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IMPROVEMENT OF MOGAS OCTANE NUMBER UTILIZING OCTANE ENHANCERS

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Abstract. In this paper different fractions of Mogas components e.g. Light Naphtha, Heavy Naphtha & Reformate produced in Aden Refinery Company beside to three blends of imported Mogas and Naphtha were studied by adding different octane enhancers and determined the increase of octane number. The petroleum streams were tested by ASTM standard methods, such as RVP, Gravity, Distillation temperatures, Sulfur content, PONA content, and octane number measuring by CFR engine. The octane enhancers used to treat Mogas and its components were organ metallic type (Ferrocene& MMT) and non-organometallic (EPT012 & OCT^{+}1025). The dosing rate was in ppm in the range of 10 to 50 for the metallic type, while for non-metallic was in % vol. from 1 to 3. Using of Ferrocene or MMT in concentration as low as 30 ppm will boost the Reformate octane by 3 numbers which enable Aden Refinery to produce Mogas 90 from Catalytic Reformer Unit with no need to blend the Reformate with imported Mogas 92^{+}. EPT012 & OCT^{+}1025 gave an increase in RON by 7.6 and 9.1 respectively when adding 2% vol. of these additives which enable Aden Refinery to upgrade part of the Naphtha into Mogas and improve the economics of the Refinery.

Keywords: *Mogas, Octane enhancer, Internal combustion Engine.*

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Abbreviation

CFR- Cooperative Fuel Engines
RON- Research Octane Number
AKI- Antiknock Index
LSRN- Light Straight Run Naphtha
Mogas- Motor Gasoline
MMT- Methylcyclopentadienyl Manganese Tricarbonyl

1. Introduction

Motor gasoline (Mogas) components vary widely in their physical and chemical properties. The fuel properties must be balanced to give satisfactory engine performance over an extremely wide range of operating conditions. The prevailing standards for fuel represent compromises among numerous quality, environmental and performance requirements. Additives are often used to provide or enhance specific performance features.

Gasoline components are blended to promote high antiknock quality, ease of starting, quick warm-up, low tendency to vapor lock, and low engine deposits. Gruse and Stevens give a very comprehensive account of properties of gasoline and the manner in which they are affected by the blending components. (Gruse & Steven, 1960)

The octane number represents the ability of gasoline to resist knocking during combustion of the air-gasoline mixture in the engine cylinder. Gasoline must have a number of the other properties in order to function properly and to avoid damage to the environment (Antos *et al.*, 1995) www.elsevier.com/locate/pecs(2017)

To boost the octane number of gasoline, refiners used from the early twenties of the last century cheap octane enhancers such as tetraethyl & tetra methyl lead. Later on in the eighties banning of lead addition was widely adopted all over the world due to its harmful effect on human and environment.

Octane ratings in gasoline are conventionally boosted by addition of aromatic and oxygenated compounds. However, as a result of increasingly stringent environmental legislation, the content of these compounds in gasoline is being restricted and thus industry has been forced to investigate alternative processes to reach the required octane levels. (Rafael *et al.*, 2008). Modern motor gasoline represents a mixture of components, which are obtained as a result of various technological processes of the petroleum.

2. Scope of the present work

Leaded Mogas is produced and consumed in Yemen with no alterations taken since those days of BP Aden until the year 2012 when Yemeni government decided to ban leaded gasoline. New regulations forced Aden Refinery Company to substitute leaded gasoline of 83 RON with unleaded gasoline with 90 RON. International specifications for petroleum products are submitted periodically for review and upgrading in accordance to technology, climate, living and environmental conditions changes. Decision of shifting from leaded to unleaded gasoline was accidently taken with no pervious arrangements. The Refinery was obliged to provide the local market with unleaded Mogas which was imported from international market while to export all its production from light and heavy naphtha which was used to produce leaded gasoline. Export of naphtha and import of unleaded gasoline heavily attacked the refinery economics and caused a big loss in profit.

