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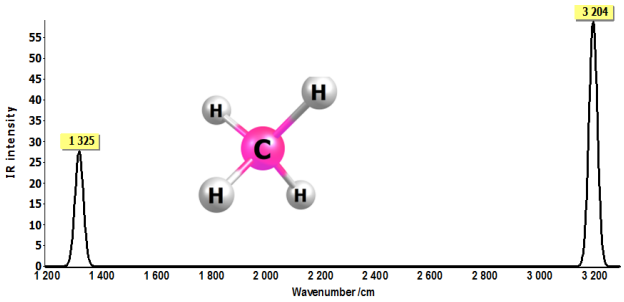

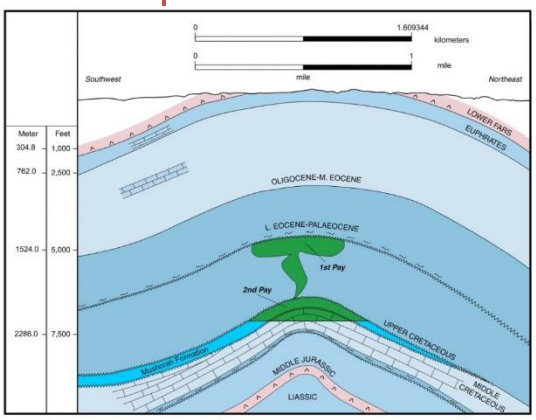

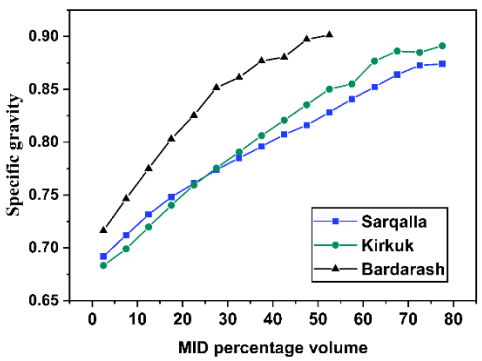

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Evaluation and Comparison between three different crude oils via chemical composition and physical properties including carbon distribution

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Abstract

For vast decision-making during the production process, knowing the physicochemical properties of petroleum and petroleum fractions is of major significance. Different types of crude oils from the Kurdistan Region and Iraq, namely (S for Sarqalla, K for Kirkuk, and B for Bardarash), have been compared, evaluated, and physicochemically characterized. American Society for Testing and Materials (ASTM), Universal Oil Production (UOP), and Institute of Petroleum (IP) standard test methods were used to estimate (density (Kg/m^3), API gravity, viscosity (cSt), salt content (ppm), H_2S content (ppm), flash point (^oC), pour point (^oC), sulphur (wt%), Reid vapor pressure (psi), asphaltene (wt%), and ash content (wt%)) to know the complexity of crude oils. Crude oils were fractionated into fractions based on their true boiling point via carbon distribution, including the paraffin, naphthenic, and aromatic (PNA) composition of their fractions through the refractive index-density-Molecular weight (n-d-M) method using a standard test method of ASTM D 3238, as well as the determination of metal elements in crude oils by inductively coupled plasma optical emission spectroscopy (ICP-OES). Afterward, Fourier transform infrared (FT-IR) spectroscopy was used for the characterization of precipitated asphaltene in crude oils and their residues (+270 ^oC). It was found that they have very similar chemical structures.

Introduction

Petroleum occurs in sedimentary rocks, whether as liquids, gases, solids, or semisolids. From a chemical viewpoint, it refers to a mixture of more than one hydrocarbon, which is naturally occurring, and other organic and inorganic species composed of oxygen, sulfur, and nitrogen atoms, as well as trace levels of metallic components, for instance vanadium, nickel, copper, and iron(1, 2). The developed industrial community utilizes crude oils in inner combustion and jet engines as fuel to obtain mobility. Petroleum fluid and its derivatives are also utilized in the production of plastics, fertilizers, paints, construction materials, medications, and clothes, as well as in the production of power (3).

In the fossil energy resource industry, information about the physical, chemical, and thermodynamic properties of crude oil mixtures is of major significance in the operation and design of vast parts of apparatus to adjust the equipment's proficiency, consumption of energy, and setting time. Petroleum and petroleum fractions are classified and characterized due to the variation and complexity of chemical composition (4).

Petroleum crude oil separates into four different groups: saturates, aromatics, resins, and asphaltenes (SARA), which is the most widely used classification approach based on their polarity and solubility (5).

Characterization of crude oils and petroleum fractions includes qualification and quantification, including traditional characterization methods that are all standardized by organizations such as ASTM, the Energy Institute (EI), and the American Petroleum Institute (API) (6) were applied. Also spectroscopic techniques such as Gas Chromatography (GC) (7), FT-IR spectroscopy (8, 9), Nuclear Magnetic Resonance (NMR) (10), Ultra Violet (UV) spectroscopy (11), mass spectrometry (12), High Performance Liquid Chromatography (HPLC) (13), atomic absorption spectroscopy (AAS) (14), an elemental analyzer Model CHNS-932 (15), molecular absorption spectroscopy (16), ICP-OES (17), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) (18), X-ray fluorescence spectrometry (19), and Thin-Layer Chromatography – Laser Desorption Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometric (TLC-LDI-MS) were used to evaluate crude oil and oil products (20).

The n-d-M approach, established by Van Nes and Van Westen in the 1950s, is the earliest known method for predicting (PNA) composition (21). After World War II, researchers at Koninklijke/Shell in Holland developed it. The purpose of this approach is to determine the carbon type distribution and demonstrate the percentage of carbon in the aromatic structure (% C_A), the percentage of carbon in the naphthenic structure (% C_N), the percentage of carbon in total (aromatic and naphthenic ring) (% C_R), and the percentage of carbon in the paraffinic structure (% C_P) (22). It equips the mean number of naphthenic (R_N) and aromatic (R_A) rings per molecule (6). It is also provided in the ASTM Manual under the ASTM D 3238 test method (23).

Kesler M.G. et al. (1976) (24) estimated the physical properties such as critical pressure, critical temperature, and molecular weight based on the boiling point and specific gravity of petroleum fractions as input data. In addition, Rodrigues Érica V.A. et al. (2018) (25) mined the physicochemical properties of crude oils by high-temperature gas chromatography associated with partial least squares (PLS) regression, which was automated, required few amounts of samples and enabled quick visualization of the oil's chemical profile. Characterization of pure and undefined petroleum fractions of Messla and Sarir crude oils of Libya using correlation models, such as Twu, Cavett, Kesler-Lee, and Riazi-Daubert correlations have been studied by Ibrahim Abou El Lei M. I. et al. (2020) (26). The computations found that there was no significant difference between correlation models and the obtained data seemed to be very close to previously published results.

Ahmed Rawaz A. et al. (2016) (27) determined the characterization, physical properties, and product distributions of Hassira and Khurmala crude oils based on the TBP distillation data and density of the-whole crude oils using Aspen HYSHYS software.

Doryani H. et al. (2016) (28) extracted asphaltene ASTM (D2007-80) by mixing n-heptane with crude oil (40:1). The solution was then stirred and shaken for 4 h and left for 48 h. Then asphaltene was filtered through Whatman filter papers. Asphaltene was re-dissolved in toluene to obtain high purity.Salim et al. (2019) (29) separated asphaltene by adding 300 mL of n-heptane into 10 g of crude oil sample then heating at 80 ^{o}C for half an hour. The mixture was kept overnight in a dark place. The mixture was filtered through a Whatman 42 membrane with a 2.5 μm pore size and 150 mm diameter. Asphaltene was extracted by utilizing toluene and soxhlet extraction at 60 ^{o}C. A rota evaporator was used at 60 ^{o}C to evaporate toluene, and for complete drying of asphaltene, it was left in an oven at 80 ^{o}C.

