

Methanol Use In Gasoline

Blending, Storage and Handling of Gasoline Containing Methanol

Methanol Blending Technical Product Bulletin

methanol.org



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Methanol Blending Technical Product Bulletin



I. INTRODUCTION

Methanol is a clean burning, high octane blending component for gasoline that is made from alternative non-petroleum energy sources such as natural gas, coal and biomass. Methanol with co-solvents has been commercially blended into gasoline (petrol) at various times and locations since the late 1970's, or for over thirty years of commercial experience and research. Although methanol has been widely manufactured for use in solvents and 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.

Following the crude oil price shocks of the 1970's, methanol blends for use in the onroad vehicle fleet began extensive studies in the later 1970's and the 1980's. Based on this early research, methanol blends containing up to 15 vol% (M15) were successfully operated by automakers or oil companies in a number of large vehicle fleet trials (\sim 1000 vehicles each) in Sweden, Germany, New Zealand and China during that



time. Also during that time period, methanol gasoline blends containing as much as 5 vol% with co-solvent alcohols were commercially introduced in Europe and the U.S.A. Because carburetted fuel systems with older elastomer parts were part of vehicle fleets on the road at that time and had limited ability to handled high oxygen content in the fuel, the fully commercial methanol blends were generally limited to 3 to 5 vol% of the gasoline blend with some co-solvents also added to provide fuel stability. However, with today's modern pressurised fuel injector systems using feedback control loops and also using more advance fuel system materials, current experience suggests that methanol blends as high as 15 vol% (M15) of the gasoline blend with adequate co-solvents and corrosion inhibitors can now be successfully used in today's more modern vehicles in use today. Many provinces in China have been commercially using M15 blends as early as 2005, and China's M15 use has been expanding because of very favourable economics compared to higher cost petroleum fuels.

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

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

Over the years, fuel methanol has been blended at refineries where it has then been distributed via pipelines, barges or railcars to the fuel product distribution terminals in the market. Where refinery distribution of methanol gasoline blends is not available, the fuel methanol premix (includes co-solvents and inhibitors) has been blended at the fuel product terminals into the tanker trucks delivering the gasoline product to the retail gasoline stations.



II. PHYSICAL PROPERTIES

Methanol is a clear, low viscosity liquid with a faintly sweet 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 used in gasoline, methanol is fully soluble in water and also miscible with gasoline-type hydrocarbons. Some cosolvent alcohols (ethanol, propanols, or butanols) are generally required in the methanol premix used for gasoline blends to provide adequate water tolerance (solubility) or phase stability where colder temperature conditions are experienced during the year. Similar to most gasolines and other alcohol fuel blends, inhibitors or additives are recommended for fuel methanol to provide added protection against corrosion of fuel system metal parts and components. Properly blended gasoline with fuel methanol is typically compatible with materials commonly used in gasoline distribution systems as well as vehicle fuel systems. In general, the fuel methanol premix is handled in a similar manner as gasoline or gasoline blending components with the exception of added precaution to keep the fuel methanol premix from being exposed to any water or moisture. Methanol gasoline blends have been successfully shipped commercially in barges, pipelines, and tanker trucks similar to conventional 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 foams approved for alcohol fires.

Extensive product research, as well as commercial experience, indicates that properly blended methanol in gasoline will provide satisfactory vehicle performance for the consumer. In fact, methanol gasoline blends have cleaner burning properties that generally reduces CO, hydrocarbon (HC), PM and other pollutants from most gasoline engine vehicles.



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

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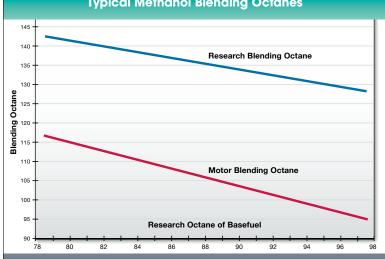


III. BLENDING PROPERTIES IN GASOLINE

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 BOV 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.



Typical Methanol Blending Octanes

Table 2: Comparison of Typical **Blending Octanes in Regular Unleaded Gasolines, RON**

	100 101
Methanol	129 – 134
MTBE	117 – 121
Toluene	112 - 115
Xylenes	111 – 114
Alkylate	92 - 96

With one of the highest RON blending values available (higher than that of MTBE, toluene, reformate 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 are shown in Table 2.

Fuel methanol blending with its lower boiling temperature is particularly well suited for blending in premium gasoline which tends to have most of its high octane components (aromatics) concentrated in the higher boiling range of the gasoline product.

Methanol also provides an effective means of improving the octane of premium gasoline without increasing its already high aromatics and olefin content, which can contribute to performance problems in some vehicles and 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 other exhaust emissions from most vehicles.

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

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

where

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

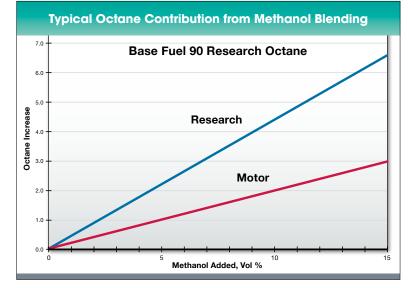
and

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

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As a result of these clean 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 governmentimposed controls on gasoline composition such as limits on aromatic or olefin content. As illustrated in the nearby figure, blending 15 vol% methanol can add over 6 Research octanes and about 3 Motor octane to refiner's gasoline product supply.





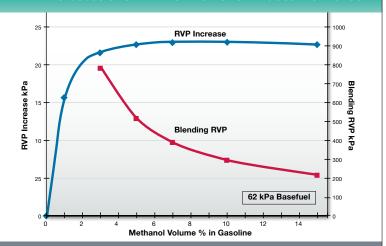
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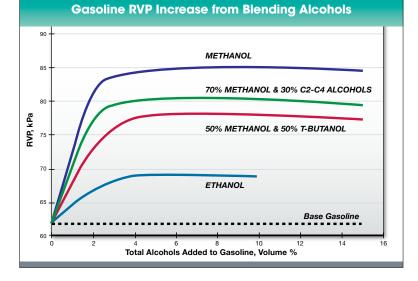
BLENDING VAPOUR PRESSURE

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 Vapour 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 further increase in RVP response which makes this portion of the curve relatively flat. Therefore, for the methanol blended above 3 vol% 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 produced from refining crude oil.

