Full Length Research Paper

Evaluation and improvement of gasoline and naphtha cut of Tawke crude oil wells, Zakho

S.A. Naman*, K.A.Maher, F. M. S. Amin

Department of Chemistry, Faculty of Science, University of Zakho, Zakho/Irak

Accepted 03 November, 2011

Gasoline cuts have been separated from crude oil of Tawke wells (fourth and eighth) according to ASTM method at one atmosphere. Physical properties of each gasoline have been determined. Also chemical constituents of these gasolines have been examined using gas chromatography and compared with Naphtha Tawke Refinery. Percent of each straight run gasoline from crude oil of both wells have been determined with their Octane Numbers (RON and MON). The current research has been performed to increase the Octane Number of both gasoline and Naphtha using series of oxygenated and organometallic additives. Also mixed additives of oxygenated and organometallic have been added to these gasoline and Naphtha in order to find the enhancement in Octane Number. These mixtures give more increases in Octane Number than pure oxygenated or organometallic additives.

Keywords: Tawke Wells Number 8 and 4(TW8, TW4), Octane Ratings, Spesific gravity(SG), Aniline Point, Flash point, Pour point, Octane Number.

INTRODUCTION

Crude Oil

Crude oil is a mixture of gaseous, liquid, and solid hydrocarbon compounds and also contains small quantities of nitrogen-, oxygen-, and sulfur-compounds as well as trace amounts of metallic constituents. Crude oil is a mixture of compounds boiling at different temperatures that can be separated into a variety of different generic fractions by distillation. And the terminology of these fractions has been bound by utility and often bears little relationship to composition (James, 2006). The composition of petroleum can vary depending on many factors, like the location and the age of the field (Anna, 2007). Organic compounds that founded in Crude oil range from methane to extremely heavy hydrocarbon molecules with up to 80 carbon atoms (Elstrott 2011). The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and various aromatic hydrocarbons (Riazi, 2005). The more important distillate products from crude oil are.

Naphtha is a liquid petroleum product. Full range naphtha is defined as the fraction of hydrocarbons in petroleum boiling between $(30\,^{\circ}\text{C})$ and $(200\,^{\circ}\text{C})$. It consists of a complex mixture of hydrocarbon molecules generally having between (5 and 12) carbon atoms. It typically constitutes $(15\text{--}30\,\%)$ of crude oil, by weight. Naphtha clasify to two types: Light naphtha is the fraction boiling between $(30\,^{\circ}\text{C})$ and $(90\,^{\circ}\text{C})$ and consists of molecules with (5--6) carbon atoms. Heavy naphtha boils between $(90\,^{\circ}\text{C})$ and $(200\,^{\circ}\text{C})$ and consists of molecules with (6--12) carbons (prestvic, 2004) (James, 2005).

Gasoline

Gasoline is a mixture of hydrocarbons that boils below 180°C (355°F) or, at most, below 200°C (390°F). The hydrocarbon constituents in this boiling range are those that have four to twelve carbon atoms in their molecular structure (James, 2002) Several compounds can be added to the gasoline e.g., antiknock, detergent, antirust, antioxidant and anti-icing additives. With the restrictions on use of lead as an

Naphtha

^{*}Corresponding author email: salah.naman@yahoo.com

Physical Properties	TW4 Crude oil	TW4 Gasoline	TW8 Crude Oil	TW8 Gasoline	Naphtha
IBP		34		32	20
FBP		190		190	78
Density at 15.6 °C (gm/cm ³⁾	0.9046	0.7366	0.8986	0.7275	0.7045
Density at 90 °C (gm/cm ³⁾		0.6890		0.6837	
S.G at 15.6 ℃	0.9054	0.7373	0.8994	0.7282	0.7056
API° gravity	24.78	60.4549	25.82	62.9989	69.1317
Water content ppm.	0.4(%V)	157	0.24(%V)	44.3	
Vis.Kin. cSt at 15.6℃	17.325	0.9087	19.11	0.8483	
Vis.Kin. cSt at 90 ℃	4.1505	0.5210	4.284	0.4251	
Total Sulphur %W		0.0768		0.0373	
Flash Point ℃		-40		-41	
Aniline Point °C		62 - 63		65 - 66	72 - 74
Refractive Index at 20 ℃		1.413540		1.407439	1.387389
Pour point, ℃	< -40		-40		
Salt content, ppm	0.0186		0.0166		
H ₂ S content ppm	14.3622		5.1256		
Ash content, W %	0.48964		0.10989		

antiknock additive, other means of octane enhancement are used today include: The metallic additive, Changes in the refining process - increase of aromatics or alkenes. Addition of oxygen containing compounds (Annsofi, 1998).

