

## Evaluation of Naphtha's Produced from Some Iraqi-Kurdistan Crude Oils Using Gas Chromatography and Determination of Their Clear (RON) by IR-spectroscopy

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**Abstract.** Three types of Crude oils namely (TQ<sub>1</sub>, TQ<sub>2</sub> from TaqTaq region and K<sub>1</sub> from Kirkuk oil field, have been fractionated to yield three different lights products (Light naphtha, Heavy naphtha and Natural gasoline) using true boiling point apparatus. All obtained light products have been fully evaluated according to Iraqi specifications. The clear Octane Number of hydrocarbon standard mixtures and petroleum products have been determined using IR-spectroscopic technique and derived equation from two statistical methods MLR (Multiple liner regression) and R.R (Ridge regression). The investigation included a hydrocarbon model composed of ten standard chemical compounds which used to prepare (333) mixtures in ratios ranged between 5% and 55%. In addition Gas Chromatographic technique with FID detector has been used for qualitative and quantitative analysis for all mentioned light products obtained from the three different Crude oils.

**Key word.** Gasoline, Naphtha, Octane Number, IR-spectroscopy, Gas Chromatography

### 1. Introduction

Gasoline consisted almost entirely of a mixture of hydrocarbons derived from Crude oil and boiling between 25°C to 220°C [1], the separation and quantization of hydrocarbon group of gasoline is difficult because it deals with a large number of very similar molecules. Therefore, the most typical method for the compositional analysis of total paraffinic, naphthenic and aromatic hydrocarbons is Gas Chromatography and near-Infrared (NIR) spectroscopy [2-4]. Octane Number is an important physical parameter of gasoline [5], it is the resistance to pre-ignition, the higher the Octane Numbers the greater the fuels resistance to knock [6]. High-Octane Number gasoline burns slower than low Octane Number gasoline. The slow burn prevents engine knock when cylinder pressure are high [7]. Gas Chromatography is the most powerful and typical separation method for the compositional analysis of a complex mixture of petroleum hydrocarbon [8,9]. The advantage of GC/FID is its sensitivity to a broad range of hydrocarbon compounds. Flame Ionization Detectors are destructive detection system because the analyte is combusted during detection [10]. Infrared spectroscopy measures the vibration (stretching and bending) that occurs when a molecule absorbs energy (heat) in the infrared region of the electromagnetic spectrum. Different functional groups and bond types have different IR absorption frequencies and intensities [11]. Alternatively, NIR spectroscopy is an excellent analytical method for the identification of petroleum product because it is fast and provides highly reproducible results with minimal maintenance and allowing simultaneous measurement of multiple components with a great precision and accuracy [12-14]. By applying spectral analysis for gasoline, one should take into account that it may contain up to 100 different chemical components (hydrocarbons), each influencing the knock-rating of the fuel. Therefore, traditional analytical methods which determine the physio-chemical characteristics of a fuel ( particularly Octane Number) from its exact composition fail in this case because of the necessity to determine the knock-rating of all constituents with allowance for their

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interaction [5]. MLR (multiple linear regressions) is one of the most popular calibration methods in NIR spectroscopy. In comparison to other calibration methods MLR is simple easy to understand and possible to clearly rationalize the relationship between the NIR spectral features and the calibration results [15]. Wong et. al. [16] used FT-IR spectrometer for the determination of > 170 gasoline samples (cracker gasoline, reforming gasoline and mixture of them with straight-run gasoline), with using multiple linear regression and partial least square (PLS) method. Aim of our research work is to production of light products (Light naphtha, Heavy naphtha and Natural gasoline) by fractional distillation from TQ<sub>1</sub>, TQ<sub>2</sub> and K<sub>1</sub> of kurdistan crude oils and full evaluation of the light mineral products according to Iraqi specification also using Gas Chromatography for qualitative and quantitative analysis for all light products obtained from TQ<sub>1</sub>, TQ<sub>2</sub> and K<sub>1</sub> of kurdistan crude oils and determination of Research Octane Number of these light products by IR – spectroscopic method and using two statistical method (MLR AND RR) for determination of their (RON).

## 2. Experimental Part

Crude oil samples: Two different Crude oils from Taq-Taq regione near Koysinjaq (TQ<sub>1</sub> and TQ<sub>2</sub>) and one from Kirkuk (K<sub>1</sub>) were used with the following general properties,

Table 1: some general properties of TQ<sub>1</sub>,TQ<sub>2</sub> and K<sub>1</sub> crude oils.

