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The Relationships between the Physical and Chemical Properties of Narrow Fractions Distilled From Mixed Kirkuk and Sharki-Baghdad Crude Oils

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Abstract

Mixed Kirkuk and Sharki-Baghdad crude oils were distilled into narrow fractions. The range of these narrow fractions were 10^{o}C, starting from IBP to 350^{o}C. The total distillates from mixed Kirkuk and Sharki-Baghdad crude oils were 58.25 vol % and 44.65 vol %, respectively.The hydrocarbons compositions (paraffin, naphthene, aromatic) in light fractions starting from IBP to 250^{o}C were determined by using PONA analysis method. The results show that the paraffin content decreases with increasing mid percent boiling point of the fraction, while the naphthene, and aromatic increase with the increase of mid percent boiling point of mixed Kirkuk and Sharki-Baghdad crude oils. Three groups of empirical equations were developed for the prediction of hydrocarbons compositions (paraffin, naphthene, aromatic) based on physical properties (mid percent boiling point, specific gravity, and refractive index) of narrow fractions distilled from mixed Kirkuk and Sharki-Baghdad crude oils. The first group relates the mid percent boiling point with the specific gravity, the second group relates the mid percent boiling point with the refractive index, while the third group relates the specific gravity with the refractive index.

***Keywords*:** Petroleum fractions analysis, Hydrocarbons content in crude oil, PONA analysis, Sulfonation method

Introduction

Crude oils and refined petroleum products consist largely of hydrocarbons, which are chemicals composed solely of hydrogen and carbon in various molecular arrangements. Crude oils contain hundreds of different hydrocarbons and other organic and inorganic substances including atoms of sulfur, nitrogen, and oxygen, as well as metals such as iron, vanadium, nickel, and chromium [1, 2].

Petroleum fractions are mixture of many hydrocarbons from different families. The most common hydrocarbon types available in petroleum fraction are paraffin, naphthene, and aromatic. Properties of hydrocarbons vary with carbon number or molecular weight as well as family type. Riazi and Daubert [3] have shown that a minimum of two parameters are required to get estimation of other physical properties. The most appropriate parameters are boiling point and specific gravity at 15.5°C. These two parameters are mainly available for petroleum fraction. Other properties may be available from laboratory measurements are refractive index, density at 20°C, and Kinematic viscosity [3].

Studies of the nature and the type of hydrocarbon constituents in crude petroleum can be carried out by PONA analysis. PONA analysis can be used for light fractions (from IBP to 250°C) and depended on sulfonation and aniline point after and before sulfonation.

Lipkin and Kurtz[4] [1941] calculated the weight percent of naphthenic ring in saturated hydrocarbons, based on density and molecular weight, using equations (1) and (2).

$$\text{Wt \% ring} = (A+190.0\,d - 217.9) / (0.539\,d - 0.249) \quad (1)$$

(For d < 0.861)

$$\text{Wt \% ring} = (A+102.8\,d - 142.8) / (0.262) \quad (2)$$

(For d > 0.861)

A: was determined by equation (3).

$$A = 55.3 + (3516) / (\text{Mol Wt} + 12) \quad (3)$$

(For Mol Wt >100)

Molecular weight is obtained with sufficient accuracy from correlation based on density and boiling point, density and viscosity, or viscosities at two temperatures.

Groenings, Kurtz, and Sankin [1945] used the refractive dispersion and bromine number for the determination of aromatic content of cracking naphtha by equation [4].

$$\text{Wt \% aromatic} = (\delta\ \text{sample} - 0.16\ \text{Br} - 99) / (\delta\ \text{aromatic} - 99) \quad (4)$$

Rossini, Rampton, and Gooding [1946] show that the Molecular-weight range, specific dispersion of the lubricating oil can be used as measure of the presence or absence of aromatic rings. Values of specific gravity below 100 are usually accepted as meaning that the sample is aromatic free [5].

Gooding [1946] had used the refractivity intercept for the determination of aromatics in straight-run fractions [6].

