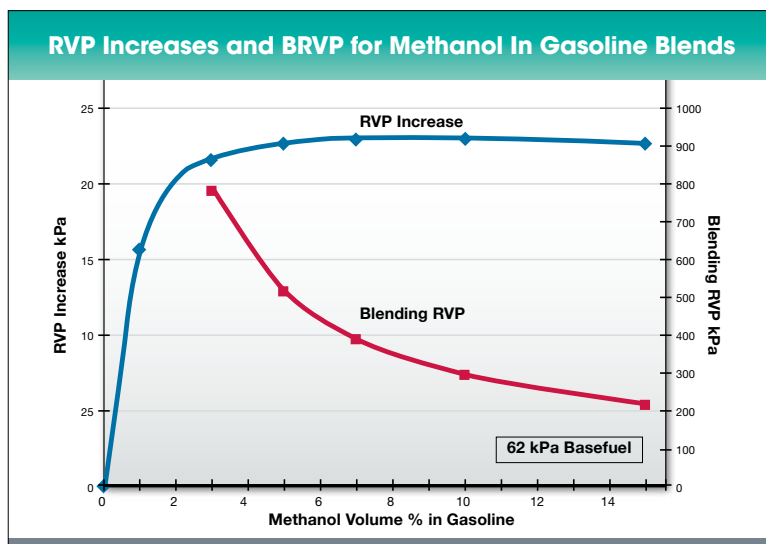
As a result of these cleaner burning octane advantages, methanol is an economically attractive alternative for those refiners who face the problem of maintaining a high quality gasoline while adhering to government-imposed controls on gasoline composition. As illustrated in the nearby figure, blending 15 volume percent methanol can add over 6 RON's and about 3 MON's to a refiner's gasoline product supply.



IV. BLENDING VAPOUR PRESSURE

Like other alcohols, methanol experiences azeotropic effects (non-ideal blending) with the vapour pressure of gasoline. Therefore, even though neat or pure methanol has a low Reid Vapor Pressure (RVP) of about 32 kPa at 38 °C, its blending RVP in gasoline can range from 200 kPa up to 800 kPa depending on the methanol concentration in gasoline, as illustrated in the nearby figure. Most of the RVP increase from blending methanol in gasoline occurs with the first 3 volume percent of methanol. When blending to a RVP specification, the refinery will need to remove some butane from the gasoline to compensate for the RVP increase from the first 3 volume percent of methanol in the blend. However, methanol blended above 3 volume percent produces little increase in RVP and the RVP response curve is relatively flat. Therefore, for the methanol blended above 3 volume percent in gasoline, little if any additional butane will need to be removed from the finished gasoline blend. The result is that the blended methanol above the first 3 volume percent displaces mostly gasoline that is refined from crude oil.

As previously mentioned, some cosolvent alcohols will need to be added to provide water tolerance and stabilise the gasoline blends under colder climate conditions. The cosolvent alcohols also provide some reduction in the methanol's RVP increase in gasoline, as illustrated in the adjacent figure. The amount of reduction in the methanol's RVP increase will be dependent on the amount and the type of co-solvent alcohols added to the methanol blend. In general, higher carbon number alcohols such as butanol (C4) will provide greater reductions that lower carbon alcohols such as ethanol (C2) or propanols (C3).

