ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Oxygenate Blending Components to prevent Phase Separation in Gasoline-Methanol Blends.

Ezis N. Awad, S.M. El-Zein, V. Ibrahim and Y. Barakat*.

Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo, Egypt

ABSTRACT

Oxygenate blending components comprising anhydrous methanol plus seven different cosolvents from c_3-c_5 alkanol isomers, were attempted to prevent phase separation in gasoline - methanol blends. Fuel blends consisting of 88.0 % vol base gasoline plus 12.vol% oxygenate blending components (10.8% M+1.2% cosolvent),were formulated and water tolerance (WT) values of these blends were measured at 0 °c and 35 °c which simulate the phase separation temperatures (PST) at winter and summer times. The obtained results reveal that neither propanol nor butanol cosolvent isomers tolerate water values exceeding 0.45 and 0.24 vol.% at 35 °c and 0 °c .At 35 °c butanol cosolvent isomers, TBA,IBA,SBA and NBA, tolerate 0.45,0.40,0.37 and 0.33 vol.% water whereas, TAA cosolvent tolerates 0.43 vol.% water. At constant gasoline concentration (88.0 vol.%) and composition, WT-PST relationship was studied using four different oxygenate blending components: (9.0 M+3.0 TBA),(8.5 M+ 3.5 IBA),(7.5 M+4.5 SBA) and (8.0 M+4.0 TAA). Fuel blends comprising TBA or TAA, gave the highest WT values. Four polynomial Fuel blends comprising equations relating WT and PST, were developed. R^2 values indicate the reliability of the fits.

Keywords: gasoline- methanol blend, cosolvent, water tolerance, phase separation temperature.

*Corresponding author

INTRODUCTION

Refiners and marketers have been turning to oxygenates to meet increase demands for gasoline pool .This is because oxygenates are gaining importance as gasoline bleding components.They supply antiknock quality, and offer potential for pollution reduction. The use of oxygenates in gasoline has been recently mandated to reduce CO emissions in urban areas of several us states during the winter months (1-4). Alcohols, as oxygenate -blending components, include methanol, ethanol, isopropanol and butanols (5-7). Because of its low cost and ready availability, methanol is the most attractive oxygenate from the economic point of view However direct use of methanol in current fuel systems could cause technical problems (8-11).Blending methanol into hydrocarbon fuels can suffer from phase separation at low ambient temperature , and when their water content exceeds a critical level, i.e, water tolerance (3,12,13).

Water tolerance (W.T) is defined as the volume percent of water a blend can retain (tolerate) in solution at a given temperature without phase separation (3) . One of the major difficulties encountered with the use of alcohol gasoline blends is their tendency to phase separate on contact with small amount of water, yelding an upper gasoline- rich phase and a lower aqueous alcohol rich phase . To avoid phase separation, in storage tanks and pipe lines must be maintained in dry conditions, which is a very difficult practical problem. Another approach is addition of cosolvents to increase water tolerance of the blend. C_2 – C_6 alcohol could be used as cosolvents however, tert- butyl alcohol is the most attractive for most commercial gasoline applications. Mixture of methanol and tert- butyl alcohol (TBA) have been marketed as an oxygenate blending component for gasoline (1, 4 ,14).

Previous work, have been carried out to examine the relative effectiveness of different cosolvent in gasoline- methanol blends (16-18). The effect of changing the level of aromatics and cosolvent on phase separation temperature (PST) , have been examined (4). The effects of boiling range and hydrocarbon- types in gasoline methanol blends on PST have been investigated without any cosolvent (15,16) . In another study, using several cosolvents and a new Laser Attenuation Technique for measuring phase separation and water tolerance (WT), Green and Yan, 1990 (1) have developed an equation relating WT of a fuel blend and temperature which is described by:

$$\mathrm{Ln}\ WT = m\ (l/T) + K$$

Where WT in vol.% , m and k are constants depending on the nature of the base fuel and the nature and concentration of the cosolvent,T is the temperature, K. They concluded that WT improves with increasing aromatics in base fuel, and the effeteness of cosolvent increases with concentration depending on its structure (3,4).

In the last decade, many interesting works have been published on multi - component systems that contain a hydrocarbon fuel, an oxygenate compound and water. Among these oxygenated compounds, ethanol and methanol have been receiving much current attention (17- 21).

EXPERIMENMTAL

Materials

Hydrocarbon- base gasoline 80 was kindly supplied by Suez Oil Processing Company. A stock, of 25 liters of this commercial fuel.was kept refrigerated in five well- stoppered containers. Methyl alcohol, 99.99% pure was kindly supplied by Methanex Egypt Co., Damietta, Egypt. C_3 - C_5 alchohol cosolvents, > 95.0% pure from Sigma Aldrich, Prolabo and Carlo Erba.

Methods and Equipment

Octane number measurements were carried out using ZX-101XL Portable Octane Analyzer. Vapour pressure was measured using ASTM D5191, IP394, EN 13016-1 (Mini Method). Water tolerance (WT) and phase separation temperature (PST) were measured according to ASTM 6422.

RESULTS AND DISCUSSION

Water Tolerance of Gasoline-Methanol Blends

Since methanol and water readily dissolve in each other,when methanol is blended into hydrocarbon gasoline, water will actually dissolve in the blended fuel to a much greater extent than in hydrocarbon gasoline. When water reaches the maximum amount that the gasoline blend can dissolve, any additional water will separate from the gasoline. The amount of water required (in vol. %) for this phase separation to take place varies with temperature. Figure I depicts water tolerance values of gasoline – methanol blends at two temperatures: 0 °C (represent winter time) and 35 °C (represents summer time). As can be seen from this figure , the hydrocarbon-base gasoline is designated MO ,i.e, methanol-free gasoline,whereas,M3,M6,M9 and M12 are gasoline-methanol blends containing 3,6,9 and 12 vol.% methanol.

Figures I illustrates water tolerance values of M0,M3,M6,M9 and M12 fuels at 0 °C and 35 °C the proposed temperatures for winter and summer times. At 0°C M0 , M3 , M6 , M9 and M12 tolerate 0.05,0.07,0.08,0.10 and 0.12 vol. % water. respectively. At 35 °C, the same blends tolerate more water which reached 0.15 ,0.17 ,0.20 , 0.22 and 0.24 vol% respectively. Figure 1 is actually a typical diagram for two water-solubility limits in gasoline – methanol blends containing from 3 to 12 vol.% anhydrous methanol . The lower line represents water-tolerance limits at 0°C which is taken as a representative temperature during winter time . The area below the 0°C line represents , two-phase region where some of the methanol/water phases out of the blend into a denser lower phase The upper line represents water tolerance limit at 35°c which is proposed to be the temperature during summer time. Below this temperature. hazing can occur depending on the concentration of blended methanol and the content of aromatics in base gasoline.

Water tolerance values at the proposed temperatures 0°C and 35 °C which represent winter and summer months. are listed in Table 1 and illustrated in Figure 1 .It is obvious that gasoline-methanol blend M12 tolerates 0.12 vol.% H_2O at 0 °C, i.e, one liter of this fuel blend can hold only 1.2 ml water. The area below the 0 °C line represents two-phase region where some of methanol/water phases out of blend solution into a denser lower phase. At the upper 35 °C line, a relatively higher water tolerance values are achieved, and as can be seen, M12 blend tolerates 0.33 volume percent water (3.3ml water per one liter of fuel blend). Below 35 °C line, hazing can occur depending on the concentration of blended methanol and the content of aromatics in the hydrocarbon-base gasoline
(1 , 22) .

Most gasoline distribution and storage systems are built on the principle that gasolines and water do not mix because the maximum water solubilities in hydrocarbon gasolines are usually less than 200 ppm , < 0.02 wt% . (10) , The employed light alcohols auch as methanol and ethanol are completely miscible with water. Therefore, when these alcohols are blended into gasoline. they will increase the maximum solubility of water in these blends. These solubility limits are mainly dependent on the type and concentration of the blended alcohol. Even without any added water in gasoline- alcohol blend, alcohol itself has a limited solubility in gasoline at the low temperature months (0 °C or below) . If alcohol separates from a gasoline- alcohol blend, and thereby forms a denser liquid phase out in vehicle’s fuel tank and it will cause significant poor engine performance and possibly make the vehicle inoperable by staling the engine if the separated alcohol was contaminated with certain amount of water. Therefore, precautions need to be developed to prevent phase separation of methanol or methanol/water mixture.