Tests	TQ <sub>1</sub>	TQ <sub>2</sub>	K <sub>1</sub>
1-specific gravity @15.6 °C	0.7904	0.9115	0.8464
2- API Gravity.	47.52	23.74	35.64
3-Viscosity @40 °C/cs	1.93	67.28	24.3801
4-Viscosity @ 50 °C/cs	1.66	40.48	31.1453
5-B.S and water content % vol.	< 0.05	0.08	0.05
6-Total sulfur content % Wt.	0.52	2.08	2.0
7-Ash content % Wt.	0.047	0.0 58	0.052

### 2.1. Procedures.

#### 2.1.1. Distillation of Petroleum Products: IP-123/ ASTM D-86

A 100 ml sample (petroleum fraction) was distilled under prescribed condition which is appropriate to its nature, systematic observation of thermometer readings and volumes of condensate were made; and from these data, the results of the test were calculate and reported.

#### 2.1.2. Determination of Trace Amount of Lead :IP-224/ASTMD-68

A known volume of sample is shaken with aqueous iodine monochloride solution when any Lead compound present passes into the aqueous phase. Organo Lead compounds are then converted to the inorganic form by boiling the solution and the excess reagent destroyed with sodium sulphate. After the addition of the buffer solution, the Lead is extracted as the dithizonate and determined colorimetrically,

#### 2.1.3. Density, Specific Gravity and API gravity of Crude oils and Petroleum Fractions;IP-160/ASTMD1298

The sample (Crude oil or petroleum fraction) was brought to the prescribed temperature. The appropriate hydrometer was allowed to settle. After the temperature equilibrium has been reached, the hydrometer scale was record, and the temperature of the sample was noted .If necessary the cylinder and its contents were placed in a constant temperature to avoid excessive temperature variation during the test.

#### 2.1.4. Determination of Aniline point : IP-2/ASTMD-611

Specified volumes of aniline and sample (petroleum fraction) or Aniline and sample plus n-heptane were placed in a tube and mixed mechanically. The mixture was heated at a controlled rate until the two phases became miscible. The mixture was then cooled at a controlled rate and the temperature at which two phases separated was recorded as the aniline point or mixed aniline point.

#### 2.1.5. Measurement of Kinematics Viscosity: IP-71/ASTM D-445

The time is measured in second; for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled temperature. The Kinematics viscosity is the measured from the flow time and the calibration constant of the viscometer used.

### 2.1.6. Calorific Value (Q)

Calorific value is another test used for these fractions which is defined as the heat of combustion of petroleum products and calculated using the following equation:

$$\text{Calorific value (Q)} = 12400 - 2100 d^2$$

### 2.1.7. Procedure for GC Analysis

1-The temperature programming was ranged from 35 to 200 °C and the temperature of the injector was adjusted at 230 °C and detector at 250 °C.

2-The flow ratio of H<sub>2</sub>/air was adjusted at 1.5/3 bar and the flow of the carrier gas (helium) at 297ml/min.

3-Inject and run 0.5µl of analyte (standard or sample) and wait for getting the chromatogram of each one. Gas Chromatographic analysis have been done for naphtha samples obtained from TQ<sub>1</sub>, TQ<sub>2</sub> and K<sub>1</sub>. Aliphatic hydrocarbons (n-pentane, n-hexane, n-heptane, iso-octane, cyclohexane, n-decane ) and aromatic (Benzene ,Toluene o,m and p-xylene) have been measured quantitatively and qualitatively in each sample .The condition which have been choosed for these sample were :

1-The detector used was type FID.

2-Sample size was 0.5µl.

3-The most suitable (GC) column have been choosen for these samples (GS-Q type column)

### 2.1.8. Procedure for IR Analysis

1-Tested background (without any standards or samples) for the detection of any peak of compounds in the air to remove them as interference from the peaks of standards or samples in the time of analysis.

2-KBr cell with 0.025 mm thickness (SPECAC) used for analysis of standards and samples.

