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Part 1-Volatility of Methanol: Blended Gasolines.

Youssef Barakat* and Ezis N Awad.

Process Design & Development Department, Egyptian Petroleum Research Institute (EPRI) , Cairo, Egypt.

ABSTRACT

Methanol – Free gasoline (M0) was formulated volumetrically from two locally produced refinery streams : 60% reformate and 40% light naphtha . Five methanol – blended gasolines were prepared using 5 to 20 vol. % anhydrous methanol . The prepared fuel blends , M5,M10, M15,M17.5 and M20 along with the M0,were examined to determine RON and six volatility terms ,T50, E70,VP,DI, VLI and $T_{v/l = 20}$, for these fuels. The measured volatility terms , were plotted against the blended methanol content.
Keywords: Methanol- gasoline blends , volalility , Vapour lock Index , drivability index, T50 and E70 , Temperature of vapour – liquid ratio

**Corresponding author*

INTRODUCTION

Oxygenates are added to S1 vehicle fuels to make them burn more clearly , thereby reducing toxic tailpipe pollution , particularly carbon monoxide [1]. Oxygenates are favoured not only for their vehicle emission benefits but also their blending properties in motor gasolines [2].Initial interest in methanol was not in its role as a sustainable fuel , but as an octane booster when lead in gasoline was banned in 1976. Interest in alternative fuels , including methanol , was also raised after the first and second oil crises .

The early interest in methanol resulted in several programs, mainly based in California. An experimental program ran during 1980 to 1990 for conversion gasoline vehicle to 85 % methanol with 15% additives of choice. Limited distribution resulted in the decision to implement flex - fuel vehicle in subsequent program [3,4]. Evaluation report for California's Methanol Program concluded that the results were technically possible but frustrated drivers are the main reason for this failure [5].

Methanol and ethanol can be renewable and sustainable energy resources due to their high oxygen content , high stoichiometric air – fuel ratio , high hydrogen – carbon ratio , and less CO emission [6] .Use of methanol and ethanol blends with gasoline can extend the supplies of fossil fuels that rely on carbon – based compounds , even the use of alcohol from non- renewable sources like methanol from natural gas , this methanol could be used as a bridging option towards transition to renewable methanol for sustainable transportation [7,8].

The need for air quality improvements and the current cost of crude oil demands alternative fuels for automobiles ⁄ IC engines [9] . Moreover, the sources of fossil fuel are dwindling day by day. According to an estimate, the fossil fuel reserves will continue until 41 years for oil , 63 years for natural gas [10,11] . At these circumstances, demand of alternative biofuels is increasing as a substitute of fossil fuel in transportation sector for energy security issues. Among the biofuels (biogas, bioalcohol , and biodiesel), bioalcohols seem to be the most attractive and promising alternative fuel [12].

MATERIALS AND METHODS

Materials

Hydrocarbon – base gasoline (HBG): was formulated volumetrically from 60% reformate and 40% light naphtha . These two refinery streams were kindly supplied from Cairo Petroleum Refining Co. Mostorod Refinery , Cairo. Detailed hydrocarbon – type GC analysis was also provided (Table 1 and 2) .

Methyl alcohol, 99.99% was kindly supplied by Methanex Co. Damietta , Egypt.

Fuel blends: were prepared volumetrically from the hydrocarbon – base gasoline (HBG) and anhydrous methanol .The prepared blends, 3- liter each , were subsequently kept refrigerated in well- stopperd labeled containers . An ice –box was used to keep these blends refrigerated when sent for octane testing.

Fuel Property Measurement Methods

Research octane number (RON): ASTM-D2699). RON values for the prepared blends (M5, M10, M15,M17.5 and M20) along with the HBG (M0) ,were determined in Cairo Petroleum Refining Co .

Specific gravity using capillary– stoppered pycnometer Method –IP 190 ⁄ 64 .

Vapour pressure of petroleum product (Reid Method) ASTM-D323 Test Method .

Vapour pressure of gasoline – oxygenate blends (Dry Method) ASTM –D5191 .