Octane Ratings

Octane rating is measured at two different operational conditions. The rating measured at the more severe operating conditions is called the Motor Octane Number (MON) and the rating measured at the less severe conditions is called the Research Octane Number (RON) (Annsofi, 1998).

Experiment

The Physical and chemical properties of crude oil, gasoline and naphtha have been determined according to specific ASTM methods. Specific Gravity (S.G) and API Gravity by Pyknometer Methods(IP 190 ASTM D 1217), Aniline Point(IP 2 ASTM D 611), Cloud Point(IP 219 ASTM 2520), Pour Point(IP 15 ASTM D 97), Flash Point by Cleveland Open Cup(IP 36 ASTM D 92) for crude oil and Pensky-Martens Closed Cup Tester (D93-97) for gasoline, Kinematic Viscosity (IP 71 ASTM 445), Water in Crude oil and gasoline(IP 74 ASTM D 95), Ash(IP 4 ASTM 482), Refractive Index Measurement (ASTM D 2159), Preliminary distillation ASTM 86 Method, fraction distillation ASTM 285.

Analysis the Research Samples by Gas Chromatography (GC), the gas chromatographic (GC) analyses were carried out on an Acme 6000, Young line instrument gas chromatography and the program Application was: Oven : 20 °C hold 2 min. rate 5 °C /min. to 250C hold 3 min. Injection temperature: 250 °C, Carrier gas: Helium flow rate 20 ml /min, Detector: flame ionization (FID) 250 °C, Injected sample volume was 2.0 μL , Column: capillary column DB-wax.

RESULTS

Physical and Chemical Properties of TW4 and TW8 Crude Oils, Gasoline and Naphtha

Some of physical and chemical properties of both crude oils, Gasoline and Naphtha measured according to specific ASTM methods are illustrated in (table 1).

Fractions Distillation for TW4 and TW8 Crude Oil

The comprehensive assay of TW4 and TW8 crude Oil requires first stage fractionation

of it by fraction distillation, then separate and collect separately the gasoline from each our crudes at $(23 \, ^{\circ}\text{C})$ and (1atm.) within a boiling range between (IBP - 190 $^{\circ}\text{C}$). The results from fractional distillation show that the weight and volume percent in TW8 is higher than TW4, figure (1) according to volume and weight percentage. A good quality old deep crude oil may yield (20%)

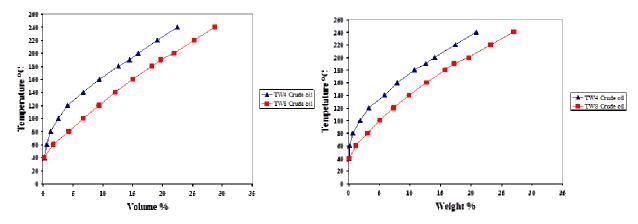


Figure 1. Fraction Distillation Curve for Cumulative Volume and Weight Distillate from TW4 and TW8 Crude.

Total Results	Crude Oil TW4	Crude Oil TW8
Volume (ml) of Crude Oil at 18 ℃	200	200
Weight (gm) of Crude Oil at 18℃	180.92	179.72
Gasoline Products % by Weight	12.5883	17.2439
Residue Volume %	76.8	70.4
Residue Weight %	78.6	72.3675
Losses by Volume %	0.75	0.9
Losses by Weight %	0.5561	0.65
Mid-boiling point °C for crude oil	171.2	155.4
Mid-boiling point ℃ for gasoline	143.8	123.3

Table 2. Totals result from Fraction distillation for TW4 and TW8 Crude oil

straight-run gasoline upon distillation (U.S. report 1995). Petroleum varies in composition from one oil field to another, from one well to another in the same field, and even from one level to another in the same well. This variation can be in both molecular weight and the types of molecules present in petroleum (James, 2006).