As previously mentioned, some co-solvent alcohols will need to be added to provide sufficient water tolerance and stabilise the gasoline blends under colder conditions. The co-solvent 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 than lower carbon alcohols such as ethanol (C2) or propanols (C3).



RVP Increases and BRVP for Methanol In Gasoline Blends

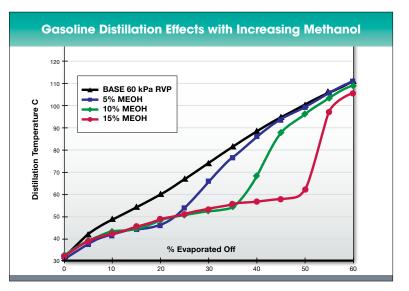


DISTILLATION PROPERTIES

Like other alcohols, methanol blending produces an azeotropic effect on the distillation temperature curve of gasoline. This produces a flattening or "knee" in the distillation 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 5, 10 and 15% methanol (without co-solvents) to gasoline is illustrated in the figure below with the most

pronounced effect being for the percent evapourated at 70 °C which is generally one of the key distillation specifications for gasoline.

The gasoline distillation curve impacts the drivability performance of the vehicle, particularly for the older carburetted fuel system that essentially operated near atmospheric pressure. The percent evapourated at 100 °C generally influences cold engine (warm up) drivability. The percent evapourated at 70 °C impacts hot engine (vapour locking) drivability with higher percentages making operation directionally worse, particularly for carburetted fuel systems. However, in the last twenty years, the automakers have mostly switched their vehicle production to fuel injector systems with their high pressure fuel systems which suppress fuel vapourisation and thereby improves hot drivability performance and significantly dampens its

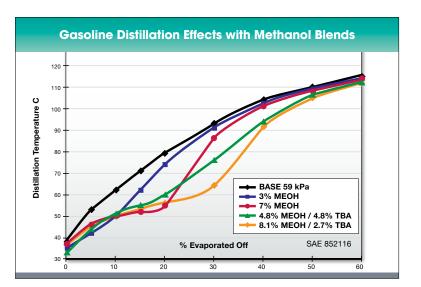


sensitivity to the more volatile (lower) distillation temperatures associated with some gasolines and alcohol blends. Therefore, unlike past carburettor fuel systems, the modern fuel injector systems on today's vehicles allows a wider range of alcohol fuels to be used in the gasoline marketplace without experiencing a loss of vehicle operating performance.

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 co-solvent alcohols with higher boiling temperatures as illustrated in the figure below. The increase in percent evapourated at 70 °C is directionally related to the amount of methanol blended

in the gasoline even when a co-solvent (TBA- tertiary butanol) 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.

In general, the cold drivability performance of the gasoline will improve as the temperatures decrease at the points where 10%, 50% and 90% volume percent evapourated off. Lower gasoline's distillation temperatures improve fuel vapourisation in the cold engine operation, and thereby improve the performance of the cold engine operation. Therefore, since adding methanol and other alcohols will lower the distillation temperatures, the cold engine drivability performance is expected to be equal or higher than gasoline without alcohols.



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IV. VEHICLE OPERATIONS AND PERFORMANCE

The automakers and the oil refining industry began investigating the use of methanol gasoline blends in the on-road vehicle fleet in the late 1970's in response to the large crude oil price increases at that time. Methanol blends at 15 volume percent (M15) were successfully used in a number of large vehicle fleets (~1000 vehicles each) in multi-year road trials to investigate the durability and performance of the fuel blend. M15 was chosen by automakers as the highest percentage of methanol that could be used in the existing vehicle fleet at that time with little or no changes in vehicle operating performance and materials used in the vehicle fuel systems. In general, properly blended M15 fuels with appropriate levels of co-solvents (for low temperature phase stability) and corrosion inhibitors (for chemical stability) were found to provide satisfactory performance with very few exceptions in the carburettors fuel systems that were most common in vehicles at that time. Since then, the automakers have generally upgraded their vehicle fuel systems to more advance materials with better M15 durability and also switched to fuel injector (pressurised) systems with feedback control that can operate on a wider range of fuel distillation volatilities and oxygen levels in the fuel without experiencing significant changes in vehicle operating performance. As a result of these fuel system improvements, most vehicles produced since 1990 are expected to perform satisfactory on properly blended methanol fuels containing sufficient co-solvents and corrosion inhibitors.





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V. MATERIAL COMPATIBILITY

Only the fuel distribution system materials are considered in this section, and not the fuel system components commonly used on vehicles. Most materials used in storing, blending, and transporting gasoline are also suitable for use with gasolinemethanol/co-solvent blends. However, sound engineering judgment is required when materials are selected for use with gasoline-methanol co-solvent blends to ensure the safety of the facilities that handle these liquids. Some commonly used materials and their compatibility with gasoline-methanol/co-solvent blends are listed in Table 3.

Before any storage system is converted to handle gasoline methanol/co-solvent blends, it should be inspected for safe operability and modified as necessary. All materials in the system should be checked for their suitability for use with gasoline methanol/ co-solvent blends, and replaced as required. Once the facility is in operation, it should be inspected periodically, and any malfunctions should be corrected promptly.

METHANOL /CO-SOLVENT-GASOLINE BLENDS

Many companies have examined the effect of gasoline blends at high concentrations of methanol (such as M15) on various materials found in automotive fuel and in gasoline distribution systems. Also, considerable commercial experience for 5% methanol blends was acquired during the 1980's. Except for a few materials, no significant detrimental effects were noted for most of the tested materials or 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. Gasoline blends containing 15 volume percent methanol (M15) have also been successfully distributed in the market place for multi-year periods of time during the late 1970's and early 1980's as part as large commercial market trials. In some cases, the M15 gasoline blends were refinery blended, and shipped via railcars and barges. In other cases, a premix of methanol, co-solvents and corrosion inhibitors were blended at the fuel product distribution terminals in the trucks used to supply gasoline to the retail gasoline stations. In more recent years, China has commercially introduce M15 by blending fuel methanol (with co-solvents and inhibitors) into gasoline at the fuel product distribution terminals. The blending of fuel methanol at gasoline distribution terminals is discussed later.

