



**Comments Regarding Low Level  
Methanol Fuel Blending Standards for  
M5-M15 Adopted by Shanxi Province  
(China)**

**September 2008**

**Prepared by:**



**TEIR Associates, INC  
160 Hidden Hills Road  
Media, PA. 19063**

***www.teira.com***

## **I. Introduction**

The Methanol Institute retained the services of William Piel of TEIR Associates, Inc. to conduct a review of the Shanxi Province low level methanol fuel blending standards for M5, M15 and Denatured Methanol. The members of the Methanol Institute appreciate this opportunity to provide comments to our colleagues in Shanxi Province based on this review. We recognize that Shanxi Province has extensive experience in methanol fuel blending, and is leading the world in the development of methanol transportation fuels. In our comments here, we have attempted to gather the experience with alcohol fuel blending in the United States and Europe to provide suggestions that Shanxi Provincial officials may wish to consider in the further development of both Provincial and National methanol fuel blending specifications. As a model for the rest of the world, Shanxi is in the unique position of demonstrating the successful adoption of methanol fuel blends on a wide scale commercial basis. Therefore, it is essential that the methanol fuel blending standards being utilized: (1) ensure the efficient performance of vehicles; (2) the facilitate the effective operation of fueling infrastructure; (3) meet applicable emission requirements, including international fuel standards being adopted in China such as Euro 3 and Euro 4; and (4) and maximize the economic value of methanol fuel blends. With these objectives, we humbly offer the following comments, and would be happy to facilitate a further discussion with the members of the Methanol Institute and our consultant, Mr. Piel of TEIR Associates.

## **II. Comparison of Fuel Standards**

The Shanxi Province methanol and methanol fuel blend standards in Table 1 are compared to China gasoline standards for the nation and Beijing as well as the Euro 3 and 4 petrol standards. The table also includes the expected RVP increases for splash blending 10% ethanol (E10) on the national gasoline standard. Except for a higher allowable RVP fuel, the M5 and M15 standards essentially use the same standards as the national gasoline for gasoline property specifications such as minimum octane, distillation temperatures, hydrocarbon composition (aromatics and olefins), other fuel stability properties such as gum formations and oxygen stability, etc. However, because the fuel's phase separation stability is a function of dissolved water in the fuel, the Shanxi methanol blend standards include three additional specifications to minimize the possibility of phase separation occurring during commercial use. The Shanxi methanol fuel blend standards also introduce the concept of a special basefuel (similar to RBOB "Reformulated (Gasoline) Blendstocks for Oxygenate Blending" in the U.S.) for methanol blending that has both sub-octane and sub-RVP fuel properties as compared to the national gasoline standards

The blending of methanol introduces gasoline property changes in four general areas of significance: (1) Fuel Blend Stability Related to Water Tolerance & Temperature; (2) Fuel Volatility of Methanol Fuel Blends; (3) Chemical Stability of Fuel Blends, and (4) Octane Contribution. The octane increase will provide added value for the methanol while the other three property changes will generally reduce the value of methanol in gasoline depending on how the fuel standards are set.

Table 1. Comparison of Fuel Standards for Gasoline used in Vehicles

Fuel Property	Units	Shanxi Methanol Blends				China Gasoline Standards			European Petrol	
		M0 Base	M5	M15	Denatured Meoh	National	E10	Beijing	Euro 3	Euro 4
<b>Oxygenate Content</b>										
Methanol	% vol	Max	0.3	5 ~ 7	13 ~15	94			3	3
	% vol	Min			7 <sup>a</sup>					
Ethanol	% vol	Max					10		5	5
Oxygenates	% mass	Max	0.5							
Oxygen Content	% mass	Max		~ 3.5	~ 7.5		2.7	~ 3.7	2.7	2.7
<b>Octane for Regular Grade</b>										
RON		Min	88	90	90		90		90	95
(R+M)/2		Min	83.5	85	85		85		85	85
<b>Volatility</b>										
<b>RVP</b>										
Summer	kPa	Max	67	82	86		74	~ 81	65	Norm (Arctic) 60 (70)
Winter	kPa	Max	81	90	90		88	~ 93	88	
<b>Distillation Temperatures</b>										
10%	°C	Max	70	70	65		70		70	210 Summer (winter) 20 (22) 48 (50) 46 71 75
50%	°C	Max	120	120	110		120		120	
90%	°C	Max	190	190	185		190		190	
FBP	°C	Max	205	205	205		205		205	
E70 C	% Evap.	Min								
E70 C	% Evap.	Max								
E100 C	% Evap.	Min								
E100 C	% Evap.	Max								
E150 C	% Evap.	Max								
<b>Density</b>										
	kg/L @ 20C									
		Max				0.810	0.775		0.775	0.775
		Min				0.791	0.720		0.720	0.720
<b>Chemical Reaction Stability</b>										
Gums	mg/100ml	max	5	5	5		5		5	
Oxygen Stability	minutes	min	540	480	480		480		480	360
Copper strip corrosion		max	1	1	1		1		1	1
Inorganic chorides	mg/L	max				2				
<b>Phase separation stability</b>										
Water Content	wt %	max		0.15	0.15	0.15				
Phasing with adding 0.15 vol% water				clear	clear	clear <sup>c</sup>				
Phases @ - 30 C <sup>b</sup> Winter only				clear	clear	clear <sup>c</sup>				
<b>Composition</b>										
Benzene	% vol	max	2.5	2.5	2.5		2.5		1	1
Aromatics	% vol	max	44	40	40		40		42	35
Olefins	% vol	max	38	35	35		35	25	18	18
Aromatics + Olefins	% vol	max						60		
Sulfur	ppm wt	max	500	500	500		500	50	150	50 / 10

a Minimum methanol content of 7% from June 1 to August 31  
b Winter test only applies from November 1 to March 31  
c Test procedure blends 30% and not 15% of denatured methanol in a gasoline blendstock

### III. Fuel Blend Phase Stability Related to Water Tolerance & Temperature

**Suggestion 1:** *Based on past experience, co-solvents are needed to produce a stable low level methanol blend for commercial use that will not likely phase separate under expected normal conditions and moisture exposure. The Denatured Methanol standard requires a 94 vol% minimum methanol content requirement, effectively limiting the use of co-solvents to 6 vol% in the Denatured Methanol, or less than 1 vol% of the finished methanol/gasoline blended fuel. To ensure that the methanol fuel blends can pass the three different fuel requirements to minimize the possibility of phase separation from occurring with the fuel blend in the marketplace, the Denatured Methanol minimum methanol content requirement should be revised from 94% to 80%.*

**Suggestion 2:** *The methanol content requirements for M5 and M15 only refer to the methanol in the fuel blend, and do not include any co-solvents that may be needed to improve the fuel blend's water tolerance. The two measurement methods (described in the annex) referenced for this content standard will only measure the amount of methanol in the fuel blend, and not any other alcohols that might be used as co-solvents. Therefore, it is unclear if any co-solvent (or denaturant) is to be included in the measured or reported methanol content for M5 or M15. Specific guidance should be provided in the M5 and M15 standards to identify acceptable co-solvents and co-solvent volumes to ensure the fuel can pass the reference measurement methods.*

**Discussion:** In general, oil and water do not mix, and therefore any risks associated with water contamination in the distribution of gasoline have not been a large concern in the past. However, alcohols, particularly light alcohols such as methanol and ethanol, will phase out (separate) from a gasoline mixture if the gasoline has been exposed to too much water before the gasoline mixture is eventually combusted. Even without any added water in the gasoline mixture, methanol itself has a limited solubility in gasoline at cooler temperatures (below 10 °C). If methanol should separate from a gasoline mixture, and thereby form a second denser liquid phase of mostly methanol in the vehicle storage tank, it will cause significant poor engine performance and possibly make the vehicle inoperable by stalling the engine. Therefore, precautions need to be developed to prevent a methanol phase separation from occurring.