In previous work, methanol was replaced by ethanol, propanol and butanol to produce a stable low level alcohol blends for commercial use that will not like phase separate under expected normal conditions and moisture exposure. (23-25). Successful low- to mid- level methanol (M3 to M15) will likely require 2 volume percent cosolvent alcohols to prevent phase separation in the consumer’s vehicles particularly during the colder winter seasons (2,7,10,11).

Effect of Cosolvent and Water Tolerance

Investigators approved the use of cosolvents to prevent phase separation. In the US.the commercial use of 5% methanol- blended gasoline that requires a minimum 2.5 vol % cosolvents (C_2 - C_7) alcohols cosolvent (10,14) . During the early 1980'S Europe commercialized gasolines containing 3 volume % methanol with 2 volume % isobutanol as a cosolvent (26) .In New Zealand , gasoline- methanol blend containing 15 volume % methanol without cosolvents , is distributed. The risk of phase separation is very low since New Zealand winter months are relatively mild and temperature do not drop below 0 °C (27-29).

In the present study. anhydrous methanol containing 10vol% of C_3-C_5 alcohol cosolvents, were employed as oxygenate blending components . Water miscibility of the employed cosolvents are given in Table 2 . In this tables , two propanol isomers, isopropyl alcohol (IPA) and n-propyl alcohol (NPA) are completely miscible with water in all proportions. Also, four butanol isomers : tert- butyl alcohol (TBA), iso- butyl alcohol (IBA),sec- butyl alcohol (SBA) and n-butyl alcohol (NBA). Tertiary amyl alcohol (TAA) is the C_5 alcohol co solvent used in this study.

Data in Table 3 show the composition and water tolerance of gasoline- methanol blends containing butonal (IPA or,NPA) cosolvents. The percentage of the main hydrocarbon- base gasoline 80 and aromatic content, were kept unchanged in the formulations of M3, M6, M9 and M12 . Figurt 3 illustrates water tolerance as a function of methanol concentration after the addition of IPA cosolvents .

It can be seen from data in Table 3 and Figure 2 the blend formulations containing methanol plus propanol cosolvents , tolerate more water than that containing methanol plus propanol cosolvents , tolerate more water than that containing methanol alone . For instance , M12 blend tolerates 0.14 and 0.35 vol% water at 0°c and 35 °C, whereas , M12 containing IPA cosolvent tolerates 0.18 and 0.37vol% water, respectively . Water – tolerance affinity difference between methanol blends containing IPA or NPA cosolvents and the corresponding blends without cosolvent. Insignificant , in water tolerance values between gasolines with the same concentration of methanol – IPA and methanol – NPA . This difference is attributed mainly to the difference in chemical structure , as the two propanol isomers are completely water soluble .Previous work proved that propanol has better affinity for water than does ethanol or methonal (20, 21) .

Data in Table 4 show the composition and water tolerance of gasoline- methanol blends containing butanol cosolvents (TBA,IBA and SBA) Hydrocarbon-base gasoline and aromatic content, were kept unchanged in the formulation of the investigated blends. Each butanol cosolvent was added to methanol in 10 volume percent as shown in Table 4.Four butanol isomers , are employed in this study: tert- butyl alcohol (TBA),iso- butyl alcohol (IBA) sec- butyl alcohol (SBA) and n-butyl alcohol (NBA) . TBA is completely water- soluble, Whereas only 12.5g of SBA, 10.0g of IBA and 9.0g of NBA are soluble per 100g of water as shown in - (Table 2) (30,31).

Figure 3 illustrates water tolerance values versus blended methanol containing butanol cosolvents at the two proposed temperature limits 0 °C and 35 °C. For instance, the addition of TBA cosolvent causes more increase in the water tolerance values if compared with that of the corresponding methanol blends without cosolvent. At 35 °C M3,M6,M9 and M12 fuel blends tolerate 0.19,0.23,0.28 and 0.33 vol.% water without addition of cosolvent and after the addition of TBA cosolvent . the corresponding fuel blends tolerate 0.34, 0.39,0.43 and 0.45 vol.% water at 35 °C, respectively (Table 4). Similarly. at 0 °C the investigated fuel blends tolerate 0.07, 0.08- 0.10 and 0.12 vol.% water without cosolvent and After addition of TBA cosolvent, water tolerance values of 0.13, 0.15, 0.20 and 0.24 vol.% water were attained, respectively (Table 4).

After using two propanol and four butanol isomers as cosolvents in gasoline- methanol blends to increase the water tolerance values of M3,M6,M9 and M12 reasonable results were achieved (Tables 3 and 4 Figures 2 and 3). However. phase separation in these blends. still occurs with only a small amount of water, when one of the pentanol isomers, Tertiary amyl alcohol, was attempted as co- solvent no improvement in water tolerance values was attained at 35 °C, whereas. At 0 °C tertiary amyl alcohol (TAA) cosolvent shows better affinity for water than does any butanol isomer (Figure 4).

In short, concerning the affect cosolvent addition on water tolerance values of the investigated gasoline- methanol blends it can be concluded that neither propanol nor butanol cosolvent isomer gave water tolerance values exceeding 0.45 vol.% and 0.24 vol.% for the proposed summer (35 °C) and winter (0 °C) times, Figures 2 and 3 In case of pentanol (TAA) cosolvent. water tolerance values reached 0.43 and 0.30 at summer and winter times. Respectively ,Figure 4.

Cosolvent-PST Relationship at Constant W·T

In the preceding experiments the effect of cosolvent on water tolerance values of the in vestigated gasoline-methanol blends were studied at two Constant temperatures, 0 °C and 35 °C, representing winter and summer times, respectively.For example gasoline-methanol blend M12,shown in Table3, consists of 88.0 vol.% gasoline, 10.8 vol.% methanol and 1.2 vol.% TBA. This blend tolerates 0.45 vol.% water at 35 °C .This temperature is the phase separation temperature of this blend. Below this temperature, phase separation occurs. At constant water-tolerance WT (0.45 vol.%), the addition of 1.5,2.0,2.5 and 3.0 vol.% TBA resulted in depression in the phase separation temperature from 35 to 30,21,9 and 0°c, respectively (Figure5)·

When IBA was used as cosolvent, M12 formulation consists of 88.0 vol.% gasoline 80,10.8 vol.% methanol and 1.2 vol.% IBA cosolvent. This blend tolerates 0.40 vol.% H_2O at 35 ^{o}c. At constant water tolerance, the phase separation temperature, was depressed from 35 to 28.0,22.0,16.5,9.0 and 0 °C when1.5,2.0,2.5,3.0, and 3.5 vol.% IBA were add to the blended methanol, respectively (Figure 6).

On parallel lines, fuel blends containing 1.2 vol.% of SBA or NBA cosolvents can tolerate 0.37 and 0.33 vol.% water at 35 °C phase separation temperature , respectively. At 0.37 vol.% water tolerance, the phase separation temperature, of fuel blend containing 1.2 vol.% SBA, was depressed from 35 °C to 32,26,21,16,10,4 and 5°c when 1.5,2.0,2.5,3.0,3.5,4.0 and 4.5vol.% SBA cosolvent were added, respectively (Figure7)·Similary at 0.33 vol.% water tolerance, the phase separation temperature, of fuel blend containing 1.2 vol.% NBA, was depressed from 35 °C to 32,26,20,15,11.5,8.5 and 5 °C when 1.5,2.0,2.5,3.0,4.0 and 4.5vol.% NBA cosolvnt were added, respectively (Figure 8).

When tertiary pentanol (tert- amyl alcohol, TAA),was employed as cosolvent in the same formulation, i.e. 88.0 vol.% gasoline 80,10.8 vol.% methanol and 1.2 vol.% TAA cosolvent. This fuel blend tolerates 0.43 vol.% water at phase separation temperature 35 °C addition of 1.5,2.0,2.5,3.0,3.5 and 4.0 vol.% TAA cosolvent depressed the phase separation temperature (PST) from 35 °C to 27,17.5,7.0,2.5,-1 and -5, respectively (Figure 9).