FUEL ADDITIVES AND INHIBITORS

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

In order to ensure "fit-for-purpose" motor gasolines, the corrosion inhibitors should be premixed with fuel methanol by the fuel methanol suppliers, distributors, or gasoline blenders. Only corrosion inhibitors that are effective in such applications and compatible with HC-only gasolines should be used for this purpose.

To ensure consistent quality in the local market place, it is generally recommended that the fuel methanol suppliers secure and add corrosion inhibitors to the fuel methanol premix at a treat rate sufficient to provide corrosion protection comparable to that of other available motor fuels. In addition to corrosion inhibitors, other gasoline additives such as antioxidants (prevent gum formation) and detergents (prevent fouling) should also be considered to prevent other vehicle performance degradation due to possible fouling in the vehicle fuel system. Lastly, some co-solvents will need to be premixed into the methanol to prevent phase separation in the methanol gasoline blend since it can contribute to metal parts corrosion in the vehicle fuel system. Co-solvents are discussed in the water solubility section.



STORAGE TANKS

Gasoline-methanol/co-solvent blends can generally be stored in aboveground or underground tanks that are the same as those used to store gasoline.

TANK MATERIALS

Unlined steel tanks are suitable for the storage of gasoline-methanol/co-solvent blends. Although the solvent characteristics of these products can cause rust from the interior walls to loosen, the rust can be removed by cleaning the tank or by flushing and filtration of the tank's contents.

Some older internally lined steel tanks may not be suitable for conversion to storage of gasoline-methanol/co-solvent blends. Many general-purpose tank liners installed in the past can be damaged by these products. In 1980, formulations were devised for linings that are compatible with gasolinemethanol/co-solvent blends. The tank-lining manufacturer should be consulted about the compatibility of a particular lining.

Fiberglass-reinforced plastic tanks may or may not be suitable for the storage of gasoline-methanol/co-solvent blends. Resins have changed since fiberglass-reinforced plastic tanks were initially fabricated, and the tank manufacturer should be consulted about the compatibility of materials. In general, most fiberglass tank manufacturers have reformulated their products to be fully compatibility with methanol gasoline blends and neat methanol since 1985.

NOTE: Sustained levels of water bottoms in gasoline storage tanks must be avoided. Water bottoms may have a higher concentration of methanol and cosolvents than the gasolinemethanol/co-solvent blend, and therefore may be more damaging or aggressive to both internally lined and fiberglass-reinforced plastic tanks.

TANK VENTS

Tank vents can be normal, gasoline-type, upward-discharging open-vent caps, or they can be pressure-vacuum vent valves. Both kinds have generally been used without significant problems. Pressure-vacuum valves should minimise product loss and moisture intake, but require periodic maintenance.

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				
Elast	tomers			
Buna-N ™ *	Buna-N ™ *			
Flurel ™				
Fluorosilicone				
Neoprene *	Neoprene *			
Polysulfide Rubber				
Viton ™				
Poly	mers			
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



PIPING AND FITTINGS

Manufacturer-approved nonmetallic pipe or cathodically protected steel pipe can be used, subject to the guidelines given for tank materials. New flanged and screwed pipe joints should be made using gaskets, thread compound, or tape that is not adversely affected by methanol.

Existing steel piping should be satisfactory for conversion from gasoline to a gasoline-methanol/co-solvent blend. Nonmetallic piping may or may not be suitable for conversion to a gasoline-methanol/co-solvent blend. The piping manufacturer or supplier should be consulted about the compatibility of the piping.

PUMPS AND DISPENSERS

The solvent characteristics of gasoline-methanol/co-solvent blends tend to loosen rust and deposits buildup in unlined steel tanks and piping. These materials should be removed by filters, since they can cause accelerated wear in meters, seals, and gaskets. Filters may initially need to be changed frequently following initial introduction to remove such deposits. Corrosion of metal components in the equipment does not appear to be of consequence unless phase separation has occurred.

STORAGE OF FUEL METHANOL PREMIXED WITH CO-SOLVENTS

As a solvent and chemical feedstock, there is substantial commercial experience in the methanol industry for shipping and storing methanol in the global markets. In general, methanol premixed with co-solvents is non-corrosive to most metals at ambient temperatures; some exceptions include lead, magnesium and platinum. Mild steel is usually selected as construction material. Many resins, nylons and rubbers, particularly nitrile (Buna-N), ethylene propylene rubber (EPDM), Teflon and neoprene are used satisfactory as components of equipment in methanol service. In general, Viton[™] and Flourel[™] flouroelastomers 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 on neat methanol material compatibility can be provided by the methanol supplier or industry organisation.



VI. WATER SOLUBILITY AND PHASE STABILITY

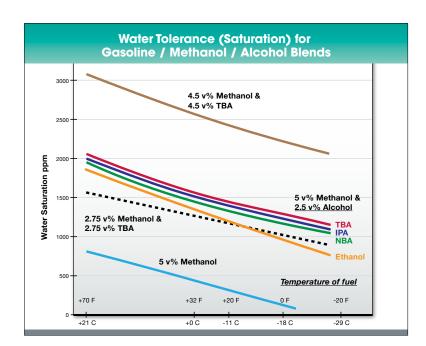
Similar to other alcohols blended into gasoline, methanol gasoline blends will separate into two phases if the gasoline blend is exposed to sufficient water that exceeds its water tolerance (solubility saturation level) for the ambient temperate conditions. Also, colder temperatures can cause the methanol gasoline blends to separate if sufficient co-solvent alcohols are not added to provide cold temperature phase stability. Beside avoiding poor vehicle operating performance, phase stability is also important to avoid fuel system degradation since the separated bottoms phase containing the water can potentially be more corrosive to some metals, and more aggressive with some non-metals. Besides containing water, the bottoms phase will also contain some of the alcohols and aromatics from the gasoline blend which will then make the water bottoms phase flammable and possibly more difficult to transfer to waste water treatment systems. Also, a vehicle will not be able to operate

if the bottom phase from retailer's fuel tank should inadvertently be pumped into a vehicle's fuel tank. Therefore, the water saturation condition should be avoided for all alcohol gasoline blends by keeping the gasoline product storage system free of excess water, and by adding sufficient water tolerance to the methanol gasoline though the use of co-solvent alcohols. Typical gasoline properties of some of the commercially used co-solvents along with methanol are listed in Table 4.