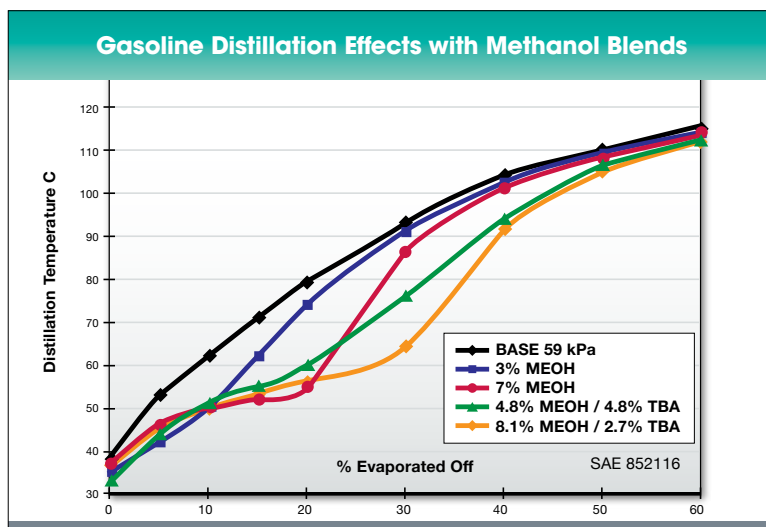


V. DISTILLATION PROPERTIES

Like other alcohols, methanol blending produces an azeotropic effect on the distillation curve of gasoline. This produces a flattening or “knee” in the distillation temperature curve of the blended gasoline that is just below the boiling point temperature of the alcohol being added (64.6 °C for methanol). In general, adding more alcohol will increase the amount of knee or flattening at a point in the distillation curve of the gasoline blend just below the boiling point of the alcohol. The distillation effect for adding 3% and 7% methanol (without co-solvent alcohol) is illustrated in the figure below.

As previously mentioned, co-solvents will dampen the RVP increase from adding methanol to the gasoline blend. However, in the case of methanol distillation effects, the amount of deflection in the distillation curve from the volume of methanol added will not be significantly affected by the addition of cosolvent alcohols with higher boiling temperatures as illustrated in the figure. The increase in percent evaporated at 60 °C is directionally related to the amount of methanol blended in the gasoline even when co-solvent tertiary butanol (TBA) is also added. With a boiling temperature of 82.6 °C, the addition of TBA will generally shift the distillation curve to the right at about 80 °C as illustrated in the nearby figure.

The cold engine drivability performance of a fuel is mostly related to its distillation temperature profile. In general, the cold engine drivability performance of gasoline will improve as the temperatures decrease at the 10, 50 and 90 volume percent evaporated points of the distillation curve. Lowering the gasoline’s distillation temperatures improves fuel vapourisation in cold engine operation, and thereby improves performance. Therefore, since adding methanol and other alcohols will lower the distillation temperatures, the cold drivability performance is expected to be equal or higher than gasoline without alcohols.



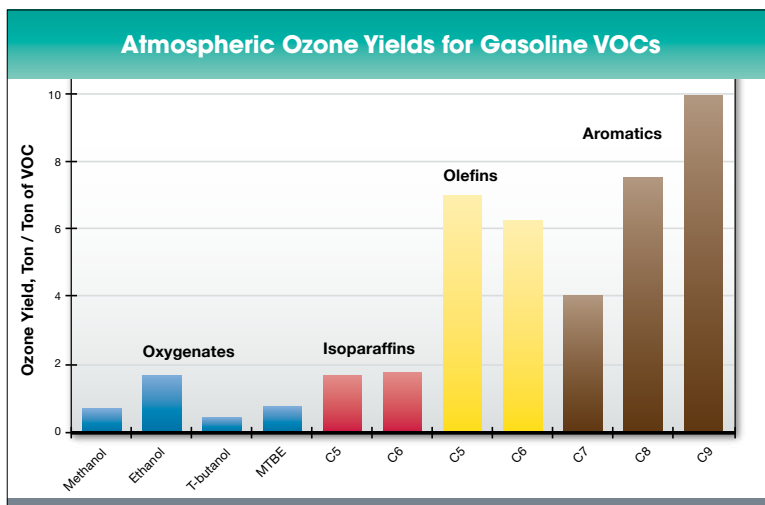
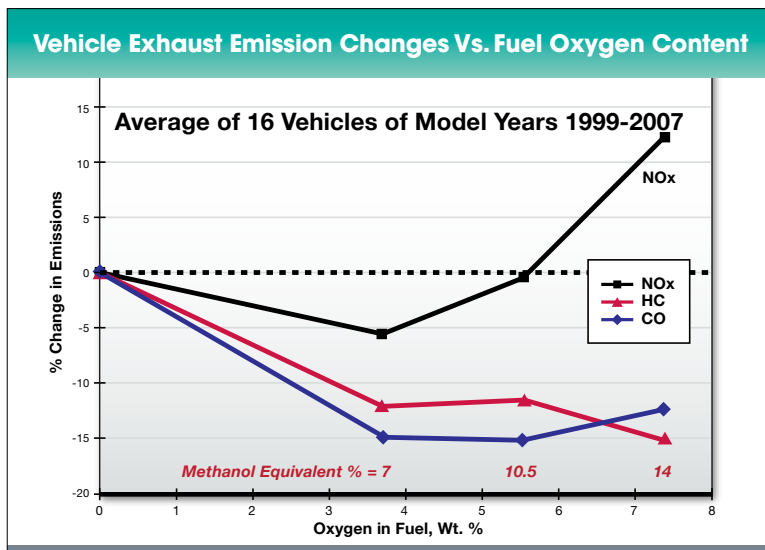
VI. VEHICLE EMISSIONS IMPROVEMENT