To reduce the economical negative effect of distribution of unleaded Mogas, the Refinery operated the reforming unit and blended the imported unleaded Mogas with reformate produced in reformer unit. Unfortunately this quantity of reformate is limited. The refinery studied the possibility of using different octane enhancers to improve the economy of unleaded Mogas production.

3. The main aims of this study

As a main aims of the paper we consider ther following items:

1. Improve the octane number of the Unleaded Mogas produced in Aden Refinery Company.
2. Reduce the production cost of Unleaded Mogas using different octane enhancers.
3. Study the optimum dose of octane enhancer added to the Mogas.

4. Upgrading of low octane heavy naphtha through processing in Reformer Unit and using reformate as Mogas product by boosting its octane number by the addition of octane.

4. Experimental work

Cooperative Fuel Research Engines (CFR), Designation: D 2699

- The Research RON of a spark-ignition engine fuel is determined using a standard test engine and operating conditions to compare its knock Characteristic with those of PRF blends of known RON.
- Compression ratio and fuel-air ratio are adjusted to produce standard AKI for the sample fuel, as measured by a specific electronic detonation meter instrument system. A standard AKI guide table relates engine CFR to RON level for this specific method. The fuel-air ratio for the sample fuel and each of the primary reference fuel blends is adjusted to maximize AKI for each fuel.
- The fuel-air ratio for maximum AKI. May be obtained:

a- By making incremental step changes in mixture strength, observing the Equilibrium AKI value for each step, and then selecting the condition that maximizes the reading.

b- By picking the maximum AKI as the mixture strength is changed from either rich-to-lean or lean-to-rich at a constant rate.

Preparation of Gasoline Samples for Testing

1. Heavy Straight Run Naphtha (HSRN) Base *(75°C - 143°C)*

A. Mother solution: 25 g of Ferrocene powder is dissolved in one liter of Heavy Naphtha and kept ready for testing. According to above 1ml of solution contains 0.025 g of Ferrocene. Referring to molecular weight of Ferrocene compound ($Fe(C_5H_5)_2$=186g/mol), molecular weight of Iron (Fe= 56g/mol). Each1 ml of solution above contains ((25/1000)*(56/186))= 0.0075g Fe/ml of solution.

B. Light Straight Run Naphtha (LSRN) Base (30°C - 124°C)

To prepare the mother solution of Light Naphtha, we repeat the same procedure as with Heavy Naphtha.

Mogas Base (RON 84) To prepare the mother solution of Mogas RON 84, we repeat the same procedure as per Heavy Naphtha.

Reformate

To prepare the mother solution of Reformate, we repeat the same procedure as per Heavy Naphtha.

Additives based on metallic compound has been taken are Ferrocene and MMT. Additives based on non-metallic compound has been taken are EPT012 and OCT^+1025.

Samples has been taken for the study

Cooperative Fuel Research (CFR):

According to ASTM the following tests has been done such as: Density, Relative Density (Specific Gravity), Sulfur in Gasoline by Energy-Dispersive X-ray Fluorescence Spectrometry, Designation: D 6445 – 99

And Distillation of Petroleum Products at Atmospheric Pressure Designation: D 86 – 08a1.

5. Results and discussion

Gasoline is produced in refinery through distillation process of crude oils. This gasoline is low octane number and needs further treatment in different refinery processing units to be a marketable product and matches the specified physical and chemical properties.

A characterization of the initial components, mainly determination of physical properties and was done as shown in Table 1.

Three blends of Mogas different octane numbers 84, 86 & 88 were prepared by mixing different portions of Light Naphtha and Imported Unleaded Mogas. The main physical properties of the blends were determined and shown in Table 2.

Effect of Organometallic Octane Boosters

Metallic octane boosters include many different types of organometallic compounds in which the carbon atoms are bonded directly to the metals. (Hartley *et al.*, 1982). Of these are methylcyclopentadienyl manganese tricarbonyl (MMT) &dicyclopentadienyl Iron (Ferrocene) which will be subject of this study.