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

In addition to the local cost and availability of individual co-solvent alcohols, the amount and type of cosolvent alcohol that should be premixed with the methanol before blending with gasoline will also be dependent on the amount of water tolerance required to prevent phase separation, given the climate and the conditions for handling and storing the methanol gasoline blend in the marketplace. With sufficient water tolerance and corrosion inhibitor protection, refinery blended gasoline with methanol and co-solvents have been successfully shipped commercially to gasoline product distribution terminals by both pipelines and oceangoing barges as well as by railcars and tanker trucks.

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



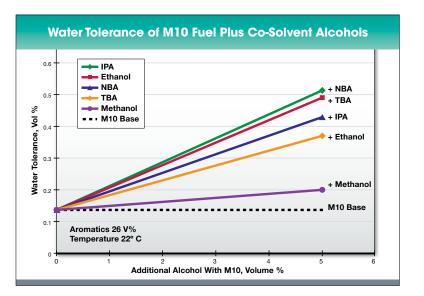
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Because of the sensitivity to water, it is important to eliminate possible sources of water in the supply chain of methanolgasoline blends. Therefore, at the gasoline distribution terminal, it is important to keep the premix of methanol and cosolvent alcohols water free or "dry" before it is blended into the gasoline at the truck loading rack. This normally requires storing the fuel methanol /co-solvent alcohol mixture in a fixed roof tank with an internal floating roof. Nitrogen blanketing of the tank headspace will also provide additional protection against any added moisture. Similarly, the methanol-gasoline blends received from refineries or gasoline blenders should be stored in fixed rook tanks with internal floating roofs to ensure maximum dryness and phase stability. Also, a common practice of clearing a product transfer pipeline of any HC by pushing water through the pipeline cannot be used following a product movement of methanol blended gasoline though it. A HC product movement will first have to be made before and after a movement of the methanol-gasoline blend in the pipeline so as to prevent water contamination.

The effectiveness of the co-solvent alcohol for adding more water tolerance to a methanol gasoline blend is related to the type of alcohol used as a co-solvent as illustrated in the following figure for a gasoline blend containing 10 vol% methanol. In general, the less polar (lower oxygen content) the co-solvent alcohol, the more water tolerance will be added to the methanolgasoline blend for the volume of co-solvent added, or the less volume of co-solvent will be needed to achieve a minimum water tolerance in the methanol-gasoline blend. As illustrated, even adding some more methanol will increase the water tolerance of the methanol blend, but the other alcohols are more effective. The data in this figure suggests that butanols (NBA and TBA) are about 50% more effective than ethanol for adding water tolerance to this particular blend which means that about 50% more ethanol will need to be used to achieve a targeted water tolerance as compared to using a butanol as a co-solvent.

Unfortunately, no standard field test exists for determining the amount of methanol/co-solvent in the gasoline-methanol/co-solvent blend at the service station. Testing for methanol and co-solvent content can only be performed by qualified laboratory personnel with the proper equipment.





METHANOL BLENDING GUIDELINES

REFINERY BLENDING

Blending mixtures of methanol/co-solvents in the gasoline at the refinery has been commercially practiced in the past by using good transportation and product segregation practices in the product distribution system as discussion in the transportation section. The methanol gasoline blend has been shipped to the product terminal via pipelines, barges, railcars and trucks. However, since most common-carrier (multi-shipper) pipelines usually do not have the flexibility and extra tanks needed to segregate alcohol blends, those refiners without direct pipelines, barging or rail access to product distribution terminals may be limited to the terminal blending of the premixed methanol with a gasoline Base fuel (BOB – Base fuel for Oxygenate Blending) that has been specially formulated to compensate for methanol's blending properties. Refinery blending may still be appropriate, however, when methanol/gasoline blends are directly supplied to the truck loading rack from the refinery.

TERMINAL BLENDING

Should an oil refiner not be able to achieve or maintain a dry gasoline product distribution supply system that prevents the introduction of excess water into the methanol gasoline blends as it is being shipped to the product distribution terminal, then it may be necessary to blend the pre-mix of methanol with sufficient co-solvents at the gasoline product terminals as the gasoline is being loaded into the gasoline 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, in this case, the refiner will generally need to produce and supply a modified gasoline blendstock (BOB) to the product terminal that is adjusted to be blended with the methanol so that the blend will still achieve the final gasoline quality specifications. The gasoline blendstock (BOB) should essentially be no different from the HC portion of the gasoline as if the methanol and co-solvents were being blended at the refinery.

Because of the lack of mixing tanks in most distribution terminals and to ensure good quality control for methanol gasoline blends, the co-solvent alcohol and inhibitors should be premixed with the fuel methanol before arriving at the gasoline terminal. To achieve good mixing of the gasoline and fuel methanol mixture before final delivery to the gasoline retail station, the methanol fuel and gasoline should preferably be simultaneously loaded into the gasoline delivery truck. However, if simultaneous (in-line) loading into the truck is not an option at the terminal, then the methanol fuel mixture should first be loaded into the delivery truck so that good mixing occurs when the gasoline portion is then loaded into the delivery truck. In this situation, a second mixing occurs when the delivery truck drops the load of methanol gasoline blend into the underground tank at the retail stations. When terminal blending of methanol procedure is used, then laboratory quality inspections should be conducted on random sampling of gasoline from the retail stations to confirm that the good mixing practices are being followed at the terminal.