In this work, three different crude oils from Kurdistan Region and Iraq are evaluated and then compared utilizing fractional distillation and standard test methods of ASTM, UOP, and IP to find their physicochemical properties via carbon distribution PNA composition of their fractions as well as determination of their metal content.

Materials and Methods

Crude oil samples and materials

The three samples of crude oils were collected from the fields of Sarqalla, Kirkuk, and Bardarash in the Kurdistan Region and Iraq, as shown in (Figure 1) (30). Nitric acid 69 % was supplied by BIOCHEM which was used for the digestion of elements. For salt content mixture of alcohol (37% methanol and 63% i-butanol) and xylene were used and supplied by Merck. For Basic Sediments and Water content, xylene was used and supplied by Merck. A standard reagent was used for elemental analysis, which was supplied by Sigma-Aldrich. n-Hexane (99 wt%) was used for asphaltene precipitation, which was supplied by BIOCHEM.

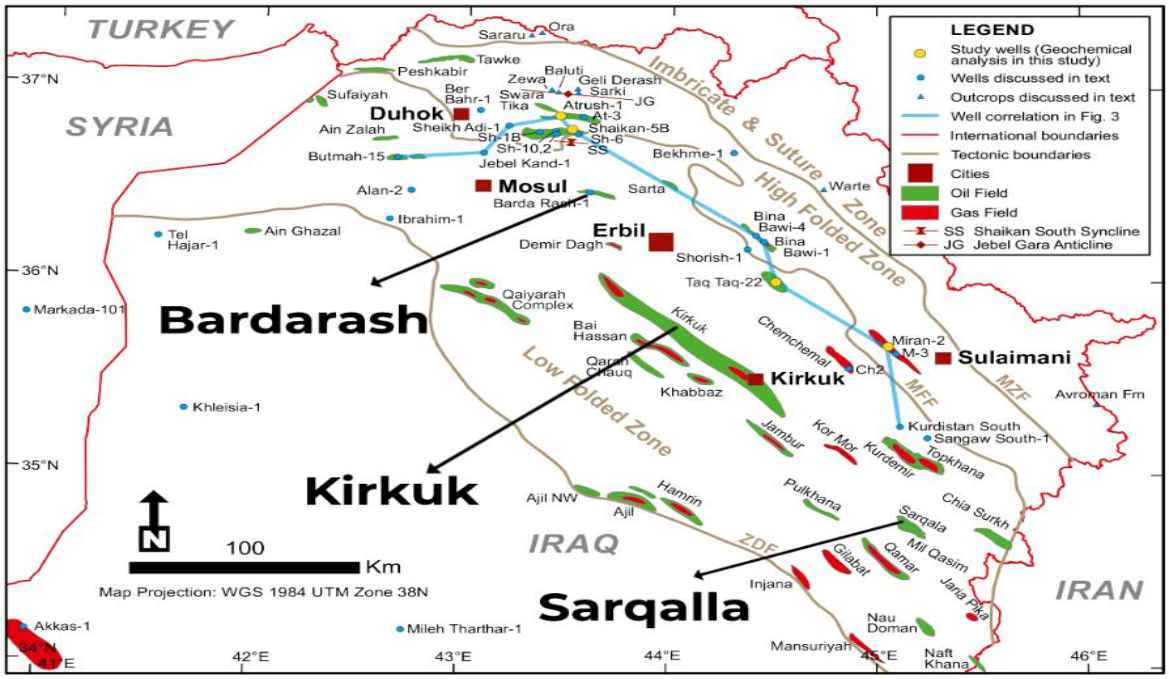

Figure 1. Location map of S, K, and B oil field (from Mohialdeen I. M. J. et al. (30) with permission).

Analysis of petroleum crude oil and petroleum fractions

Crude oils and their fractions were characterized according to standard methods such as ASTM, UOP, and IP. As shown in (Table 1), these standards are density (ASTM D 1298) was determined by Anton Paar-DMA 45000M, API gravity (ASTM D 4052), flash point (ASTM D 93), pour point (ASTM D 97), kinematic viscosity (ASTM D 445), basic sediment and water content (ASTM D 4007) was determined by centrifuge SETA, color (ASTM D 1500), hydrogen sulphide (UOP 163) by SPARAGE method, copper corrosion (ASTM D 130), ash content (ASTM D 482), Reid vapor pressure (ASTM D 6377) was determined by MiniVapour Pressure Tester (Grabner) MINI VAP, distillation (ASTM D 86), carbon distribution and group analysis (ASTM D 3238), refractive index (ASTM D 1218), salt content (ASTM D 3230) was determined by STANHOPE-STA salt-in-crude analyzer and sulfur content (ASTM D 4294) was determined by Portable Sulphur content analyzer (NEX QC). Elemental analysis was determined by ICP, model Perkin-Elmer ICP-OES Optima 2100 DV. The IR spectra of precipitated asphaltene were recorded on Nicolet iS 10 FTIR Spectrometer in the range (400–4000cm^{-1}).

Table 1. Physicochemical parameters of Kurdistan Region and Iraq crude oils.

Test	Unit	Methodology	Sarqalla	Kirkuk	Bardarash
Density at 15.6 ºC	Kg/m^3	ASTM D 1298	822.70	843.50	928.68
Specific gravity at 15.6 ºC		ASTM D 1298	823.50	844.30	929.50
API gravity at 15.6 ºC		ASTM D 4052	40.30	36.10	20.70
Salt	ppm	ASTM D 3230	10.83	8.26	138.00
H_2S	ppm	SPARAGE Method (UOP 163)	0.00	1.00	0.00
Sulphur	Wt%	ASTM D 4294	1.089	2.274	4.965
Basic Sediment and Water	Vol%	ASTM D 4007	0.00	0.00	0.00
Reid vapour pressure	psi	ASTM D 6377	3.77	2.48	2.10
Pour point	ºC	ASTM D 97	-36	-50	-20
Flash point	ºC	ASTM D 93	+15	+15	+18
Viscosity at 40 ºC	cSt	ASTM D 445	3.14	5.23	260.50
Viscosity at 50 ºC	cSt		2.46	4.31	139.77
Viscosity at 70 ºC	cSt		1.79	2.98	76.24
Viscosity at 80 ºC	cSt		1.64	2.36	38.12
ASTM Color		ASTM D1500	Darker than 8.0	Darker than 8.0	Darker than 8.0
Ash content	Wt.%	ASTM D 482	0.02988	0.01394	0.05577
Asphaltene	Crude oil wt.%	IP 143	0.44	3.93	19.45
	Residue (+270) wt.%		1.24	5.14	23.95

Fractional distillation of crude oil

Distillation of crude oil samples into fractions was conducted in a laboratory distillation unit according to ASTM D 86, consisting of a distillation flask, electrical heating mantle, condenser, fractional column, graduated receiver, ice bath with water recirculation, and thermometer.

A 100 ml crude oil sample was distilled in a 250 ml distillation flask. The temperature was recorded at each 5% v/v of distillate obtained, up to a maximum of 350 ºC or when the distillation was stopped, as shown in (Table 2). Another type of distillation into five fractions (IBP-80 ºC), (80-120 ºC), (120-170 ºC), (170-210 ºC), and (210-270 ºC) was achieved by taking 200 ml of petroleum crude oils in a 250 ml round-bottom flask, as shown in (Table 3, 4, and 5) (31).