Figures 5-9 reveal some results concerning the impact of butanol and pentanol cosolvents addition on phase separation temperature (PST) of the fuel blend · First, phase separation temperature can be depressed from 35 °C to 0 °C by the addition of relatively small concentration of certain butanol or pentanol cosolvent isomers . Secondly, gasoline blended with 12 vol.% methanol without cosolvent addition. tolerates only 0.12 and 0.33 vol. % water at 0 °C and 35 °C. When the same gasoline was blended with 10.8 vol.% methanol +1.2.vol% TBA the blend tolerates 0.24 and 0.45 vol.%. water at 0 °C and 35 °C PST respectively Increasing the added TBA cosolvent from 1.2 vol.% to 3.0 vol.% in the blended methanol, causes a depression in PST from 35 °C to 0 °C. (Figure 4). Similarly, fuel blend consiststing of 88 vol.% gasoline +(10.8 vol.% M+1.2 vol.% TAA). can tolerate 0.43 vol.% water at 35 °C PST. Increasing the concentration of TAA in methanol from 1.2 to 3.5 vol. causes a depression in PST from 35 °C to 0 °C without hazing or phase separation (figure 9).

PST-WT Relationship at Constant Cosolvent Concentration

The relationship between water tolerance (WT) and phase separation temperature (PST) at constant cosolvent concentration for three different formulation of gasoline-(methanol+cosolvent) blends, are illustrated in Figure 10. The first blend consists of 88 vol.% gasoline, 9.0vol.% M+3.0 vol.% TBA. This blend tolerates 0.45 vol.% water at 0 °C PST. Increasing WT from 0.45,0 to 50,0.55,0.60,0.65, 0.70 and 0.75 vol.% necessitates a subsequent increase in phase separation temperature from 0 °C to 2.5,5.0,8.0,13.5,21.5 and 36.0 0 °C, respectively.The secand blend consists of 88 vol.% of the same gasoline,8.5 vol.% M+3.5 vol.% IBA. This blend tolerates 0.40 vol.% water a 0 °C PST. Increasing WT from 0.40 to 0.45,50,0.55,0.60,0.65 and 0.70 vol.% necessitates subsequent increase in PST from 0 °C to 2.5,4.0,8.0,13.0,19.0 and 34 °C, respectively. The third blend consists of 88 vol.% of the same gasoline 7.5 vol.% M+4.5 vol.% SBA. This blend can tolerate 0.37 vol.% water at 0°C PST. Increasing.WT from 0.37 vol.% to 0.40,0.45,0.50 and 0.55 vol.% necessitates subsequent increase in PST from 35 °C to 3.0,7.5,14.0 and 31. 0°C, respectively.

Similarly, the relationship between WT and PST at constant tertiary amyl alcohol (TAA) cosolvent , is constructed in Figure11, In this figure , the fuel blend which consists of 88 vol.% of the same gasoline plus 8.0 vol.% M+4.0 vol.% TAA cosolvent.This blend tolerates 0.40 vol.% water at

-5 °C PST without hazing or phase separation.

Increasing WT from 0.40 vol.% to 0.45,0. 50,0.55,0.60,0.65,0.70 and 0.75 vol.%, necessitates subsequent increasing WT from 0.4 vol. to o.50 ,0.55 ,0.65,0.70, and 0.75 vol. % necessitates subsequent increasing PST from -5.0°c to -4.0,-1.5,2.0,5.0,10.5,21.0,36.5 °C, respectively·Effect of butanoal cosolvent isomers on PST at constant WT are given also in Table 5 (A-D).

Based on the obtained results concerning the relationship between WT and PST at constant butanol or pentanol cosolvent values in four blends · Four polynomial equation are developed , R^2 values indicate the rebliability of the fits · The oxygenate blending component , (methanol + butanol or pentanol cosolvent), is kept constant in each blend , moreover the amount and composition of the employed base gasoline are kept unchanged Formulation and oxygenate blending component for each gasoline – methanol blend ·

Fuel Blend (vol.%) : 88·0 G + (9.0M) + 3·0 TBA)
PST = 440·48 (WT) ^{2} – 418·21 (WT)+ 100·31 R^2 = 0·9871 (1)

Fuel blend (vol.%) : 88·0 G + (8·5M) + 3·5 IBA)
PST = 414·48 (WT) ^{2} – 352·86 (WT)+ 76·107 R^2 = 0·9813 (2)

Fuel blend (vol.%) : 88·0 G + (7·5M) + 4·5 SBA)
PST = 926·04 (WT) ^{2} – 690·13 (WT)+ 129·6 R^2 = 0·9860 (3)

Fuel blend (vol.%) : 88·0 G + (8·5M) + 4·0 IBA)
PST = 505·09 (WT) ^{2} – 460·21 (WT)+ 100·12 R^2 = 0·9414 (4)

CONCLUSIONS

- Oxygenate blending components comprising propanol , butanol and pentanol cosolvent isomers , gave WT values not exceeding o·45 and 0·24vol· % at 35 °C and 0 °C·
- Tertiary amyl alchol (TAA) cosolvent shows better water affinity at 0 °C than does any other propanol or butanol cosolvent isomers ·
- At 35 °c oxygenate blending components comprising 1·2 vol· % TBA , IBA, SBA and NBA cosolvent , tolerate 0·45, 0·40,0·37 and 0·33vol· % water , whereas , that comprising 1·2 vol· % lending components consisting of : M+TBA, M+ 1BA, M+SBA and M+TAA
- TAA , tolerateso·43vol· % water at the same PST ·
- Four polynomial equations were developed relating WT and PSA of four different oxygenate blends.

Table 1- Composition and Water Tolerance of the Investigated Gasoline- Methanol Blends

Fuel Blend Components	**Blend composition, vol.%**				
	M0	M3	M6	M9	M12
Gasoline 80	100	97	94	91	88
Methanol	------	3	6	9	12
total	100	100	100	100	100
Density,@15 °c	0.7242	0.7259	0.7276	0.7296	0.7313
Aromatics , vol. %	21.5	20.9	20.3	19.6	18.9
Water Tolerance					
Vol.% at 0 °c	0.05	0.07	0.08	0.10	0.12
Vol.% at 35 °c	0.15	0.19	0.23	0.28	0.33

Table 2- Water Miscibility of Some Alcohols Employed as Cosolvents is Fuel Blends

Cosolvent	Abbr	Solubility g alcohol/100g H_2O
2-Propanol (iso-propyl alcohol)	IPA	Completely miscible
1- Propanol (n-propyl alcohol)	NPA	Completely miscible
2-Methyl-2-propanol (tert-Butanol)	TBA	Completely miscible
2- Methyl-2-propanol (iso-Butanol)	IBA	10.0g
2-Butanol (sec-Butanol)	SBA	12.5g
1-Butanol (n- Butanol)	NBA	9.0g
2,2-Dimethyl-1-propanol (tert-Amyl alcohol)	TAA	11.5g

Table 3-Composition and Water Tolerance of the Gasoline- Methanol Blends Containing Propanol Cosolvent.

Fuel Blend components	Blend Compostion ,vol.%				
	M0	M3	M6	M9	M12
Gasoline 80	100	97.0	94.0	91.0	88.0
Methanol	-----	2.7	5.4	8.1	10.8
Propanol isomers	-----	0.3	0.6	0.9	1.2
Total	100	100	100	100	100
Aromatic, Vol.%	21.5	20.9	20.3	19.6	18.9
Density@ 15°C ASTM D4052:					
Of blends+IPA	---	0.7278	0.7313	0.7350	0.7383
Of blends+NPA	---	0.7279	0.7298	0.7352	0.7386
Water Tolerance of Blends + IPA:					
Vol.% at 0 °C	-----	0.08	0.12	0.15	0.18
Vol.% at 35 °C	-----	0.21	0.27	0.32	0.37
Water Tolerance of Blends + NPA:					
Vol.% at 0 °C	-----	0.08	0.11	0.12	0.14
Vol.% at 35 °C	-----	0.20	0.25	0.29	0.35

Table 4-Composition and Water Tolerance of the Gasoline- Methanol Blends Containing Butanol Cosolvent.