VII. TRANSPORTATION OF METHANOL GASOLINE BLENDS

TRANSPORT VIA MULTI-PRODUCT PIPELINES

Because of potential commingling concerns with other distillate fuels (jet, diesel) with low flash point temperatures being shipped in multi-product pipelines and also water collecting in system low points, the alcohols gasoline blends are not generally transported in common carrier (multi shippers) fuel product pipelines from refineries to product distribution terminals. However, methanol gasoline blends have been successfully shipped in single owner, multi-product pipelines for distances over 500 kilometers.

If pipelines are to be used for this purpose, they must be dehydrated prior to the first shipment of methanol/gasoline blends because of the affinity of methanol for residual water. If methanol gasoline blends are transported via a pipeline system, more frequent cleaning and inspection should occur due to the capacity of methanol to pick-up dirt (rust, sediments, etc.) throughout the system. Corrosion inhibitors that are effective with methanol gasoline blends should be selected to protect the pipeline system.

TRANSPORT BY ROAD AND RAIL

In principle, the distribution of methanol/gasoline blends by tanker trucks and by railcars is done in the same way as conventional motor gasoline. However, special precautions should be taken to avoid contamination of the methanol/gasoline blend with water, dirt, rust, and gum buildup in the gasoline tanks. In addition, the methanol/gasoline blend should not be mixed with other HC-only fuel in order to avoid increases in vapour pressure in the mixture which can raise the 'flash' temperature in the case of distillate fuel products.

TRANSPORT BY BARGE

Due to the affinity of methanol for water, the transport of methanol/gasoline blends by barge requires additional attention. Methanol gasoline blends have been successfully shipped from refineries via ocean going barges to product terminals in the past. However, extra precautions and procedures should be put in place to ensure safety, cleanliness, and product integrity following transport. In particular, vessels that occasionally use product tanks as ballast water tanks should not be used for transporting methanol/gasoline blends. Any commingling of methanol/gasoline blends and water should be strictly avoided.



VII. STORAGE AND HANDLING

Motor fuels that consist of a blend of gasoline and methanol containing sufficient co-solvent or co-solvents, and corrosion inhibitors have properties similar to those of gasoline that is not blended with alcohols. With some exceptions, the facilities required for the handling of gasoline-methanol/co-solvent blends are also similar to those required for gasoline. There are, however, some differences that must be recognised by those who store, handle, or provide fire protection for the blended product.

These guidelines describe recommended practices for the storage, handling, and fire protection of gasoline-methanol/cosolvent blends at fuel product distribution terminals and service stations. Co-solvent alcohols improve a gasoline-methanol blend's water-tolerance properties that are needed to provide phase stability when exposed to colder temperatures or excess moisture in the storage system or the fuel tanks of vehicles. In addition, co-solvents also help control the effects of methanol on the vapour pressure of a finished gasoline-methanol/co-solvent blend.

Though fuel methanol premixed with co-solvent alcohols and its gasoline blends can generally be stored and handled in much the same way as most other gasoline-type hydrocarbons, there are certain differences that need to be considered which require some precautions. These precautions will be addressed separately for the methanol/co-solvent premix and the methanol gasoline blends.

METHANOL PREMIXED WITH CO-SOLVENTS

The importance of keeping the fuel methanol water–free or dry has been discussed in the 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 such as using carbon filter breathing masks when the probability of high vapour exposures exists. Additional guidance can be found in the Methanol Institute's Methanol Safe Handling Manual, available on the web site at <u>www.methanol.org</u>.

Before introducing methanol/co-solvent premix into the system, the transfer and storage systems must be checked for flouroe-lastomers such as Viton[™] elastomer and polyurethane which may fail unexpectedly, and thereby lead to releases of methanol into the environment and unplanned equipment downtime. However, flouro-elastomers have generally been found to be satisfactory for use with methanol-gasoline blends.

Since methanol is water soluble, it will reduce the effectiveness of a fire 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 may need to increase the flow rate for the fuel methanol storage area. (Fire safety discussed later)



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 now be slightly different from before. This change in solvency may cause some of the long–term gum and dirt build-up in the 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 many need to be switched to a type with smaller micron opening that is designed for alcohol gasoline blends. The performance of vehicles during this initial phase should be unaffected as long as good house–keeping practices are maintained at the retail gasoline outlets.

As part of the good house keeping practices at the retail gasoline stations, the station attendant will routinely check for any potential buildup of water bottoms phase at the bottom of the underground gasoline tanks which needs to be removed. The water detection paste that is normally applied to the bottom of inventory checking stick 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. Also, those tanks with electronic inventory detection may need to have the level sensor adjusted to reflect the difference in water bottoms composition.

Since excess water can sometimes build up in the gasoline storage and distribution systems, a water phase can form at the bottom of gasoline storage tanks. In the case of alcohol blends, the water bottoms will also contain some alcohol and aromatics from the gasoline. As a result, the water bottoms must be handled as a flammable liquid, and should be properly 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 waste treatment systems, and therefore should not lead to an increase in BOD or COD in the waste water effluent.

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 <u>www.methanol.org</u>. It is strongly recommended that these documents be accessed for thorough review of this subject. However, in general, facilities which handle or store methanol 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 feasible.



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TERMINAL CONVERSIONS TO METHANOL BLENDS AND TERMINAL BLENDING

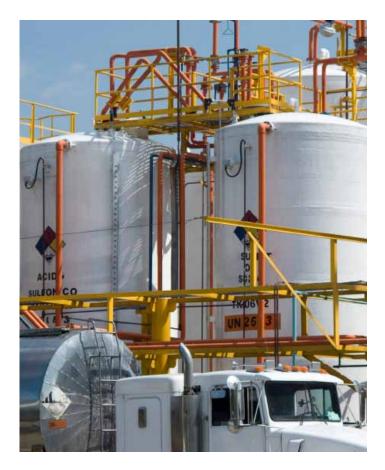
A gasoline-methanol/co-solvent blend must conform to government environmental regulations and final product specifications. If a gasoline-methanol/co-solvent blend is stored at and transported from a product distribution terminal, the facilities required and the methods of handling are essentially the same as those at a service station (discussed later). However, there are a few steps that should be taken at the terminal level to ensure the trouble-free implementation and ongoing operation of the methanol gasoline blend program. The terminal operator should consider developing a checklist for personnel orientation to avoid mishaps especially for truck blending of the fuel methanol premix with the gasoline.