Table 2. Fractional distillation of S, K, and B crude oil.

Vol. %	S			K			B		
	T (ºC)	Sp.gr at 15.6 ºC	Cummula-tive wt. %	T (ºC)	Sp.gr at 15.6 ºC	Cummula-tive wt. %	T (ºC)	Sp.gr at 15.6 ºC	Cummula-tive wt. %
IBP	56			59			62		
5	87	0.6920	4.21	84	0.6834	4.05	140	0.7164	3.86
10	120	0.7120	8.53	95	0.6991	8.20	173	0.7464	7.88
15	137	0.7316	12.98	116	0.7198	12.46	210	0.7751	12.05
20	150	0.748	17.53	124	0.7403	16.85	245	0.8030	16.37
25	165	0.7611	22.15	142	0.7595	21.35	280	0.8254	20.82
30	178	0.7739	26.85	170	0.7754	25.95	300	0.8515	25.40
35	197	0.7850	31.63	181	0.7908	30.64	320	0.8613	30.04

40	210	0.7958	36.46	208	0.8063	35.42	335	0.8768	34.76
45	216	0.8073	41.37	233	0.8208	40.28	340	0.8803	39.50
50	234	0.8161	46.33	259	0.8353	45.23	347	0.8973	44.33
55	261	0.8281	51.36	286	0.8501	50.27	350	0.9012	49.18
60	285	0.8408	56.47	309	0.8551	55.34	-	-	-
65	305	0.8523	61.65	320	0.8766	60.54	-	-	-
70	321	0.8638	66.90	335	0.8861	65.79	-	-	-
75	333	0.8726	72.20	345	0.8850	71.03	-	-	-
80	340	0.8740	77.52	350	0.8910	76.32	-	-	-
85	-	-	-	-	-	-	-	-	-
90	-	-	-	-	-	-	-	-	-
95	-	-	-	-	-	-	-	-	-
100	-	-	-	-	-	-	-	-	-

Table 3. Distillated cumulative volume and weight percentage of different temperature for S crude oil.

Temperature ºC	**Specific Gravity at 15.6 ºC**	**vol. %**	**cumulative vol. %**	**wt. %**	**cumulative wt. %**
IBP-80	0.6848	1.50	1.50	1.25	1.25
80-120	0.7102	7.50	9.00	6.47	7.72
120-170	0.7498	14.80	23.80	13.49	21.21
170-210	0.7871	11.45	35.25	10.95	32.17
210-270	0.8175	17.00	52.25	16.89	49.06
Residue (+270 ºC)		37.75	90.00		

Table 4. Distillated cumulative volume and weight percentage of different temperature for K crude oil.

Temperature ºC	**Specific Gravity at 15.6 ºC**	**Vol.%**	**Cumulative vol. %**	**Wt.%**	**Cumulative wt.%**
IBP-80	0.6806	2.50	2.50	2.02	2.02
80-120	0.7067	7.55	10.05	6.33	8.34
120-170	0.7496	11.55	21.60	10.26	18.61
170-210	0.7874	8.40	30.00	7.84	26.45
210-270	0.8248	13.45	43.45	13.15	39.60
Residue (+270 ºC)		47.55	91.00		

Table 5. Distillated cumulative volume and weight percentage of different temperature for B crude oil.

Temperature ºC	**Specific Gravity at 15.6 ºC**	**Vol.%**	**Cumulative vol. %**	**Wt.%**	**Cumulative wt.%**
IBP-80	0.6785	0.95	0.95	0.69	0.69
80-120	0.7095	3.45	4.40	2.64	3.33
120-170	0.7542	8.75	13.15	7.11	10.44
170-210	0.7928	6.25	19.40	5.34	15.77
210-270	0.8382	13.25	32.65	11.96	27.73
Residue (+270 ºC)		56.35	89.00		

n-d-M Approach

The refractive index, density, and molecular weight were used as input data in this method; the value of PNA was then calculated using the standard test method of ASTM D 3238.

Asphaltene Preparation

To precipitate asphaltene from crude oil and residue (+270 ºC), IP-143 was carefully utilized. n-hexane was added to the crude oil or residue (+270 ºC) in a ratio of 40:1. The mixture was then refluxed, boiled for 1h and left in the darkness for 1h. Then, the solution of precipitated asphaltene was filtered using Whatman 42 filter paper. The precipitate was washed several times with n-hexane until a clear solution was obtained. Finally, the asphaltene was dried at 80 ºC in an oven.

Results and Discussion

Physicochemical Properties of Petroleum Crude Oils

Specific gravity, API gravity, and sulfur content are significant parameters, particularly utilized for the classification of petroleum crude oil samples. In general, the API gravity of crude oil increases while the specific gravity decreases. API gravity has also been reported to have an inverse relationship with the sulfur content of crude oil. Also, the sulfur content of crude oil is known to increase as the specific gravity increases (32).

As shown in (Table 1), API gravity and sulfur content determine the quality of crude oils. A comparison of the values of API gravity and sulfur content obtained from Kurdistan Region and Iraq crude oils in this study shows that S crude oil can be classified as a light sour crude oil, the K light sour crude oil, but the B sulfur content was 4.965 wt% which means intermediate sour crude oil.

Fractional Distillation of Petroleum Crude Oils and Their fractions

Nowadays, crude oil distillation is a significant operation in all refineries. The process of separating hydrocarbons in crude oil based on their boiling points is known as crude distillation.

(Table 2) illustrated the fractional distillation data of each type of S, K, and B crude oils. A temperature was recorded at every 5 mL distilled until 360 ºC at volume zero. The specific gravity was measured, as well as the cumulative volume and weight percent were calculated. The initial boiling point of the crude oils is different from one to another, the volume of the final boiling point is different from S, which has a wide volume range starting from 0 to 80 ml. K started from 0 to 79.4 mL, and B started from 0 to 55 mL. The volume and weight percent increased with increasing boiling temperature as shown in (Figure 2 and 3). This indicates that, with increased mass, the number of carbon atoms has increased. (Figure 4) shows the relation between the specific gravity values and the mid-percent volume of the fractions distilled from S, K, and B crude oils. With increasing mid-percent volume of the fractions, the specific gravity increases. This is due to the increase in aromatics and the decrease in paraffinic content (33).

Table 3,4, and 5 showed another type of fractionating crude oils to produce various fractions like (IBP-80 ºC, 80-120 ºC, 120-170 ºC, 170-210 ºC, 210-270 ºC, and residue +270 ºC) that could be collected below (300 ºC) to avoid the thermal decomposition of remaining petroleum constituents (31); so the test was stopped at (270

°C). The specific gravity of each fraction was measured, and also the cumulative weight and volume perecent were computed.