Distillation of petroleum products – ASTM –D86 Test Method .

Standerd specification for automotive spark- ignition engine fuel ASTM-D4814- 98a -EPA .

Driveability index (DI) -ASTM –D4814-98. Society of Automotive Engineer SAE paper 881668.

Vapour – Liquid Ratio of Spark – Ignition Engine Fuels T V/L =20 , ASTM-D5188 .

Oxidation Stability of Gasoline (Induction Period Method)- ASTM-D525.

Calorific value for gasoline and gasoline – alcohol blends (Bomb Calorimeter Method) – ASTM-D240-02.

Corrosivity - Copper Strip Test , 3 hour , 50 OC (122 OF) ASTM –D-130 .

RESULTS AND DISCUSSION

Methanol- Blended Gasolines

Physical and chemical properties of the investigated fuels including the hydrocarbon –base gasoline (HBG). This methanol free - gasoline (MO) and the other five blended with 5,10,15,17.5,and 20 vol.% methanol (M5,M10, M15,M17.5 and M20), were tested mainly for their octane number and volatility .

Date in Table 3 reveal that addition of 5,10,15,17.5 and 20 vol.% methanol to the HBG resulted in noticeable linear increase in RON as shown in Figure 1 .

The contribution of these methanol additions reached 4.1, 7.1,10.6,12.1. and 14.1 research octane number (RON) . This broad octane benefits can enable petroleum refiners to market several grades of gasoline – methanol blends for old and new – model vehicles . Also , upgrading low octane fuels is possible by the addition of the required methanol concentration . The linear increase of RON as a result of methanol addition (Figure1) is very close to what had been reported [13]. However , this increase in RON is not matching well with the results achieved by [14].

Concerning the effect methanol addition on the volatility of HBG, the study will extend to a number of volatility criteria listed in Table 3 . From the distillation data of HBG and the other five gasoline – methanol blends, a number of '' T '' points (T10 , T50, and T90) and " E " points such as E70 can be located on distillation curves [15-17] .T10,T50 and T90 values listed in Table 3 represent the temperatures (OC) at which 10 vol.% , 50 vol.% and 90 vol.% evaporated . From these T- values , driveability index , DI , values are calculated as one of the considerable volatility measures . Moreover , T50 values are important mid-range volatility term. E70 values of the examined fuel and fuel blends have the same importance when volatility is considered. E70 is the volume percent evaporated at 70 OC , The vapour pressure (VP) and E70 values are important fuel properties from which vapour – lock index (VLI) values are calculated [18-20] . Vapour lock and hot fuel handling problems occur when excessive gasoline vapour accumulates somewhere in fuel system of vehicle and reduces or interrupts the fuel supply to the engine [21] . Overheated or highly volatile fuel is the main reason for vapour lock problem.

The effect of methanol addition on the VP of hydrocarbon- base gasoline (M 0) is shown in Table 3. A sudden rise in VP from 59.30 to 80.60 occurs after the addition of 5 vol.% methanol . Addition of more methanol to the base fuel , the VP of the blend reached a flat plateau till 10 vol.% methanol . Further methanol addition causes a slight decrease in VP .Other investigators reported that most of the VP increase occurs with the first 3 vol.% methanol addition [2] . These results strongly agree with what have been achieved by Salaheldin Safwat, 2016 . Vapour pressure of S1 engine varies with the season , the normal range is 48.2 KPa to 103.o KPa (7 psi to 15 psi) The obtained vapour pressure values , Table3 , are within the specifited range .

T50 represents the mid- range volatility of the investigated fuels . Based on the ASTM regulations, hydrocarbon – base gasoline has T50 value of 89 OC which is far from the minimum (77 OC) value required for any fuel before blending . any alcohol. After the addition of 5 and 10 vol % methanol , T50 dropped to 85 OC and 81 OC , respectively . However , T50 dropped to 63-62 OC when methanol addition reached 15-20 vol.% According to ASTM volatility regulations , M5 and M10 blends match with the international gasoline volatilities [21,22] . The effect of methanol addition on T50 values of the investigated blends is illustrated in Figure 2 .