TANKS AND TANK LININGS

Tanks used to store gasoline-methanol/co-solvent blends should comply with generally accepted standards for storage of flammable liquids for local government codes. Riveted tanks are likely to leak and should not be used unless a liner resistant to the gasoline-methanol/co-solvent blend is installed. Tankage needs to be sized to volume requirements and the size and frequency of anticipated deliveries. A fixed roof tank with a floating internal cover is recommended to minimize moisture exposure. In order to minimise vapour loss, a pressure/vacuum vent should be installed. Be sure and confirm that the storage tank is designed to tolerate the required pressure before the pressure/vacuum vent is installed. The petroleum equipment supplier can help with the proper selection of the vent based upon the size of the fitting and whether the storage tank is above or below ground.

PIPING

If existing lines are to be used, they must be thoroughly flushed with the blended product beforehand. Line flushing practices used to clear products from pipelines should avoid using water before and after any movements or transfer of methanolgasoline blends or fuel methanol mixtures. The solvency effect of gasoline-methanol/co-solvent blends will loosen scale, rust, gum, varnish and dirt buildup from the interior surface of piping and tanks. A 40 mesh basket strainer should be installed in the line at the loading rack. The strainer should be removed and cleaned as necessary.



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RETAIL GASOLINE STATION CONVERSION TO METHANOL BLENDS

NEW FACILITIES

In addition to the recommendations given in this publication, underground storage tanks and piping systems should be installed according to the applicable requirements and recommendations of API Bulletin I615 and API Recommended Practice 2003. Care should be exercised to assure that nonmetallic parts are not adversely affected by the gasoline-methanol/ co-solvent blend. The nonmetallic-parts manufacturer should be consulted about possible adverse effects.

CONVERTING EXISTING RETAIL FACILITIES FROM USE WITH OTHER PRODUCTS

To ensure trouble free operation and maintain good quality gasoline product to the consumers, there are items to be covered so as to prepare a storage tank and piping system for use with a gasoline-methanol/co-solvent blend. The items are as follows:

- 1. If the tank has a liner or is of nonmetallic construction, consult the supplier or manufacturer to determine the tank's compatibility with the gasoline-methanol/co-solvent blend.
- 2. Inspect the fill-pipe cap and adapters to ensure that they are in good condition, and will prevent water from entering the tank. Take corrective action if necessary.
- 3. Strip the tank bottom of all water and sludge, using a thief pump if necessary. Tank bottoms and sludge should be disposed of in accordance with appropriate environmental regulations.
- 4. Pump gasoline down to as low a level as is possible. This may be accomplished by sales through the service station dispenser. If regulations require that the exact gasoline-methanol/ co-solvent blend percentage be posted, remove all gasoline from the tank.
- 5. Install filters in the dispensing system to ensure the delivery of clean product to the customers' vehicles.
- 6. Fill the tank 85-90 percent full with gasoline-methanol/co-solvent blend for the first fill.
- 7. Change the dispenser filter and/or clean the dispenser strainer as necessary. Periodically inspect the pumping equipment for any evidence of leaks due to shrinking of gaskets or other causes.
- 8. Calibrate the dispenser's liquid meter at the time of conversion and at 2-3 months after conversion to verify the meter's accuracy. Particulate matter may increase wear of the meter, which would then require more frequent calibration.
- 9. Check the storage tanks daily for water bottoms.
- 10. Educate all operating personal to the change in procedures.



IDENTIFICATION UPDATE

The identification on the converted dispensers and the underground tank's fill pipe should be corrected to reflect the use of methanol gasoline blends. Corrections should include the following items:

- 1. The dispenser's product identification panel. (The product supplier should be consulted regarding the correct information.)
- 2. The required government and/or supplier labeling.
- 3. The identification tag, fill box, and/or manhole cover.

RECORD KEEPING

Daily inventory records should be maintained in the same manner as for any other gasoline motor fuel. Since water is a serious problem in the storage and handling of gasoline-methanol/co-solvent blends, it is important to check tanks for water and to record the results of these tests with the inventory records. Some underground tanks use electronic inventory and water detection probes for monitoring inventory. To confirm continued accuracy of inventory and water detection when switching to methanol gasoline blends, the equipment supplier should be contacted for guidance. The conventional method for monitoring gasoline inventory and water detection has been to use tank inventory measuring sticks with water detection paste applied to the bottom 10 centimeters of the stick before inserting the stick into the tank for daily checks. Some of the older water detection paste do not change colours for tanks water bottoms containing alcohol. Therefore, water detection paste especially designed for also detecting alcohol containing water bottoms should be used. At the time of this writing, the following two suppliers had distributed a water detection paste suitable for use with alcohol gasoline blends. There may be other acceptable suppliers of such water detection pastes for retail gasoline tanks.

The Sartomer Company	KolorKut Products Co.
468 Thomas Jones Way	P.O. Box 5415
Exton, PA 19341	Houston, TX 77262
(610) 363-4100	(713) 926-4780

The following page contains a one page checklist for conversion of retailer gasoline stations from conventional gasoline to methanol gasoline blends.



Gasoline Methanol Blend Program – Retail Station Operator Checklist Investigation and Preparation

Verify material compatibility of tanks and submersible pumps

Investigate any prior tank water problems and correct by reviewing history of each underground tank.

Tight seals on fill caps and proper water run off from surface covers. Remove water bottoms (if present). Check for tilted tanks. Clean integrity of tank's bottom wall, if necessary.

If using an electronic tank inventory system, verify compatibility and operation with methanol gasoline blends.

Conversion Plan (before first delivery of methanol gasoline blend)

Equip the fuel pump or dispenser with a 10 micron filter. Supply extra filters for first few weeks.

Recheck for water at bottom of the tanks and remove any that is present.