Past experiences suggest that successful low level methanol blends (M3 to M15) will likely require 2 vol% co-solvent alcohols to prevent phase separation in the consumers' vehicles, particularly during the colder winter seasons. The U.S. approved the commercial use of 5 vol% methanol blend waivers that required a minimum 2.5 vol% of co-solvents (C2 to C7 alcohols). Europe commercialized the 3/2 methanol blends (3 vol% methanol and 2 vol% butanols) during the early 1980s. Norway successfully demonstrated M15 blends with 2 vol% isobutanol as a co-solvent. Although BP operated a 3 year fleet demonstration program using M15 with no reported co-solvents in New Zealand, the risk of phase separation is very low since New Zealand winters are relatively mild since temperatures do not drop below 0 °C.

The Shanxi methanol fuel standards add three different fuel requirements to minimize the possibility of phase separation from occurring with the fuel blend in the marketplace. The first requirement is a maximum for the soluble water content of 0.15 wt%. The second phase separation test determines if the methanol fuel blend has a working water tolerance of at least

0.15 vol% before the fuel blend would begin to phase separate at room temperature conditions (~20 °C). The 0.15 vol% water tolerance would be approximately the same as that experienced with 5 vol% ethanol blends which are successfully used in Europe, and therefore would be expected to be sufficient working water tolerance for methanol blends as well. The third phase separation test is a “winter season only” test conducted at – 30 °C which visually inspects for hazing or phase separation in the sample with out adding any additional water. This test only applies during the winter months from November 1 to March 31.

The denaturant requirement for methanol blends becomes more complicated because in addition to the M5 and M15 fuel blend being required to meet the three different phase separation tests, the standard for Denatured Methanol requires that it ‘also’ meet the same three phase tests by making it into a M30 fuel blend (and not a M15 test blend) with some methanol blendstock. The amount of denaturant needed in the Denatured Methanol will likely be defined by the requirement to meet this 30 vol% blend sample testing, and not by the M5 or M15 fuel blend standards. As a result, the winter – 30°C test will likely require that 2 to 3 vol% co-solvent be incorporated in the M15 blend during the five winter months.

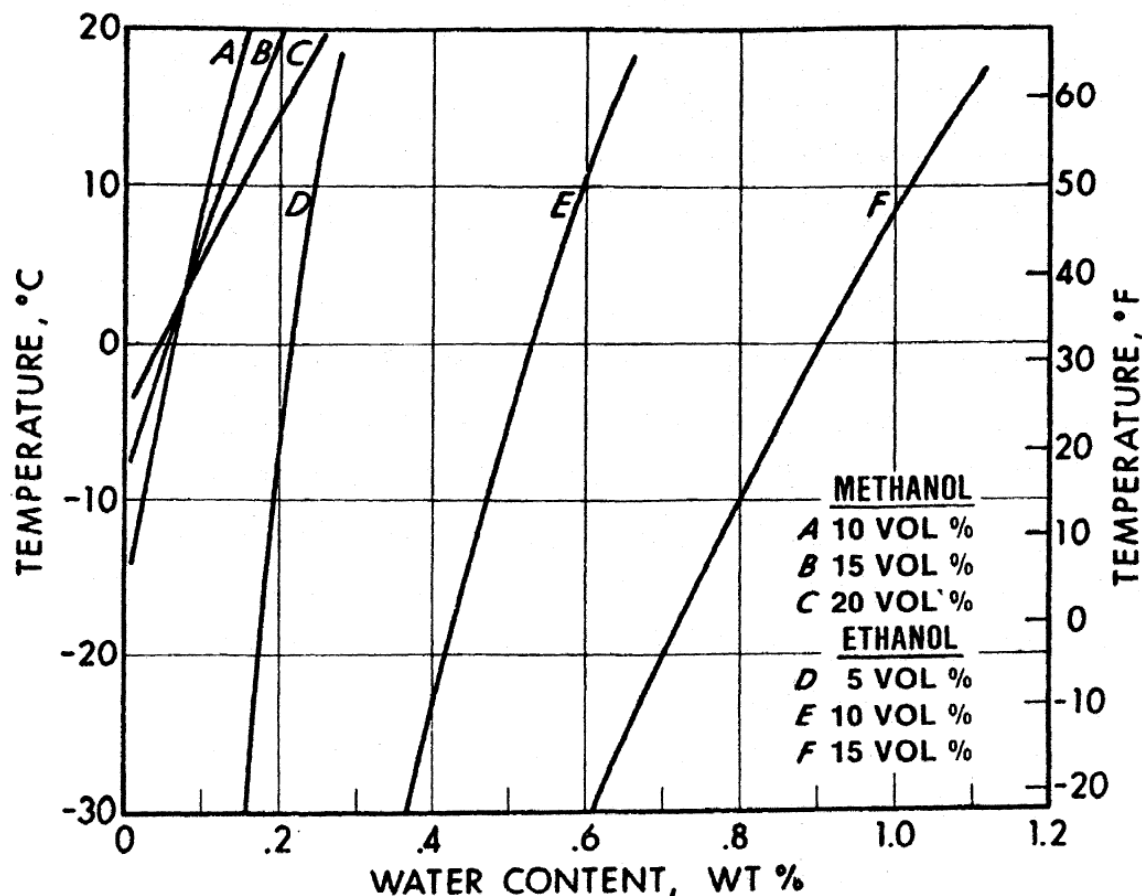
Most gasoline distribution and storage systems are built on the principle that oil and water do not mix because the maximum water solubilities in hydrocarbon gasolines are usually less than 200 ppm (< 0.02 wt%). However, light alcohols such as methanol and ethanol are totally miscible with water. Therefore, when the alcohols are mixed in gasoline, they will increase the maximum solubility of water in gasoline and that is dependent on the type and concentration of alcohol. Chart 1 illustrates the water solubility levels (tolerance) for different concentrations of methanol or ethanol. At room temperature (~ 20 °C), the more alcohol added, the greater is the water solubility. However, as observed for methanol, there is an inflexion point at lower temperatures where adding more methanol reduces the water solubility of the methanol gasoline blend. The line intercepts on the Y axis of the chart also show the solubility limits of methanol for dry methanol gasoline blends at the colder temperature.

The water solubility lines represent the points of phase separation where some of the alcohol and water will begin to phase out of solution and thereby form a second denser phase. When an alcohol gasoline blend reaches its solubility limits, it will generally form a haze of tiny suspended droplets that will eventually fall to the bottom of the solution. The regions to the right of these solubility lines are essentially two phases which need to be avoid in commercial practice because the new second denser liquid phase of mostly alcohol and water in the vehicle storage tank will cause significant poor engine performance and possibly make the vehicle inoperable by stalling the engine. This second denser phase is also more electrically conductive, and therefore could lead to increased corrosion risk of metals if insufficient and proper corrosion inhibitors are not added to the fuel blend.