Van Nes and Van Weston[7] show that the percent ring carbons in the hydrogenated fractions from five crude oils can be determined accurately from refractivity intercept correlation. They also showed that there is an approximate relation between viscosity gravity constant (VGC) and percent paraffin carbon, percent naphthene carbon and percent aromatic carbons. Equation (5) described this relation.

$$\text{VGC} = 0.00743\ \%\ C_p + 0.00925\ \%\ C_N + 0.0110\ C_A \quad (5)$$

Kesler-Lee, in 1976, predicted the physical properties of petroleum fractions such as molecular weight, critical temperature, and critical pressure based on boiling point and specific gravity of fractions as input data [8].

Hajek, and Skelnar, in 1978 analyzed heavy crude oil using NMR spectroscopy and they determined the amount of aromatic and aliphatic carbon [9].

Misbah and Mohammad (1983) estimated the aliphatic and aromatic content, average paraffinic chain length, and hydrogen, methyl and alkyl bearing aromatic carbons for six fractions of Saudi Arabian heavy crude oils based on N.M.R. spectroscopy [10].

Riaze and Daubert, in 1987, proposed a general empirical correlation to predict physical properties of pure hydrocarbons and undefined petroleum fractions. These correlations are applicable in the molecular weight range 70–300 and normal boiling point range 32– 210o C [11].

Riazi and Sahhaf, in 1995, proposed an empirical correlation for the calculation of critical properties of heavy petroleum fraction based on molecular weight and PNA as input data [12].

Experimental Work

In this work empirical correlations to predict paraffin, naphthene, aromatic content of petroleum fraction based on simple physical properties such as mid percent boiling point, specific gravity, and refractive index were developed.

Feed stocks

The feed stocks used in this investigation were mixed Kirkuk and Sharki-Baghdad crude oils. The properties of mixed Kirkuk and Sharki-Baghdad crude oils are given in Table 1.

Table 1 property of mixed Kirkuk and Sharki-Baghdad crude oils

Item	Tests	Mixed Kirkuk crude oil	Sharki-Baghdad crude oil
1	Specific gravity at 15.6/15.6 °C	0.8810	0.9296
2	API gravity	29.1	20.6
3	R.V.P. at 37.8°C, psi	2.2	-----
4	Salt content, mg/L	15.2	26.4
5	Pour point, °C	-9	-24
6	Water content, vol %	nil	0.2
7	C.C.R, wt %	5.4	8.1
8	H2S content, ppm	7.73	12.8
9	Total sulphur content, wt %	3.3	3.39
10	ASTM distillation, Vol %		
	Recovery at IBP	57	62
	50 °C	----	----
	75 °C	0.6	2.3
	100 °C	4.6	5.0
	125 °C	9.6	7.0
	150 °C	14.6	9.3
	175 °C	20.6	12.3
	200 °C	26.3	17.3
	225 °C	31.3	20.6
	250 °C	36.0	24.0
	275 °C	42.0	28.3
	300 °C	46.3	36.3
	Total distillate, vol %	48.4	37.6
	Total residue, vol %	50.6	61.4

Distillation unit

Distillation of mixed Kirkuk and Sharki-Baghdad crude oils into narrow fractions (every 10°C) was achieved in laboratory distillation unit according to ASTM D 2892-78 consisting of distillation flask, heating mantle, distillation column, condenser, timer, reflux divider, thermometers, fraction collector, variac, gauge pressure, and vacuum pump.

The size of distillation flask was 6 liters, and provided with two side arm, the first side arm was used to charge the crude oil and the second sidearm contains glass bulb for thermometer. The distillation flask was mounted with 2.4 KW heating kettle connecting with variac to control the heat input to the flask.

The distillation column consisted of 10 trays, and has 40 mm inside diameter and 450 mm length. The column was isolated by highly vacuum jacket to minimize the heat loss.

Reflux ratio was controlled by using a magnetic valve connected with reflux timer. A reflux ratio 5:1 was used for atmospheric distillation and 3:1 for vacuum distillation.