Ferrocene Addition:

Ferrocene was added at different concentrations to Light & Heavy Naphtha produced in Aden Refinery directly from processing of indigenous Mareb Crude oil in Crude Distillation Units. Octane number was measured by CFR engine the results are shown in (Fig. 1).

Addition of Ferrocene in concentrations as low as 10 to 50 ppm Fe increased the Octane number (RON) gradually at an average of 1.1 Octane number per each 10 ppm Fe addition.

Table 1. Physical Properties of Mogas Components

PROPERTY	LIGHT NAPHTHA	HEAVY NAPHTHA	IMPORTED MOGAS	REFORMATE
RON	71.0	59.1	90.5	88
DISTILLATION,				
IBP	30	75	35	42
10%	41	87	54	70
20%	45	91	62	86
30%	49	96	71	100
40%	53	101	83	111
50%	58	106	98	122
60%	65	110	111	132
70%	73	115	123	142
80%	83	121	138	152
90%	97	130	160	160
FBP	124	143	199	205
S.G. @ 60/60 F	0.6773	0.7508	0.74	0.7667
RVP @ 37.8 C, PSI	13.1	2.7	9.0	5.4
SULPHUR	0.0015	0.0042	0.02	0.0007

The promised results encouraged to apply the Ferrocene addition to Mogas product with different RON. Octane number was measured by CFR engine the results are shown in (Fig. 2). Addition of Ferrocene to Mogas in concentration of 50 ppm Fe increases the Octane number from 2.2 to 3.5 numbers depending on the Mogas RON, the lower octane the higher the effect. These results in accordance with Stratiev & Kirilov findings. *(*Stratiev & Kirilov, 2009).

Table 2. Physical Properties of Mogas Blends

PROPERTY	MOGAS 84 RON	MOGAS 86 RON	MOGAS 88 RON
DISTILLATION			
IBP	36	37	40
10%	52	55	57
20%	58	62	64
30%	69	71	73
40%	79	81	85
50%	94	97	100
60%	104	109	111
70%	116	120	122
80%	129	135	136
90%	152	158	161
FBP	190	194	196
S.G. @ 60/60 F	0.7249	0.7320	0.7413
RVP @ 37.8 C, PSI	9.6	9.4	9.2
SULPHUR MASS%	0.0203	0.0229	0.0256