The effect of methanol addition on Vapour – lock index (VLI) is best illustrated in Figure 2 . VLI= 10VP+ 7 (E70) where VP in KPa and E70 is the vol.% evaporated at 70 OC (located from the distillation curve) . As illustrated in Figure 3, the VLI of base (M0) is 803 , a sharp increase to 1092 occurs after the addition of

5 vol.% methanol (M5). The calculated VLI for M10, M15 , M17.5 and M20 reached 1102,1100 ,1129, and 1158 respectively . VLI varies with the same season, the normal range is 800 to 1250 . The examined fuel and fuel blends are within the specified VLI range. The lower VLI values provide greater protection against vapour lock and hot fuel handling problems [21].

The effect of methanol addition on temperature of vapour liquid ratio of 20 (T V/L =20) in OF is illustrated in Figure 4. T V/L =20 is the temperatures at which a gasoline exists as 20 volumes of vapour in equilibrium with one volume of liquid at atmospheric pressure. T V/L =20 is calculated from the formula [22].

T V/L =20 , (OF) = 114. 6 - 4.1(VP)+ 0.2(T10) + 0.17(T50)

Where VP (psi) ; T10 and T50 (OF).

Figure 4 illustrates that a sharp decrease in the temperatures of V/L =20 by the addition of 5 and 10 vol.% methanol , more methanol addition causes insignificant decrease in this temperature .T V/L =20 varies with the season , the normal range is 95 OF to 140 OF. The calculated values of T V/L =20 are in the range 138-116 OF (Table 3) . Gasolines or gasoline blends with OF higher value provide greater protection against vapour lock and hot fuel handling problems [21].

The driveability index (DI) has been developed to predict a fuel's cold – start and warm – up driveability , using T10 , T50 , and T90 (the temperatures for 10% , 50% and 90 % evaporated and the vol.% of added alcohol [22].

DI is calculated from these formulae :

DI(OF – derived) = 1.5(T10) + 3.0 (T50)+ 2.4(methanol vol.%) .
DI(OC - derived) = 1.5(T10) + 3.0 (T50)+ 1.33 (methanol vol.%) .

DI varies with gasoline grade and season , the normal range in the U.S. is 850 to 1275 (OF – derived) , 375-610 (OC - derived) . In other parts of the world, the range may be narrower. Lower values of DI generally result in better cold start and warm - up performance , but once good driveability is achieved , there is no benefit to further lowering the DI .[21,22].

Figure 5 depicts the effect of methanol addition on DI. It can be seen from this figure that increasing the concentration of blended methanol resulted in lowering the DI of the blend up to M15, further methanol addition does not cause any significant lowering of DI. The calculated DI values of investigated fuel blends , (M5-M20) are in the range from 1038 to 943 (OF – derived) which are lower than DI of the base fuel . Results pictured in Figure 5 indicated that the driveability index of a vehicle improves by using methanol blended gasolines (M5-M20) than methanol – free gasoline (M0) .

CONCLUSIONS

From this study, one can reach some conclusions :

1-Upgrading low – octane hydrocarbon fuel is possible by blending the required methanol content.
2-Gasoline blended with 5-10 vol.% methanol gave T50 values within the specified volatility requirement and match well with ASTM gasoline volatility regulations .
3-All the examined gasoline methanol blends are within the specified VLI range and provide greater protection against vapour lock and hot fuel handling problems .

Table 1-GC Analysis of Reformate

Hydrocarbon Totals by Group Type			
GROUP Type	Wt %	Vol.%	Mol.%
Total Aromatics	73.661	69.074	73.449
Total Iso- Paraffins	13.279	15.885	13.704
Total Naphthenes	3.081	3.294	3.132
Total Olefins	1.527	1.759	1.504
Total Paraffins	6.520	7.803	6.726
Total Unknowns	1.931	2.184	1.485
Total	100.00	100.00	100.00