Extensive product research and decades of commercial experience indicate that blending oxygenates into gasoline can improve automobile fuel performance and reduce exhaust emissions. In general, the reduction or change in exhaust emissions is related to the amount of oxygen added to the fuel. Adding oxygenates generally reduces many ozone precursor emissions from vehicles such as CO, HC, and nitrogen oxides (NOx) by the addition of oxygen and octane, and by also improving fuel distillation temperatures. Total air toxic emissions are also reduced by the addition of the oxygen as well as the octane replacement of benzeneproducing aromatics in gasoline. The oxygen and improved volatility characteristics achieved by using oxygenates also contribute to lower PM emissions in the exhaust.

The nearby chart shows an example of the emissions reductions that are associated with the addition of oxygenates for three blends of varying oxygen content. Although this emission study conducted by the U.S. DOE used ethanol as the oxygenate, the emissions effect is expected to be similar if methanol is instead used as the source of the fuel oxygen.

Based on the oxygen content, adding 7 volume percent methanol to the fuel blend (equivalent to 3.5% oxygen by weight) would reduce the CO by about 15% and the HC emissions by about 12% as compared to having no oxygen in the fuel. At this oxygen level, the NOx also decreased by approximately 5%. Using the octane from the methanol to further reduce the aromatics in the gasoline would reduce all of the emissions even further. A significant advantage of reformulating gasoline with oxygenates such as methanol is that the emissions benefits occur immediately across all classes and ages of vehicles using the cleaner burning gasoline. This generally provides immediate air pollution benefits without the need to wait for new emission reduction technology to penetrate the vehicle fleet population.

Reactive HC's or volatile organic compounds (VOC's) react with NOx and sunlight in the atmosphere to form ozone during hot summer daytime conditions. However, the type or chemical composition of the HC emitted from the vehicle into the atmosphere significantly impacts the yield of ozone formed from a VOC emission. The nearby figure compares typical ozone yields for some of the different chemical classes of HC's. Of all the VOC's found in gasoline, oxygenates with their lower reactivity generally form the lowest amount of ozone in the atmosphere, and methanol and T-butanol form the least ozone. Unsaturated gasoline VOC's such as olefins and aromatics produce as much as 10 to 15 times more ozone than methanol in the atmosphere.



VII. MATERIAL COMPATIBILITY

METHANOL/CO-SOLVENT-GASOLINE BLENDS

Many suppliers of fuel system components have examined the effect of gasoline blends at higher concentrations of methanol on various materials used in automotive fuel systems and in gasoline distribution systems. Also, considerable commercial experience for 5% methanol blends was acquired during the early 1980's. Except for a few materials, no significant detrimental effects were noted for most of the tested materials or those used in commercial practice. Based on experience developed by the oil refining industry, Table 3 lists the recommendations for commonly used materials in the storage, handling and distribution of gasoline that may contain 5% methanol.

As is common with other alcohols that are blended in gasoline, and with commercial gasoline in general, corrosion inhibitors are usually added to mitigate any risk of corrosion of metals commonly used in the fuel distribution systems and vehicle fuel systems. As with the other commercial alcohols for fuel blending, appropriate dosage levels of corrosion inhibitors are strongly recommended for the fuel methanol mixture (including co-solvents) that will be used in gasoline blends.