Issue alcohol compatible paste for checking water bottoms, and discard any older incompatible pastes.

Change any necessary identification labels to reflect the use of methanol gasoline blends.

Confirm any applicable accounting procedures.

First Delivery

Check for water. Water bottoms must be removed before first delivery of methanol blends.

Follow normal delivery procedures, and ensure that accurate tank gauge and dispenser readings are taken.

Verify (with transport driver) correct compartment for each tank.

Dispenser pumps should be shut down during initial delivery. (check company policy)

Purge lines from tanks to dispensers. (check company policy)

Fill tanks to at least 80% of capacity.

Test for water bottoms at the beginning of each shift for the first 48 hours after initial delivery. Check for water bottoms daily.

Notify designated personnel if water is detected, and have it removed at once. Replace filters if pump/dispenser is running slow. Carry extra filters at each retail station for first few weeks after the methanol blend introduction.

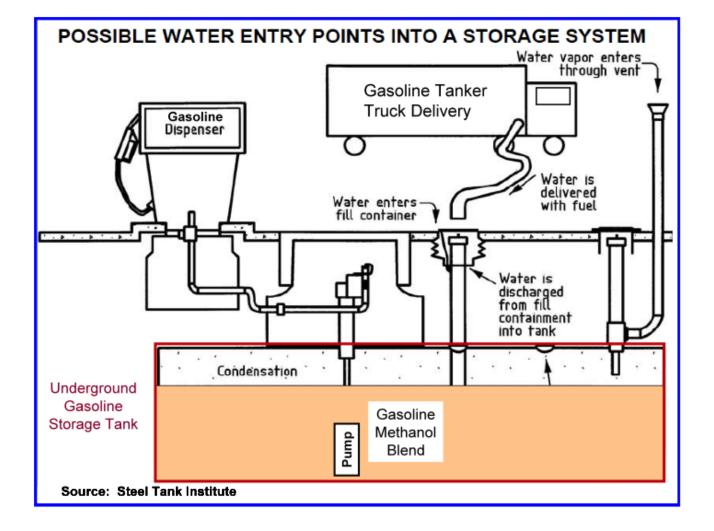
Check pump calibration two weeks after initial load conversion

Ongoing Maintenance

Check for water phase at bottom of the tank. No water level is acceptable.

Use proper size pump filter, and change out regularly to maintain good pump flow.







IX. GLOBAL METHANOL FUEL BLEND REGULATIONS

In many regions of the globe, the blending of oxygenates such as alcohols and ethers are controlled by government regulations that specify the limits for the various oxygenates allowed in commercial gasolines. The maximum levels of total oxygen from the oxygenates in gasoline had been generally established to maintain and ensure the fuel blend's drivability performance in the vehicle fleet on the road at the time the regulation was implemented. As for methanol blending, the maximum limit in gasoline had generally been established based on the compatibility of the nonmetal materials of the older vehicles on the road at the time that the regulation was being established.

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 U.S. set a maximum oxygen limit of 3.7 wt% which reflects the drivability performance limits of the carburetted fuel metering systems that were used on vehicles at the time these fuel oxygenate regulations were first established. However, most vehicles on the road today now have fuel injection systems with more alcohol tolerant fuel system materials. With the improved fuel systems, many provinces in China have established methanol blends with oxygen levels that are about twice as high as that established in the 1980's in Europe and U.S. markets. The higher allowable oxygen levels in China gasoline markets reflect the greater flexibility of current vehicle fuel system technology which is 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 materials, the vehicles on the road today can manage a wider range of oxygen level and alcohol content in fuel without suffering a loss in drivability performance or durability.

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 the methanol gasoline blend may experience in the commercial market place. During the early commercial introduction of methanol blends, the conservative regulatory practice was to add an amount of co-solvent alcohols that is equal 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 tolerance targets have been established such as in China.

Although fuel system material compatibility (metals and non-metals) concerns during the commercial introduction of methanol blending during the early 1980's had initially limited methanol content to 5 vol% or less in Europe and U.S. markets, the advancement of fuel systems materials and the improvement of corrosion inhibitors to address the growing use of alcohol blends such as ethanol (up to 25 vol% in Brazil) in global markets allows today's vehicle on the road to use much higher levels of methanol with little risk of incompatibility or performance degradation. To take advantage of the greater flexibility of all vehicles on the road today to operate on higher levels of methanol, the Shanxi Province of China successfully implemented a M15 fuel program which is now under consideration for a national program in China.

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	\geq 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						

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

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XI. FIRE AND SAFETY

SAFE HANDLING

Similar safety equipment and precautions should he used when handling either gasoline-methanol/co-solvent blends or gasoline.

SURFACE SPILLS

Gasoline-methanol/co-solvent blends should be handled in accordance with the applicable environmental regulations. Spills should be treated in the same manner as gasoline spills, including notification of the proper authorities.

LEAKS

Underground leaks of gasoline-methanol/co-solvent blends should be handled in the same manner as underground leaks of gasoline with notification to proper authorities and corrective actions. Because alcohols are soluble in water, they will preferentially dissolve into water if the leak should reach an underground water table or surface water. Unlike hydrocarbons, alcohols cannot be easily separated from water using the conventional techniques used to recover hydrocarbons. The leak response and remediation plan should be reviewed and modified if necessary before methanol blends are introduced into the market.

FIRE PROTECTION

Personnel should approach a gasoline-methanol/co-solvent blend fire with the same caution as they would approach a gasoline fire, and similar fire-fighting techniques should be used. Information on the control and extinguishment of flammable liquid fires is provided in API Publication 2021, and API Publication 2300.



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FIRE-FIGHTING AGENTS

DRY CHEMICAL

All types of gasoline-methanol/co-solvent blend fires (spill, pressure, three-dimensional, and fuel in-depth) can be extinguished with dry chemical at the same rate of application required to extinguish gasoline fires.

CARBON DIOXIDE, HALON 1211, AND HALON 1301

Spill fires involving a gasoline-methanol/co-solvent blend can be extinguished using carbon dioxide, Halon 1211, or Halon 1301 at the same volumetric concentration or rate of application required to extinguish gasoline fires.