Chemical composition

Analysis the Research Samples by Gas Chromatography (GC) Application:

Crude Oil Analysis by Gas Chromatography

(Figures 2) shows, GC chromatogram for TW4 and TW8 crude oils, there are no large different between these two crude oils in chemical constituents, but a large different in the intensity of these chemical constituents can be noted. the different in the well depths which was (350-400 meters) for TW4 and (3000-3250 meters) for TW8, and that explain why the hydrocarbons in a non deep wells was easy exposed to volatilization, and also in non deep wells the pressure is

low so that's lead to exist of immature hydrocarbons and hence hydrocarbons with high molecular weight.

Naphtha Analysis by Gas Chromatography

The chromatogram of Naphtha (Boiling Range 20-78 ℃) figure (4) shown evident that peaks differing by three main peaks having retention time in (0.4500, 0.5625 and 2.2325

min.), this figure shows that the current Naphtha consisting of light hydrocarbons.

Gasoline Analysis by Gas Chromatography

Figures (5) and (6) show GC chromatogram for TW4 and TW8 gasoline. Appears number of peaks at the same retention time can be perceived, from comparison between GC chromatogram for TW4 and TW8 gasoline. The Area % or the intensity of these peaks in TW8 gasoline was more than in TW4 gasoline and this result illumine that the TW8 gasoline contained of hydrocarbons compound lighter than the TW4 gasoline

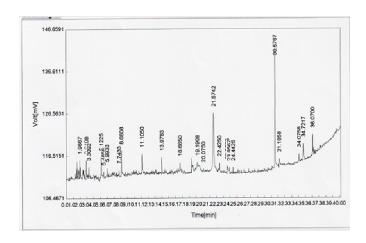


Figure 2. GC Chromatogram for TW4 Crude Oil

Table 3. Octane Numbers for TW4, TW8 Gasoline and Naphtha Measured by Zeltex 101C and Shatox instruments

Fuel	By Zel	tex 1010	2	By Sh	By Shatox			
	RON	MON	AKI	RON	MON	AKI		
TW4 Gasoline	72.9	69.4	71.2	73.2	69.9	71.6		
TW8 Gasoline	72.5	69.2	70.9	73.0	69.7	71.4		
Naphtha	71.2	70.2	70.7	71.8	69.9	70.9		

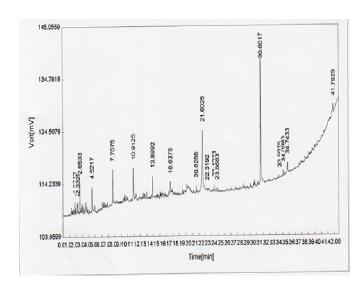


Figure 3. GC Chromatogram for TW8 Crude Oil

hydrocarbons.

Enhancements of Gasoline and naphtha Octane Number

The RON, MON and AKI values for TW4, TW8 gasoline and Naphtha measured by Zeltex and Shatox instrument without additives are shown in table 3.

Oxygenate Additives. [Measured by Zeltex instruments

Addition of Ethanol

According to our data in table (4) and figure (4) the addition of ethanol at low percentage is suitable for TW4 gasoline, but at high addition percentage the ONs increased suitably for Naphtha more than TW4, TW8