To reduce the probability of two phases from occurring in a vehicle gasoline tank, the production of commercial alcohol gasoline blends should provide a working water tolerance which is the difference between the measured soluble water in the gasoline blend and its solubility limit where phasing begins to occur. The room temperature water tolerance test in the Shanxi Province methanol blend standards has essentially chosen a working tolerance of 0.15 vol% water in the blend (~0.20 wt% water) before hazing or separation begins. Based on

successful use of E5 fuels (5 vol% ethanol) in Europe, this working tolerance appears to be sufficient since the E5 blend in Chart 1 will also likely provide a net working water tolerance of 0.2 wt % (0.15 vol%) at 20 °C after adjusting for the water contribution of the 1 vol% water that may be contained in the neat ethanol product itself (~0.07 wt% water in an E5 blend).

**Chart 1**  
**Phase Temperatures for Methanol and Ethanol Gasoline Blends**



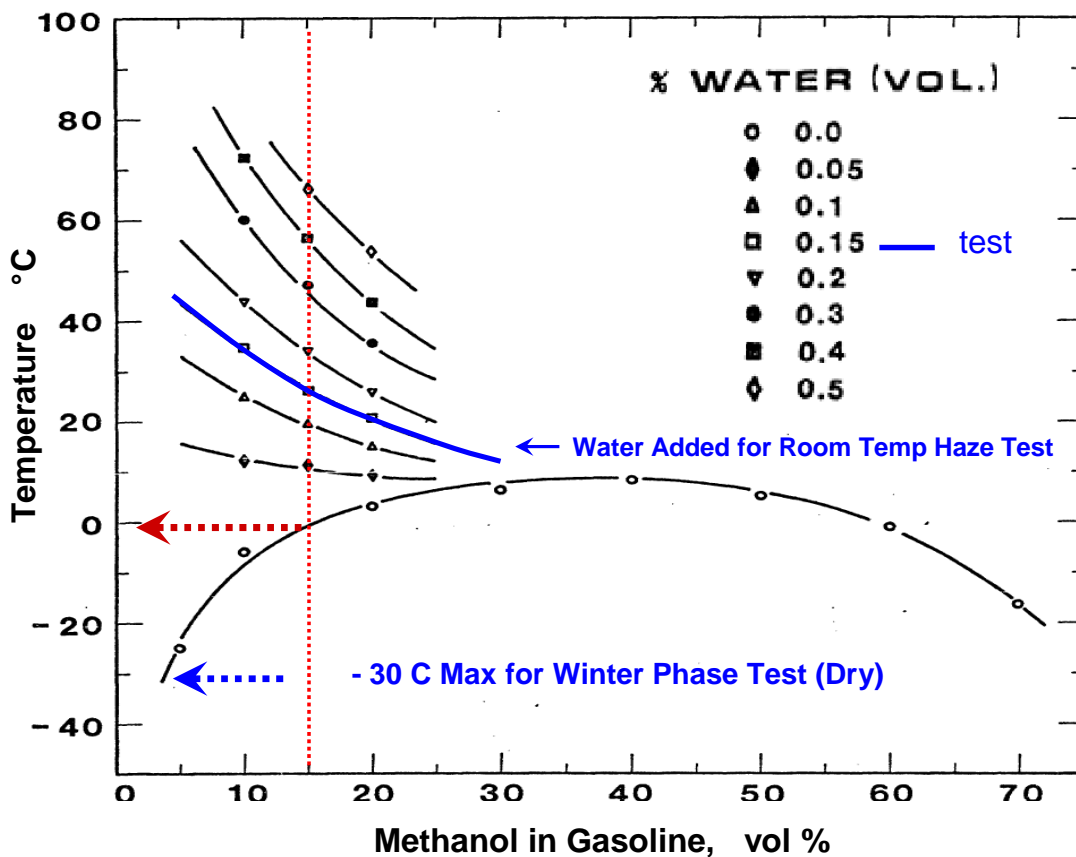
As illustrated in Chart 1, the higher polarity of methanol can limit the range of methanol solubility conditions in solutions with hydrocarbons such as gasoline, especially if small amounts of highly polar water are also dissolved in the solution. Chart 2 illustrates a typical diagram for methanol solubility limits in gasoline for various amounts of dissolved water where the areas below the lines represent two phase regions where some of the methanol and water phases out of solution into a denser lower phase.

The colored dashed lines represent the two important control points for phase separation testing in the M15 standards. The red vertical dashed line represents 15 vol% methanol and intersects the solubility line for zero water a little below 0 °C which does not achieve the ‘no phasing or hazing’ test temperature of – 30 °C that is required during the five winter months. Therefore, a thoroughly dry 15 vol% methanol solution would fail this requirement without the

addition of some co-solvent alcohols needed to shift the dry methanol solubility line downward. The winter temperature test is even more severe in the Denatured Methanol standard since the test is conducted with a M30 sample which raises the cold solubility line upward to more than 5 °C which would then require that even greater amounts of co-solvent be added to the Denatured Methanol to meet the no-haze requirement.

As for the 0.15 vol% water addition test, the diagram in chart 2 suggests that the M15 blend without co-solvents might fail the test (hazing) since the 20 °C point is located below the 0.15 vol% water solubility line. However, it appears that the M30 without co-solvents might pass the test (no haze) since the M30 at 20 °C point is above the 0.15 vol% water line. If this is the case, then using a M30 sample level for the water addition test in the Denatured Methanol standard is less constraining than the M15 water addition test, and therefore would understate the need for adding co-solvents (denaturants) in the Denatured Methanol for eventual use in the commercial M15 fuel blend.

**Chart 2**  
**Phase Separation Temperatures for Water in Methanol Gasoline Blends**



Based on the diagram in Chart 2, it would appear that the M15 blend without co-solvents might fail both the 0.15 vol% water addition test conducted at room temperature and as well as the winter time - 30°C test conducted with no added water. Therefore, it is apparent that some type and amount of co-solvent is needed to produce a stable M15 blend for commercial use that

will not likely phase separate under expected normal conditions and moisture exposure. The following discussion provides some guidance on the amount of co-solvent alcohols that may be needed to achieve the two phase prevention test discussed above.

Chart 3 illustrates the expected impact of adding isobutanol (IBA) on the phase separation temperature for a M15 blend containing 0.25 wt% water (~0.19 vol% water) relative to three different aromatic contents in the base gasoline. One observation is that with no IBA (co-solvent) increasing the aromatic content of the gasoline blendstock alone by about 10% will reduce the water saturation temperature by about 15 °C. Assuming the high aromatic content of fuel C, the M15 blend would not phase separate above 10 °C without the use of co-solvents, and would therefore not form a haze at room temperature (20°C). However, the lower intermediate aromatic fuel (B) would require about a 0.05 ratio of IBA to prevent a phase separation at room temperature and fuel A about a 0.15 ratio. This ratio is equal to about 0.75 vol% IBA in the final M15 blend.