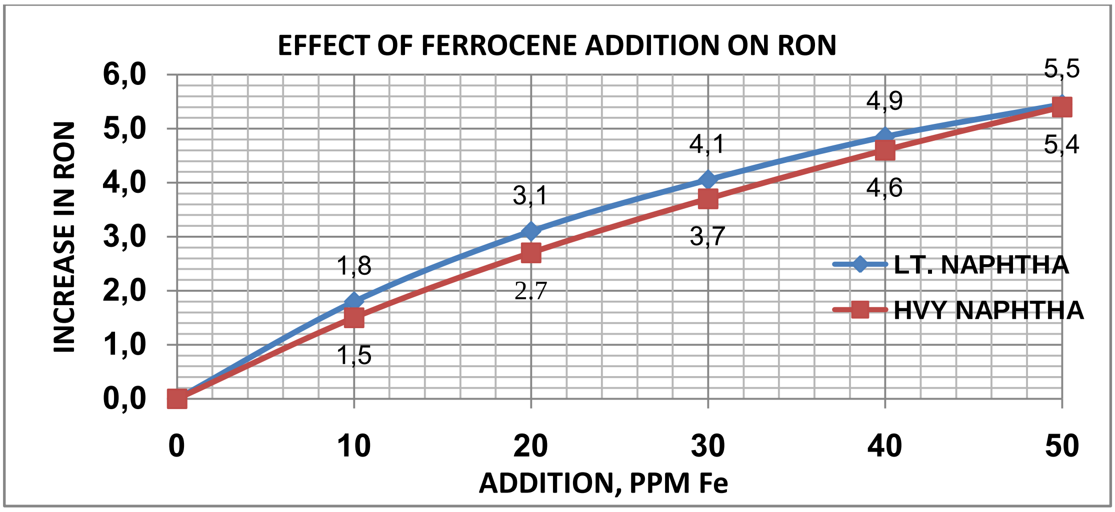

Figure 1. Addition of Ferrocene to Light & Heavy Naphtha

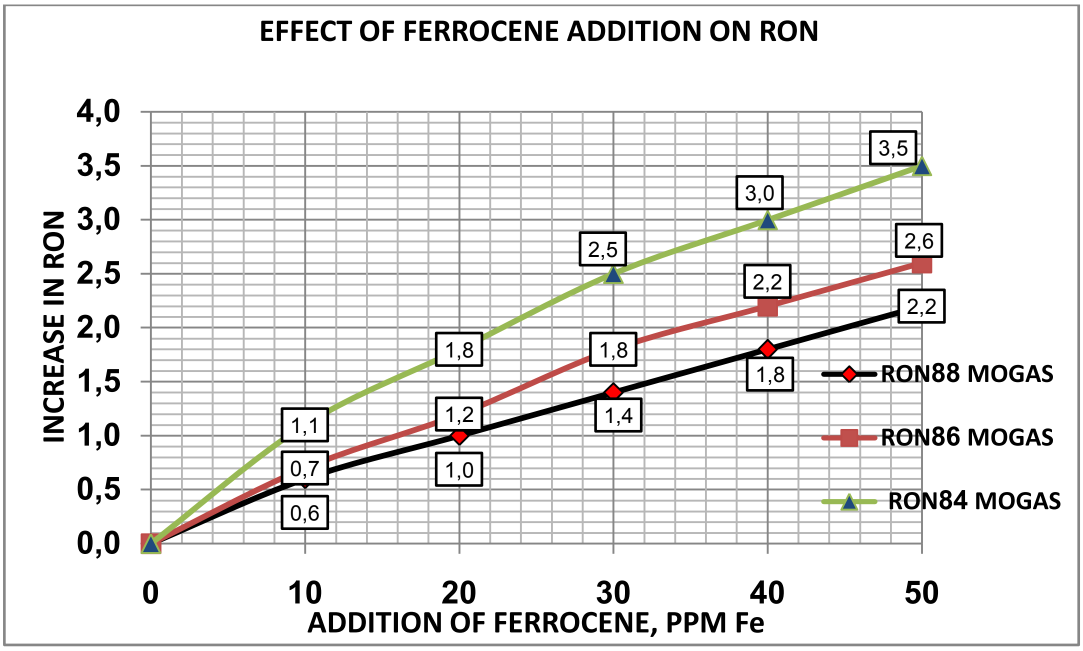

Figure 2. Addition of Ferrocene to Mogas Different RON

Addition of Ferrocene also tried on Reformate product with different RON produced in Aden Refinery from Catalytic Reforming Unit. Octane number was measured by CFR engine the results are shown in (Fig. 3). Addition of Ferrocene in 50 ppm Fe led to increase of RON from 3.5 to 4.2 depending on Reformate RON, the lower octane the higher the effect. The results are courageous and will help to produce Unleaded Mogas (RON=90) directly from the unit with no need to blend it with Imported Mogas high octane number e. g 92+ as it is practiced. Addition of Ferrocene even in low concentration as low as 30 ppm will compensate the deficit in Octane number and reduce the severity of the Catalytic Reforming Unit conditions. Production of Reformate with 87 RON plus 30 ppm Ferrocene will ensure on specification Mogas product (RON=90).