The vacuum was achieved by using vacuum system consisted of vacuum pump, trap, and vacuum gauge. When the temperature of crude oil inside the distillation flask reach 300oC, the distillation column is connected with the vacuum system. The vacuum system lines for both the condenser and the receiver are gathered by T shape joint to produce 100 mm pressure. Vacuum pump type Edward, 2008, GES Machines LTD, was used for vacuum production.

PONA analysis

This method was used for light fractions (IBP to 250 °C) to determine the aromatic, naphthene, and paraffin content. Aromatic determination was achieved by sulfonation method; naphthene by empirical equation and paraffin by subtracting aromatic and naphthene % from 100.

Determination of aromatic

The sulfonation method was used to separate the aromatic-olefin fraction from distillated fraction by using concentrated sulfuric acid according to (ASTM D 1019-68). The apparatus was used for this method consists of sulfonation flask, pipette of 10-ml, cooling bath, and thermometer.

The sulfonation flask is made of heat resistance glass. The calibrated neck of the flask is graduated from zero to 100 in 2 increments.

Estimation of naphthenes and paraffines

The estimation of the percentage of naphthenes was done by the determination of the aniline point of the fraction before and after removing the aromatic fraction [9].

Naphthenes percentages were calculated from equation [6,9].

$$N\,\% = (Ap - As) / (Ap - An) * 100 \qquad (6)$$

The paraffines percentage were calculated by equation 7

$$P\,\% = 100 - (A\,\% + N\,\%) \qquad (7)$$

Aniline point

The aniline point of all narrow fractions produced from crude oil distillation unit was determined according to ASTM D 611-82.

5 ml of aniline with 5 ml of the tested sample were added in the test tube and mixed by stirrer and the heat was supplied to heat bath until homogenous one phase of sample and aniline was obtained. The sample then cooled until the appearance of two phases. The measured temperature at two phase appearance is called aniline point.

Density and Specific gravity

Density, specific gravity of all narrow distillation fractions from mixed Kirkuk and Sharki-Baghdad crude oils were determined according to ASTM D 1298-80, by using 25 cm^3 Pycnometer.

Refractive Index

Refractive index of all narrow fractions of mixed Kirkuk and Sharki-Baghdad crude oils were determined according to ASTM D 1218-82.

The apparatus used consisted of Abbe refractometer having rang 1.33 to 1.64 for the sodium D line, thermometer for recording temperature, circulating pump and chiller to keep the temperature at 20°C.

Results and Discussion

True boiling point of mixed Kirkuk and Sharki-Baghdad crude oils:

Figures 1 and 2 show the true boiling point curves of mixed Kirkuk and Sharki-Baghdad crude oils, respectively.