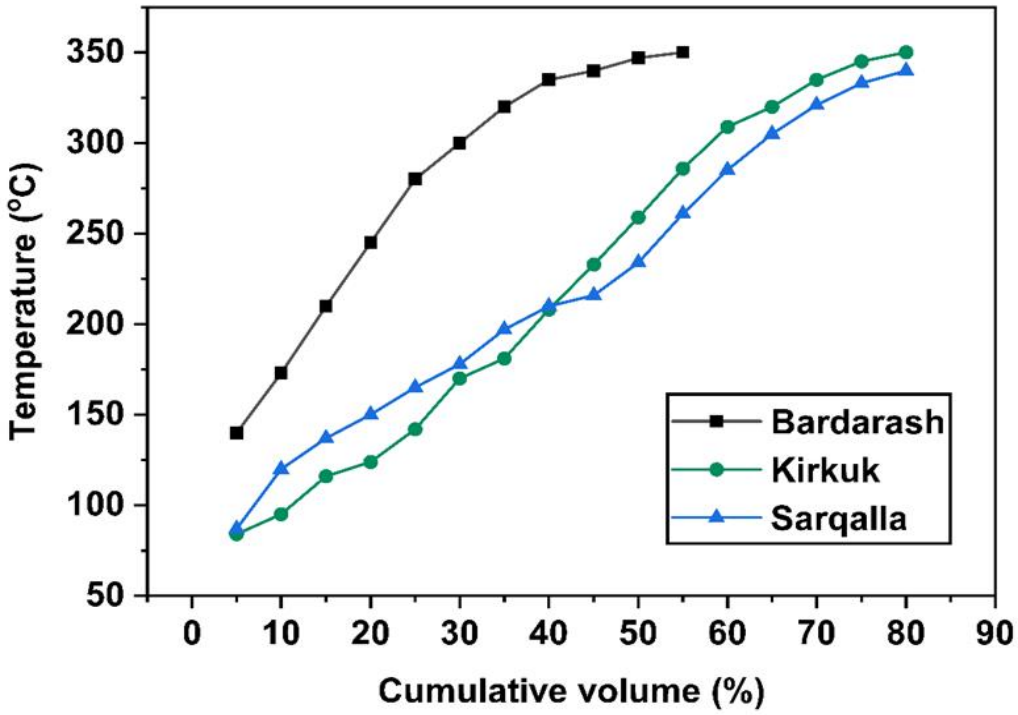

Figure 2. Relation between boiling point of fractions with cumulative volume percent.

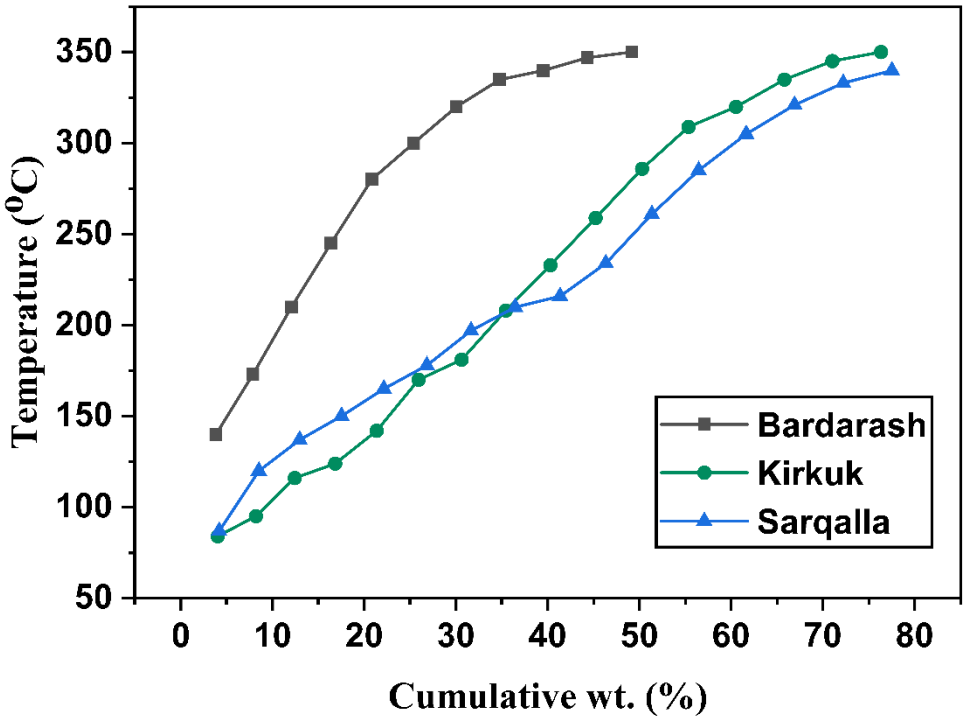

Figure 3. Relation between boiling point of fractions with cumulative weight percent.

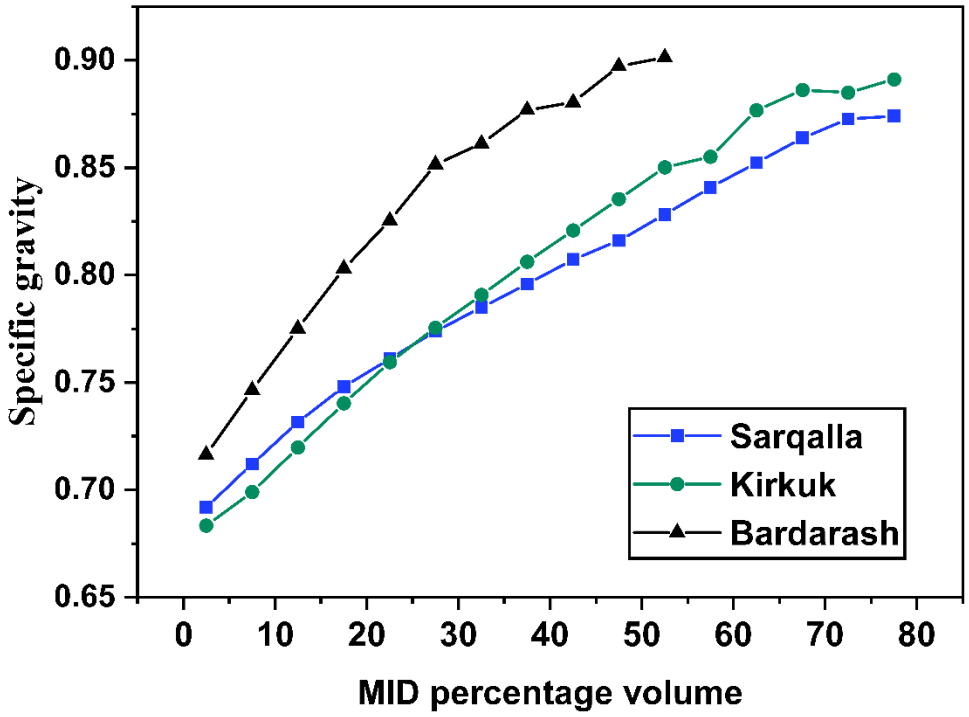

Figure 4. Relation between Specific gravity with mid-percent boiling point of fractions.

Figure 5 and 6 show the relation between cumulative weight and volume percent with the boiling point temperature of each fraction distilled from S, K, and B. The results indicated that S crude oil is lighter than K crude oil because the cumulative weight and volume percent of S crude oil are higher (49.06% and 52.25%) than K crude oil (39.60% and 43.45%), and B crude oil (27.73% and 32.65%) is heavier than K crude oil. (Figure 7) shows the yield percentage (vol.%) of each fraction for S, K, and B crude oils. It is observed that both S and K crude oils contain similar amounts of light products, but B crude oil contains a low amount of light products. On the other hand, S crude oil contains the highest amount of medium products compared to K and B crude oils. And B crude oil contain the heighest amount of residue (+270 ^{o}C) compared to K and S crude oils.