3-Standards prepared freshly and immediately run to avoid any evaporation of the constituents, the standard mixture were prepared from ten pure hydrocarbons n-pentane, n-hexane, n-heptane, cyclohexane, iso-octane, n-decane, benzene, toluene, ethylbenzene and p-xylene. The set was composed of (333) mixtures containing from 5% v/v to 55% v/v of each pure hydrocarbon to give RON ranging from 39.2 to 112.2. Table (2) illustrate the RON for the pure standard hydrocarbons used [1].

Table 2: Research Octane Number of pure hydrocarbons

Hydrocarbon compounds	Research Octane Number	Hydrocarbon compounds	Research Octane Number
n-heptan	0	Iso-octane	100
n-decane	0	Cyclohexane	110
n-hexane	19	Ethylbenzene	124
n-pentane	62	Toluene	124
Benzene	98	p-xylene	145

## 3. Result and Discussion

### 3.1. Fractionation of Crude Oil to Obtain Different Naphtha Cuts (Different boiling points)

Table (3) is a tabulation of the fractional distillation data for each type of these Curdes and it shows the yield (% v/v) of Light naphtha, Heavy naphtha and Natural gasoline obtained from TQ<sub>1</sub>, TQ<sub>2</sub> and K<sub>1</sub> Crudes.

Table 3: The fractions obtained from TQ1, TQ2 and K1 Room temperature = 15-17 °C

Name	TQ <sub>1</sub>		TQ <sub>2</sub>		K <sub>1</sub>	
	b.p °C	Yield (% v/v)	b.p °C	Yield (% v/v)	b.p °C	Yield (% v/v)
Light naphtha	28-82	16.6	41-82	2.2	29-82	11.14
Heavy naphtha	82-171	28	82-171	6.9	82-171	20.12
Natural gasoline	23-150	37.8	37-150	5.1	23.5-150	26.2

### 3.2. Evaluation of Fractions

Table (4), (5), (6) show some general physical properties of natural gasoline and naphtha obtained from TQ<sub>1</sub>, TQ<sub>2</sub>

It is very clear from these results that all properties are within the Iraqi specification or requirements of these light products.[30]

### 3.3. Gas Chromatographic Analysis

Qualitative and quantitative analysis of light products obtained from TQ<sub>1</sub>, TQ<sub>2</sub> and K<sub>1</sub> Crudes were carried out using Gas Chromatography type CSI 200 (England). Qualitatively show that the signal of all hydrocarbon compounds in all fractions is in the boiling range of gasoline and naphtha [for example fig.(1) show Chromatogram for Light naphtha obtained from TQ<sub>1</sub>] as compared with the chromatogram [Fig. (2)] for standard mixtures. These indicate that these light products have the best composition for gasoline and naphtha]. Also the results from Tables (7) quantitatively determined the amount of all hydrocarbon compounds present in the fractions by calculating the area percent for each separated compound. These retention times of separated compounds are compared with the retention time of known standard reference hydrocarbon compounds [Table (8) ] This quantitative analysis approved that all light products, obtained are paraffinic products of straight chained isomers (except in heavy naphtha contain approximately equal amount paraffinic and aromatic), and little amount of branch chained isomers. This explains why the Octane Numbers of these light products are low, as it is clear from literature branch chained isomers have higher Octane Numbers than non branch straight chained isomers .On the other hand aromatic hydrocarbons present in these light products composition are of side branched isomers which have low Octane Number in composition with simple non-side branching aromatic compound.

### 3.4. Determination of Octane Number by IR spectroscopy

Using IR-spectroscopy, minute spectral difference hydrocarbons could be identified and those spectral differences provide enough quantitative information, which is necessary to make the calibration using multiple linear regression and ridge regression method. The results of the spectrophotometric calibration of RON for standard hydrocarbon mixtures using statistic methods , multiple linear regression (MLR) and ridge regression (RR) are shown in fig.(3)&(4),while the calibration statistics are summarized in Table(11) . Two IR-spectra are shown in fig.(5)and (6) as an example of synthetic hydrocarbon mixture and real naphtha obtained from crude oils .The calculated value of (RON) using MLR method gives better standard error in comparison with values of (RON) obtained by using (RR) method .Also (R-square ) for calibration curve between actual RON and RON predicted from MLR is (0.9423) indicate better result than that obtained from (RR) method which is (0.8734)

Equations were obtained by least square method for the correlation between the (RON) and many possible absorption aromatic and paraffinic bonds are shown in Table (9) & (10) . IR-spectrum offers quantitative information about the structural group as well as the identification of the chemical nature of the samples .These equations show a good relation to determine (RON) which is a physical property that has a order dependence on concentration.