Table 4. Ethanol Effect on the ONs Value of TW4, TW8 gasoline and naphtha

No.	Additives	TW4 g	TW4 gasoline			gasoline		Naphtl	ha	
	% V.	RON	MON	AKI	RON	MON	AKI	RON	MON	AKI
1	0	72.9	69.4	71.2	72.5	69.2	70.9	72.5	69.2	70.9
2	1	75.7	70.4	73.0	75.5	69.4	72.4	75.5	69.4	72.4
3	1.9	81.0	71.3	76.1	74.3	69.6	72.0	74.3	69.6	72.0
4	2.9	74.2	70.4	72.3	74.8	70.0	72.4	74.8	70.0	72.4
5	3.8	77.4	71.0	74.2	75.1	70.2	72.7	75.1	70.2	72.7
6	4.8	77.5	70.8	74.1	75.5	70.5	73.0	75.5	70.5	73.0
7	5.7	77.8	71.2	74.5	75.9	70.6	73.2	75.9	70.6	73.2
8	6.6	78.2	70.3	74.2	75.2	70.9	73.1	75.2	70.9	73.1
9	7.4	78.5	71.7	75.1	75.2	71.0	73.1	75.2	71.0	73.1
10	8.3	78.7	71.0	74.8	75.1	71.2	73.1	75.1	71.2	73.1
11	9.1	78.8	71.8	75.3	76.1	71.6	73.8	76.1	71.6	73.8
12	10	79.3	71.6	75.5	76.0	72.0	74.0	76.0	72.0	74.0

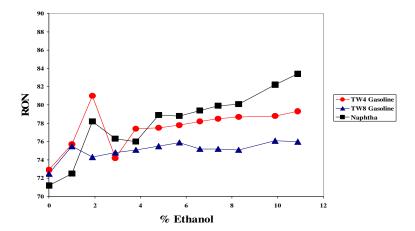


Figure 4. TW4, TW8 Gasoline and Naphtha Octane Numbers Effected by Ethanol

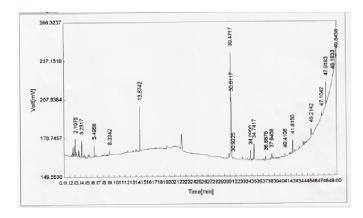


Figure 5. GC Chromatogram for TW4 Gasoline

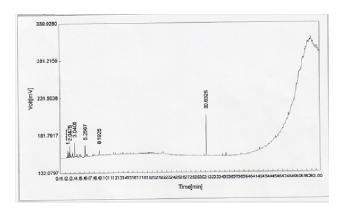


Figure 6. GC Chromatogram for TW8 Gasoline

Table 5. Methanol Effect on the ONs Value of TW4, TW8 gasoline and naphtha

No.	Additive	TW4 gasoline			TW8 ç	gasoline		Naphtl	ha	
	s % V.	RON	MON	AKI	RON	MON	AKI	RON	MON	AKI
1	0	72.9	69.4	71.2	72.5	69.2	70.9	71.2	70.2	70.7
2	1	79.0	68.8	73.9	75.6	67.4	71.5	79.3	69.7	74.5
3	1.9	77.9	68.3	73.1	76.3	67.5	71.9	76.0	68.7	72.3
4	2.9	78.7	68.5	73.6	76.4	67.0	71.7	78.5	69.7	74.1
5	3.8	80.9	69.1	75.0	76.6	66.5	71.5	82.5	70.3	76.4
6	4.8	79.4	68.6	74.0	76.7	68.6	72.6	81.7	69.4	75.6
7	5.7	77.9	68.5	73.2	79.9	70.7	75.3	83.6	70.4	77.0
8	6.6	77.4	67.6	72.5	81.6	70.5	76.1	82.8	71.0	76.9
9	7.4	77.2	68.2	72.7	82.1	71.0	76.5	81.1	70.2	75.7
10	8.3	77.7	67.6	72.7	81.1	72.2	76.6	81.6	71.3	76.4
11	9.1	77.7	68.2	73.0	82.4	72.1	77.3	83.2	72.1	77.6
12	10	78.6	69.5	74.0	82.9	73.4	78.1	88.3	73.6	81.0

gasoline

Addition of Methanol

According to our data in table (5) and figure (5) the addition of Methanol at low and high percentage is suitable for Naphtha. At low percentage the addition of Methanol is more suitable for TW4 gasoline compared with TW8 gasoline, but at high percentage is more suitable for TW8 gasoline.

Addition of Iso-propanol

According to our data in table (6) and figure (6) the addition of 2-Propanol at low and high percentage is suitable for TW4 gasoline. As in tables (6) the effect of addition IPA is approximately same for TW4, TW8

gasoline and Naphtha.