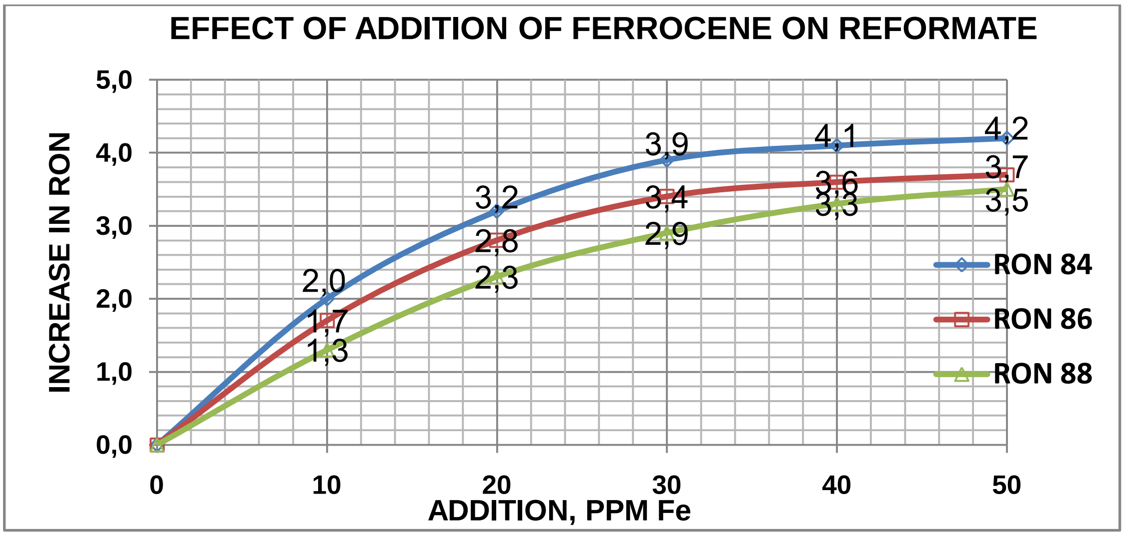

Figure 3. Addition of Ferrocene to Reformate different RON

MMT (HITEC® 3000) Addition:

Addition of MMT as **HiTEC®3000** to Naphtha in low concentration (10 to 50 ppm MMT) increased the RON. Light Naphtha positively affected by the dosing for the rates 10 to 30 ppm MMT, further addition has slight effect on RON. The effect of MMT on Heavy Naphtha was nearly linear proportional to the studied concentration 10 to 50 ppm MMT.

As shown in (Fig. 4). Addition of metallic additives Ferrocene& MMT to Light & Heavy naphtha in the range of 50 ppm metal increased the RON by 5.0 to 5.5 unit. It is visible that they have nearly the same effect.

MMT as **HiTEC®3000** was added to Mogas different in RON (84, 86 & 88) in concentration of 10 to 50 ppm MMT. Octane number was measured by CFR engine the results are shown in (Fig. 5).

Addition of MMT to Mogas in the range of 10 to 50 ppm increased the RON from 3.1 to 4.6 units depending on the Mogas RON, the lower the RON the higher the effect, these results agree with Hollrah& Burns study. (Hollrah & Burns, 1991).

The addition of the first 10 ppm MMT increased the RON significantly while further addition shows less effect.

In comparison between Ferrocene and MMT regarding their effect on Mogas different RON, MMT shows better effect where it increased the RON in the studied range of addition (3.1-4.6) while Ferrocene increased the RON (2.2-3.5). MMT is better by nearly one unit octane.

To discuss the effect of octane boosters, it is important to know what happens in the internal combustion engine. At some conditions, normal combustion of fuel/air mixture may be destroyed and becomes knocking combustion. Knocking combustion is characterized with formation of knocking waves. It is sign of incomplete burning in the combustion chamber and associated with smoking (Petkov *et al.*, 1995).

The main reason for knocking is formation and accumulation of active peroxides which decompose in the next phase of combustion giving up their excessive energy and causing an explosive combustion of the fuel with accelerating of the flame velocity up to ten times. Peroxides (R-O-O-R) and hydroperoxides (R-O-O-H) are the first products of hydrocarbons oxidation, further oxidation leads to accumulation of aldehydes, organic acids, alcohols and other compounds. Final products are carbon dioxide and water.