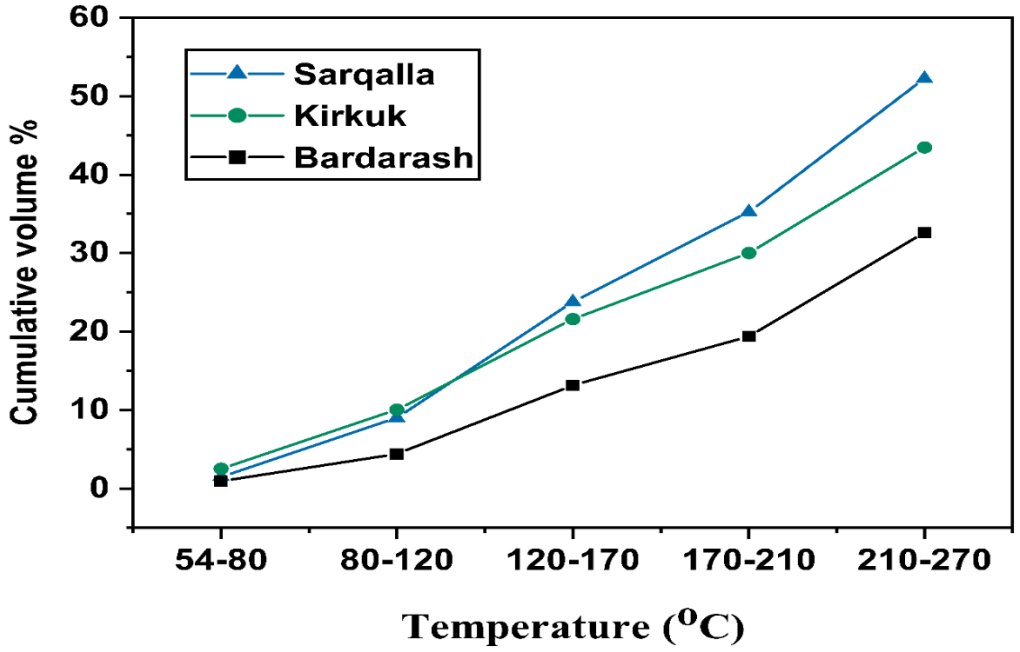

Figure 5. Relation between cumulative volume percent with boiling point temperature of five fractions of S, K, and B crude oil.

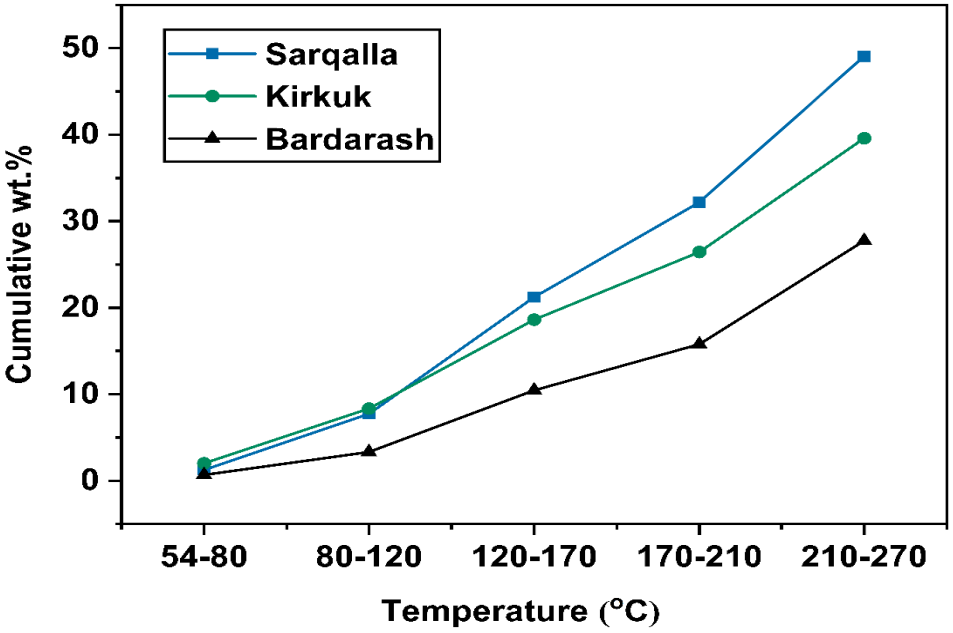

Figure 6. Relation between cumulative weight percent with boiling point temperature of five fractions of S, K, and B crude oil.

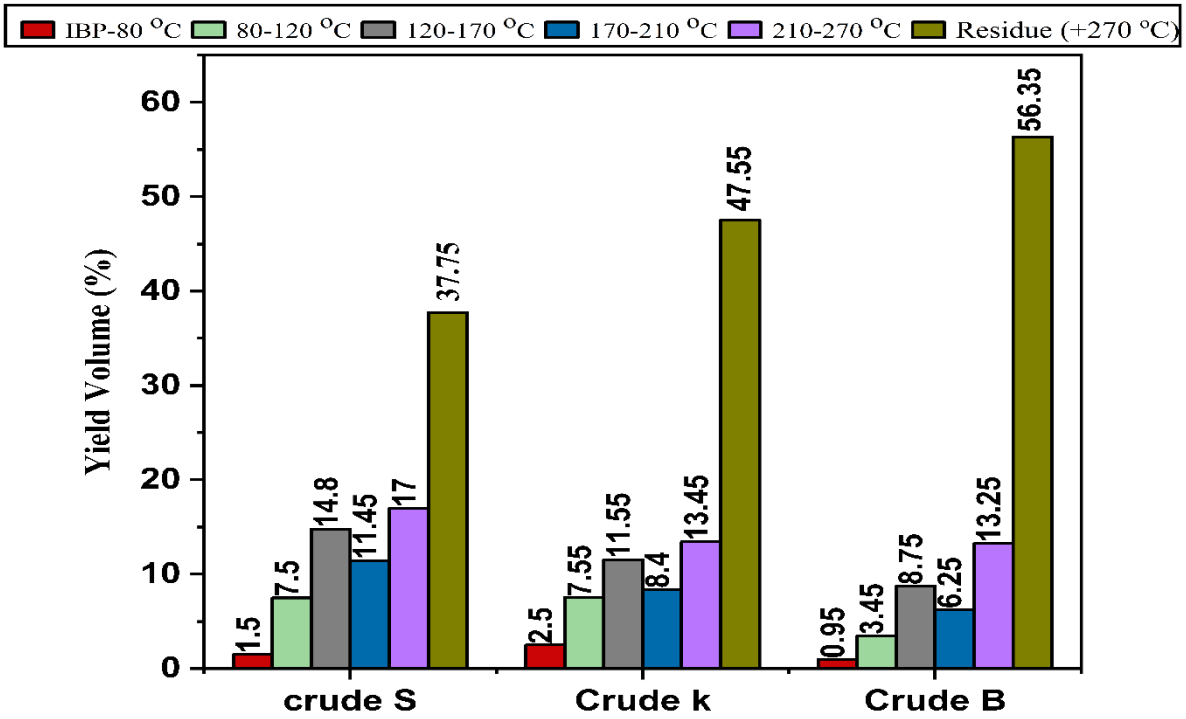

Figure 7. yield percentage (vol.%) of each fraction for S, K, and B crude oils.