FUEL METHANOL STORAGE

Methanol is non-corrosive to most metals at ambient temperatures; exceptions include lead, magnesium and platinum. Mild steel is usually selected as the construction material. Many resins, nylons and rubbers, particularly nitrile rubber (Buna-N), ethylene propylene rubber (EPDM), Teflon and neoprene are used satisfactorily as components of equipment in methanol service. However, Viton™ and Flourel™ fluoroelastomers as well as polyurethanes experience appreciable loss in some of their properties when in contact with methanol. The extent to which this effect may lead to a shorter service life of the materials involved is dependent on their specific applications. Further guidance can be provided by the engineering and construction company, or the equipment supplier.

Table 3: Material Compatibility of Commonly Used Materials with Gasoline / Methanol / Co-solvent Blends

Recommended	Not Recommended
Metals	
Aluminum	Galvanised metals
Carbon Steel	
Stainless Steel	
Bronze	
Elastomers	
Buna-N™ *	Buna-N™ *
Flurel™	
Fluorosilicone	
Neoprene *	Neoprene *
Polysulfide Rubber	
Viton™	
Polymers	
Acetal	Polyurethane
Nylon	Alcohol-based pipe dome
Polyethylene	
Teflon™	
Fiberglass-reinforced	

™ - Trademark * Okay for hoses and gaskets but not seals

Source: Storage and Handling of Gasoline-Methanol / Cosolvent Blends API 1627 Recommended Practices, 1986



VIII. WATER SOLUBILITY

Similar to other alcohols blended into gasoline, the methanol-gasoline blends will separate into two phases if exposed to water in excess of the water tolerance (solubility saturation level) for the ambient temperate conditions. The larger top phase will contain the HC portion of the gasoline and some of the alcohols (methanol and co-solvents) while the smaller bottoms phase will contain the water and some of the alcohols. As a result of the solubilised methanol and HC, the water bottoms must be handled as a flammable liquid, and should be properly recovered and disposed of in a waste water treatment plant. In the refinery, gasoline tank water bottoms are usually fed to a waste treatment plant for disposal. Laboratory studies and field experience show that methanol is biodegradable in acclimated waste treatment systems, and therefore should not lead to an increase in BOD or COD in the waste water effluent.

Also, a vehicle cannot operate if the bottoms phase should inadvertently be pumped into its fuel tank. Therefore, water saturation conditions should be avoided for all alcohol-gasoline blends by keeping storage and distribution systems free of excess water, and by increasing the water tolerance of methanol-gasoline blends through the use of cosolvent alcohols. Key gasoline properties of some of the commercially used co-solvents along with methanol are listed in Table 4.

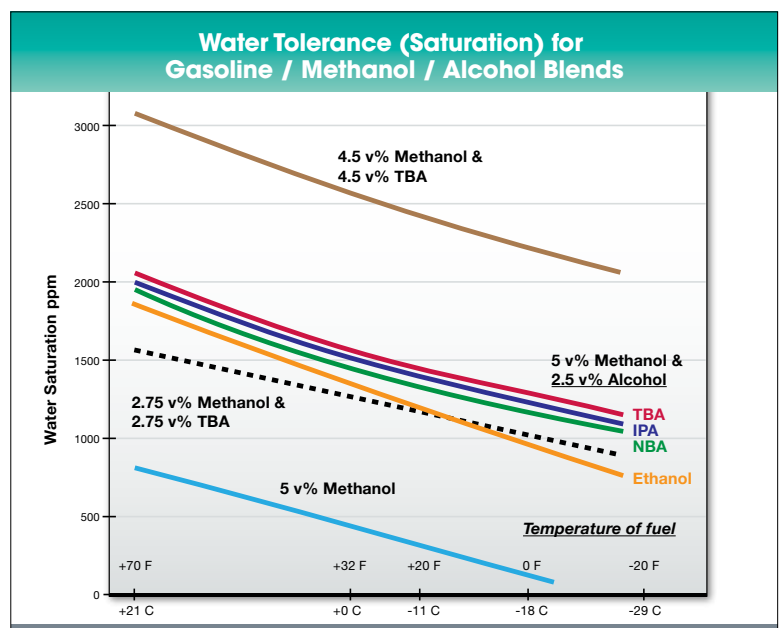
The amount and type of cosolvent alcohol that should be added to a methanol-gasoline blend is dependent upon the amount of water tolerance required to prevent phase separation, given the climate and the handling and storing conditions. With sufficient water tolerance and corrosion inhibitor protection, refinery-blended gasoline with methanol and cosolvents has been successfully shipped commercially to gasoline product distribution terminals by pipeline, ocean going barge, as well as by tanker truck.