**Chart 3**

**Methanol Blend Phase Temperatures Relative to Gasoline Aromatic and Iso-Butanol Co-Solvent Content**

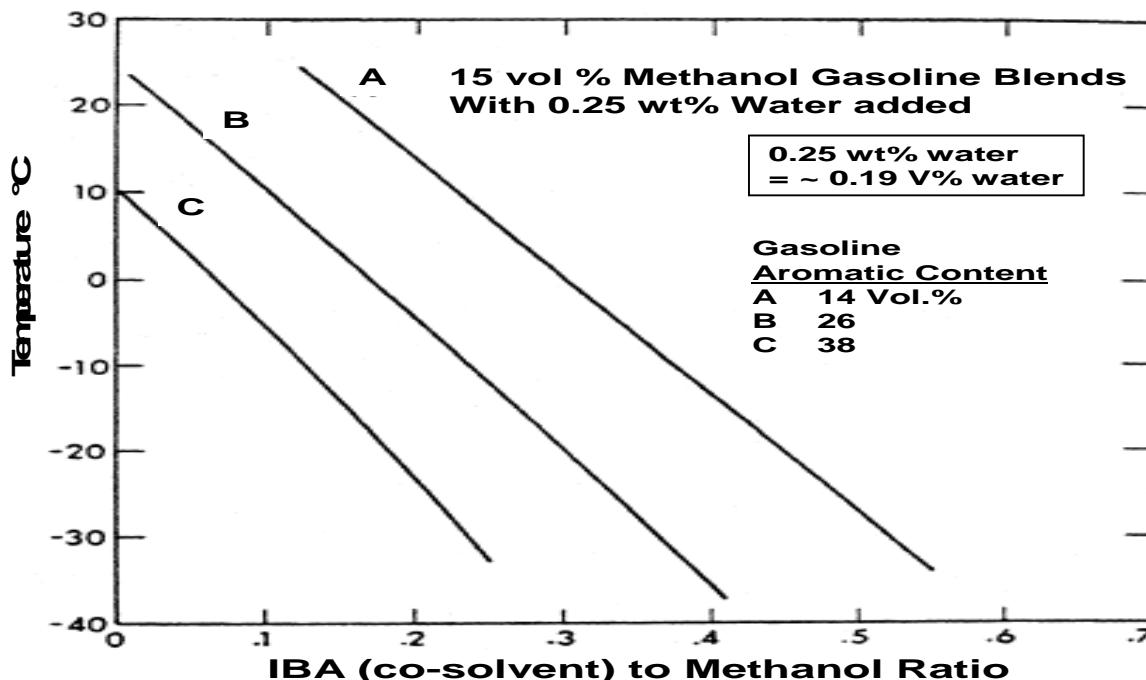
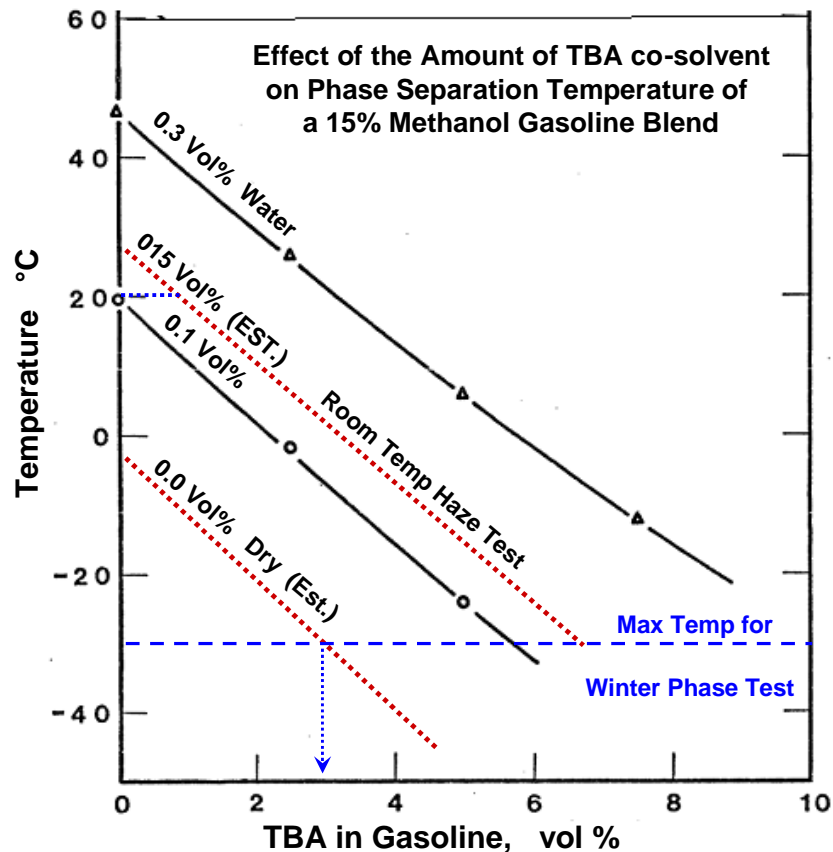


Chart 4 shows another water solubility diagram for a 15 vol% methanol blend using tertiary butanol (TBA) instead of IBA as a co-solvent. The aromatic content of this gasoline blendstock is not reported for these results. Two red dashed lines have been estimated and added to this diagram to represent 0.15 vol% water solubility and a 0% water solubility line for a M15 gasoline blend. The 20 °C temperature intersects the estimated 0.15 vol% water line at about 0.75 vol% TBA which suggests this fuel would need this amount of TBA in the M15 blend to meet the room temperature haze test. This amount of TBA would be the same as the amount of

IBA needed to prevent hazing or phase separation for fuel B (26 vol% aromatics) in the previous Chart 3.

**Chart 4**



Meeting the  $-30\text{ }^{\circ}\text{C}$  test applied during the five winter months would increase the co-solvent requirement as illustrated in Chart 4. To prevent the methanol from phase separating out of the gasoline blend at this low temperature, approximately 3 vol% TBA might be required based on this estimated line for a dry M15 gasoline blend with no water added. To achieve this amount of co-solvent, the Denatured Methanol needs to contain 20 vol% TBA which would lower the methanol content in the Denatured Methanol to 80 vol% which is much less than the 94 vol% minimum methanol content requirement. Therefore, it is unclear how the winter season low temperature test can be achieved if the minimum methanol content effectively limits the co-solvent content to 6 vol% or less.

The proposed standards require that ‘Denatured Methanol’ be used for making the M5 and M15 fuel blends. The English translation of the standard uses the following language to describe it: *“Methanol for industrial use added with additives for blending low methanol content gasoline products for motor vehicles is simply called denatured methanol”*. This description might mean that any co-solvents are additives or denaturants, and therefore are considered part of the Denatured Methanol. The minimum methanol content for Denatured Methanol is 94 vol% which implies that co-solvents are limited to 6 vol% of the Denatured

Methanol product mixture. If the Denatured Methanol is blended at 15 vol% in gasoline, then the co-solvent would be limited to slightly less than 1% in gasoline. The low level of co-solvent might provide insufficient protection, particularly during the colder winter months.