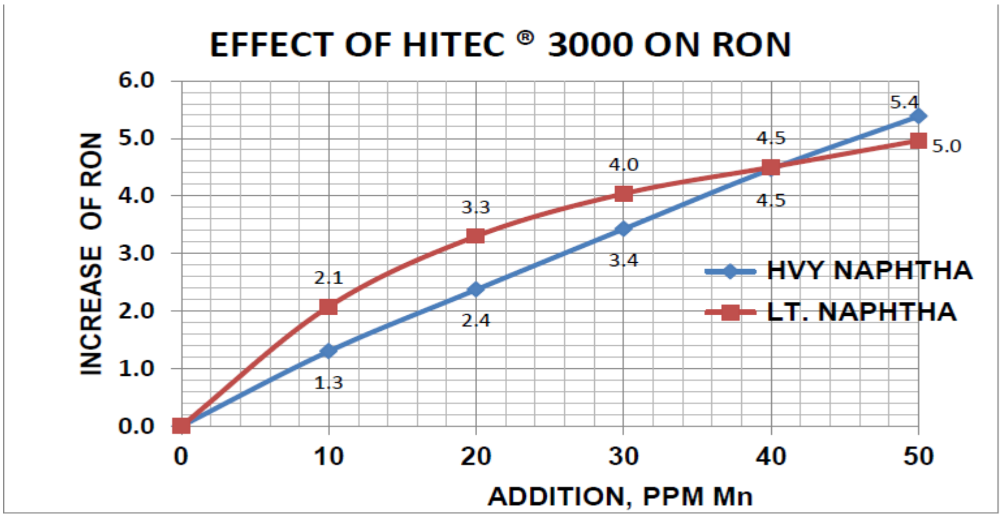

Figure 4. Addition of MMT (HITEC®3000) to Light & Heavy Naphtha

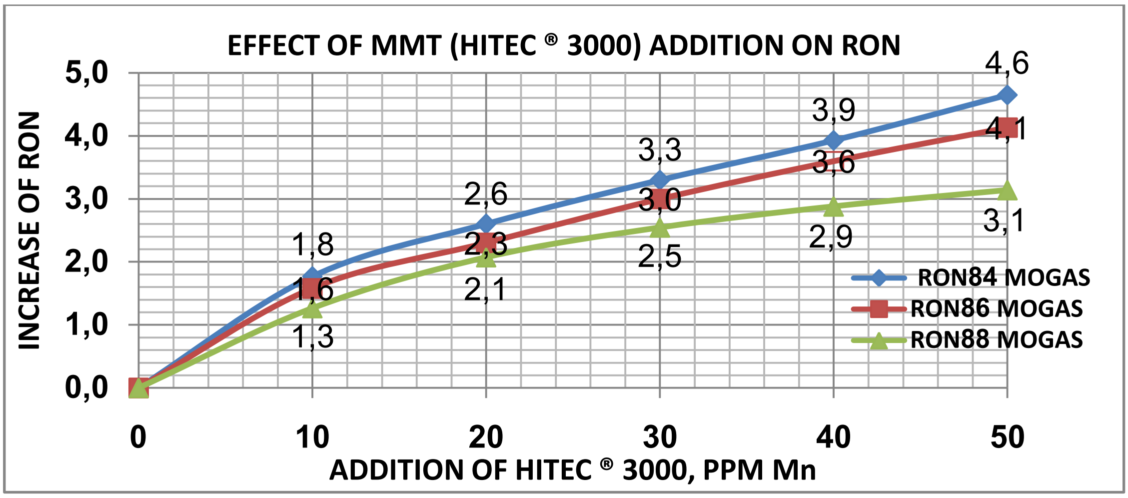

Figure 5. Addition of MMT (HITEC®3000) to Mogas different in RON

The products of oxidation are instable active compounds, which again decompose with releasing heat to be as a source for oxidation reactions

In the engine, oxidation of the fuel with oxygen from the air begins since the fuel/air mixture enters the combustion chamber. The temperature and the pressure of the chamber proportionate with the compression ratio. Increasing the temperature and the pressure in the chamber lead to increase the rate of oxidation process and formation of the peroxides. Hydrocarbons with different structures begin to oxidize when they reach a limited temperature. For example propane, toluene and ethyl alcohol begin to oxidize at 295, 550 and 445 °C respectively.