Volume average boiling point and mean average boiling point are calculated by applying equations 1, 2, 3, and 4. The characterization factor (k), correlation index (CI), and molecular weight (M.wt) are calculated by equations 5, 6, and 7. (Table 6) shows the k factor values (12.51-11.82), (12.48-11.78), and (12.55-11.88) for fractions of S, K, and B crude oils, respectively. These results show that all fractions consist of naphthenic hydrocarbons. It is well known that highly paraffinic oils have k in the range (12.5–13.0) and cyclic (naphthene) oils have k in the range (10.5–12.5) (1). CI values for two light fractions of S and K crude oils contain paraffin hydrocarbon, while for B crude oil, three fractions at the first contain paraffin hydrocarbon. Other fractions of three different crude oils contain either naphthenes or mixtures of paraffins, naphthenes, and aromatics.

$$\mathrm{VABP} = \frac{(t10+t30+t50+t70+t90)}{5} \quad (1)$$

$$\mathrm{MeABP} = VABP - \Delta \quad (2)$$

$$\mathrm{Slope} = \frac{(t90-t10)}{90-10} \quad (3)$$

$$Ln\Delta = -0.94402 - 0.00865(VABP - 32)^{0.6667} + 2.99791(slope)^{0.333} \quad (4)$$

$$\mathrm{k} = \frac{(MeABP)^{1/3}}{Sp.gr.\ at\ 15.6\ ^{\circ}\mathrm{C}} \quad (5)$$

$$\mathrm{CI} = \frac{473.7d-456.8+48640}{K} \quad (6)$$

$$M.Wt = 60 + 0.3t + 0.001(t)^2 \quad (7)$$

Where MeABP is the average boiling point in degrees Rankine (°F+ 460) and VABP is the volume average boiling point in °C. Where t is the average boiling point in °C and k is the characterization factor. Where K for

a petroleum fraction is the average boiling point determined by the Standard Bureau of Mines distillation method, in ºK (ºC + 273.15), and d is the specific gravity at 15.6 ºC/15.6 ºC. Where CI is the correlation index.

Table 6. Basic data for calculating the structural group composition.

Fractions	S			
	R.I	k-factor	C.I	M.Wt
IBP-80 ºC	1.39399	12.51	4.62	86.65
80-120 ºC	1.39886	12.26	10.74	96.93
120-170 ºC	1.41627	11.98	17.55	115.70
170-210 ºC	1.43445	11.78	24.78	139.94
210-270 ºC	1.45143	11.82	26.62	180.52
Fractions		**K**		
IBP-80 ºC	1.38814	12.48	5.87	89.75
80-120 ºC	1.40274	12.26	10.60	99.10
120-170 ºC	1.41822	11.94	18.91	116.12
170-210 ºC	1.43635	11.76	25.07	141.82
210-270 ºC	1.45610	11.78	27.58	180.08
Fractions		**B**		
IBP-80 ºC	1.39302	12.55	3.47	82.65
80-120 ºC	1.40080	12.33	8.18	91.78
120-170 ºC	1.41916	12.08	14.76	111.75
170-210 ºC	1.43824	11.87	22.40	135.78
210-270 ºC	1.46168	11.88	25.24	175.14

Figure 8 shows the relation between k-factor and CI with five fractions of S, K, and B crude oils. It is well known that the CI values for the index between 0 and 15 indicate a predominance of paraffin hydrocarbons in the fraction. A value between 15 to 50 indicates a predominance of either naphthenic or a mixture of paraffinic, naphthenic, and aromatic. An index value of more than 50 indicates a predominance of aromatic species (6). In general, low boiling point fractions have higher paraffinic and lower aromatic contents, while as the boiling point of the fraction increases, the amount of aromatic content also increases (3).

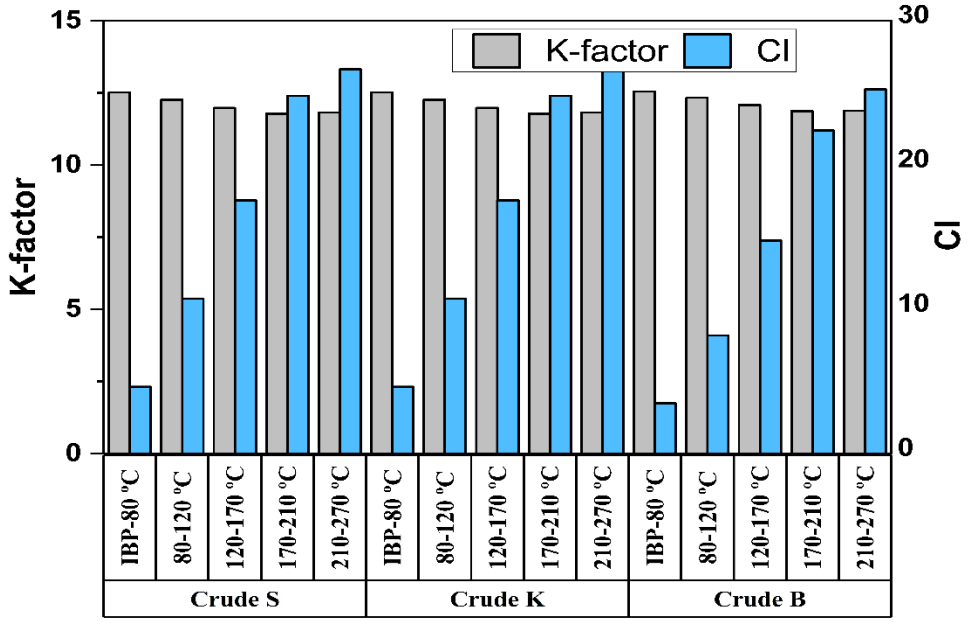

Figure 8. Relation between K-factor & CI with five fractions of S, K, and B crude oils.

PNA Composition

Determination of structural group analysis (PNA) composition for S, K, and B fractions are shown in (Tables 7 a, b, and c). The results show that the % C_R for fractions of S, K, and B crude oils increased with temperature from (9.69 % to 47.46 %), (11.53 % to 50.10 %), and (10.85 % to 59.48 %) respectively. And the % C_P for the fractions of S, K, and B decreased with temperature, meaning the paraffinic decreased from (90.31 % to 52.54 %), (88.47 % to 49.90 %), and (89.15 % to 40.52 %), respectively. The % C_P for the first fraction of S crude oil is equal to 90.31 %, which means it contains a high content of saturated hydrocarbons. The relationship between carbon distribution % with five fractions of the three different crude oils is given in (Figure 9). The molecular structure of S, K, and B fractions are composed mainly of polycyclic cores containing aromatic and/or naphthenic rings (R_T) increased with temperature from (0.11 % to 1.05 %), (0.13 % to 1.09 %), and (0.12 % to 1.19 %), respectively. The relationship between ring distribution with five fractions of the three different crude oils is shown in (Figure10). The results of structural group analysis are in accordance with the results of k-factor and CI.

Table 7. Indicators of PNA composition for (a) S (b) K (c) B fractions.