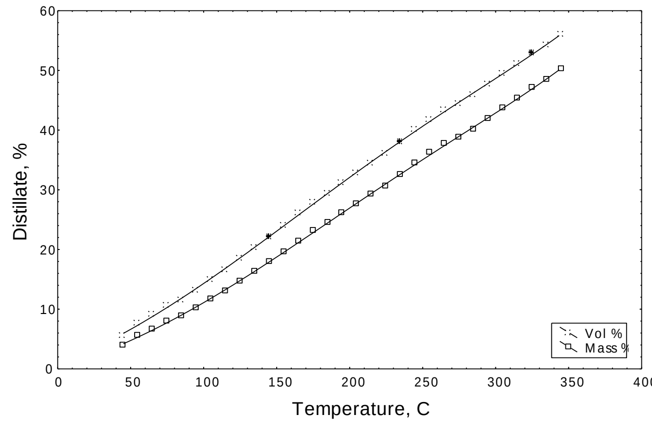

Fig. 1: True boiling point curve of mixed Kirkuk crude oil

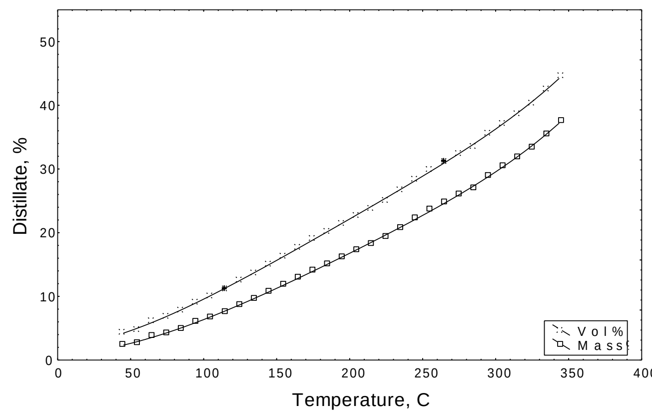

Fig. 2: true boiling point curve of Sharki-Baghdad crude oil

Relationship between mid percent boiling point with specific gravity and API:

Figure 3 shows the relation between the specific gravity values with mid percent boiling point temperature of the narrow fractions distilled from mixed Kirkuk and Sharki-Baghdad crude oils. The specific gravity of the narrow fractions increases with the increase of mid percent boiling point of the fractions. This is due to the increase of the aromatic and decrease of paraffinic content, and this is in agreement with Nelson. [14] Usually the specific gravity of aromatic hydrocarbon is higher than those for paraffin hydrocarbon having the same number of carbon atoms. Figure 4 shows the relation between the degree API gravity with the mid percent boiling point temperature of the narrow fractions distilled from mixed Kirkuk and Sharki-Baghdad crude oils. Degree API gravity decrease, with the increase of mid percent boiling point temperature of the narrow fractions, because the value of API is inversely related to specific gravity.

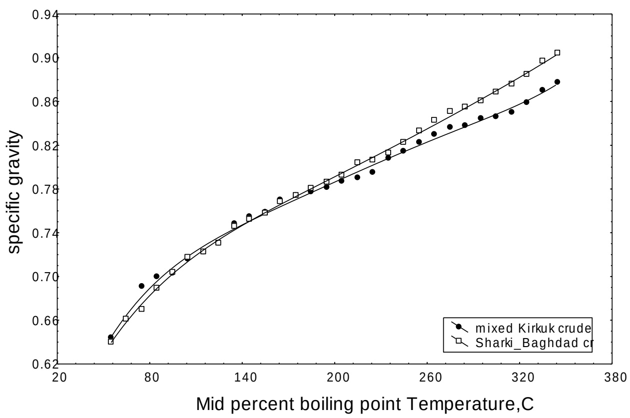

Fig. 3: Relation between mid percent boiling point of the narrow fraction with the specific gravity

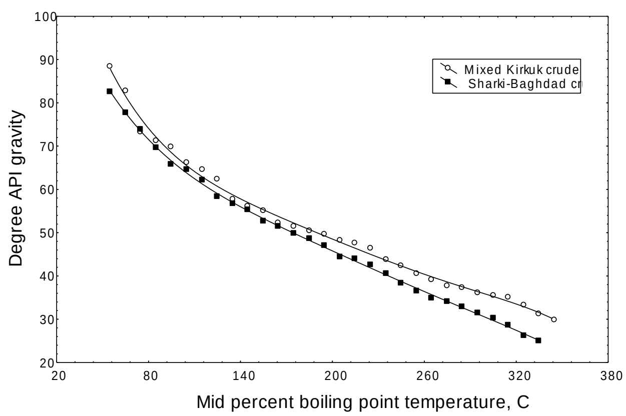

Figure 4: Relation between mid percent boiling point of the narrow fraction with the degree API

Relationship between mid percent boiling point and refractive index:

Figure 5 shows the relation between the refractive index of the distilled narrow fractions with mid percent boiling temperature of mixed Kirkuk and Sharki-Baghdad crude oils. It was noted that the refractive index increases with the increase of mid percent boiling point temperature of the fractions because the refractive index of high molecular weight hydrocarbon is higher than that for low molecular weight fractions [15]. The results show that the refractive index of the narrow fractions up to 200°C distilled from both crude oils is approximately the same and the difference in RI value increases after 200°C. This is because the higher naphthenic hydrocarbons content of Sharki-Baghdad crude oil narrow fraction compared with fractions distilled from mixed Kirkuk crude oil (see Fig 8).

