

WATER TOLERANCE OF GASOLINE-METHANOL BLENDS

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ABSTRACT

A new method based on laser attenuation was devised to accurately measure the phase separation and, in turn, the water tolerance of gasoline-methanol blends with and without cosolvents. Water tolerances were quantified for a variety of blends in model and actual gasolines, as well as in major refinery streams--alkylate, FCC gasoline, and reformat--which make up commercial gasoline pools. Regression analysis of the data shows that the water tolerance behavior of blends with each cosolvent well-described by a correlation which includes cosolvent concentration, temperature, and base fuel hydrocarbon type.

INTRODUCTION

Refiners and marketers have been turning to oxygenates to meet increasing demands for gasoline pool octanes in light of more stringent volatility and fuel composition controls. Oxygenates which have become important as gasoline blending components include methanol (MeOH), ethanol (EtOH), isopropanol (IPA), t-butyl alcohol (TBA), and methyl t-butyl ether (MTBE). MeOH is generally the most attractive oxygenate from a strictly economic point of view, but its direct use as a blending component in current fuel systems can cause technical problems [1]. The most serious of these is the separation of blends into hydrocarbon and methanol phases when the water content exceed a critical level, i.e. the water tolerance. This problem is exacerbated at low ambient temperatures.

Water tolerance is defined as the volume % water that a blend can retain in solution--"tolerate"-- at a given temperature without phase separation. The water tolerance of gasoline-MeOH blends can be improved by the addition of a cosolvent, which is typically a higher alcohol such as IPA or TBA. TBA has been identified as the most attractive cosolvent for most commercial gasolines, and mixtures of MeOH and TBA have been marketed as an oxygenate blending component for gasoline for some time [2] although such mixtures are currently in very limited use in the U.S.

Previous studies on the water tolerance of gasoline-methanol (MeOH) blends have been both qualitative [3,4] and quantitative [5,2] in nature. One quantitative study has investigated the water tolerance of gasoline-MeOH blends to compare the relative effectiveness of IPA vs. TBA as cosolvents in a regular grade leaded gasoline [5]. Other quantitative work [2] has examined the relative effectiveness of other alcohols in gasoline, as well as the effect of changing aromatics and cosolvent levels on phase separation temperatures. One study has reported findings on the effect of boiling point and hydrocarbon type in gasoline-MeOH mixtures with no cosolvent [6]. However, the effect of base gasoline composition over a wide range on the water tolerance of gasoline-MeOH-cosolvent blends has remained largely unexplored.

In the current study, the water tolerance behavior of various gasoline-MeOH

blends using several cosolvents was investigated to determine and compare the efficacy of the cosolvents and the effect of fuel composition over a wide range. As part of this work, a useful, new technique based on laser attenuation was devised to rapidly and reliably measure phase separations.

EXPERIMENTAL

Preparation of Blends

Three unleaded gasolines--designated as Gasoline A, B, and C--representing both regular and premium grades, and three gasoline blending stocks taken directly from refinery streams--Light Alkylate, FCC Gasoline, and Reformate--were included for study as base fuels. Properties of these materials are given in Table 1.

Three classes of gasoline hydrocarbon types were simulated by model compounds, as follows: 1) Saturates - 85 vol% i-octane/15 vol% n-heptane; 2) Olefins - 50 vol% 1-hexene/25 vol% 1-heptene/25 vol% 1-octene; and 3) Aromatics - 33 vol% benzene/34 vol% toluene/33 vol% xylenes.

The following reagent grade oxygenates were dried over 3A molecular sieves before use in the blends: MeOH, EtOH, IPA, TBA, and MTBE.

Blends were prepared by mixing the base fuel with 5 vol% MeOH, and 0, 2.5, or 5 vol% cosolvent--EtOH, IPA, TBA, or MTBE. The water content of each MeOH/gasoline cosolvent blend was adjusted using a precise gravimetric method and was measured directly using a Brinkmann Model 652 Karl Fischer Coulometer.

Measurement of Phase Separation

The method of determining the water tolerance of a blend was based on measuring the optical attenuation of a laser beam as it passes through a fuel sample which is undergoing cooling [7]. A photodiode equipped with a laser line filter is used to measure the intensity of the transmitted laser beam, while a thermocouple is used to simultaneously measure the temperature of the sample. The output voltages from the photodiode and thermocouple are continuously monitored and recorded via a calibrated dual-pen strip chart recorder. A schematic diagram of the apparatus is shown in Figure 1.