Examples of the water tolerance of methanol-gasoline blends as a function of the amount and type of cosolvent alcohol, as well as the ambient temperature, are illustrated in the nearby figure.

Because of the sensitivity to water, it is important to eliminate possible sources of water in the supply chain of methanol-gasoline blends. Therefore, it is necessary to keep the methanol and co-solvent alcohols water free or “dry” before blending into gasoline. This normally requires storing neat methanol or the methanol/co-solvent alcohol mixture in a fixed roof tank with an

Table 4: Potential Co-Solvent Alcohols for Methanol in Gasoline

Alcohol	Methanol	Ethanol	Iso-Propanol	Tertiary butanol	Normal butanol
	MEOH	ETOH	IPA	TBA	NBA
Carbon Number	C1	C2	C3	C4	C4
Oxygen, wt%	49.9	34.7	26.6	21.6	21.6
Solubility in Water, wt%	100%	100%	100%	100%	7.5%
Spec. Grav (15/15 C)	0.796	0.794	0.789	0.791	.814
Boiling Temp. C	64.6	78.3	82.3	82.6	117.7
RVP (kPa @ 38C)	32	15.9	12.4	12.4	2.8
Typical Blending Octanes					
Research	133	131	120	106	94
Motor	100	97	96	94	81



internal floating roof. Nitrogen blanketing of the tank headspace also provides added protection against moisture exposure and accumulation. Similarly, gasoline-methanol blends should be stored in fixed roof tanks with internal floating roofs to ensure maximum phase stability. Also, the common practice of clearing pipelines of HC's by flushing with water cannot be used before or after a product movement of a methanol-gasoline blend. To prevent water contamination, a HC movement must be made before and after any movement of a methanol-gasoline blend.

TERMINAL BLENDING

It may be that an oil refiner is unable to achieve or maintain a dry gasoline product distribution supply system that prevents the introduction of excess water into methanol-gasoline blends as they are being shipped to the distribution terminal. In such case, it may be necessary to blend the methanol (premixed with sufficient cosolvents and corrosion inhibitors) directly at the gasoline product terminals as the gasoline is being loaded into the tank trucks that deliver the methanol-gasoline blends to the retail fuel stations. This procedure of truck blending of the alcohol in gasoline is the common commercial practice used for blending ethanol into gasoline before delivery to retail service stations. However, when blending methanol, the refiner must produce and supply a modified gasoline blendstock so that the resulting methanol gasoline blend will still achieve the final gasoline quality specifications.



IX. STORAGE AND HANDLING

Though methanol and its gasoline blends can generally be stored and handled in much the same way as most other gasoline-type HC's, there are certain differences that need to be considered which require some precautions. These precautions are addressed separately for neat fuel methanol and its gasoline blends. Additional guidance can be found in the Methanol Institute's Methanol Safe Handling Manual, available on our web site at www.methanol.org.

FUEL METHANOL

The importance of keeping the methanol dry has been discussed in an earlier section. Another important precaution is to minimise worker exposure to high doses of methanol vapours. This risk can be minimised by employing good industry safety practices for handling petroleum products.

Before introducing neat methanol into the system, the transfer and storage systems must be checked for fluoroelastomers such as Viton™ elastomer and polyurethane which may fail unexpectedly and thereby lead to releases of methanol (and cosolvents) into the environment, possible personnel exposure, and unplanned equipment downtime. However, fluoroelastomers have been found to be satisfactory for use with methanol-gasoline blends.