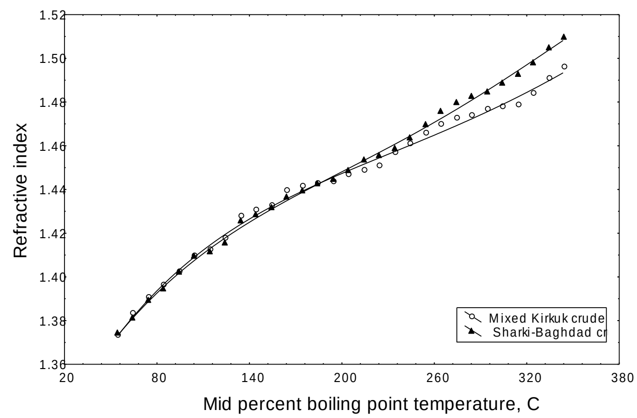

Fig. 5: Relation between mid percent boiling point of the narrow fraction with the refractive index

Relationship between mid percent boiling point and aniline point:

Figure 6 shows the relation between mid percent boiling point and the aniline point of narrow fraction of mixed Kirkuk and Sharki-Baghdad crude oils. The results show that the aniline point increases with the increase of mid percent boiling point of the narrow distillated fractions and this is due to the increase of molecular weight of the fractions (14).

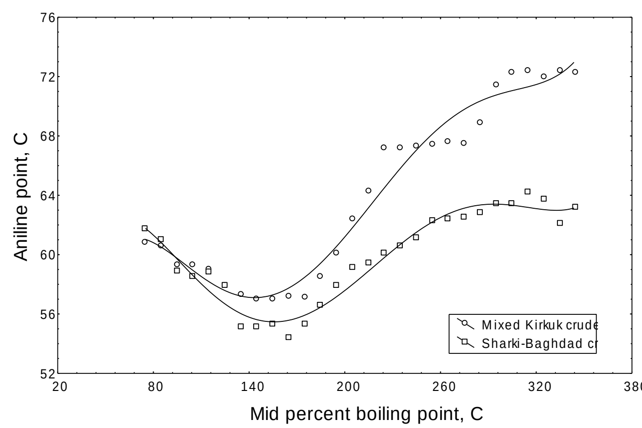

Fig. 6: Relation between mid percent boiling point of the narrow fraction with the aniline point

Effect of narrow fraction boiling point on the hydrocarbon content:

Figure 7 shows the relation between mid percent boiling point of the distillate fractions and the paraffin content of mixed Kirkuk and Sharki-Baghdad crude oils. The result shows that the paraffin content decreases with the increasing of mid percent boiling point of the narrow fractions.

Figure 8 shows the relation between mid percent boiling point of the distillate fractions and the naphthene content of mixed Kirkuk and Sharki-Baghdad crude oils. The result shows that the naphthene content increases with increasing mid percent boiling point of the narrow fractions. This agrees with the results of Hajek and others [35].

Figure 9 shows the relation between mid percent boiling point and the aromatic content of narrow fractions distilled from mixed Kirkuk and Sharki-Baghdad crude oils. Its noted that the aromatic content of mixed Kirkuk narrow fractions less than the Sharki-Baghdad narrow fractions. The result also shows that the aromatic content increases with increasing mid percent boiling point of the narrow fractions. These results agree with those obtained by other authors [14,16].