FOAM

Gasoline-methanol/co-solvent blend spill fires (fuel depth less than 6 mm) can be extinguished with aqueous-film forming foams (AFFFs), polar-solvent (alcohol-resistant) foams, fluoroprotein foam, or regular protein foams in accordance with the recommended application rates from the supplier. Gasoline-methanol/co-solvent blend in-depth fires (fuel depth of 6 mm or greater) can be extinguished with AFFFs, polar-solvent (alcohol-resistant) foams, or fluoroprotein foam in accordance with the recommended application rates given by the supplier. Subsurface foam injection is not recommended for extinguishing gasoline-methanol/co-solvent blend tank fires. Detailed information on controlling and extinguishing fires involving gasoline/alcohol blends can be found in API Publication 2300.

WASTE WATER HANDLING

Unlike for gasoline, any water removed from storage tanks of methanol-gasoline blends at terminals or retail gasoline stations will have sufficient methanol and other hydrocarbons solubilised in it to make it flammable. Therefore, it should be handled as flammable hazardous waste water. The waste water with alcohols and hydrocarbons can usually be disposed in the waste water treatment facilities since it is generally biodegradable. However, some precautions are necessary as discussed below.

Methanol and co-solvent alcohols can be difficult to remove from waste water because it is very soluble in water. For this reason, the only way to efficiently remove methanol is through biological treatment. If the bacteria in treatment facilities have not been acclimatised to methanol, much of the methanol may initially pass through the treatment plant before it is fully degraded. Several weeks to a month may be required before a treatment plant can efficiently process methanol-containing waste streams. Facilities can gradually increase the methanol content in their waste water system as the bacteria become more efficient at degrading methanol. It is important to test degradation performance in the laboratory and analyse the plant effluent for methanol content over time in order to determine the degradation rate.

Because fuel product distribution terminals do not usually have biological treatment facilities, methanol will most likely pass through the mechanical treatments that are commonly used. If the terminal sends its waste water to a municipal treatment plant, it is important to check with the treatment plant operators whether their facility can handle methanolcontaining waste water. In any case, the disposal of waste water must be done in accordance with all local regulations and permits.

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XII. 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 other components in gasoline that could increase health risks.

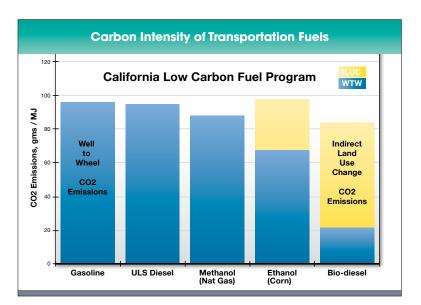
ENVIRONMENTAL

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 LIS. Ontions for						

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



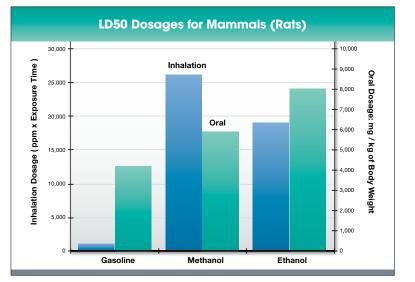
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HEALTH RISK FROM EXPOSURE

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.





XIII. OTHER REFERENCES

- API Recommended Practice 1627, Storage and Handling of Gasoline-Methanol/Co-solvent Blends at Distribution Terminal and Service Stations, August 1986
- API publication 1642, Alcohol, Ethers, and Gasoline–Alcohol and Gasoline–Ether 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
- 'Distribution of Gasoline Containing Oxygenates', BP Oil International, London, UK, , <u>VII International</u> <u>Symposium on Alcohol Fuels</u>, Paris, October 1986, page 497-501
- 'Retail Distribution of MAS Blended Gasoline In The Commercial Network: First Large Distribution,' F. Monti, et.al., AgipPetroli, Italy, <u>VII International Symposium on Alcohol Fuels</u>, Paris, October 1986, page 502-507
- "THE USE OF ALCOHOL MIXTURES AS GASOLINE ADDITIVES", B.C. Davis & W.H. Douthit, Sun Refining & Marketing, NPRA AM-80-47, NPRA Annual Meeting, March 1980, New Orleans, Louisiana
- "Methanol In Gasoline, The Fuel of Tomorrow-Today", ARCO Chemical Company, 1985
- "Methanol-Gasoline Blended Fuels in West Germany Specification and Early Field Experience", B. Nierhauve, ARAL Research Center, West Germany, Proceedings of the IV International Symposium on Alcohol Fuels Technology, Brazil, October 1980, Volume 1, pgs 319-324
- "The M-15 Blend Test Programme of the New Zealand Liquid Fuels Trust Board", J. Duncan, Proceedings of the IV International Symposium on Alcohol Fuels Technology, Brazil, October 1980, Volume 2, pgs 523-531
- "Methanol Gasoline Blends in New Zealand", W.G. Dyer, BP Zealand Limited, Proceedings of the IV International Symposium on Alcohol Fuels Technology, Brazil, October 1980, Volume 2, pgs 533-540
- "Road Trials to Assess the Hot Weather Driveability Characteristics of Gasoline Containing Oxygenates in European Cars", SAE 831706, F.H. Palmer (BP Oil) & A. Tontodonati (ENI), SAE 1983
- "Engine and Vehicle Concepts for Methanol-Gasoline Blends, SAE 831686, Holger Menrad, Volkswagen Research, Bernd Nierhauve, Aral AG, Germany, 1983
- "Vehicle Operating Experience with Methanol as a Substitute for Petrol and Diesel", SAE 830899, R.J. Joyce, et.al., Liquid Fuels Trust, New Zealand, 1983
- "ALCOHOL FUELS: THE LAST TEN YEARS AND THE NEXT TEN YEARS', VII International Symposium on Alcohol Fuels, Paris, October 1986, pgs 9 -35
- "A Review of the Study on Alcohol Fuels for Automotive Engines," SAE 890433, Chen Xiaofu, Shanghai Automobile and Tractor Research, Shanghai, China, 1989



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