When the sample undergoes a phase separation, the transmitted laser beam intensity is attenuated due to scattering caused by small droplets of a second immiscible phase. The temperature which corresponds to the initial rapid loss of photodiode signal is recorded as the phase separation temperature. This is the temperature of phase separation for the given water level in a base fuel/MeOH blend. Accordingly, the water tolerance at this temperature is equal to the measured water content of this sample. Measurements were made over a temperature range of -116 to 44°C, depending on the fuel blend under consideration.

RESULTS AND DISCUSSION

Laser Attenuation Technique Improves Data Acquisition

Water tolerance data were obtained on over 50 gasoline-MeOH-cosolvent blends (~200 data points) in this study using the laser attenuation technique. The collective results (to be more extensively reported elsewhere) demonstrated

the utility of this electro-optic approach for routine and reliable laboratory measurement of phase transition temperatures in fuel blends. Previous techniques for such measurements, including ASTM methods, have generally relied on visual observation by an operator and manual recording of the temperature as read from a thermometer. These techniques are often time consuming and subject to inconsistent visual observation by one or more operators, and their accuracy can be influenced by ambient lighting conditions. The current technique significantly alleviated these problems.

Water Tolerance Improves With Increasing Temperature

The water tolerance of gasoline/MeOH blends increases with temperature. To illustrate this, water tolerances are plotted versus $1/T$ for gasoline A/MeOH/EtOH blends (Figure 2), for FCC gasoline/MeOH blends with and without TBA as the cosolvent (Figure 3), for refinery streams containing MeOH alone (Figure 4), for reformat/MeOH blends with various cosolvents (Figure 5), and for alkylate/MeOH blends with various cosolvents (Figure 6).

The relationship between the water tolerance of a fuel blend and temperature is adequately described by equation (1):

$$\ln WT = m (1/T) + k \quad (1)$$

where

WT is water tolerance, vol%

m, k are constants depending on the nature of the base fuel and the nature and concentration of the cosolvent

T is temperature, °K

This linear relationship between log of water tolerance and the reciprocal of temperature was found to be valid for all fuels, cosolvents, and concentration levels investigated in this study.

In general, the higher the water tolerance of a given blend set, the less sensitive that fuel/MeOH/cosolvent combination tends to be with respect to temperature (Figures 3-6). Table 2 gives the constants m and k derived from linear least squares fits of the data from representative blend sets, as well as the corresponding water tolerances at 0 and 20°C calculated for these blends. The slope, m, represents the sensitivity of the water tolerance of the blend with respect to temperature.

For any given MeOH/cosolvent combination, the temperature sensitivities (slopes, m) tend to decrease in the order of alkylate, FCC gasoline, and reformat, and similarly decrease in the order of saturate, olefin, and aromatics. This decrease in temperature sensitivity correlates with increasing water tolerance as illustrated by the calculated water tolerances at 0 and 20°C for each blend set shown in Table 2. This sensitivity decreases as cosolvent is added (Figure 3) and as the efficacy of the cosolvent improves (Figures 5 and 6).

Water Tolerance Improves As Aromatics In Base Fuel Increase

The composition of the base gasoline has a significant effect on the water tolerance of blends containing MeOH. As indicated in Figure 4 and Table 2,

water tolerance increases in the following order for the refinery streams:

Reformate > FCC Gasoline >> Alkylate

For example, at 0°C the water tolerances are 0.0724, 0.0309, 0.0019 vol% for 5 vol% MeOH blends of reformat, FCC gasoline, and alkylate, respectively, based on the data shown in Table 2. This relative ordering of water tolerance among base fuel types is generally maintained even upon addition of cosolvents, as indicated by the data in Table 2. For example, at 0°C the water tolerances are 0.2152, 0.1649, and 0.0411 vol% for 5 vol% MeOH/5 vol% EtOH blends of reformat, FCC gasoline, and alkylate.

The relative water tolerance behavior observed for the refinery streams is coupled to the specific hydrocarbon types present in the stream, improving in the order of increasing concentrations of:

Aromatics >> Olefins >> Saturates.

This finding is confirmed by the model compound data shown in Figure 7 for MeOH blends with no cosolvent. Here, the water tolerance is 0.1575, 0.0431, and 0.0038 vol% for 100% aromatics, 100% olefins, and 100% saturates, respectively. As before, this relative ordering persists in the presence of cosolvents as well, and is consistent with the relative contributions of both polar and hydrogen bonding effects of each hydrocarbon type [8].