Table 4: General properties of gasoline and naphtha obtained from TQ1

Test	Test method	Light naphtha	Heavy naphtha	Natural gasoline
Specific gravity @ 15.6 °C	ASTMD 1298	0.656	0.7308	0.7035
API gravity	ASTMD 1298	84.20	62.12	69.63
Visc @37.8 °C	ASTMD 445	0.400	0.640	0.522
Distilled @ 100 °C %v	ASTMD 86	-----	10	55.5
Distilled @ 145 °C %v	ASTMD 86	-----	77.5	95
Aniline point	ASTMD 611	66	65	65.75
Final boiling point	ASTMD 86	85	174	153
Trace lead content (ppb)	ASTMD 68	Null	Null	Null
Calorific value (Kcal/Kg)	IP-12	11496.29	11278.58	11360.68

Table 5: General properties of gasoline and naphtha obtained from TQ2

Test	Test method	Light naphtha	Heavy naphtha	Natural gasoline
Specific gravity @ 15.6 °C	ASTMD 1298	0.6924	0.7541	0.7338
API gravity	ASTMD 1298	72.86	56.14	61.33
Visc @37.8 °C	ASTMD 445	0.509	0.842	0.711
Distilled @ 100 °C %v	ASTMD 86	83	3.5	33.5
Distilled @ 145 °C %v	ASTMD 86	-----	51	70
Aniline point	ASTMD 611	66.5	61	64
Final boiling point	ASTMD 86	109	186	167
Trace lead content (ppb)	ASTMD 68	Null	Null	Null
Calorific value (Kcal/Kg)	IP-12	11393.22	11205.79	11296.22

Table 6: General properties of gasoline and naphtha obtained from K<sub>1</sub>

Test	Test method	Light naphtha	Heavy naphtha	Natural gasoline
Specific gravity @ 15.6 °C	ASTMD 1298	0.6560	0.7490	0.7110
API gravity	ASTMD 1298	84.20	57.41	67.51
Visc @37.8 °C	ASTMD 445	0.400	0.705	0.570
Distilled @ 100 °C %v	ASTMD 86	-----	8	45
Distilled @ 145 °C %v	ASTMD 86	-----	61.3	85.5
Aniline point	ASTMD 611	63.5	57.75	60
Final boiling point	ASTMD 86	86	174	153.5
Trace lead content (ppb)	ASTMD 68	Null	Null	Null
Calorific value (Kcal/Kg)	IP-12	11496.29	11221.89	11338.40