Organometallic Additives [Measured by Shatox Instrument]

Bis [Hydrazine dithiocarbamato Nickel (II)]

According to our data in table (7) and figure (6) the addition of *Bis [Hydrazine dithiocarbamato Nickel (II)*] at low and high percentage is suitable for TW4 gasoline.

Bis [Hydrazine dithiocarbamato Manganest (II)]

According to our data in table (8) and figure (8) the addition of *Bis [Hydrazine dithiocarbamato Manganest (II)]* at low and high percentage are suitable for TW4 gasoline

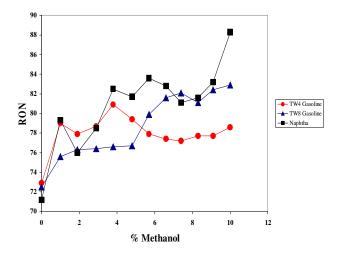


Figure 5. TW4, TW8 Gasoline and Naphtha Octane Numbers Effected by Methanol

Table 6. Iso-Propanol Effect on the ONs Value of TW4, TW8 gasoline and naphtha

No.	Additives	TW4 ç	TW4 gasoline			jasoline		Napht	ha	
	% V.	RON	MON	AKI	RON	MON	AKI	RON	MON	AKI
1	0	72.9	69.4	71.2	72.5	69.2	70.9	71.2	70.2	70.7
2	1	76.9	72.1	74.5	74.8	71.2	73.0	77.1	73.7	75.4
3	1.9	77.1	73.0	75.0	76.1	72.3	74.2	78.0	74.5	76.3
4	2.9	77.5	74.1	75.8	77.3	73.1	75.2	78.3	75.1	76.7
5	3.8	76.8	74.6	75.7	75.7	73.3	74.5	78.6	75.7	77.1
6	4.8	76.6	74.9	75.7	76.2	74.0	75.1	77.2	75.8	76.5
7	5.7	77.7	75.7	76.7	76.4	74.0	75.2	80.2	76.5	78.4
8	6.6	78.4	76.3	77.3	76.8	74.7	75.7	80.4	76.9	78.6
9	7.4	79.1	76.8	77.9	79.2	75.5	77.4	79.0	76.9	78.0
10	8.3	80.2	77.5	78.8	80.5	76.1	78.3	80.0	77.8	78.9
11	9.1	80.5	77.8	79.2	79.9	76.4	78.1	82.7	78.6	80.6
12	10	83.4	78.6	81.0	79.8	76.8	78.3	81.7	78.7	80.2

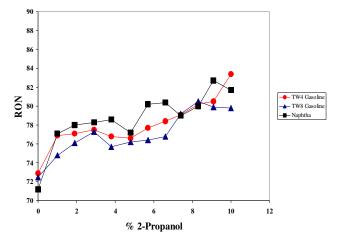


Figure 6. TW4, TW8 Gasoline and Naphtha Octane Numbers Effected by 2-Propanol

Table 7. Effect of Addition of Bis [Hydrazine dithiocarbamato Nickel (II)] on the ONs of TW4, TW8 gasoline and naphtha

No	Additives	TW4	TW4 gasoline			jasoline		Napht	Naphtha			
•	Weight in ppm	RON	MON	AKI	RON	MON	AKI	RON	MON	AKI		
1	0	73.2	69.9	71.6	73.0	69.7	71.4	71.8	69.9	70.9		
2	0.5	79.8	71.3	75.6	74.8	71.7	73.3	72.2	70.3	71.3		
3	1	78.8	70.6	74.7	78.4	73.1	75.8	72.4	70.5	71.5		
4	2.5	78.7	70.6	74.7	77.9	72.7	75.3	72.7	70.7	71.7		
5	5	80.0	72.5	76.3	77.3	72.3	74.8	73.5	70.9	72.2		
6	10	79.8	72.2	76.0	78.6	73.2	75.9	77.4	71.7	74.6		
7	20	79.4	71.7	75.6	80.0	73.4	76.7	78.3	71.9	75.1		
8	30	80.3	72.9	76.6	77.2	71.9	74.6	78.4	72.0	75.2		