The rate of oxidation sharply increases after the fuel is ignited and the front of flame proceeds. At the combustion of fuel/air mixture, the temperature and pressure of the combustion chamber increases leading to increase the rate of oxidation of the unburned hydrocarbons in the end part of the chamber. The quantity of peroxides increases and reaches a critical limit at which a self-ignition occurs associated with an explosion.

Effect of Non- Organometallic Octane Boosters

The plasma hydrogen decomposed from this additive when is heated, then combine with active Free Radical of gasoline together, will produce stable molecular which can reduce the Free Radical that comes from Thermal Radiation and reduce the burning point. This additive can help gasoline to fully homogenous combustion, increase power, eliminate carbon deposition and save energy. (www.czbaolong.com)

EPT012 was added to Mogas product with different RON, octane number was measured by CFR engine, and the results are listed in (fig. 6). Due to limited quantity of EPT012, study was restricted on two types ofMogas 84 & 88 RON.

Addition of EPT012 significantly increased the RON of the Mogas, the lower is the RON the higher is the effect. The increase in RON is gradually decreased by increasing the rate of addition.

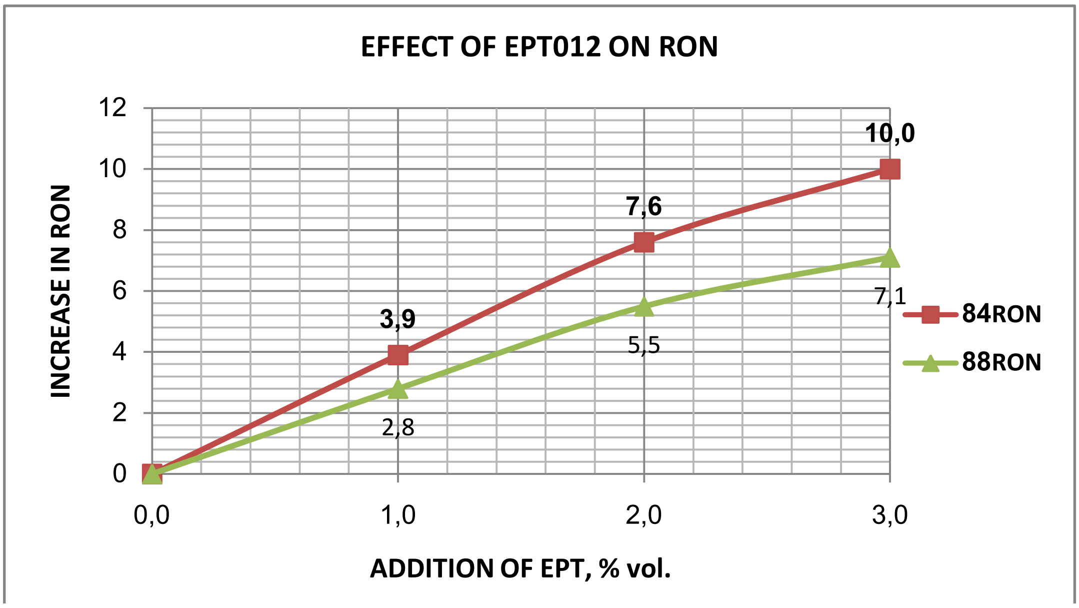

Figure 6. Effect of EPT012 Addition on Mogas Different in RON

The increase of RON for the Mogas under study was ranged from 7.1 to 10.0 Octane number by addition of 3% vol. of the EPT012 additive.

Another non-metal additive **OCT$^+$1025** was added to Mogas product with different RON, octane number was measured by CFR engine, and the results are shown in (Fig. 7).