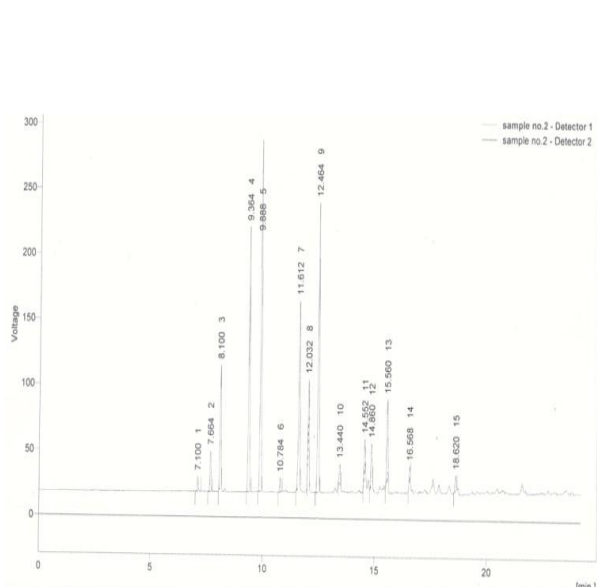


Fig. 1: Chromatogram for Light naphtha obtained from

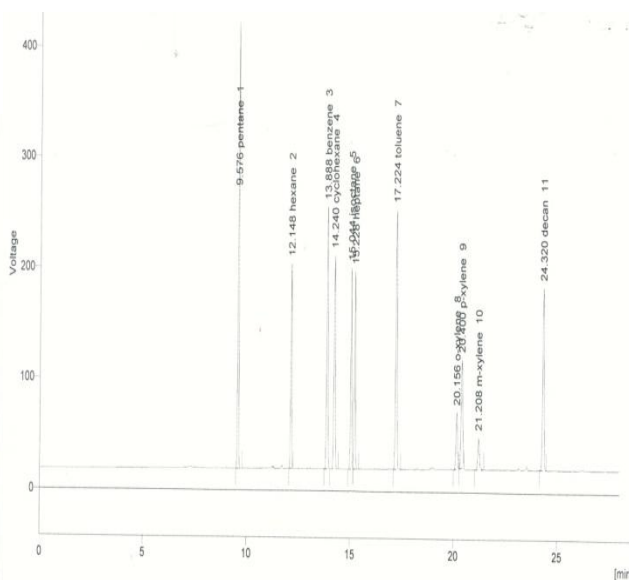


Fig. 2: Chromatogram for standard mixture TQ<sub>2</sub>

Table 7: Result for the analysis of light naphtha

N. O.	Ret. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	7.10	35.97	11.21	0.9	1.0
2	7.66	102.0	30.86	2.5	2.6
3	8.10	295.1	92.22	7.2	7.9
4	9.36	693.8	202.6	17.0	17.3
5	9.88	926.4	269.6	22.6	23.1
6	10.78	38.17	10.43	0.9	0.9
7	11.61	558.4	141.2	13.7	12.1
8	12.03	90.73	39.32	2.2	3.4
9	12.46	831.3	221.3	20.3	18.9
1	13.44	55.58	14.93	1.4	1.3
1	14.55	79.20	23.67	1.9	2.0
1	14.86	111.3	30.77	2.7	2.6
1	15.56	206.4	59.89	5.0	5.1
1	16.56	22.16	8.77	0.5	0.8
1	18.62	44.01	11.40	1.1	1.0
	Total	4090.	1168.	100.	100.0

Table 8: Results for the analysis of standard mixture

NO.	Ret. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	Name of standard
1	9.576	1305.48	403.83	16.1	20.7	n-pentane
2	12.14	656.07	185.29	8.1	9.5	n-hexane
3	13.88	1059.72	236.89	13.0	12.1	benzene
4	14.24	847.71	193.06	10.4	9.9	cyclohexane
5	15.04	726.34	181.95	8.9	9.3	iso-octane
6	15.22	699.66	178.64	8.6	9.1	n-heptane
7	17.22	1051.79	234.40	12.9	12.0	toluene
8	20.15	254.23	50.74	3.1	2.6	o-xylene
9	20.40	557.37	97.20	6.9	5.0	p-xylene
10	21.20	158.49	28.26	1.9	1.4	m-xylene
11	24.32	816.69	164.92	10.0	8.4	n-decane
	Total	8133.5	1955.2	100	100	

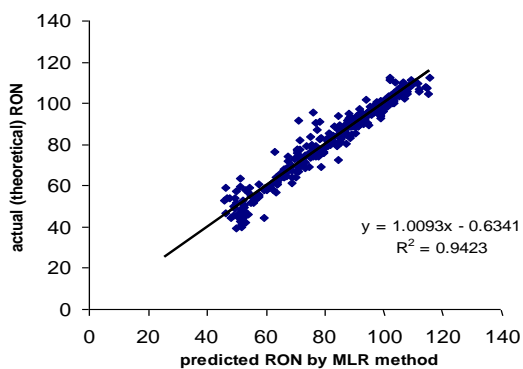


Fig. 3: Calibration curve for Actual (theoretical) predicted RON by the MLR method

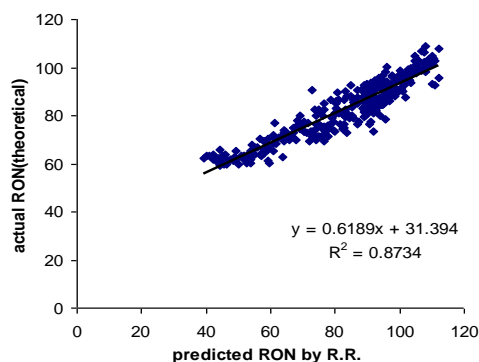


Fig. 4: Calibration curve for actual (theoretical) RON vs. predicted RON by the RR method

Table 9: Equation used for the calculation of (RON) [Actual O.N.(theoretical MLR equation RR Equation]