Since methanol is water soluble, it will reduce the effectiveness of a fire extinguishing foam system designed for HC fires. To compensate for this water solubility, the fire spray monitors should be switched over to an alcohol-resistant fire foam, and flow rates may need to be increased for the fuel methanol storage area.

METHANOL-GASOLINE BLENDS

There are a few potential nuances that may occur with the initial introduction of methanol blends into the gasoline distribution system. One is that the solvency of the gasoline may be slightly different from prior gasoline. This change in solvency may cause some of the long-term gum and dirt build-up in the gasoline storage system to readily dissolve, and then be released abruptly from the walls of the gasoline distribution system. As a result, a slight colouration may be found in the initial gasoline batch containing methanol, and a temporary increase in fuel filter replacements may be required at the gasoline dispenser pumps to capture any dislodged dirt. In addition, the pump dispenser filters may need to be switched to a type with smaller micron openings specifically designed for alcohol-gasoline blends. The performance of vehicles during this initial phase should be unaffected as long as these procedures are followed, and good housekeeping practices are maintained at the retail outlets.

Retail fuel station attendants must routinely check for any potential accumulation of a water bottoms phase which needs to be removed from underground gasoline tanks. The water detection paste that is normally applied to the bottom of inventory checking sticks may not be effective for water bottoms that occur with alcohol blended gasoline. Therefore, it is important to replace the old paste with a type that is designed for detecting water bottoms with alcohol-gasoline blends.



SPILLS AND LEAKS

The Methanol Institute has published a Methanol Safe Handling Manual and a Crisis Communication Guidebook, both of which can be found at www.methanol.org. It is strongly recommended that these documents be accessed for thorough review of this subject. However, in general, facilities which handle or store methanol. Premixes of methanol and cosolvents, and methanol-gasoline blends should implement the requisite spill prevention, leak detection and emergency response plans. These plans should address issues such as the following:

- Detection of spills and leaks
- Emergency notification procedures
- Community contacts for notification and advice on evacuation needs
- Fire prevention and protection
- Provisions for spill containment and clean-up
- Environmental protection
- Compliance with applicable storage tank regulations or laws

Because of its solubility in water, methanol is fairly mobile in soil, and should be prevented from migrating to the groundwater or nearby surface water when possible.



X. GLOBAL METHANOL FUEL BLENDING REGULATIONS

In many regions of the globe, the blending of oxygenates such as alcohols and ethers is controlled by government regulations that specify the limits for the various oxygenates allowed in commercial gasolines. The maximum levels of oxygen from the oxygenates in gasoline have generally been established to maintain and ensure the fuel blend's drivability performance in the vehicle fleet operating on the road at the time when the regulations had been implemented.

Table 5 summarises the current fuel regulations for blending methanol in major gasoline market regions. Oxygenate blending regulations established in the 1980's in Europe and the U.S. set a maximum oxygen limit of 3.7 wt%, which reflects the drivability performance limits of the carburetted fuel metering systems that existed at the time. More recently, some provinces in China have established methanol blends with oxygen levels that are about twice as high as those established in the 1980's in Europe and the U.S. markets. The higher allowable oxygen levels in Chinese gasoline markets reflects the greater flexibility of current vehicle fuel system technology, which employs high pressure, multi-port fuel injection systems with computerised feedback control loops using oxygen sensors. As a result of these advancements in fuel metering technology and improved materials, the vehicles on the road today can manage a wider range of oxygen levels and alcohol content in fuel without suffering a loss in drivability performance.



For reasons discussed earlier in the water solubility section, co-solvent alcohols are needed to prevent phase separation during the range of seasonal temperatures that methanol-gasoline blends may experience in the commercial marketplace. During the early introduction of methanol blends, the regulatory practice was to add an amount of co-solvent alcohols that was equal to or greater than the amount of methanol being added into the gasoline. Since then, the amount of co-solvent in newer methanol regulations has been decreased to a minimum of 2.5 volume percent, or even less when minimum water tolerances have been established such as in China.