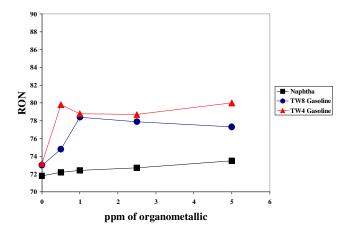


Figure 7. TW4, TW8 Gasoline and Naphtha O. N. Effected by Bis [Hydrazine dithiocarbamato Nickel (II)]

Table 8. Effect of Addition of Bis [Hydrazine dithiocarbamato Manganest (II)] on the ONs Value of gasoline of TW4 Gasoline

No.	Additives	TW4	gasolin	е	TW8 g	jasoline		Napht	ha	
	Weight in ppm	RON	MON	AKI	RON	MON	AKI	RON	MON	AKI
1	0	73.2	69.9	71.6	73.0	69.7	71.4	71.8	69.9	70.9
2	0.5	78.9	70.6	74.8	74.7	72.3	73.5	72.0	70.2	71.1
3	1	79.1	72.9	76.0	74.6	72.6	73.6	72.5	70.5	71.5
4	2.5	79.5	73.4	76.5	75.1	72.8	74.0	75.0	70.7	72.8
5	5	79.8	70.3	75.1	76.4	72.9	74.7	74.3	70.4	72.3
6	10	80.3	72.9	76.6	75.9	72.3	74.1	74.8	70.4	72.6
7	20	81.3	71.1	76.2	76.3	72.8	74.6	74.6	70.3	72.4
8	30	80.4	72.0	76.2	78.4	73.1	75.8	74.6	70.4	72.5

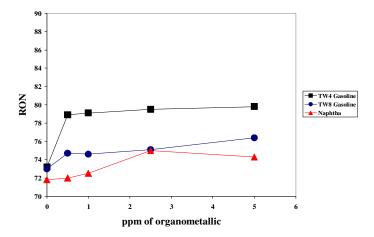


Figure 8. TW4, TW8 gasoline and Naphtha o. N. Effected by Bis [Hydrazine dithiocarbamato. Manganest (II)]

Table 9. Mixture of Ethanol and 1 ppm of *Bis [Hydrazine dithiocarbamato Nickel (II)]* with of TW4, TW8 Gasoline and naphtha

No	ppm of	%Ethanol	TW4	gasoline		TW8 g	jasoline		Napht	ha	
	Organo- metallic		RON	MON	AKI	RON	MON	AKI	RON	MON	AKI
1	0	0	73.2	69.9	71.6	73.0	69.7	71.4	71.8	69.9	70.9
2	1	1	80.1	73.9	77.0	77.6	75.4	76.5	74.8	70.1	72.5
3	1	2	81.8	76.4	79.1	79.9	77.2	78.6	78.4	73.1	75.8
4	1	3	83.2	77.2	80.2	81.3	79.9	80.6	81.5	77.6	79.6
5	1	4	85.5	77.8	81.7	82.2	80.8	81.5	84.3	80.3	82.3
6	1	5	88.6	79.0	83.8	85.4	81.2	83.3	86.9	82.1	84.5

Addition of Oxygenated and Organometallic Additives to TW4, TW8 Gasoline and naphtha Measured by Shatox Octane Meter

Ethanol with 1 ppm of Bis[Hydrazine dithiocarbamato Nickel (II)]

Mixture with (1 ppm) of organometallic additives and different percentage of Ethanol was prepared. Table (9) show the ONs for TW4, TW8 gasoline and Naphtha with this mixture.

According to our data in plot figure (9), TW4, TW8 gasoline and Naphtha ONs value were increasing linearly with increasing the percentage of Ethanol in this mixture. TW4 gasoline has the best compliance to this mixture. TW4 gasoline gives best value of ONs (88.6), then Naphtha (86.9) and at last TW8 gasoline (85.4). The best enhancement of the Octane Numbers value for TW4, TW8 gasoline and Naphtha, which is the aim of this study, was happened with this mixture.

Ethanol (5%) with Bis [Hydrazine dithiocarbamato Nickel (II)]

Mixture with constant concentration of Ethanol additives (5%) and different percentage of Bis [Hydrazine dithiocarbamato Nickel (II)] was prepared, the data illustrated in tables (10).