Name	Equations
Actual O.N. (theoretical)	Y1= Combination[ (percent *O.N.) for each standard in standard mixture /100]
MLR equation	$Y_2 = 119.511 + 0.191382X_1 + 0.825139X_2 + 9.55316 X_3 + 154.633X_4 - 52.0947X_5 + 319.453X_6 - 70.7921X_7 - 3.36523X_8 - 31.6506X_9$
RR Equation	$Y_3 = 77.62266 - 0.632249X_1 + 3.550272X_2 + 11.20891X_3 + 112.8803X_4 + 9.289726X_5 + 184.09551X_6 - 29.70123X_7 - 11.10275X_8 - 14.20538X_9$

Table(10) Absorption bands for different group in IR-region

Peak type	Absorption-position( $cm^{-1}$ )	Frequency type
$X_1, X_2$	600-750 (683.55, 734.4)	Aromatic C-H out of plane bending
$X_3$	750-860 (799.1)	C-H Aromatic out of plane bending (o, m and p) substituted.
$X_4$	880-980 (914.65)	C-H Paraffinic in plane bending.
$X_5$	980-1080(1043)	Aromatic C-H in plane bending
$X_6$	1080-1300(1261.3)	C-C bending (paraffinic)
$X_7, X_8$	1300-1590(1389.7, 1466.6)	Paraffinic C-H bending (for $CH_2$ and $CH_3$ )
$X_9$	2500-3300(2930.3)	C-H stretching (paraffinic and naphthenic)

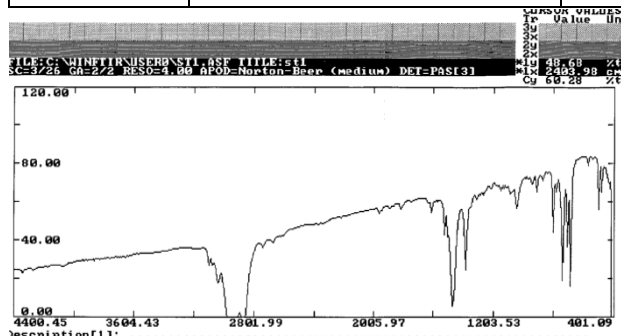


Fig. 3: IR spectra (transmittance) for standard obtained by mixing [ 55% n-pentane , 5% n-Decane, 5% Benzene , 5% cyclohexane , 5% Isooctane , 5% n-Heptan , 5% n-Hexane , 5% Ethylbenzene , 5% Toluene , 5% P-xylene

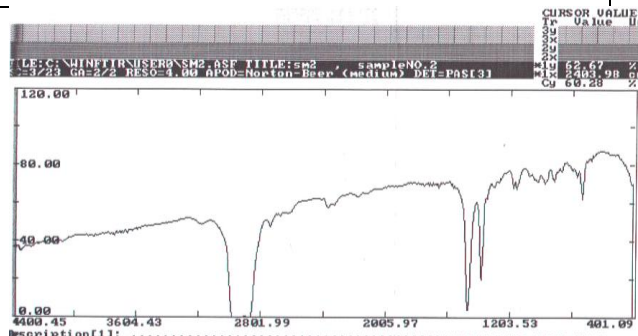


Fig. 4: IR spectra (transmittance) for Light mixture naphtha obtained from TQ<sub>1</sub>

## 4. Conclusions

1-It was found that Crude oils from TQ<sub>1</sub> and K<sub>1</sub> contain high amounts of light products according to the (API=47.52) for TQ<sub>1</sub> and (API=30.47) for K<sub>1</sub> than that of TQ<sub>2</sub> (API=23.47), However, TQ<sub>1</sub> is more suitable for the production of Light naphtha, Natural gasoline and Heavy naphtha than K<sub>1</sub> and TQ<sub>2</sub> as it contains 16.6%, 37.8% and 28.0% by volume percent for TQ<sub>1</sub> 11.14%, 26.2% and 20.12% by volume percent for K<sub>1</sub> and 2.2%, 5.1% and 6.9% by volume percent for TQ<sub>2</sub>, the above percentage are of Light naphtha, Natural gasoline and Heavy naphtha, respectively.

2- The clear Octane Number determined by IR spectroscopic method. Show that these light products obtained from these Crudes have a low Octane Number.

## 5. Acknowledgements

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