Fuel blend components	Blend compostion ,vol.%				
	M0	M3	M6	M9	M12
Gasoline 80	100	97.0	94.0	91.0	88.0
Methanol	-	2.7	5.4	8.1	10.8
Butanol isomers	-	0.3	0.6	0.9	1.2
Total	100	100	100	100	100
Aromatic. Vol.%	21.5	20.9	20.3	19.6	18.9
Density@ 15 °c ASTM D4052					
Of blends+TBA	---	0.7278	0.7313	0.7350	0.7383
Of blends+NPA	---	0.7278	0.7314	0.7352	0.7385

Of blends+ SBA	---	0.7278	0.7314	0.7352	0.7385
Water Tolerance of Blends + TBA					
Vol. % at 0 °C	-----	0.13	0.15	0.20	0.24
Vol. % at 35 °C	-----	0.34	0.39	0.43	0.45
Water Tolerance of Blends + IBA					
Vol. % at 0 °C	-----	0.10	0.12	0.15	0.20
Vol. % at 35 °C	-----	0.30	0.33	0.38	0.40
Water Tolerance of Blends +SBA					
Vol. % at 0 °C	-----	0.09	0.11	0.12	0.17
Vol. % at 35 °C	-----	0.27	0.31	0.35	0.37

PST=phase stability temperature TBA= tert-butyl alcohol
IBA=isobutyl alcohol SBA= sec-butyl alcohol
NBA=N-butyl alcohol TAA= tert-amyl alcohol

Table 5A- Effect of TBA Cosolvent on PST at 0.45 vol.% W.T.

Fuel Blend Formulation, vol.%	PST (°C)
88% BG+10.8% M+1.2 TBA	35.0
88% BG+10.5% M+1.5 TBA	30.0
88% BG+10.0% M+2.0 TBA	21.0
88% BG+9.5% M+2.5 TBA	9.0
88% BG+9.0% M+3.0 TBA	0.0
88% BG+8.5% M+3.5 TBA	-10.0

Table 5B- Effect of IBA Cosolvent on PST at 0.40 vol.% W.T.

Fuel Blend Formulation, vol.%	PST (°C)
88% BG+10.8% M+1.2 IBA	35.0
88% BG+10.5% M+1.5 IBA	28.0
88% BG+10.0% M+2.0 IBA	22.5
88% BG+9.5% M+2.5 IBA	16.5
88% BG+9.0% M+3.0 IBA	9.0
88% BG+8.5% M+3.5 IBA	0.0

BG=base gasoline 80, M=methanol
PST=phase stability temperatur

Table 5C- Effect of SBA Cosolvent on PST at 0.37 vol.% W.T.

Fuel Blend Formulation, vol.%	PST (°C)
88% BG+10.8% M+1.2 SBA	35.0
88% BG+10.5% M+1.5 SBA	32.0
88% BG+10.0% M+2.0 SBA	26.0
88% BG+9.5% M+2.5 SBA	21.0
88% BG+9.0% M+3.0 SBA	16.0
88% BG+8.5% M+3.5 SBA	10.0
88% BG+8.0% M+4.0 SBA	4.0
88% BG+7.5% M+4.5 SBA	1.0-0.0

Table 5D- Effect of TAA Cosolvent on PST at 0.43 vol.% W.T.

Fuel Blend Formulation, vol.%	PST (°C)
88% BG+10.8% M+1.2 TAA	35.0
88% BG+10.5% M+1.5 TAA	27.0
88% BG+10.0% M+2.0 TAA	17.5
88% BG+9.5% M+2.5 TAA	7.0
88% BG+9.0% M+3.0 TAA	2.5
88% BG+8.5% M+3.5 TAA	-1.5
88% BG+8.0% M+4.0 TAA	-5.0

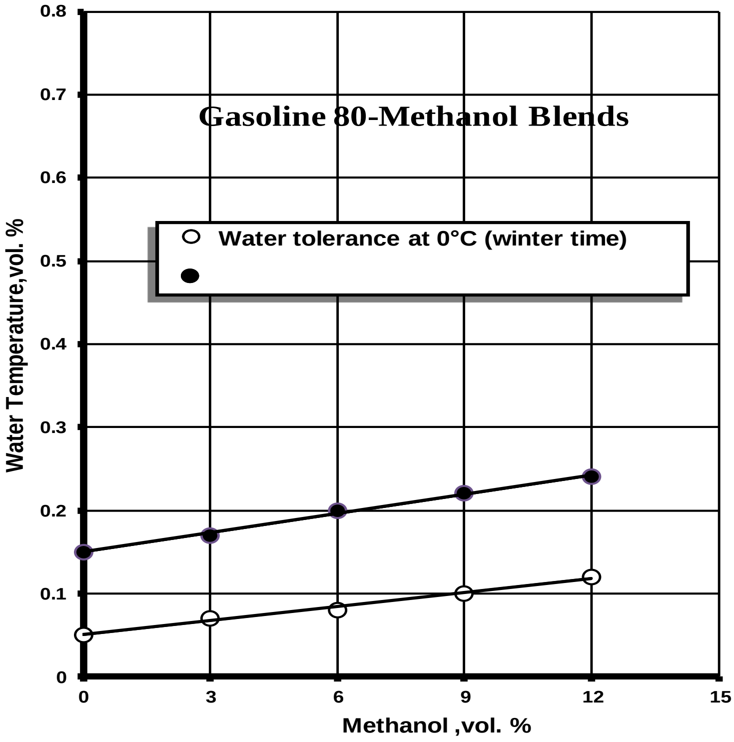

Figure 1 - Water Tolerance vs Methanol Concentration at 0 °C and 35 °C.

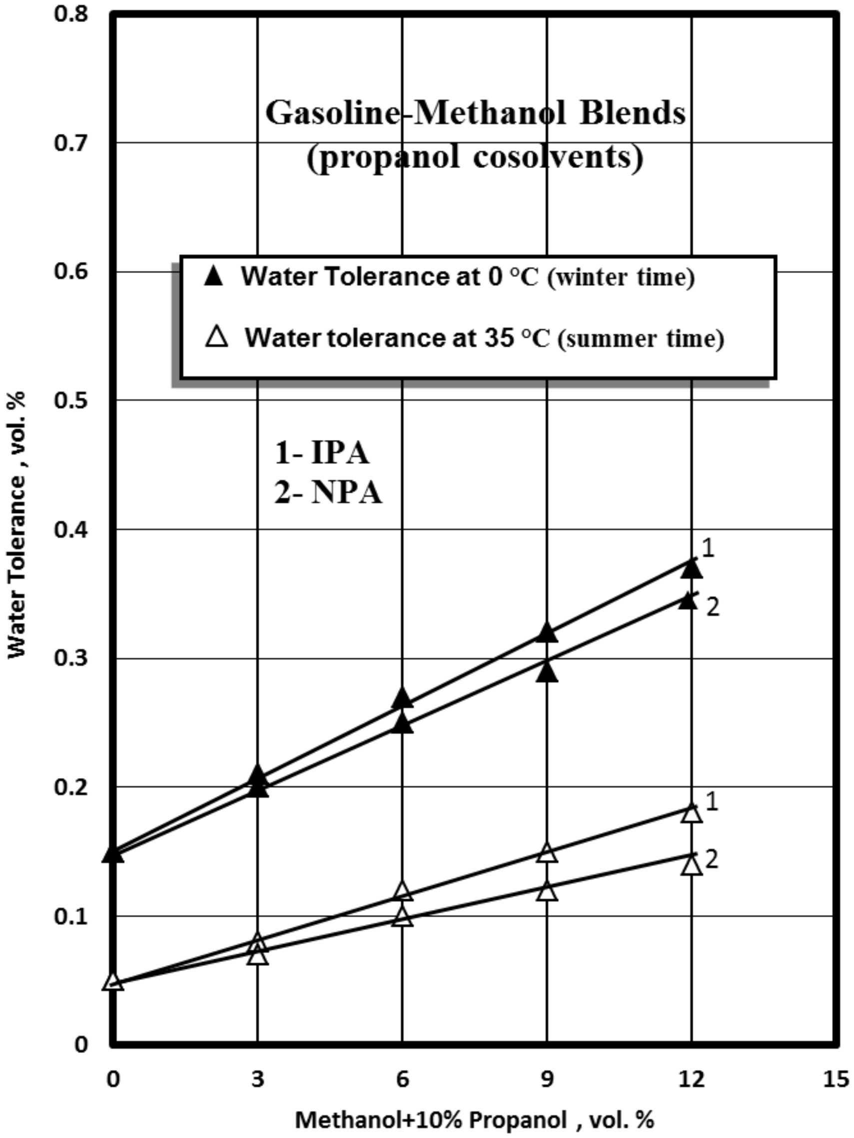

Figure 2 - Water Tolerance vs Methanol Conentration Containing 10% Propanol Cosolvent at 0°C & 35 °C .