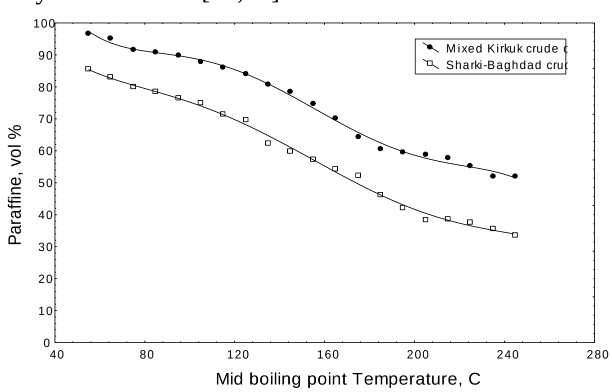

Fig.7: Relation between mid percent boiling point of the narrow fraction with the Paraffin content

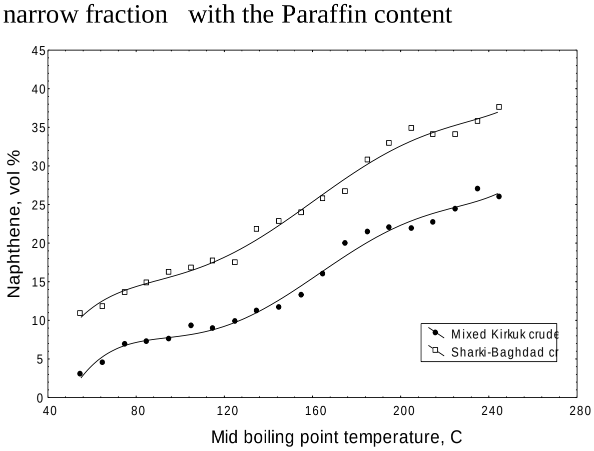

Fig. 8: Relation between mid percent boiling point of the narrow fraction with the Naphthene content

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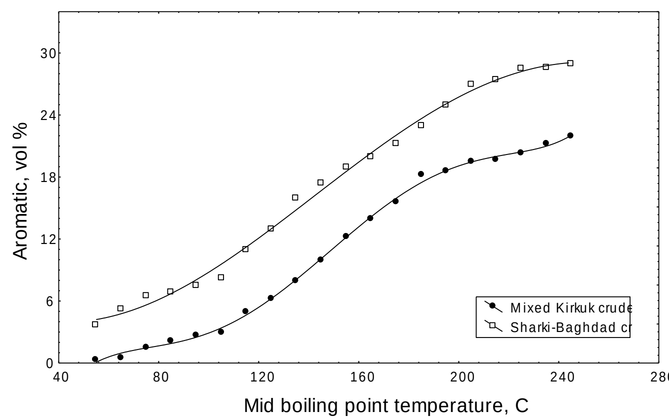

Fig. 9: Relation between mid boiling point of the narrow fraction with the Aromatic content

Prediction of hydrocarbon composition based on physical properties of narrow fractions:

Raize and Daubert were proposed a general equation (4.1) for the estimation of some important properties from other simple properties [11].

$$\theta = A_1 \theta_1^{A2} \theta_2^{A3} \tag{4.1}$$

Where: θ = property needed to predict

θ_1, θ_2 = simple physical properties

A1, A2, A3= constants

Raize and Doubert were estimated the molecular weight, critical temperature, critical pressure and a centric factor of wide range fraction distilled from some American crude oils based on specific gravity and boiling point [11].

Based on the general equation (4.1) some new relationships for the prediction of hydrocarbon composition of narrow fractions distilled from mixed Kirkuk and Sharki-Baghdad crude oils were developed.

A computer program package (statistica) was used to develop the necessary correlations. The program performs least square fitting of a proposed function for given set of data.

Table (4.1) shows the relationships for the estimation of hydrocarbon composition for narrow fractions distilled from mixed Kirkuk crude oil, while table (4.2) shows the relationships for narrow fractions distilled from Sharki-Baghdad crude oil.

Equations (1, 2) and (3) relates the percent of paraffin, naphthene and aromatic, respectively with the mid boiling point and specific gravity of narrow fractions distilled from mixed Kirkuk crude oil, while equations (10, 11) and (12) related the same properties for narrow fractions distilled from Sharki-Baghdad crude oil.

Equations (4, 5) and (6) relates the percent of paraffin, naphthene and aromatic, respectively with the mid boiling point and refractive index of narrow fractions distilled from mixed Kirkuk crude oil, while equations (13, 14) and (15) related the same properties for narrow fractions distilled from Sharki-Baghdad crude oil.