Use of an aromatics-rich gasoline not only improves the water tolerance for a given MeOH blend, but also minimizes the cosolvent volume required to attain a given water tolerance. For example, when TBA was used as the cosolvent to maintain a water tolerance of 0.1 vol% at 0°C, the TBA concentration required was 1.0, 2.2, and 4.8 vol% for 5 vol% MeOH blends of reformat, FCC gasoline and alkylate, respectively.

Effectiveness of Cosolvent Increases With Concentration

The water tolerance of gasoline/MeOH blends improves significantly by the addition of a cosolvent in increasing concentrations. For example, by adding 2.5 and 5 vol% of TBA to FCC gasoline/5 vol% MeOH blends, the water tolerances at 0°C were increased from 0.032 to 0.11 and 0.24 vol%, respectively (Figure 3). Similar effects were observed in the other base fuel blends. However, the effect of base fuel composition on water tolerance diminishes as the concentrations of cosolvent are increased.

Effectiveness of Cosolvent Depends on Its Structure

The collective results confirm that higher alcohols are effective cosolvents for improving the water tolerance of MeOH/gasoline blends. The cosolvent behavior of MTBE, although poorer than the alcohols, indicates that ethers also can improve water tolerance of gasoline/MeOH blends. To illustrate this finding, the water tolerances of FCC gasoline/MeOH blends at 0°C are plotted against cosolvent concentration in Figure 8. Between the dosages of 2.5 and 5 vol%, the cosolvent efficacies are 0.056, 0.056, 0.030, and 0.012 vol%/vol% for TBA, IPA, EtOH, and MTBE, respectively. Consistent with this finding, and as illustrated in Figures 5 and 6, cosolvent performance for other fuel blends also generally follows the order:

TBA ~ IPA > EtOH > MTBE

The relative cosolvent effectiveness shown above is consistent with trends

in solubility parameters [8] which show the balancing between contributions to nonpolar, polar, and hydrogen bonding for each of these oxygenate cosolvents as a function of structure.

As the temperature increases, the relative differences in efficacy of each cosolvent begin to diminish (Table 2). At 20°C, EtOH begins to approach the effectiveness of TBA and IPA in many blends. However, because wintertime transport, storage, and use of gasoline/MeOH blends is where phase separation problems are likely to occur, higher alcohols such as IPA or TBA would be preferred cosolvents.

Regression Analysis Provides Good Correlation for Water Tolerance Prediction

The water tolerance of a MeOH/cosolvent blend can be expressed in terms of the collective effects of temperature, base fuel hydrocarbon type, and cosolvent concentration as follows:

$$WT = c \text{ Conc}_{\text{cosolvent}} + t_1 T + t_2 T^2 + s \text{ Sat} + o \text{ Olef} + a \text{ Arom} \quad (2)$$

where

$\text{Conc}_{\text{cosolvent}}$ is in vol%
 T is temperature in °C
 Sat , Olef , Arom are in vol% and derived from FIA analysis of the base fuel

Equation 2 closely approximates the observed water tolerance behavior of all base fuel/MeOH/cosolvent blends examined in this study and is the result of a multiple linear regression analysis of all data obtained for all blends prepared in this study. The results of the analysis are summarized in Table 3, which gives the coefficients (at the 95% significance level) for each term in Equation 2 for each cosolvent. The correlation coefficient for each fit, r , is also given, as is the number of data points considered.

The correlation coefficients indicate that Equation 2 fits the observed data well, despite that the temperature dependence was linearized in terms of a quadratic instead of a log c vs. $1/T$ relationship for convenience. Non-linearities evident in the cosolvent concentration dependence data (Figure 8) were not statistically strong enough over the whole range to warrant a non-linear concentration term.

The results shown in Table 3 tie together the main findings discussed separately above. For example, the relative ordering of cosolvent efficacy is reflected in the values of the relative coefficients c across a wide range of temperatures and compositions (TBA > IPA > EtOH >> MTBE). Similarly, the relative ordering of chemical type effects on water tolerance is reflected in the relative coefficients s , o , and a across a wide range of temperatures and compositions (Aromatics >> Olefins >> Saturates). Although this correlation may not accurately predict water tolerances at the extremes of concentration, temperature, and composition (for example, 100% saturates at 0°C and no cosolvent), it offers the potential to be a useful tool for predictive evaluation of MeOH/cosolvent blend behavior in a variety of practical gasoline compositions.