Hydrocarbon Totals by Carbon Number			
GROUP	Wt %	Vol.%	Mol.%
Butanes	0.049	0.069	0.086
Pentanes	2.013	2.612	2.856
Hexanes	10.826	11.251	13.644
Heptanes	33.736	43.349	36/382
Octanes	29.587	28.808	28.120
Nonanes	14.190	13.467	12.003
Decanes	6.379	6.117	4.815
C11's	2.130	2.247	1.417
C12's	0.946	0.924	0.588
C13's	0.127	0.137	0.071
C14's	0.017	0.018	0.009
Total	100.00	100.00	100.00

Table 2- GC Analysis of Light Naphtha

Hydrocarbon Totals by Group Type			
GROUP Type	Wt %	Vol.%	Mol.%
Total Aromatics	2.800	2.076	2.819
Total IsoParaffins	46.290	46.994	45.646
Total Naphthenes	5.978	5.206	5.920
Total Paaffins	44.933	45.723	45.615
Total	100.00	100.00	100.00

Hydrocarbon Totals by Carbon Number			
GROUP	Wt %	Vol.%	Mol.%
Butanes	0,033	0.037	0.044
Pentanes	46.872	48.623	51.148
Hexanes	53.089	51.334	48.803
Heptanes	0,007	0.007	0.005
Total	100.00	100.00	100.00

Table 3 – Properties of The Investigated Fuels

Fuel Designation	M0*	M5	M10	M15	M17.5	M20
Fuel Compositions, vol.%						
HC-Base Gasoline	1oo	95	90	85	82.5	80
Methanol	——	5	10	15	17.5	20
Total	100	100	100	100	100	100

Distillation- ASTM- 86						
IBP , ^{O}C (F^{O})	36 (96.8)	36 (96.8)	36 (96.8)	36 (96.8)	36 (96.8)	36 (96.8)
10%, ^{O}C (F^{O})	55 (131)	44 (111.2)	45 (113.0)	45 (113.0)	44 (111.2)	43 (109.4)
50 %, ^{O}C (F^{O})	89 (192.2)	85 (185.0)	81 (177.8)	63 (145.4)	63 (145.4)	62 (143.6)
90 %, ^{O}C (F^{O})	152 (305.6)	151 (303.8)	152 (305.6)	149 (300.2)	150 (302.0)	149 (300.2)
FBP ,^{O}C (F^{O})	185 (365.0)	186 (366.8)	184 (363.2)	185 (365.0)	184 (363.2)	184 (363.2)

Driveabilily Index (DI)						
D I (^{O}C - derived)	402	479	456	426	428	426
DI(^{O}F – derived)	1079	1038	1033	942	945	943

Fuel Properties, vol.%						
Density	0.7544	0.7576	0.7598	0.7635	0.7639	0.7611
Aromatices, wt%	45.13	43.04	40.78	38.51	37.38	36.25
Benzene , wt%	——	0.73	1.51	2.34	2.79	3.25
Oxygen content, wt%	2.89	2.74	2.60	2.46	2.38	2.31
Oxidation stabilily , min.	480›	480›	---	480›	---	480›
Corrosivity , 3hr , 50 °C	1	1	1	1	1	1
Calorific value , MJ ⁄ Kg	43.28	43.26	43.21	43.17	43.12	43.08
Octane number , RON	83.4	87.5	90.5	94.2	95.5	97.5

Volatility Criteria						
VP, KPa at 37.8	59.30	80.60	80.10	74.30	75.10	75.85
E70, vol.% evaporated at 70 °C	30	38	43	52	54	58
VLI= 10(VP) + 7(E70)	803	1092	1102	1100	1129	1158
T_{VL} = 20 , ^{O}F	138	129	117	118	117	116