#### **IV. Fuel Volatility of Methanol Fuel Blends**

**Suggestion 3:** *The methanol content standard for M15 reports the methanol volume content as “13 ~ 15” percent with no reference to a minimum or maximum as is the case with other specifications used for defining other fuel properties. Therefore, it is not clear if the 13 vol% is the minimum allowed in M15, or a target range for the methanol. Further, footnote “a” of the M15 fuel standard states that the lower methanol limit should not be under 7 vol% between June 1 and August 31 of every year. This summer season requirement is similar to the U.S. requirement that the ethanol blends must contain at least 9 % ethanol to qualify for the 1 psi RVP exemption during the summer control months. The U.S. requirement is based on having sufficient exhaust emission reduction from oxygen enleanment to offset the increased evaporative emissions resulting from the 1 psi exemption so as to make the E10 fuel “emission neutral” during the summer ozone season. The 7 vol% minimum in the footnote would also suggest that the 13 vol% is not a minimum, but may be part of a preferred target range. To ensure market certainty, the M15 standard should clarify the use of the 13 vol% methanol content , and a 7 vol% minimum content requirement for summer months.*

**Suggestion 4:** *To ensure that low level methanol blends can economically comply with new national fuel standards and to also limit the need to back-out low cost butane from the methanol blendstock, consideration should be given to raising the RVP exemption of M5 to 12kPa (same as M15), and that these RVP exemptions be applied to all regional lower RVP fuel standards such as that for Beijing.*

**Discussion:** Alcohols, being polar compounds, form minimum-boiling azeotropes when blended with hydrocarbons of similar boiling points in the gasoline, and will therefore ‘act’ more volatile in a gasoline blend than the alcohol in its pure state. As a result, this non-ideal blending phenomenon with alcohols causes the gasoline’s vapor pressure to increase and its distillation temperatures to decrease. The amount of deviation from ideal blending laws is a function of the alcohol type and the amount of alcohol blended. Methanol, being the most polar alcohol because of its high oxygen content produces the greatest deviation from ideal blending relationships.

China has two separate alternative fuel blending programs that extend their gasoline supplies by blending alcohols into the gasoline: E10 and M15. It appears that both programs use truck blending methods at the gasoline distribution terminals. This distribution practice for alcohol blends is similar to that used for blending ethanol in both Europe and the U.S. The addition of either of these light alcohols will raise the RVP (“Reid Vapor Pressure”) of the gasoline base-fuel, and therefore will require an RVP exemption if the RVP of the base-fuel is not lowered to compensate for the alcohol’s RVP increase.

Similar to what is typically allowed for ethanol blends, the Shanxi methanol blends standards allow some RVP exemption (increase) above the national gasoline RVP standard for methanol blended fuels. One unexplained observation is that the allowed RVP increase in the

summer is different for M5 grade (82 kPa) or M15 grade (86 kPa) fuel blends even though the RVP increases from blending 5% methanol and 15% methanol are expected to be about the same. However, the winter RVP spec for both M5 and M15 grades is the same (90 kPa). Since the summer RVP maximum for national gasoline is 74 kPa, the RVP exemptions are 8 kPa for the M5 and 12 kPa for M15. These RVP exemptions are not large enough to accommodate the RVP increase from mixing methanol into gasoline which can be as great as 24 kPa without using co-solvents. To help meet the RVP standards for M5 and M15, the summer RVP for the methanol blendstock standard is limited to no higher than 67 kPa which is 7 kPa below the national gasoline standard for summer RVP (74), 15 kPa below the M5 RVP summer standard and 19 kPa below the M15 summer RVP standard. The M5 summer RVP standard is a more restrictive standard, and will require a blendstock RVP that is much lower than the 67 kPa in the methanol blendstock RVP standard.

Summer RVP exemptions for the methanol fuels might become an issue if China should move to lower summer RVP fuel standards similar to those required in Beijing and Europe. Like the U.S., Europe is considering allowing the RVP increase with ethanol blends to be exempt because of the offsetting exhaust emission reductions from ethanol's oxygen enleanment. This emission offsetting logic should apply to methanol blends as well. The evaporative emission increases associated with methanol blend RVP increases are mostly methanol, and these methanol vapors are considered to be relatively low in atmospheric reactivity during summer pollution conditions. Methanol blends also provide proportionally more oxygen enleanment than ethanol for reducing exhaust emissions because of methanol's higher oxygen contribution to the fuel blend. Using a low-emission fuel logic, the methanol blends should qualify for even larger RVP exemptions during the summer months since the overall reactive organic emissions from the vehicles should be much lower.

Chart 5a illustrates the estimated RVP increases for ethanol blended into a summer national gasoline (74 kPa), and also for methanol and methanol containing co-solvents blended into a summer sub-RVP methanol blendstock (M0) of 67 kPa. As illustrated in the chart, even when using the sub-RVP blendstock, the resulting RVP for the various methanol fuel blends will still be higher than that for the ethanol blends using the higher national gasoline. Also, methanol containing 30 to 50 percent higher alcohols will have RVPs that are lower than that for blending pure methanol.

**Chart 5a**

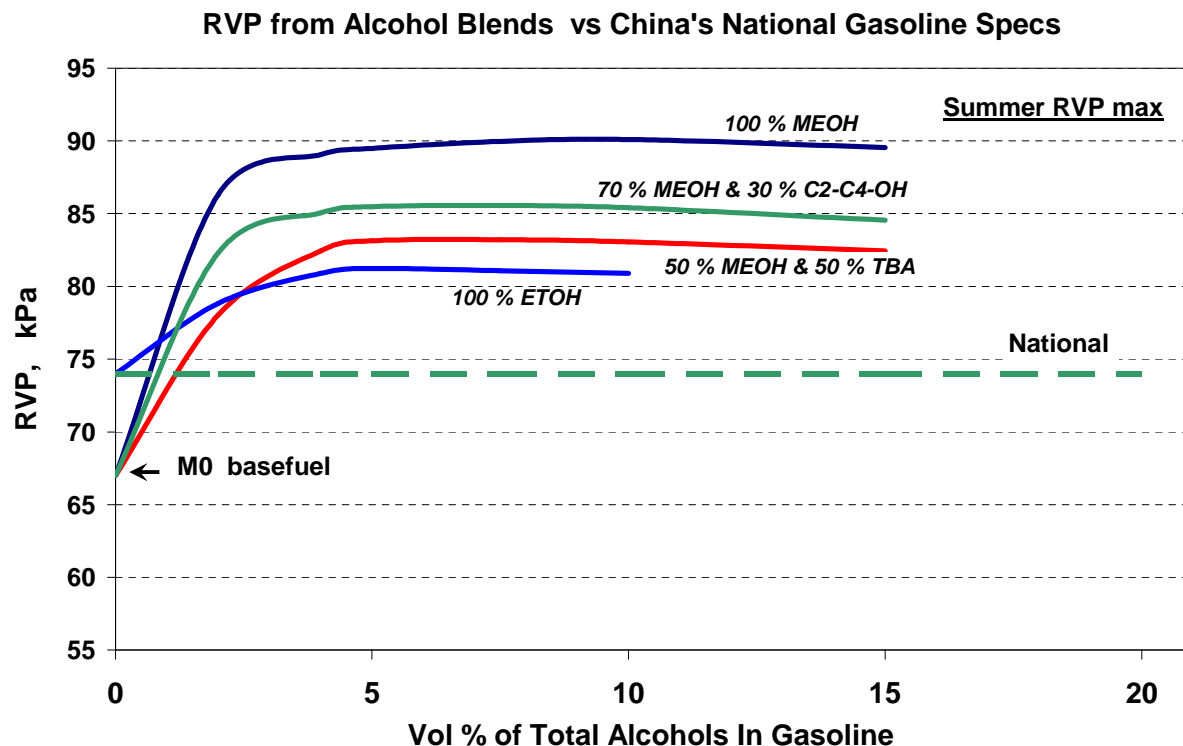
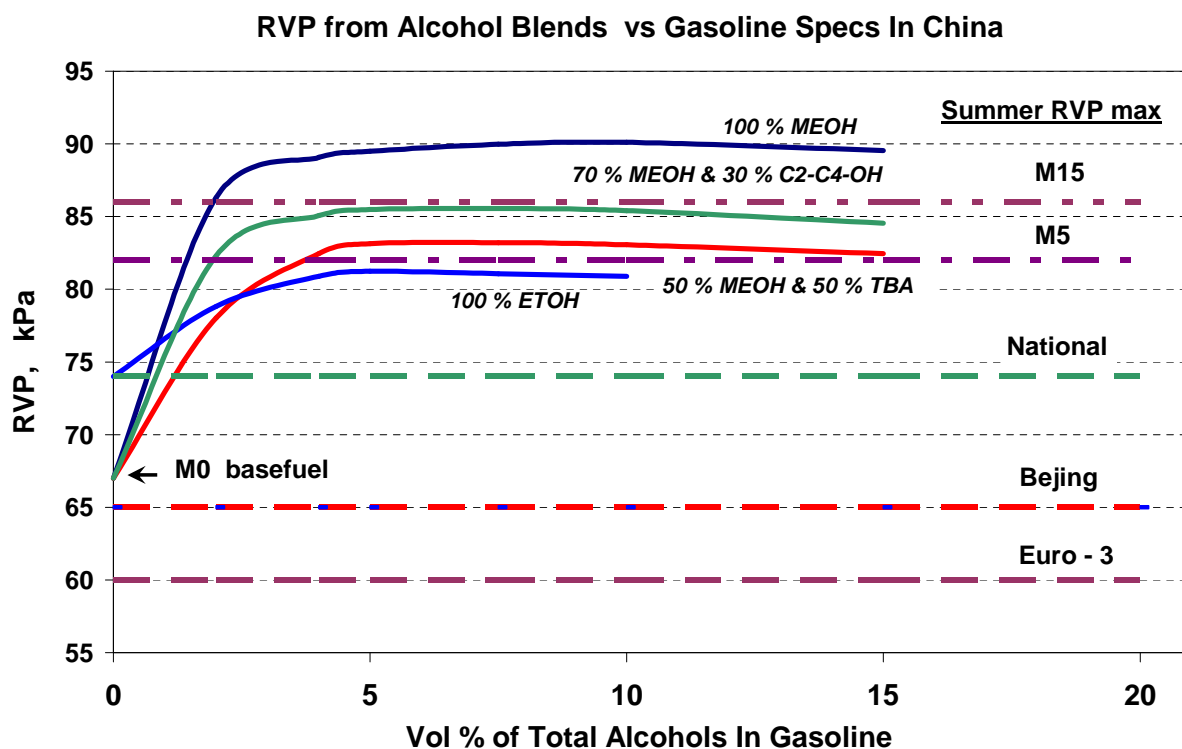