During the commercial introduction of methanol blending during the 1980's, the limit of 3.7 wt% maximum oxygen was also driven by concerns of fuel system material compatibility (for both metals and non-metals). However, the advancement of fuel systems materials and the improvement of corrosion inhibitors to address the growing use of alcohol blends (such as up to 25 volume percent ethanol in Brazil) allows today's vehicles to use much higher levels of methanol with little risk of incompatibility. To take advantage of the greater flexibility, the Shanxi Province of China successfully implemented an M15 fuel program (15 volume percent methanol) which is now under consideration for a national program in China.

Table 5: Approved Methanol Gasoline Blends with Requirements for Co-solvent Alcohols and Additives

Market Region		Introduction Year	Maximum Volume % Methanol	Minimum Volume % Co-solvent	Maximum Wt % Oxygen	Corrosion Additives
Europe	EC Directive	1985	3.0	≥ Methanol	3.7 %	
U.S.A	Sub Sim *	1979	2.75	≥ Methanol	2.0 %	
U.S.A	Fuel Waiver	1981	4.75	≥ Methanol	3.5 %	Required
U.S.A	Fuel Waiver	1986	5.0	2.5	3.7 %	Required
China, Shanxi	M15 Standard	2007	15.0	For Water Tolerance	~7.9 %	Required

* U.S. EPA's Substantially Similar Regulation for commercial gasolines

XI. ENVIRONMENTAL AND HEALTH EFFECTS

Methanol is one of the most tested and evaluated components in gasoline and in commerce. Respected, authoritative research bodies have evaluated methanol and have determined that methanol cannot be classified as a cancer hazard to humans. Furthermore, studies have shown that exposure to low levels of methanol does not cause human risks for birth defects, reproductive disfunction, or genetic damage. High acute exposure can be deadly, or may damage the optic nerve and cause blindness in humans. Scientific weight-of-evidence demonstrates that methanol use in gasoline does not increase overall health risks; in some ways, it may even reduce such risks. Methanol obviates or reduces the need to use some components in gasoline that could increase health risks.

ENVIRONMENTAL

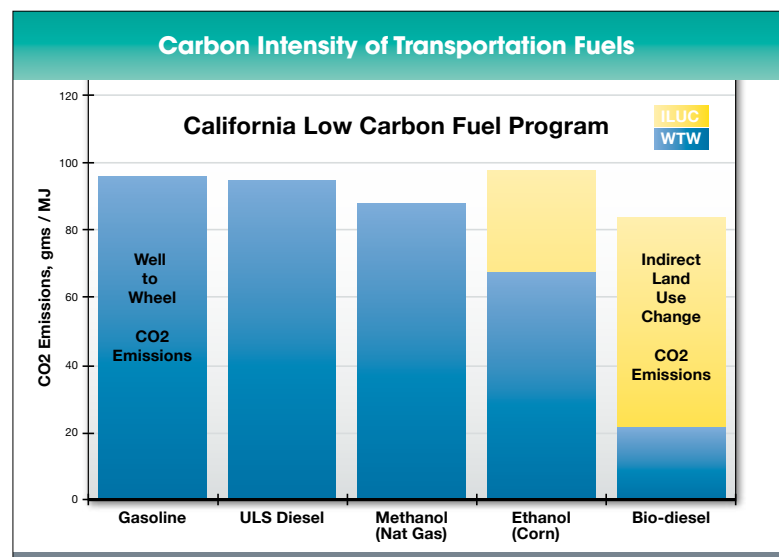
Besides being synthetically produced from many carbon-based energy sources, methanol is also a naturally occurring alcohol that is easily biodegraded in the environment. Compared to common aromatics (benzene and toluene) used for adding octane to gasoline, methanol released into the environment has much shorter half-lives in soil and water mediums as illustrated in Table 6. In the case of a release into the air, methanol is more resistant to oxidation in the atmosphere, and thereby has much longer half-lives compared to gasoline, aromatics and ethanol. However, compared to other gasoline VOC's, methanol's resistance to air oxidation is also beneficial since slow oxidation of VOC's reduces the amount of ozone production that contributes to peak ozone exceedances as discussed previously in the section on vehicle emissions.

Based on California's Low Carbon Fuel Standard (LCFS) program, the carbon emission intensity of the methanol supply chain made from natural gas is about 6% lower than that for average gasoline and about 10% lower than bio-ethanol produced from corn, as illustrated in the figure below.