.

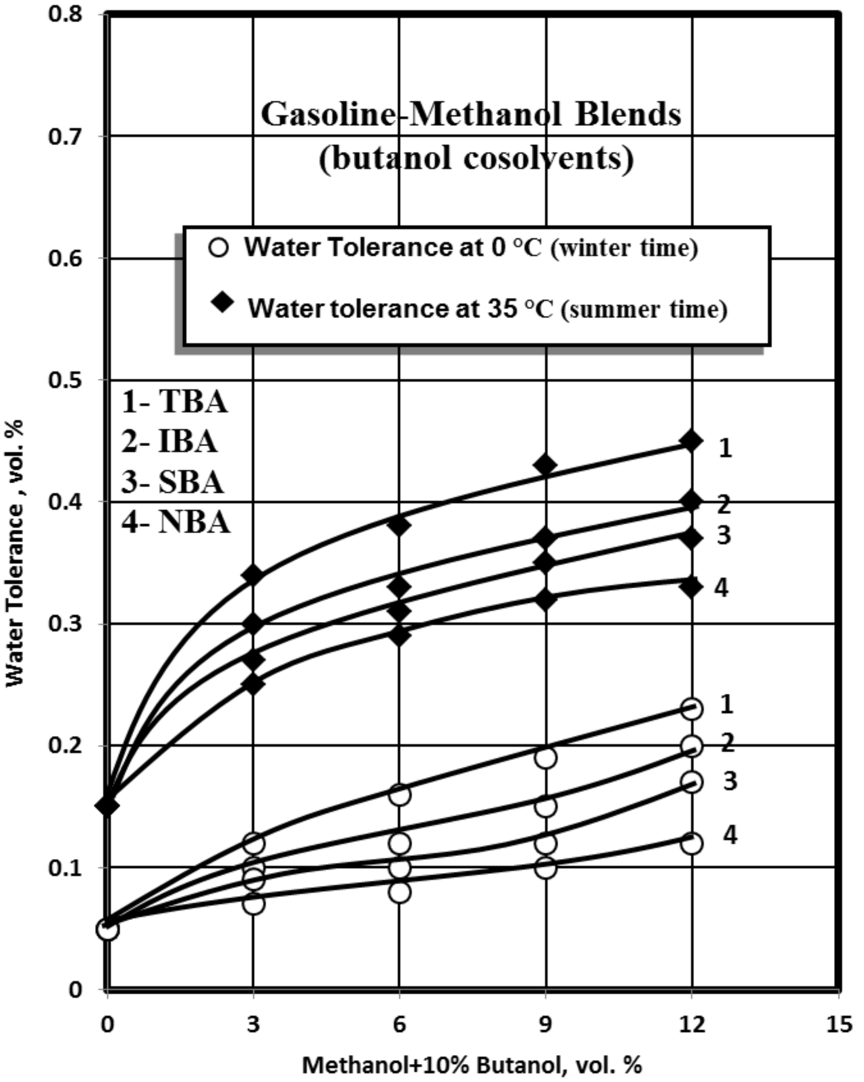

Figure 3 - Water Tolerance vs Methanol Conentration Containing
. 10% butanol Cosolvent at 0°C & 35 °C

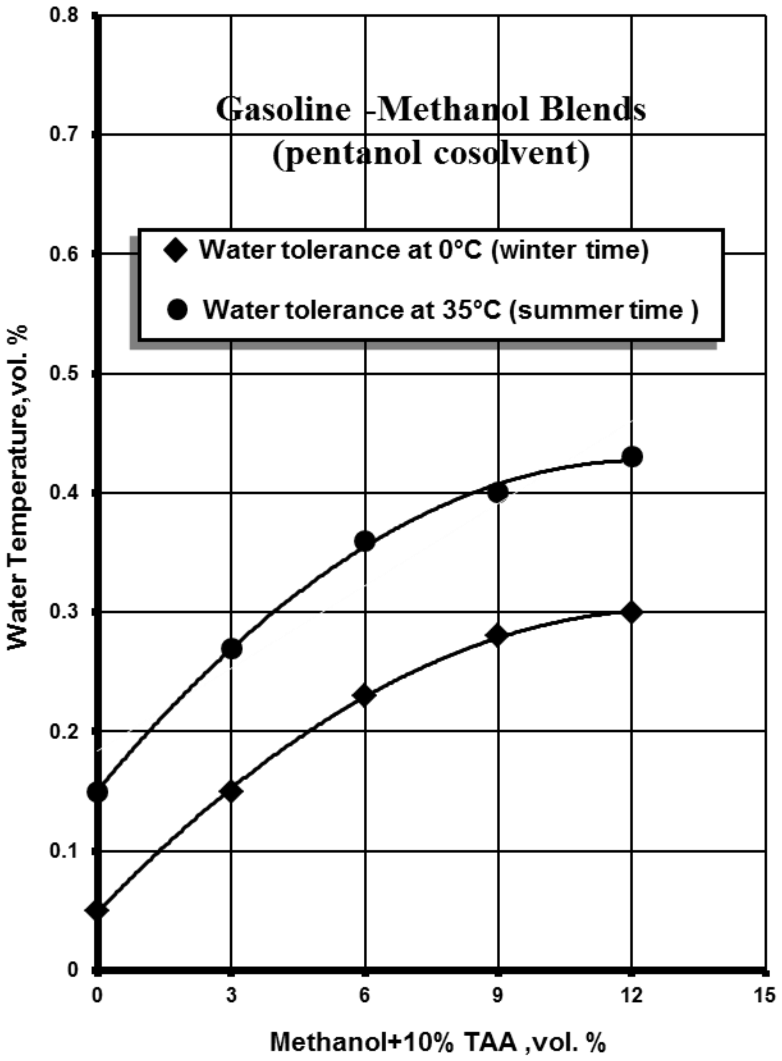

Figure 4 - Water Tolerance vs Methanol Concentration Containing 10% TAA Cosolvent at 0 °C and 35 °C .

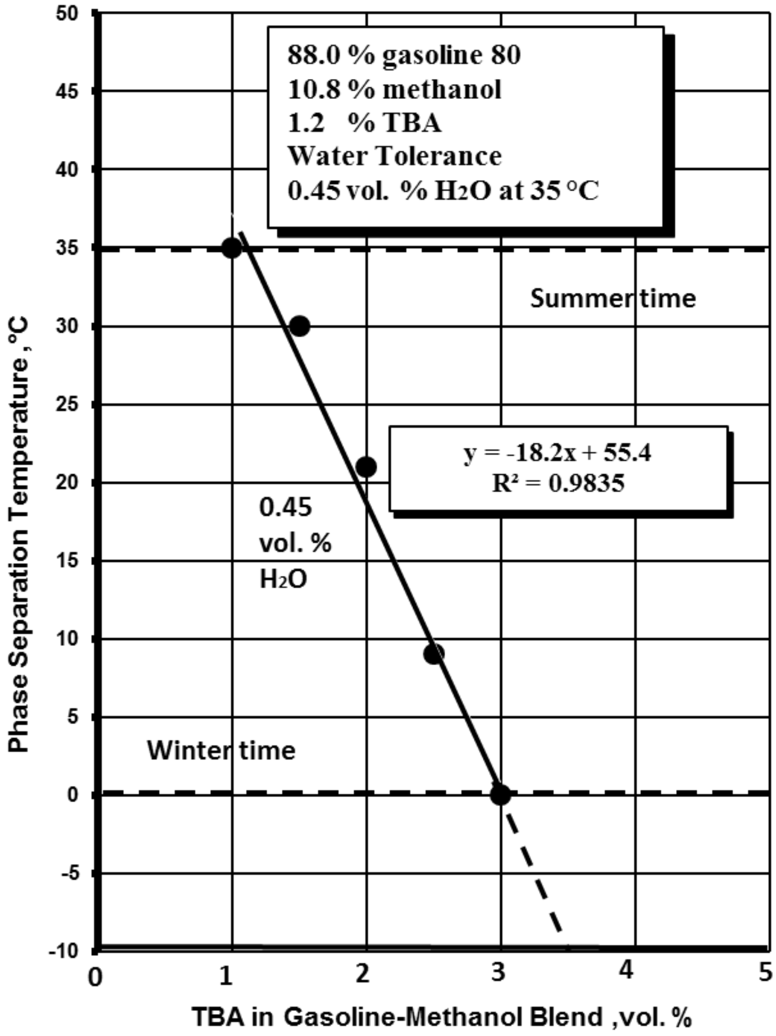

Figure 5 - Effect of TBA cosolvent on Phase Separation Temperature of Gasoline-Methanol Blend.