(a)

Fractions	**Values**		**Percentage of C atom in fraction**				**Number of rings per a molecule**		
	v	**w**	**% C_A**	**% C_R**	**% C_N**	**% C_P**	**R_A**	**R_T**	**R_N**
IBP-80 °C	-0.037135	-0.076278	16.40	9.69	6.71	90.31	0.18	0.11	0.06
80-120 °C	-0.050311	-0.056284	4.05	28.26	24.21	71.74	0.05	0.35	0.3
120-170 °C	-0.046212	-0.036009	0.67	39.65	38.98	60.35	0.01	0.58	0.56
170-210 °C	-0.037880	-0.018889	0.77	48.31	47.54	51.69	0.02	0.84	0.83
210-270 °C	-0.025660	-0.007337	3.08	47.46	44.38	52.54	0.07	1.05	0.98

(b)

Fractions	**Values**		**Percentage of C atom in fraction**				**Number of rings per a molecule**		
	v	**w**	**% C_A**	**% C_R**	**% C_N**	**% C_P**	**R_A**	**R_T**	**R_N**
IBP-80 °C	-0.047618	-0.073985	8.87	11.53	2.65	88.47	0.10	0.13	0.04
80-120 °C	-0.037072	-0.064091	12.09	14.62	2.53	85.38	0.15	0.19	0.04
120-170 °C	-0.041117	-0.038374	3.97	35.82	31.85	64.18	0.06	0.52	0.46
170-210 °C	-0.033411	-0.020698	3.42	44.50	41.08	55.50	0.06	0.78	0.72
210-270 °C	-0.021239	-0.005221	6.09	50.10	44.00	49.90	0.13	1.09	0.96

(c)

Fractions	**Values**		**Percentage of C atom in fraction**				**Number of rings per a molecule**		
	v	**w**	**% C_A**	**% C_R**	**% C_N**	**% C_P**	**R_A**	**R_T**	**R_N**
IBP-80 °C	-0.033269	-0.081502	21.99	10.85	11.14	89.15	0.22	0.12	0.10
80-120 °C	-0.044742	-0.059138	9.90	30.28	20.38	69.72	0.11	0.35	0.24
120-170 °C	-0.043358	-0.034817	3.70	44.17	40.47	55.83	0.05	0.61	0.56
170-210 °C	-0.034067	-0.017396	4.13	52.03	47.90	47.97	0.07	0.86	0.79
210-270 °C	-0.020633	0.001985	7.07	59.48	52.96	40.52	0.15	1.19	1.04

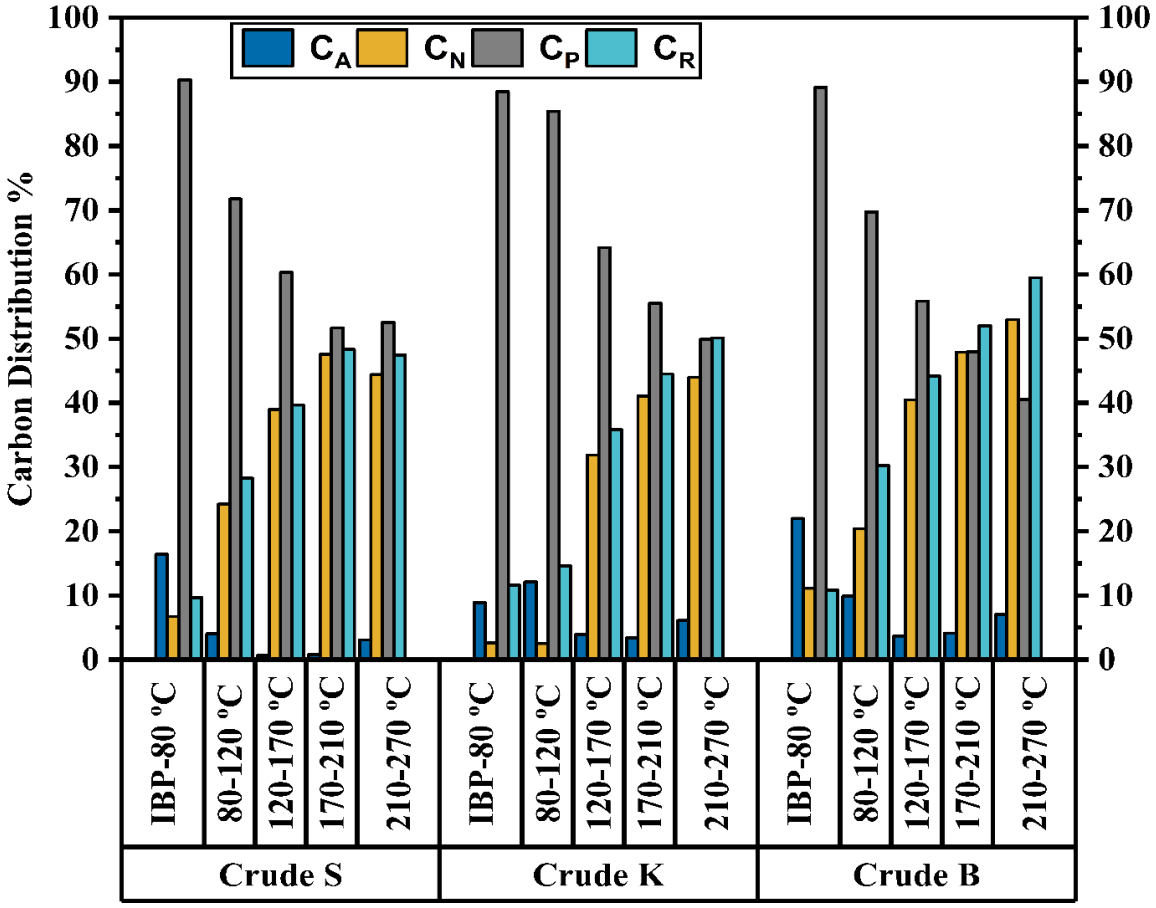

Figure 9. Relation between carbon distribution with five fractions of S, K, and B crude oils.

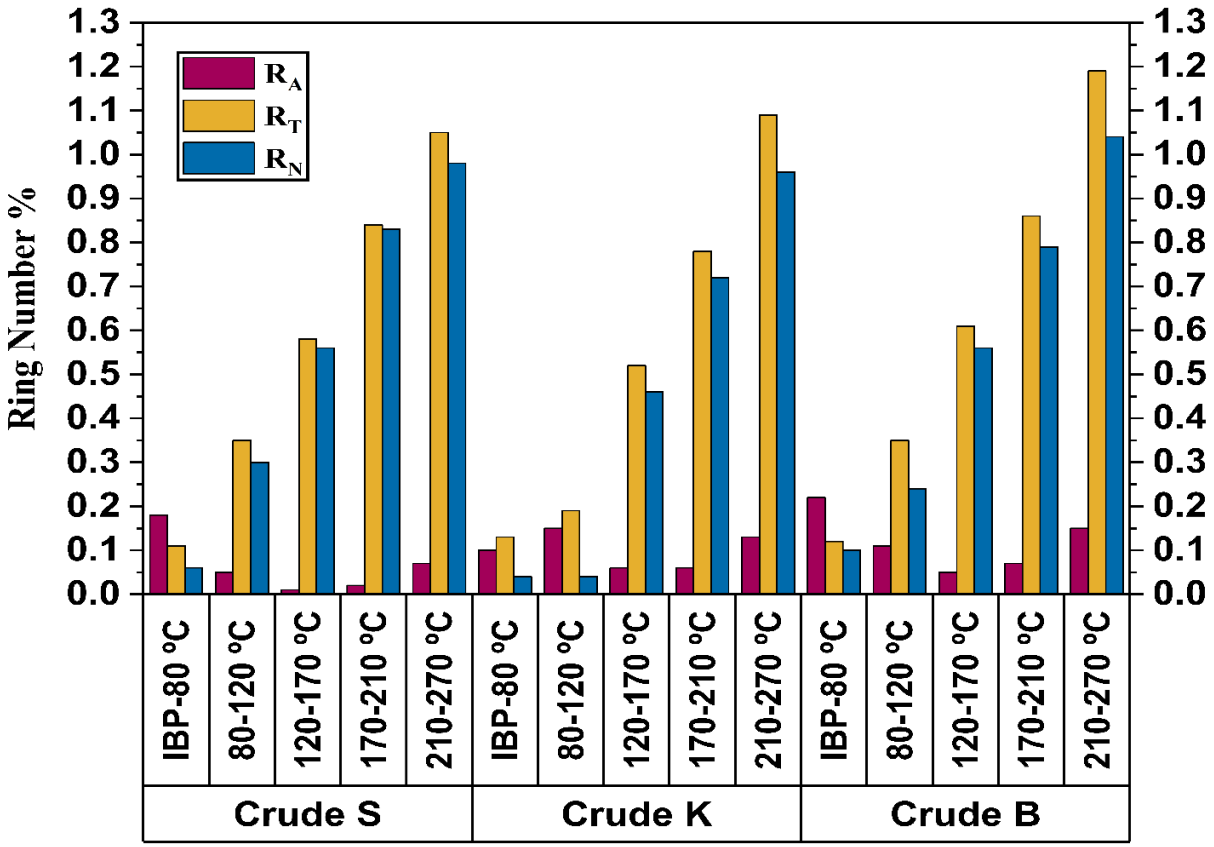

Figure 10. Relation between ring number with five fractions of S, K, and B crude oils.