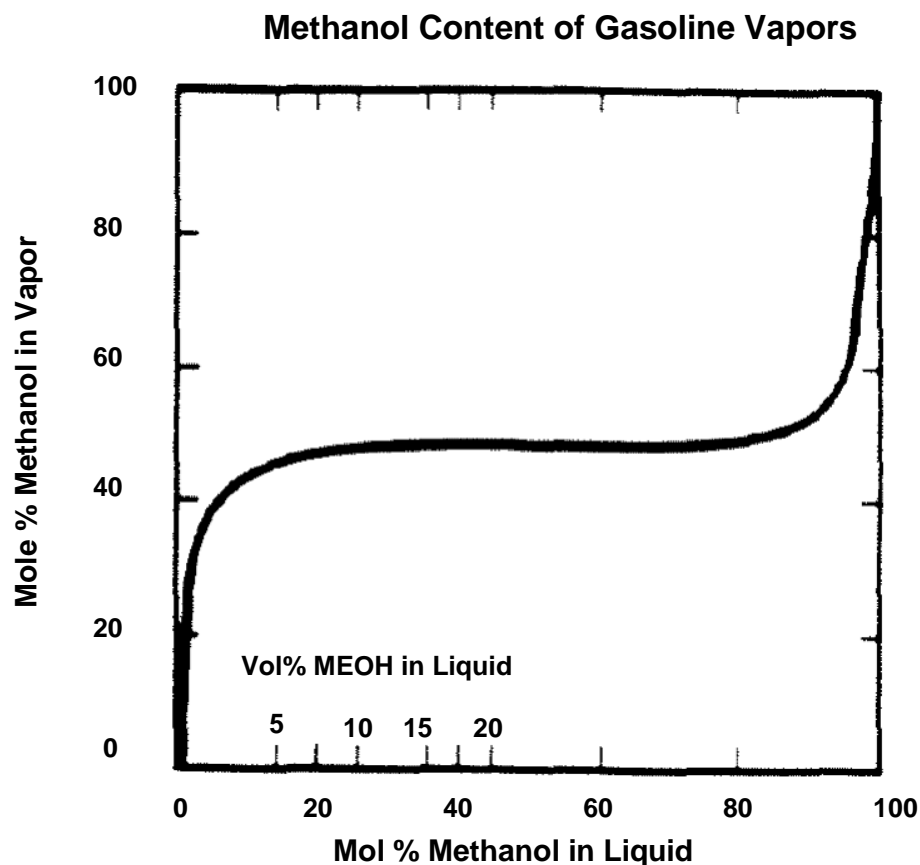
Chart 5b shows the same information as Chart 5a except that it also includes the summer RVP maximum limits for the M5, M15, Beijing and Euro 4 gasoline standards. This comparison illustrates a number of RVP issues for the methanol blends. One is that it will be difficult to meet the M15 maximum RVP without either the methanol containing some RVP-decreasing co-solvents, or the lowering of the methanol blendstock's RVP to about 63 kPa instead of the 67 kPa maximum. Another issue is that the summer Beijing RVP standard and the Euro 3 (and 4) RVP standard for gasoline are less than that for the M0 blendstock. For M15 to be commercial with these lower summer RVP fuels, it will likely need a similar size RVP exemption (~13 kPa) applied to any such lower RVP fuel standard. This would mean that M0 methanol blendstock would still need to be about 7 kPa lower than the gasoline RVP standard.

Chart 5b



Since the basis for lowering the summer RVP of gasoline appears to be for air pollution reasons and not for vehicle engine performance, there might be a good justification for granting methanol blends some amount of RVP exemption from the low summer RVP standards. Most of the RVP increase for blending methanol into gasoline is due to methanol's high partial pressure in the fuel's vapor. As a result, most of increase in vapor from the vapor pressure increase is methanol which is a relatively low reactive organic compound in summer time pollution conditions. Therefore, most of the increase in evaporative emissions should be considered low-polluting. Chart 6 illustrates the methanol composition of the vapor above a methanol gasoline blend. Just as the methanol blend RVP increase is essentially the same from 5 liquid percent to 20 liquid percent methanol, the vapor composition above this methanol blend is approximately a constant 45 mole percent. Another emission advantage of adding methanol to gasoline is the addition of oxygen to the gasoline which will generally lower the exhaust emissions from the engine, and therefore the vehicle's tailpipe. Generally, the greater amount of oxygen added to gasoline with methanol, then the greater will be the exhaust emissions reduction for the lower methanol fuel blends (less than 20 vol%) before it reaches a point of diminishing returns.