ACKNOWLEDGEMENT

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Table 1
Base Fuel Properties

	Light Alkylates	Reformats	FOG Gasoline	Gasoline A	Gasoline B	Gasoline C
Gravity, °API	72.7	46.5	56.1			
Research Octane Number	92.8	98.9	93.4	97.6		
Motor Octane Number	91.2	89.1	80.7	87.3		
Resid Vapor Pressure, psi	6.3	7.7	9.5	13.7		
Distillation, °F						
- 10%	165	141	116			
- 50%	215	247	223			
- 90%	232	330	382			
Composition (FIA), vol%						
- Aromatics	1	62	33	54	31	36
- Olefines	1	2	36	1	3	15
- Saturates	98	36	31	45	66	49

Table 2
Effect of Temperature on Water Tolerance:
Constants for Eq. (1) $\ln C = m \cdot 1000/T + k$
and calculated water tolerance at 0°C and 20°C

Fuel Blend ^a	m	k	W.T. @ 0°C	W.T. @ 20°C
Alkylate/MeOH	-7.082	19.54	.0019	.0109
+ MTBE	-4.729	12.99	.0133	.0432
+ EtOH	-3.386	9.205	.0411	.0958
+ IPA	-1.917	4.670	.0955	.1542
+ TBA	-1.726	4.178	.1173	.1805
FCC Gasoline/MeOH	-2.143	4.369	.0309	.0528
+ MTBE	-1.342	2.484	.0881	.1232
+ EtOH	-1.716	4.480	.1649	.2532
+ IPA	-1.425	3.734	.2270	.3240
+ TBA	-1.037	2.321	.2287	.2963
Reformate/MeOH	-1.781	3.822	.0724	.1125
+ MTBE	-0.835	0.907	.1275	.1570
+ EtOH	-0.814	1.444	.2152	.2638
+ IPA	-0.429	0.169	.2462	.2741
+ TBA	-0.451	0.313	.2623	.2938
100% Saturates/MeOH	-4.739	11.789	.0038	.0126
+ MTBE	-4.234	11.279	.0147	.0423
+ EtOH	-5.899	18.057	.0293	.1280
+ TBA	-1.948	4.998	.1193	.1939
100% Olefins/MeOH	-2.061	4.401	.0431	.0721
+ MTBE	-2.000	4.875	.0709	.1188
+ EtOH	-1.821	4.133	.1851	.2474
+ TBA	-1.142	2.671	.2209	.2939
100% Aromatics/MeOH	-1.852	4.932	.1575	.2502
+ MTBE	-0.737	1.116	.2055	.2471
+ EtOH	-0.755	1.920	.4300	.5192
+ TBA	-0.627	1.382	.4011	.4691

^a Fuel blends contain 5 vol% MeOH and, for those containing a cosolvent, 5 vol% cosolvent.

Table 3
Results of Regression Analysis
of Collective Water Tolerance Data:

$$WT = c(\text{Conc})_{\text{cosolvent}} + t_1(T) + t_2(T^2) + s(\text{Sat}) + o(\text{Olef}) + a(\text{Arom})$$

C O E F F I C I E N T S

Cosolvent ^a	c	t ₁	t ₂	s	o	a	Number of Data Points	Correlation Coefficient, r
None	-	.00174	-.00001	-.00024	.00042	.00140	19	.8492
MTBE	.01089	.00189	.00001	-.00040	.00023	.00140	68	.9289
EtOH	.03136	.00304	.00001	-.00104	.00013	.00200	73	.9060
IPA	.03376	.00226	.00001	-.00055	.00030	.00150	46	.9182
TBA	.03975	.00263	.00001	-.00077	.00020	.00166	62	.9804