Equations (7, 8) and (9) relates the percent of paraffin, naphthene and aromatic, respectively with the specific gravity and refractive index of narrow fractions distilled from mixed Kirkuk crude oil, while equations 16, 17 and 18 related the same properties for narrow fractions distilled from Sharki-Baghdad crude oil.

Table 4.1 predict equations of mixed Kirkuk crude oil

NO	equation	A_1	A_2	A_3	R
1	$P=A_1 T^{A2} S^{A3}$	7503.86	-0.7885	2.54	0.93
2	$N= A_1 T^{A2} S^{A3}$	0.015	1.368	0.029	0.98
3	$A= A_1 T^{A2} S^{A3}$	92E-6	2.176	-2.508	0.974
4	$P= A_1 T^{A2} RI^{A3}$	564.83	-0.398	-0.241	0.93
5	$N= A_1 T^{A2} RI^{A3}$	0.0296	1.55	-4.508	0.98
6	$A= A_1 T^{A2} RI^{A3}$	418E-6	1.539	6.677	0.97
7	$P= A_1 S^{A2} RI^{A3}$	3286.5	0.1966	-10.59	0.93
8	$N= A_1 S^{A2} RI^{A3}$	23396.6	12.369	-10.96	0.98
9	$A= A_1 S^{A2} RI^{A3}$	1E-7	-2.2574	52.163	0.96

Table 4.2 predict equations of Sharki-Baghdad crude oil

NO	equation	A_1	A_2	A_3	R
10	$P= A_1 T^{A2} S^{A3}$	0.099	0.776	-8.629	0.95
11	$N= A_1 T^{A2} S^{A3}$	0.258	0.911	0.099	0.989
12	$A= A_1 T^{A2} S^{A3}$	1E-7	3.322	-12.312	0.99
13	$P= A_1 T^{A2} RI^{A3}$	1513850	1.4706	-49.213	0.96
14	$N= A_1 T^{A2} RI^{A3}$	0.1479	0.7844	3.251	0.989
15	$A= A_1 T^{A2} RI^{A3}$	2.352	2.8125	-33.90	0.99
16	$P= A_1 S^{A2} RI^{A3}$	205958E3	6.28372	-37.424	0.95
17	$N= A_1 S^{A2} RI^{A3}$	2.182	3.198	9.215	0.98
18	$A= A_1 S^{A2} RI^{A3}$	4403E3	14.309	-23.67	0.98

CONCLUSIONS

The total distillate from mixed Kirkuk crude oil was 50.29 wt % while the total distillate from Sharki-Baghdad was 37.64 wt %, and thus denoted that mixed Kirkuk crude oil lighter than Sharki-Baghdad crude oil. Paraffinic content decreases with the increasing mid percent boiling point of the narrow fractions, while naphthenic and aromatic contents increase with the increasing mid percent boiling point of the fraction. The specific gravity, refractive index of the narrow fractions increase with increasing the mid percent boiling point of the fractions. The predicted equations of hydrocarbon group based on mid percent boiling point and specific gravity were identical for both the mixed Kirkuk and Sharki-Baghdad crude oils, while the equations based on specific gravity and refractive index and those based on the mid percent boiling point and specific gravity has were identical for mixed Kirkuk and Sharki-Baghdad crude oils.

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NOMENCLATURE

A	Aromatic
An	Aniline point of naphthenic hydrocarbon, °C
Ap	Aniline point of paraffinic hydrocarbon,°C
ASTM	American standard test measurement
Br	Bromine number
CCR	Conradson carbon residue
D	density at 20 oC in g / ml
G	Specific gravity
IBP	Initial boiling point
M	Moleculer weight
N	Naphthene
P	Paraffin
PNA	paraffin naphthene aromatic
RI	Refractive Index
RVP	Reid vapor pressure
Sp.gr	Specific gravity
T	Average boiling point temperature in °C
TBP	True boiling point
VGC	Viscosity gravity constant
δ	Refractive dispersion

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