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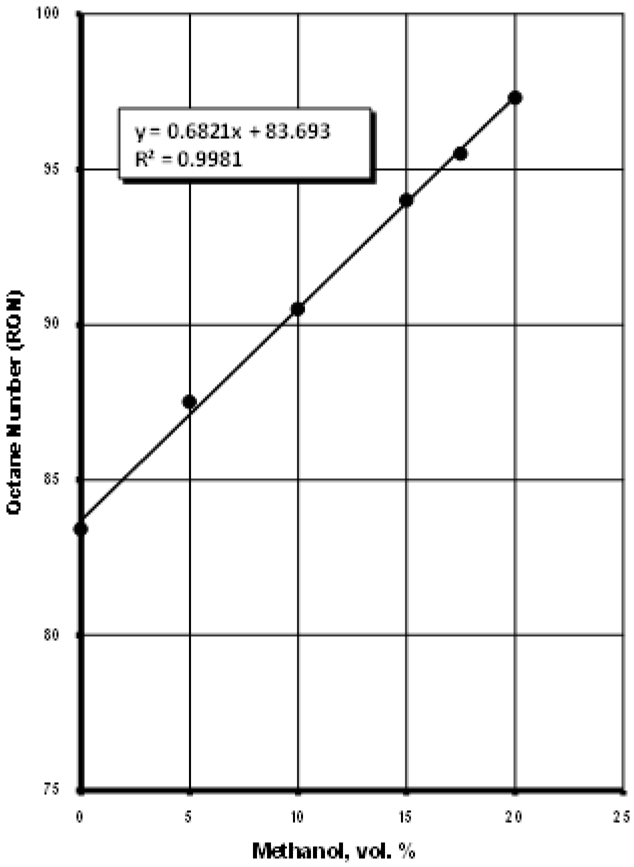

Figure 1 - Effect of Blended Methanol on Octane Number (RON) of HBG.

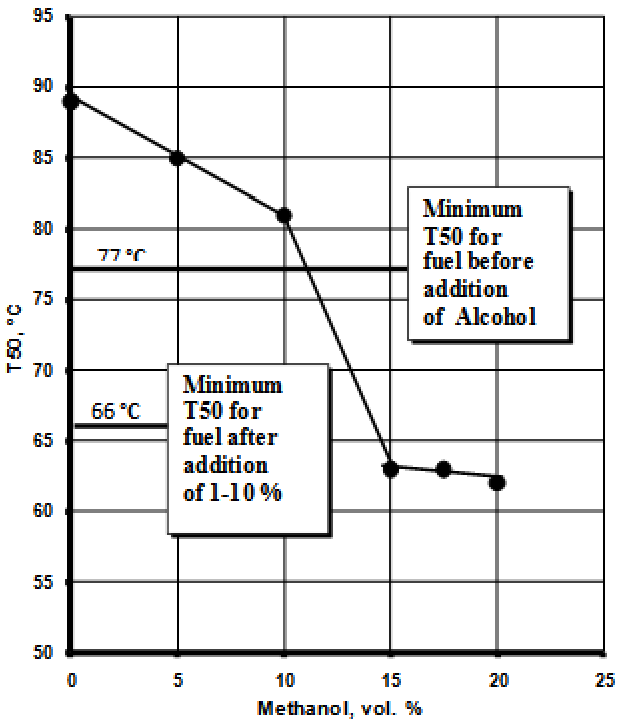

Figure 2 - Effect of Blended Methanol on T50 Value of HBG.