OCT$^+$1025 shows positive effect in increasing the RON even at lower percentages (fig.7). By the addition of 2% vol. an Increase of 7.3 to 9.1 was obtained for Mogas RON 88 & 84 respectively. In comparison with EPT012 this increase was 5.6 to 7.6 for the same % vol. of addition and RON. It is concluded that OCT$^+$1025 more efficient than EPT012 for the Mogas under study.

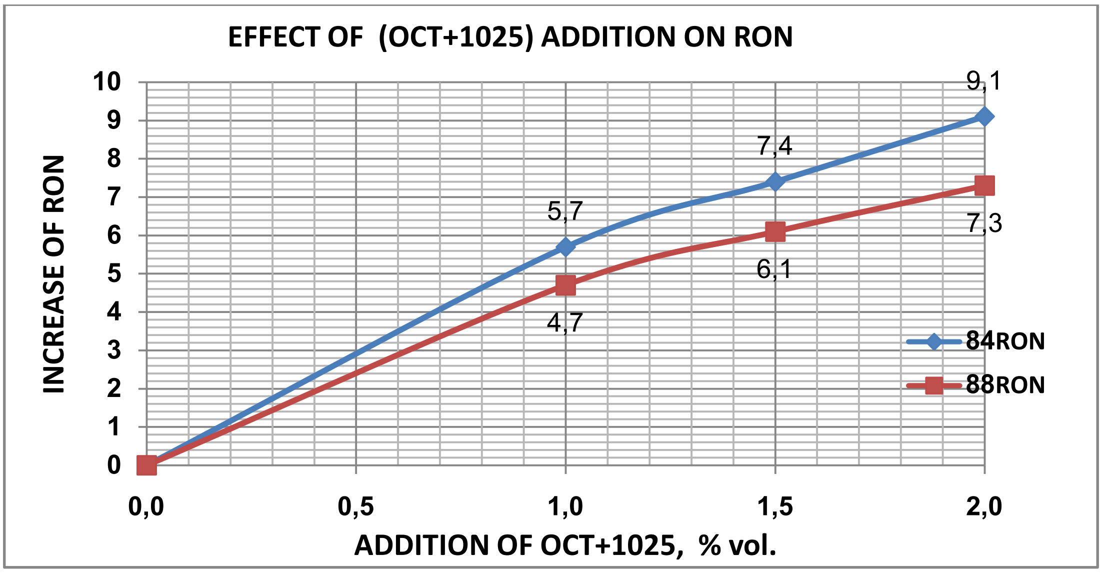

Figure 7. Effect of (OCT+1025) Addition on Mogas Different RON

6. Conclusion

In this study metallic (Ferrocene& MMT) and non-metallic additives (EPT012 & OCT^+1025) were used to treat Mogas and its components. Treatment of Mogas different RON (84, 86 & 88) and its components i.e. Light & Heavy Naphtha and Reformate with additives led to increase in RON. Increase in RON depends on Mogas neat RON, the lower the RON the higher is the effect (increase). The dosing rate was in ppm in the range of 10 to 50 for the organometallic type, while for non-organometallic was in % vol. from 1 to 3.

The effect of organometallic additives Ferrocene& MMT was nearly the same for the Light & Heavy Naphtha with an average increase of 1.1 RON for each 10 ppm additive in the studied range. This effect on Mogas RON (84, 86 & 88) is slightly less.

Using of Ferrocene or MMT in concentration as low as 30 ppm will enable to produce Mogas 90 from Catalytic Reformer Unit with no need to blend Reformate with imported Mogas 92^+.

EPT012 & OCT^+1025 gave an increase in RON by 7.6 and 9.1 respectively when adding 2 % vol. of the additives.

OCT^+1025 shows a significant effect rather than EPT012. Application of EPT012 or OCT^+1025 in Aden Refinery Company will depend on economical evaluation, price of the additive in relative to RON increase.

It is recommended to study other new generation of non-metallic additives that contains no N-Methyl aniline such as ETP045.

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