^a In fuel blends containing 5 vol% MeOH

FIGURE 2

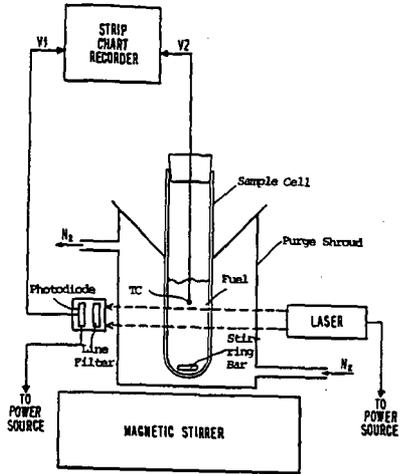


FIGURE 3

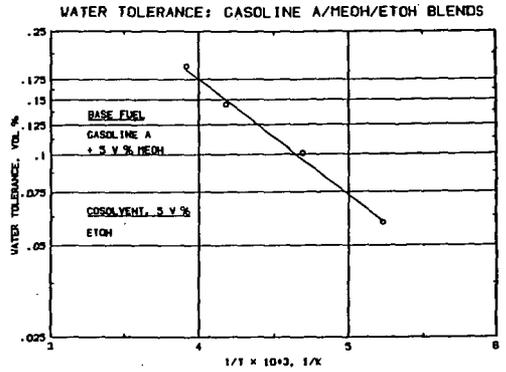


FIGURE 3

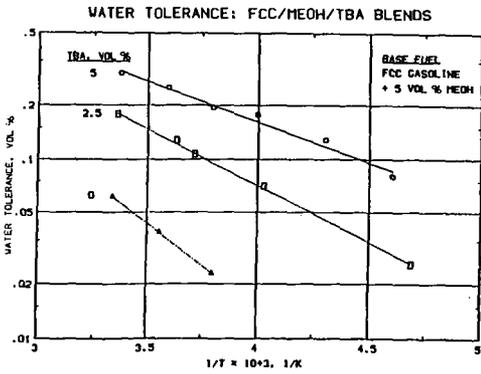


FIGURE 4

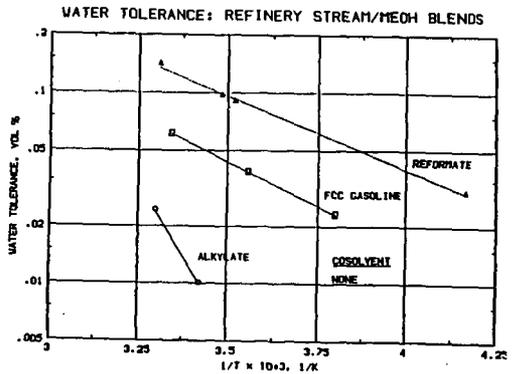


FIGURE 5

WATER TOLERANCE: REFORMAT/MEOH/COSOLVENT BLENDS

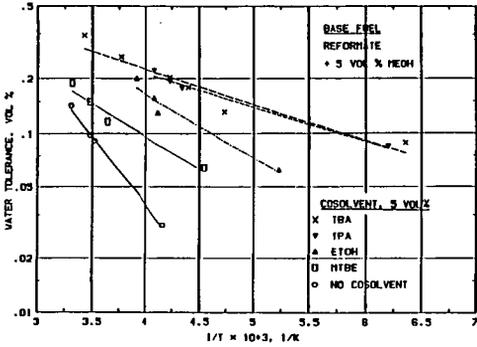


FIGURE 6

WATER TOLERANCE: ALKYLATE/MEOH/COSOLVENT BLENDS

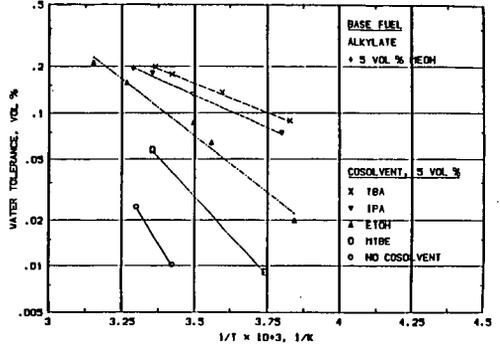


FIGURE 7

WATER TOLERANCE: MODEL FUEL/MEOH BLENDS

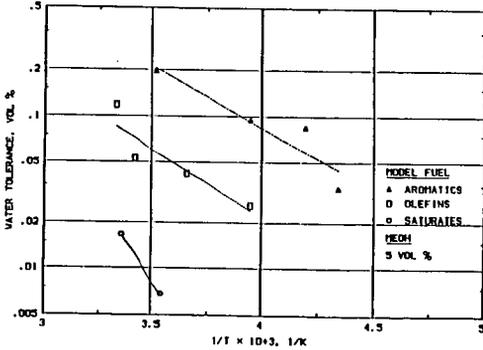


FIGURE 8

WATER TOLERANCE: EFFECT OF COSOLVENT TYPE AND CONC