Chart 6

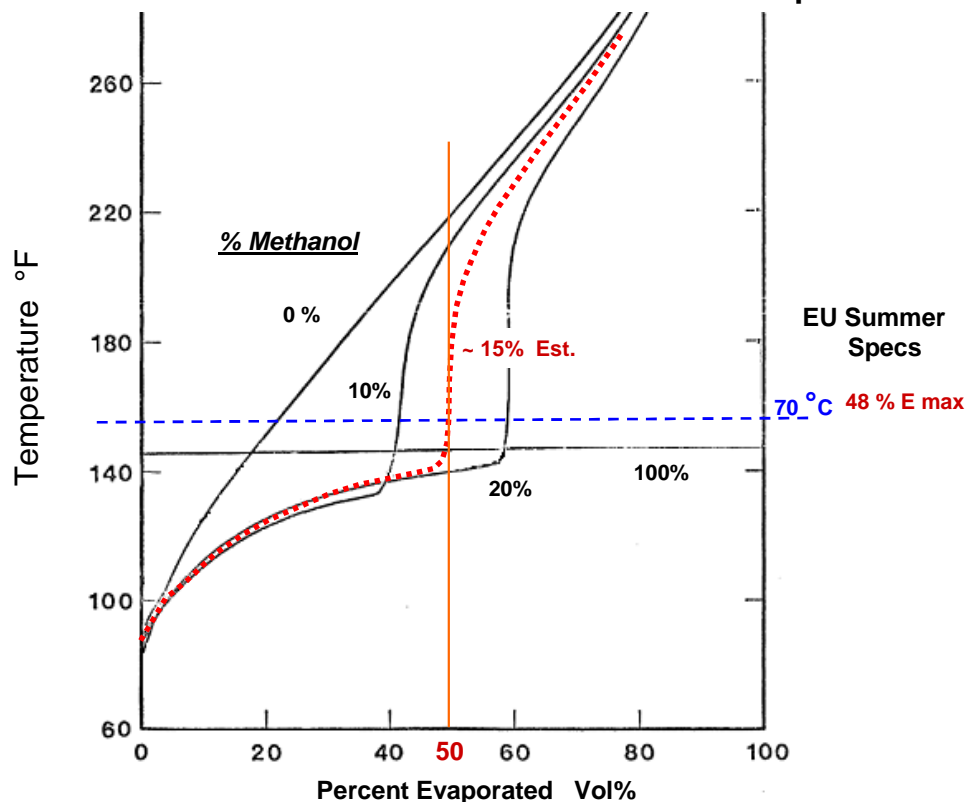


As mentioned earlier, when alcohols are mixed with hydrocarbons, they form minimum boiling temperature azeotropes with those hydrocarbons with boiling point temperatures that are near that of the alcohol itself. The effect is that light alcohols (such as methanol and ethanol) will increase the front-end volatility by raising the gasoline's RVP and lowering the gasoline's distillation temperatures. Chart 7 illustrates the impacts of blending methanol to the gasoline distillation curve or profile. Since the 15 vol% blend was not tested by this source, the associated distillation curve has been estimated with the red dashed line. The effect of adding methanol greatly increases the amount of gasoline that distills off below the boiling point of methanol. For 15 vol% methanol, the amount of gasoline that distills off below methanol increases from about 20% to 50% which is a 30% increase for adding 15 % methanol.

For gasoline distillation standards, China currently only applies a minimum volatility specification (maximum temperature constraints at targeted percentages distilled off), and contains no maximum distillation volatility constraint like that applied in the Euro petrol standards. European standards apply maximum volume percentage evaporated at 70 °C (E70) and at 100 °C (E100). Since blending methanol can significantly increase the distillation volatility of gasoline, applying the summer E70 of 48 vol% maximum can potentially restrict the amount of methanol blended in China gasoline to less than 15 vol%. As illustrated in Chart 7, the M15 distillation curve bumps up against this mid-range distillation constraint.

## Chart 7

### Effect of Methanol Content on Gasoline Distillation Temperatures

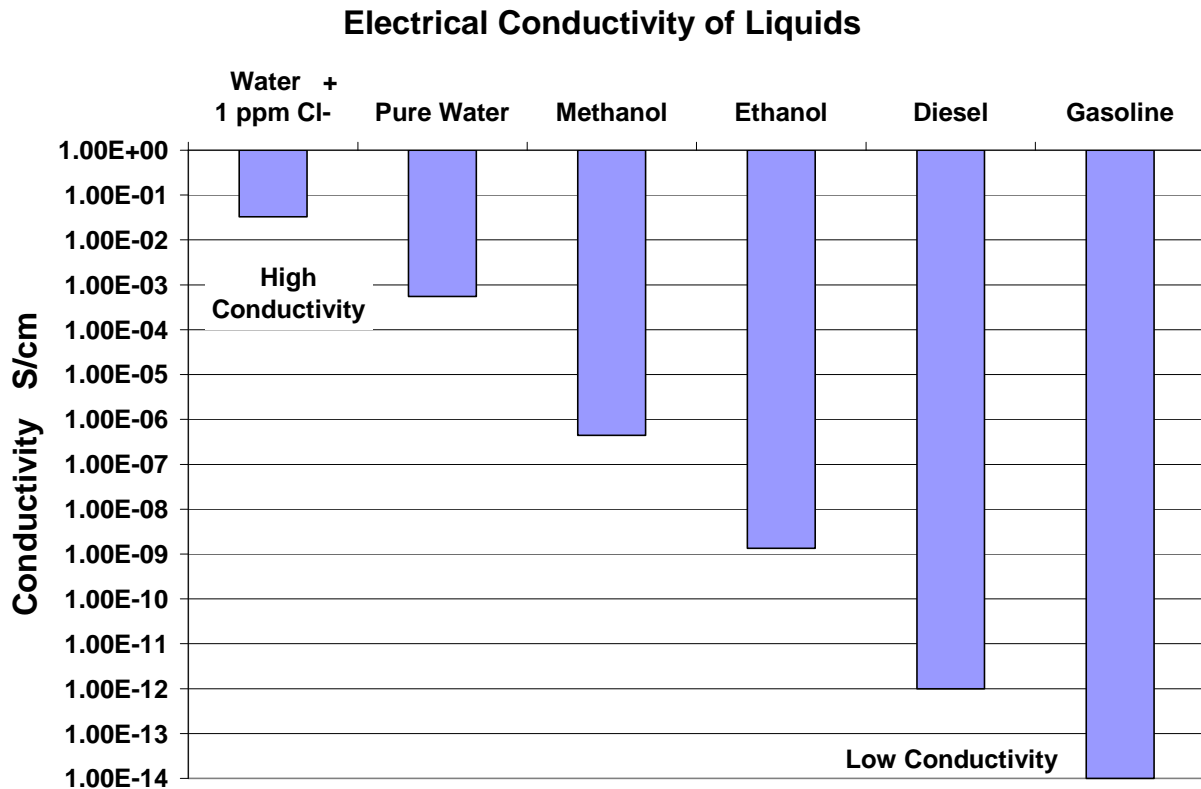


## V. Chemical Stability of Fuel Blends

**Suggestion 5:** *The Shanxi standards do not provide specific guidance on the need for additives to control against corrosion, effectively leaving responsibility for controlling corrosion risk to the discretion of the various Denatured Methanol suppliers. This introduces a significant amount of market risk, in that inadequate corrosion inhibitors may be used by suppliers that risk damage to vehicles and threatening the success of the methanol fuel blending program. The standards should include some discussion of allowable additives for corrosion protection and establish minimum content requirements, or alternatively, add some performance standard for corrosion risk control.*

**Discussion:** Beside needing co-solvents to provide phase separation stability for exposure to moisture, the gasoline blends with lighter alcohols such as methanol and ethanol can require more corrosion inhibitors because the alcohol can be more chemically aggressive toward metals (particularly less dense metals) in the fuel storage and vehicle fuel systems. Much of the corrosion risk concern with alcohols has to do with their higher electrical conductivity compared to gasoline as observed in Chart 8. Note that these conductivities are reported in orders of magnitude using a log scale. Although pure methanol appears more conductive than gasoline, it is still much less conductive than either pure water or water with 1 ppm chloride ions which are only potentially corrosive to metals.