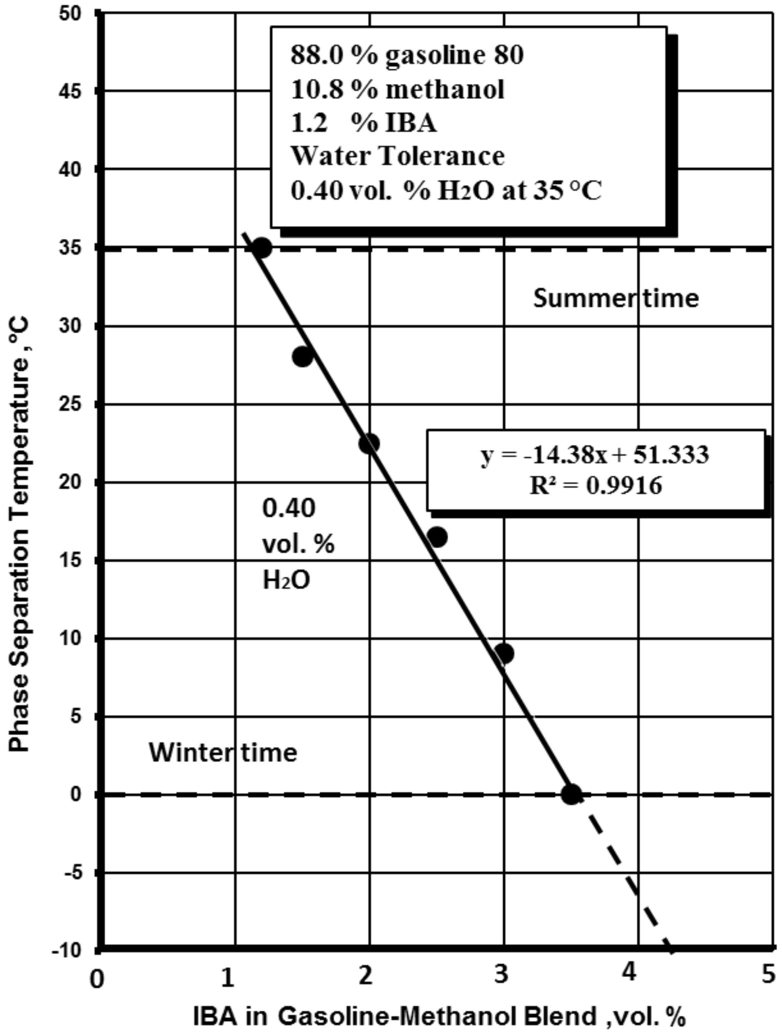

Figure 6 - Effect of IBA cosolvent on Phase Separation Temperature of Gasoline-Methanol Blend.

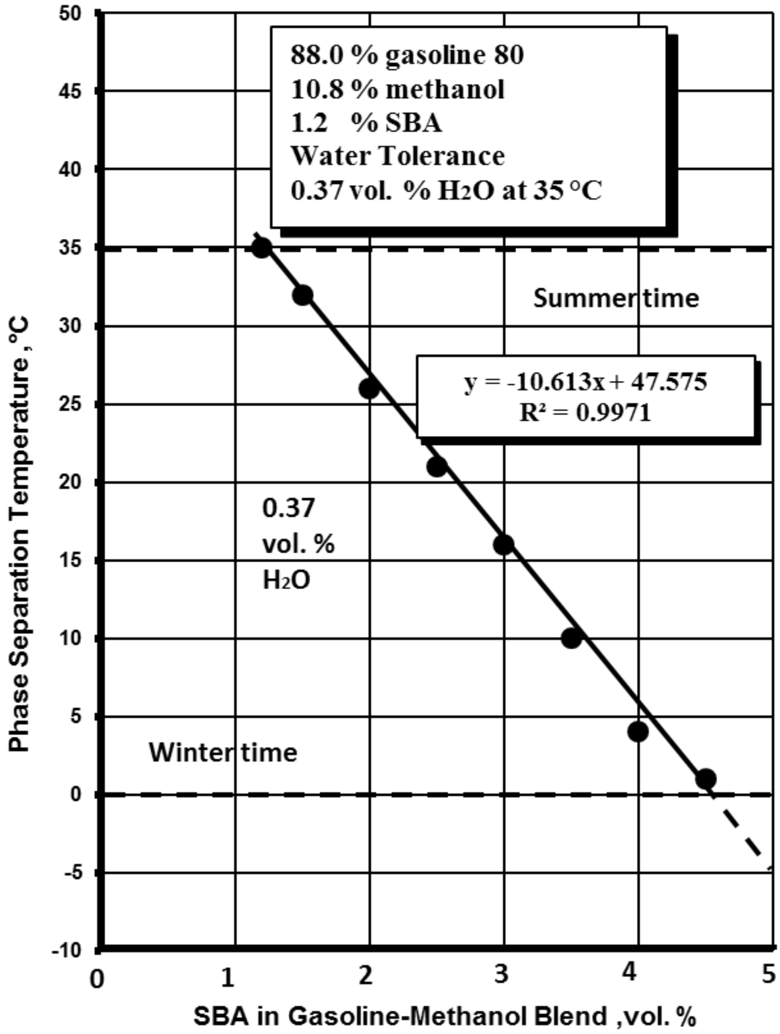

Figure 7 - Effect of SBA cosolvent on Phase Separation Temperature of Gasoline-Methanol Blend.

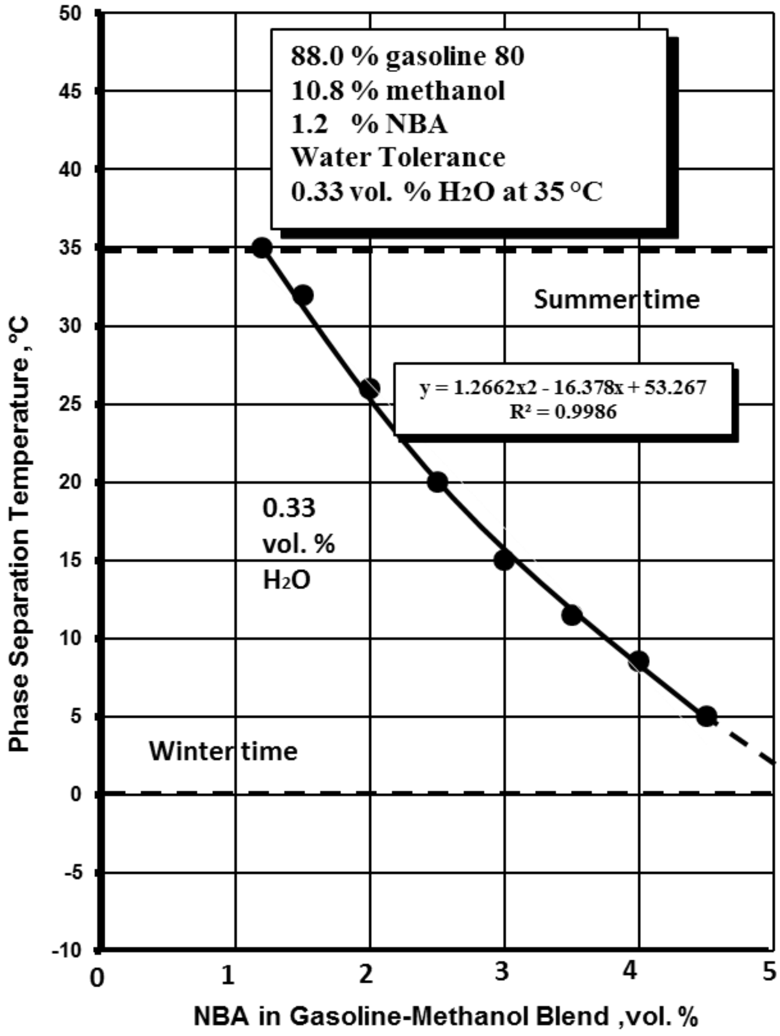

Figure 8 - Effect of NBA cosolvent on Phase Separation Temperature of Gasoline-Methanol Blend.