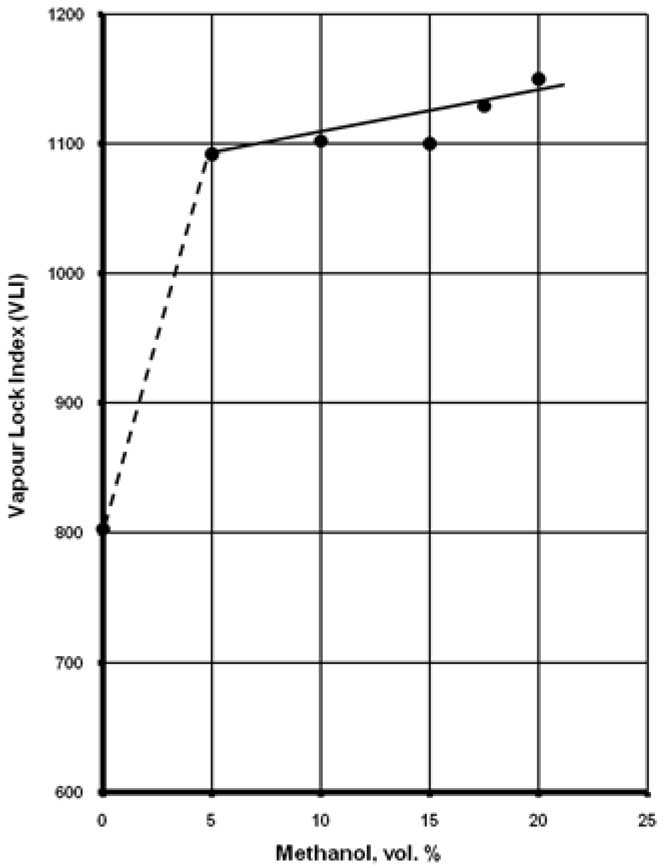

Figure 3 -Vapour Lock Index as a Function of Blended Methanol .

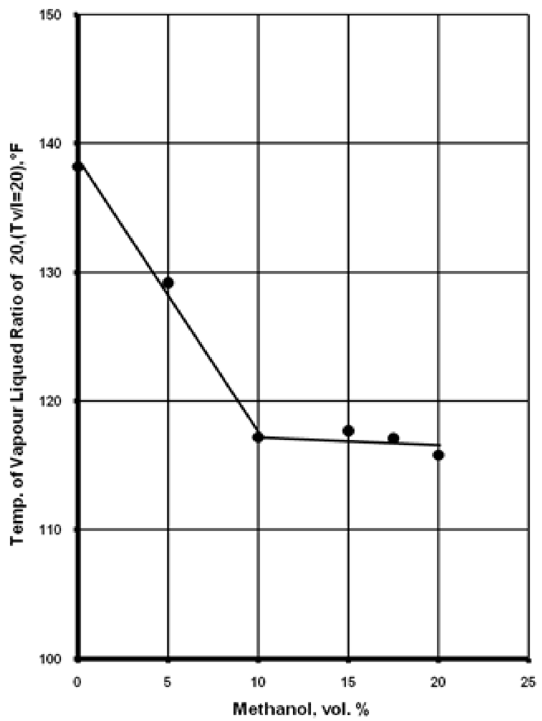

Figure 4 -Temperature of Vapour Liquid Ratio of 20 as a Function of Blended Methanol .

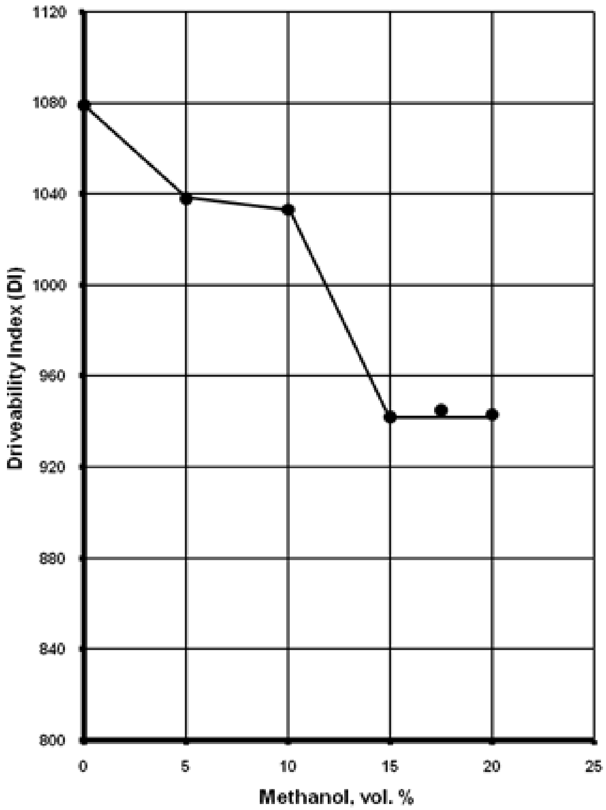

Figure 5 -Relationship Between Driveability Index and Blended Methanol .

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