Chart 8



Prior corrosion studies with alcohol fuels have shown that introducing water and anions (such as chlorides) into the fuel are responsible for most of the increase of the observed metal corrosion tendency of the alcohol fuels, particularly with more active metals such as magnesium, zinc and aluminum. Although metals such as magnesium and aluminum would normally create a metal oxide film (passive anodization) to protect against further oxidation corrosion, potent anions such as chlorides in the solution can break through this protective film to create a corrosion pitting point, and therefore need to be minimized in the alcohol and the fuel blend. In addition, to decrease the potential risk of galvanic corrosion of metals, the electrical conductivity of liquids in the fuel system need to be reduced by minimizing water content as well as preventing water induced phase separation of the methanol fuel blend by using adequate co-solvents. Other corrosion mitigating methods are the use of corrosion inhibitors such as organic amines (protective film on metals) and anti-oxidants (scavenge oxygen radicals).

The Shanxi standards provide few requirements to control the general corrosion properties of the gasoline or methanol fuel blends other than noting that “effective metal corrosion inhibitors should be added.” There is a copper corrosion test which is used for detecting mercaptans and the standard does cap inorganic chlorides (salts) at 2 mg/kg (ppm) in the Denatured Methanol which is important since chlorides not only increase the electrical conductivity of the liquid, but are also very potent anions for breaking down the insoluble protective oxide film layer that develops on metal surfaces such as aluminum. Therefore, the standards essentially allow the

gasoline suppliers to determine the appropriate type and amount of corrosion inhibitors to use in gasoline and methanol blends for providing adequate protection against abnormal corrosion. This lack of guidance seems somewhat risky for introducing and expanding methanol fuel blends, as automakers routinely point to methanol's higher corrosivity as a significant concern for materials compatibility.

## VI. Octane Contribution

**Suggestion 6:** *The Shanxi methanol fuel standards take some advantage of the methanol's octane contribution to a limited extent by establishing a sub-octane standard for the gasoline blendstock used for methanol blending. The 2 RON lower gasoline blendstock used for blending M5 is appropriate to that fuel. However, the 2 RON reduction does not take full advantage of the higher octane contribution from M15 fuel blends. To give M15 full economic credit for its octane contribution – and to limit the need to back-out low cost butane from the blendstock – for M15 blending a 6 RON reduction for the gasoline blendstock would be more appropriate.*

**Discussion:** Of all the alcohols, methanol provides the highest octane contribution in gasoline blending. The high octane from alcohols can be used to further reduce the cost of gasoline production by allowing the refiners to lower the octane of the base fuel (blendstock) gasoline used for blending with the alcohol. As illustrated in Table 2, blending 15 vol% methanol would be expected to add about 6 RON's (research octane numbers) and about 4.5 (R+M)/2 octanes (average of research and motor octanes). Blending 5 vol% methanol would provide about one-third of these octane increases (+2 RON and +1.5 (R+M)/2). The Shanxi methanol fuel standards take some advantage of the methanol's octane contribution to a limited extent by establishing a sub-octane standard for the gasoline blendstock used for methanol blending. However, the sub-octane standard for the methanol gasoline blendstock is only 2 RON lower (88) and 1.5 (R+M)/2 octanes (83.5) lower than the national standard for regular grade gasoline in China. The small sub-octane decrease will allow the addition of 5 vol% methanol to meet the final octane minimums for gasoline standards, but will result in most of the higher octane contribution from M15 blends being given away as excess octane in the marketplace. Using the same sub-octane blendstock with M15 should produce a 94 RON blend which might be sold as 93 octane mid-grade gasoline. Therefore, the small 2 RON sub-octane standard for the methanol blendstock will limit the potential value contribution that can be realized by methanol when used in a M15 fuel blend since about two-thirds of methanol's high octane contribution will not be utilized to reduce the refiners' gasoline production cost.

To make a sub-RVP blendstock that fully offsets the whole 23 kPa increase requires removing about 7 vol% of low cost butanes from the gasoline. However, removing this full amount of low cost butane from the summer grade gasoline would significantly reduce the economic incentive to blend the methanol in gasoline, particularly for lower content M5 fuel blends. The current 7 kPa reduction for summer M0 blendstock only requires the removal of about 2 vol% butane from the gasoline which is smaller economic debit that can be somewhat offset by the 2 RON decrease with the M0 blendstock.

However, to make the M15 blend even more economical, it would be beneficial to lower the M0 blendstock octane by 5 or 6 RON (instead of 2 RON) which is the expected octane contribution from M15 blending. Also, the 12 kPa exemption is necessary to reduce the butane removal penalty for using the M15 blend during the summer since removing 7 vol% butane would undermine much of the gasoline supply extender benefits of M15 (~ 10 gasoline energy). Therefore, if Euro 4 or Beijing's lower summer RVP fuel standards were to be applied nationwide in China, the economic viability and energy supply benefits of M15 would significantly depend on extending the current 12 kPa exemption for these low RVP fuels.

Table 2. Comparison of Octane Standards and expected Octane from adding Methanol

Octane Type	Shanxi Octane Specifications				Expected Octane	
	M0 Base	Regular	Mid-grade	Premium	5% Meoh	15% Meoh
RON min	88	90	93	97	90.1	94.3
(R+M)/2 min	83.5	85	88	report	85.8	90.5
<u>Delta above M0</u>						
RON	--	2	5	9	2.1	6.3
(R+M)/2	--	1.5	4.5		2.3	7.0

## VII. Glossary

ETOH	Ethanol
E5	5 vol% ethanol fuel blend
E10	10 vol% ethanol fuel blend
E70 °C	Percent of gasoline evaporated at 70 °C
kPa	kilo-Pascal
MEOH	Methanol
psi	pounds per square inch
MON	Motor Octane Number
RON	Research Octane Number
RBOB	Reformulated blendstock for oxygenate blending
RVP	Reid Vapor Pressure at 37.8 °C
vol%	Volume percent
mol%	Mole percent
wt%	Weight percent
M5	5 vol% methanol fuel blend
M15	15 vol% methanol fuel blend
M85	85 vol% methanol fuel blend

***Report Contact:***

**William J. Piel**

**Phone: (610) 566-1483**

**Fax: (775) 255-4472**

**Email: [William.Piel@teira.com](mailto:William.Piel@teira.com)**

---

**TEIR Associates, INC  
160 Hidden Hills Road  
Media, PA. 19063**

***[www.teira.com](http://www.teira.com)***