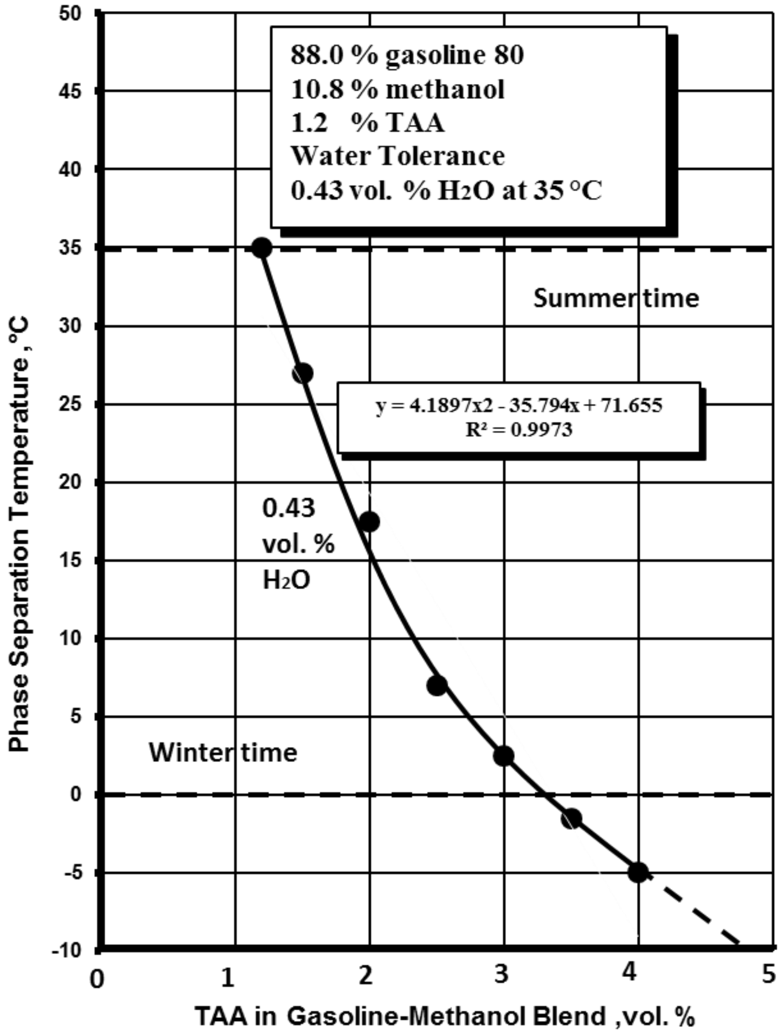

Figure 9 - Effect of TAA cosolvent on Phase Separation Temperature of Gasoline-Methanol Blend.

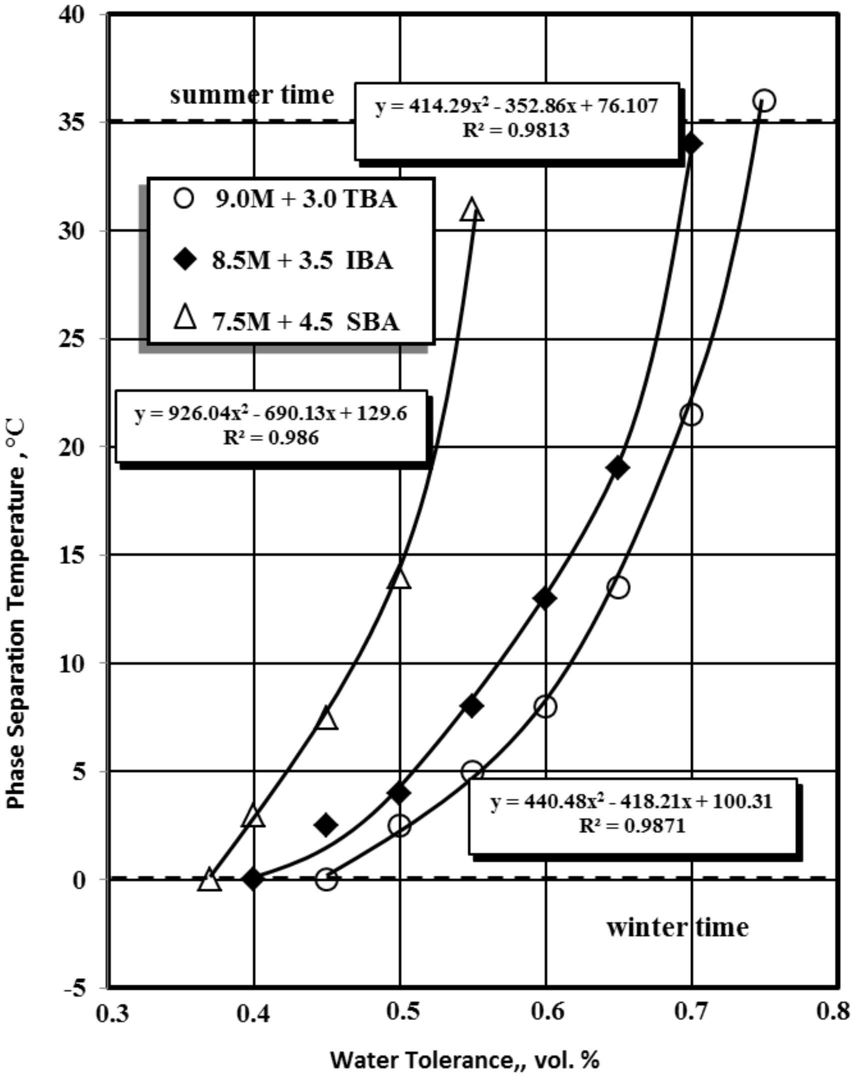

Figure 10 - Water Tolerance - PST Relationship of

○ Gasoline - (9.0 vol.%M+3.0 vol. % TBA)

◆ Gasoline - (8.5 vol.%M+3.5 vol. % IBA)

△ Gasoline - (7.5 vol.%M+4.5vol. % SBA)