Table 6: Environmental Half-Lives in Days

	Soil	Air	Surface Water	Ground Water
Methanol	1 - 7	3 - 30	1 - 7	1 - 7
Ethanol	0.1 - 1	0.5 - 5.1	0.25 - 1	0.5 - 2.2
Benzene	5 - 6	2 - 21	5 - 16	10 - 720
Toluene	4 - 22	0.4 - 4.3	4 - 22	7 - 28

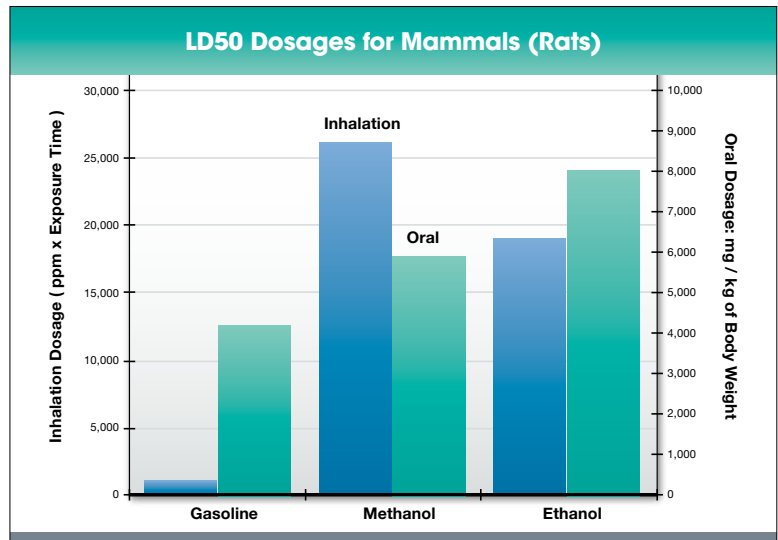
Methanol as an alternative transportation fuel in the US: Options for sustainable and/or energy-secure transportation, MIT Nove 2010



HEALTH RISK FROM EXPOSURE

Methanol is a naturally occurring alcohol which leads to very low dosage exposures to humans and other mammals over their lifetimes, primarily through dietary exposure (fruits, juices, beverages). Also, higher levels of methanol exposure have been safely experienced in activities involving a number of consumer products such as with racing fuels, windshield washer fluid, camp stove fuel, and shellac solvent, as well as others. Also, M85 fuel (85% methanol and 15% gasoline) was commercially supplied in California from about 1988 to 2000 without any known incidences of unfavourable health effects. Similarly, no known negative health effects were reported for the 5% methanol-gasoline blends that were commercially marketed from 1981 to 1986 in eastern U.S. gasoline markets.

Rat exposure studies of the median lethal dosages (LD50) for methanol by oral and inhalation are shown to be much higher (less toxic) than that for gasoline as illustrated in the figure below. Methanol's LD50 for rats is somewhat comparable to that for ethanol. However, high acute oral exposure for humans is known to cause blindness and even death. In general, based on long commercial experience and health testing studies, commercial methanol-gasoline blends are not expected to contribute to increased health risk.



XII. OTHER REFERENCES

API Recommended Practice 1627

Storage and Handling of Gasoline-Methanol/Cosolvent Blends at Distribution Terminal and Service Stations, August 1986

API publication 1642

Alcohol, Ethers, and GasolineAlcohol and GasolineEther Blends: A report on Fire-Safety Considerations at the Petroleum Marketing Facilities, February 1996

API Publication 4261

Alcohols, Ethers: A Technical Assessment of Their Application as Fuels and Fuel Components, July 1988

Effects of Intermediate Ethanol Blends on Legacy Vehicles and Small Non-Road Engines, Report 1 – Updated
NREL/TP-540-43543, ORNL/TM-2008/117, February 2009

Methanol as an alternative transportation fuel in the US: Options for sustainable and/or energy-secure transportation
L. Bromberg and W.K. Cheng, Sloan Automotive Laboratory, Massachusetts Institute of Technology
Cambridge MA 02139, Revised November 28, 2010

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