Figure (3.13), shows that TW4, TW8 gasoline and Naphtha ONs have the maximum value with (mixing 0.5 ppm 0f Organometallic with 5% Ethanol). After this point the ONs was decreased with increasing concentration of organometallic compounds in mixture. However, TW4 gasoline has the best ONs value (89.3), then TW8 gasoline (87.2), and at last Naphtha (87.1).

CONCLUSION

These results show that Octane Number of TW4, TW8 Gasoline and naphtha can be increased by addition

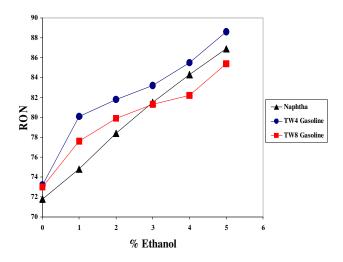


Figure 9. TW4, TW8 Gasoline and Naphtha O. N. Effected by Different Percent of Ethanol with 1 ppm of Bis [Hydrazine dithiocarbamato Nickel (II)]

Table 10. Mixture of (5%) Ethanol and *Bis [Hydrazine dithiocarbamato Nickel (II)]* with TW4, TW8 Gasoline and naphtha

No.	ppm of	%Ethanol	TW4	gasoline	9	TW8 g	gasoline		Naphtha			
	Organo metallic		RON	MON	AKI	RON	MON	AKI	RON	MON	AKI	
1	0	0	73.2	69.9	71.6	73.0	69.7	71.4	71.8	69.9	70.9	
2	0.5	5	89.3	79.8	84.6	87.2	83.8	85.5	87.1	82.9	85.0	
3	1.0	5	88.6	79.0	83.8	85.4	81.2	83.3	86.9	82.1	84.5	
4	1.5	5	85.4	77.6	81.5	84.7	79.6	82.2	83.0	79.7	81.4	
5	2.0	5	81.6	75.8	78.7	81.1	77.0	79.1	80.5	76.3	78.4	
6	2.5	5	80.2	74.3	77.3	80.5	75.2	77.9	78.6	72.4	75.5	

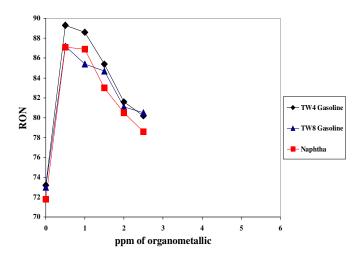


Figure 10. TW4, TW8 Gasoline and Naphtha O. N.Effected by (5%) Ethanol with Different Percent of *Bis[Hydrazine dithiocarbamato Nickel (II)*]

Table 11. Summary of the Best Effect of Oxygenated Additives

No.	Sample	Range of changing	Δ in ON
1	TW4 gasoline	72.9-83.4	10.5
2	TW8 gasoline	72.5-82.9	10.4
3	Naphtha	71.2-88.3	17.1

Table (12): Summary of the Best Effect of Organometallic Additives

No.	Sample	Range of changing	Δ in ON
1	TW4 gasoline	73.2-81.3	8.1
2	TW8 gasoline	73.0-80.0	7.0
3	Naphtha	71.8-78.4	6.6

Table 13. Summary of the Best Effect of Mixture of Oxygenated and Organometallic Additives

Sample	ppm of organometallic	%Ethanol	Range of Changing	Δ in ON
TW4 gasoline	0.5	5	73.2-89.3	16.1
TW8 gasoline	0.5	5	73.0-87.2	14.2
Naphtha	0.5	5	71.8-87.1	15.3

oxygenated additives, and the best results obtained are shown in table (11). Also the Octane Numbers value changed for each of our samples with the organometallic additives as shown in table (12). This increase in ONs value return to straight run gasoline, it may become more higher if we can produced other type of gasoline from these crude oils by thermal or

catalytical cracking, in future suggest refinery to these wells. Mechanism of these increasing in Octane Numbers is not easy to suggest as it is a function of complex constituents of crude oil and it needs more advanced research in this field. The best result obtained in this study is when, the mixture of oxygenated and organometallic additives has been adding to the samples, as shown in table (13).

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