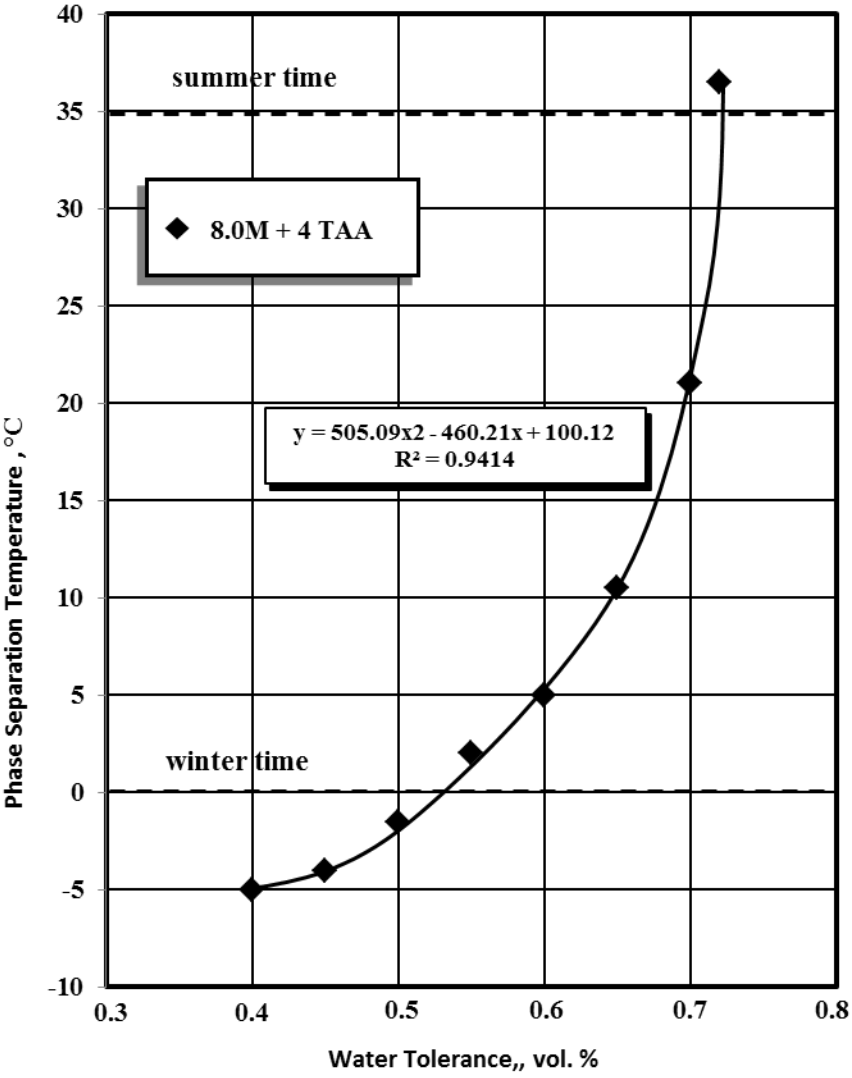

Figure 11 - Water Tolerance - PST Relationship of Gasoline - (8.0 vol.%M+4.0 vol. % TAA)

REFERENCES

[1] Frank Cox "The Physical Properties of Gasoline/ Alcohol Automotive Fuels" U.S. Department of Energy Proceedings of the Alcohol Fuels Technology Third International Symposium ,Vol. II, (1979) May 28-31.

[2] American Petroleum Institute "Alcohols and Ethers- A Technical Assessment of their Application as Fuels and Fuel Components" API Publication 4261, (1988) 2nd Ed., Washington, D.C.

[3] Green, G.J. and Yan, T.Y. " WaLer Tolerance of Gasoline- Methanol blends" Ind. Eng. Chem.Res., 29, (1990) 1630- 1635. ; Green, G.I (1989) US patent 4,804,274

[4] Roberta J.Nichols " The Methanol Story: A Sustainable fuel for the Future"J. Scientific & Industrial Research, vol. 62, (2003) 97- 105.

[5] El- Kady, M.Y, El- Zein, S.M., Ibrahim, V, Awad, E.N and Barakat, Y. "Environmental Impacts of Some Oxygenated Gasoline Formulations" , I. Environ. Sci, vol.11, No. 1 (2005) 1- 29.

[6] Ibrahim, V. ,Awad, Ezis N. and Barakat, Y. " Volatility and Enviromental Impacts of some Oxygenated Gasoline Blends" Egypt. J. Petrol., 16,no1, (2007) 29-50.

[7] Mingfa Yao, Zhengchen, and Zun- qingZheng "Investigation of the Effects of Injection Timing on thermo Atmosphere combustion of Methanol", SAE paper (2007) 01- 0197.

[8] Ryan, T.W, Bond, T.J, Schieman, R.D Understanding the Mechanism of Cylinder Bore and Ring Wear in Methanol Fueled SI Engineers, SAE Paper No ·861591, (1986). Society of Automotive Engineers ,Warrendale, Pa.

[9] Schwartz, S.E, Smolenski, D.I., Chark, S.I Entry and Retention of Methanol fuel in Engine Oil,SAE paper No. 880040, (1988). Society of Automotive Engineers, Warrendale, Pa.

[10] TEIR Associates, INC Comments Regading Low LeveLMethanol Fuel Blending Standards for M5-M15 Adopted by Shanxi Province, China, transportation energy information resources, Methanol Institute, (2008). 1- 19.

[11] Li , L,Ge,Y., Wang,M.,Li,J, Peng,Z., Song,Y.,& Zhang, L. Effect of gasoline i methanol blends on motorcycle Emissions : Exhaust and Evaporative emissions, Atmospheric Environment, 102, (2015). 79-85.

[12] Osten, D.W.,shell, N.J. Methanol –gasoline blends: Blending agents to prevent phase separation , Fuel, 62, (1983). 268.

[13] Unzelman, G.H Problems Hinder Full Use of Oxygenates in Fuel. Oil Gas J.82, (1984). 59- 65.

[14] Rawat, R.S.; Khanna, M.K., Nagpal, J.M, Gulati, 1.B. Water Tolerability of Gasoline- Methanol Blends. Res. 1nd., 29 (2), (1984) 114 – 122.

[15] Hart, P.R, Meyer, E.M ;Clavert N.RStabilizer blends for alcohol in hydrocarbon fuel, US . (2004) 0093789 Al.

[16] Eccleston, B.H.;Cox,F.W. Physical properties of Gasoline – Methanol Mixtures. Report BERC/RI- 76/12, (1977). Energy Research and Development Administration. Bartlesville , OK .

[17] Alexios KyriaKides, Vasilis Dimase, Eleni lymperopoulou, Dimitris karonis, Evripidislois Lois Evaluation of gasoline- ethanol- water ternary mixtures used as a fuel for an Otto engine. Fuel 103, (2013) 208-215

[18] Magin lapuerta, Octavio Armas, Reyes Garcia- Contranas Effect of Ethanol on Blending Stability and Diesel Engine Emissions. Energy Fuels, 23, (2009). 4343 – 4354.

[19] Johansen and Schraman , J. Low- Temperature Miscibility of Ethanol Gasoline- Water Blends in Flex Fuel Applications. Energy Sources, Part A ,31, (2009). 1634- 1645.

[20] Singgih Nitiarhardio and H. Michael Cheung Effect of Susfactants and Cosurfactants on the Phase Separation Temperature and Volatility of Methanol- Hydrocarbon- Water Blends. Energy &Fuels, 4, (1990) 303- 307.

[21] Salaheldine S.O.Khalil "Environmental Impact of The Use of Methanol- Gasoline Blends as a Fuel for Vehicles" MSc Thesis Institute of Graduate Studies and Research, University of , Alexandria , Egypt(2016)..

[22] Methanol Institute "Use of Methanol as a Transportation Fuel" Methanol Blend Physical and Chemical Property Impacts, (2007). 12-45.

[23] Bata, A.M Enhancement of Octane Number and Emission of Blend Gasoline via Reformulation of Addition of Oxygenated Compounds. Ph. D Thesis Chemistry Department, Faculty of Science, Suez Canal University, Ismaelia, Egypt. (2008).

[24] Bayrakter, H. Experimental and Theoretical Investigation of Using Gasoline- Ethanol- Blends in Spark-Ignition Engines, .Renew. Energy, 30 (11): (2005). 1733- 47.

[25] Muzikova, Z., Pospisil, M.;sebor, G. Volatilily and phase stability of petrol blends with ethanol, Fuel, 88, (2009). 1351- 1356.

[26] Coordinating Research Council "Performance Evaluation of Alcohol Gasoline Blends in 1980 Model Automobiles Phase 11- Methanol –Gasoline Blends " , U.S Department of Energy , DOE report No · DOE/ CS/ 50003-1(1984).

[27] Rolfsen, B., and Bang, J. "Methanol Gasoline Blends in Norway" Proceedings of the Fifth International Alcohol Fuel Technology Symposium, (1982) May 13-18 , Auckland, New Zeeland .

[28] Shears, T.W. and Judd, B.T. "Operating a Vehicle Fleet on Methanol Blend Fuels – 1978 to 1981" proceeding of the Fifth International Alcohol Fuel Technology Symposium, (1982) May 13-18 , Auckland, New Zeland .

[29] Shirley Schwartz "laboratory studies of the Effects of Methanol Fuel on Engine Oil and Malerials" Proceedings of the VI International Symposium on Alcohol Fuels Technology, Vol. I, (1984) May 21-25, Ottawa, Canada.

[30] Klass, D.L. "Synthetic Oxygenated Liquid Fuels, Biomass For Renewabale Energy, Fuels, and Chemicals" Chapter 11, (1998) 383 – 443.

[31] Linstromberg, W.W Organic Chemistry – A- Brief Course , 3rd Eddition, Chapter 8 , (1974). 177-183.