D. Metals Content Determination in Crude Oils

Metallic constituents during recovery, transportation, and storage pick up in petroleum. Even trace concentrations of these metals can significantly impair refining processes, particularly those that involve catalysts. Trace components, such as metallic constituents, have negative impacts on refining, either by causing corrosion or by affecting the quality of refined products. As a result, having test procedures that can determine metals is essential. The ICP technique was used for the determination of metals in crude oils. Twenty-one elements were analyzed in crude oils as shown in (Table 8). Heavy crude oil B has the highest concentration of the following metals: (Na, Ni, Mo, Mg, Li, and Ca). Light crude oil S has the highest concentration of (K and Fe) metals, and medium crude oil K has the highest concentrations of (Al and Si).

Table 8. Concentration of some metals in Kurdistan region and Iraq crude oils.

Elements (ppm)	Sarqalla	Kirkuk	Bardarash
Aluminum (Al)	0.1011	0.2163	0.1175
Antimony (Sb)	0.0329	0.0421	0.0280
Barium (Ba)	0.0489	0.0375	0.0403
Boron (B)	0.0744	0.0524	0.0214
Cadmium (Cd)	0.0374	0.0376	0.0376
Calcium (Ca)	0.0650	0.0607	0.1426
Chromium (Cr)	0.0446	0.0441	0.0378
Cobalt (Co)	0.0364	0.0369	0.0391
Cupper (Cu)	0.0680	0.0501	0.0742
Iron (Fe)	0.2380	0.0745	0.1035
Lead (Pb)	0.0487	0.0450	0.0480
Lithium (Li)	0.0864	0.0608	0.1765
Magnesium (Mg)	0.1048	0.1952	0.3987
Manganese (Mn)	0.0408	0.0408	0.0491
Molybdenum (Mo)	0.0427	0.0388	0.5501
Nickle (Ni)	0.1667	0.1220	0.4979
Phosphor (P)	0.0777	0.1777	0.0777
Potassium (K)	0.7368	0.5991	0.5863
Silicon (Si)	0.2867	0.5101	0.1726
Sodium (Na)	0.7189	0.6685	1.5990
Titanium (Ti)	0.0416	0.0428	0.0471

FT-IR Analysis

The FT-IR characterization of the asphaltene fraction from S, K, and B crude oils and their residues (+270 ^{o}C) is reported in (Figure 11). As predicted, in (Table 9), the spectra of three types of crude oils and their residues (+270 ^{o}C) exhibited very similar chemical structures.

Table 9. Assignments of the IR spectrum bands of Asphaltene fraction.

Functional groups	Absorption bands (cm^{-1})
CH_3 (asym stretch)	2957
CH_2 (asym and symm stretch)	2920 and 2851
C=C aromatic	1598
CH_3 (asym and symm bending)	1455 and 1375
Sulfonate	1150 and 1025
Aromatic C-H (oop) bending	720 and 850

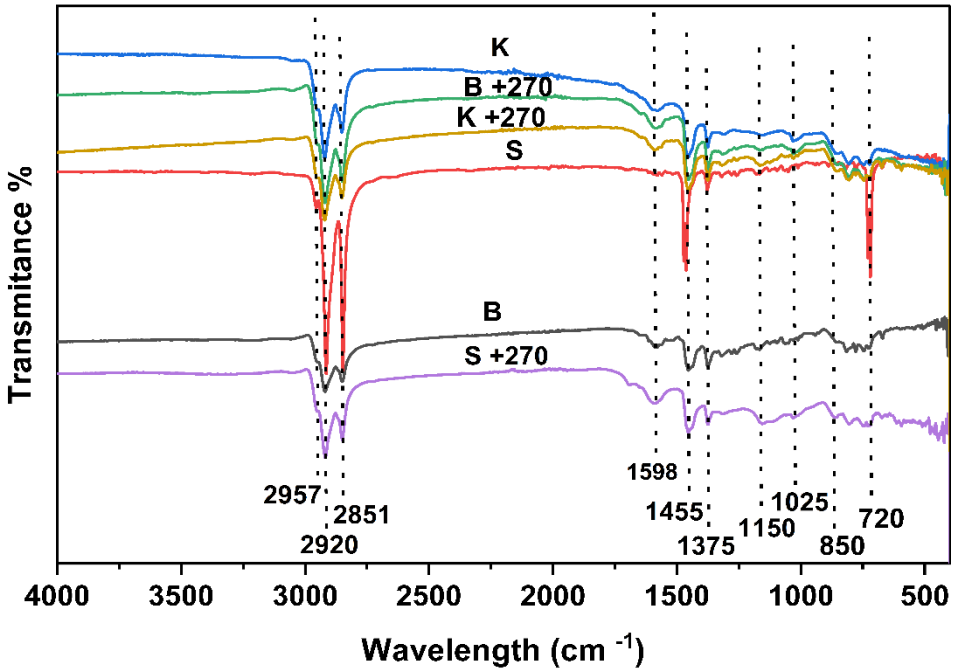

Figure 11. Infrared spectra of asphaltene fraction from S, K, and B crude oils and their residues (+270 °C).

The frequencies of the asphaltene fraction of the vibration spectra of hydrocarbons have been found in the stretching frequencies of the C-H (CH_2, CH_3 asym, symm) bond of alkyl at 2800-3000 cm^{-1}. The stretching of carbon-carbon double bonds of aromatic (C=C) is at 1598 cm^{-1}. The broad band structure between 1000 and 1200 cm^{-1} was assumed to be related to both sulfur structures and oxygenated structures. From the aromatic region bending (out of plane) between 720 and 850 cm^{-1}, it is observed that the aromatic structures are similar in terms of the number of adjacent hydrogens on aromatic rings for asphaltenes.

Conclusions

According to specific gravity and API-gravity, it was found that S crude oil (823.50 and 40.30) is lighter than K and B crude oils (844.30 and 36.10) and (929.50 and 20.70), respectively. And also, S and K crude oils give high amount of light fractions compared to B crude oil. In this study, sulfur content was obtained for Kurdistan Region and Iraq crude oils. S crude oil (1.089 wt%) can be classified as a light sour crude oil, K (2.274 wt%) as a light sour crude oil, and also B sulfur content (4.965 wt%), which means intermediate sour crude oil.

The total distillate from S crude oil was 49.06 wt% and from K crude oil was 39.60 wt%, while the total distillate from B crude oil was 27.73 wt%, and this revealed that S crude oil is lighter than K and B crude oil. The metallic constituent was determined in crude oils, which contain high amounts. They are problematic because they are poisons to the catalysts and can also cause significant corrosion to the refining equipment during the refinery, so they should be removed before the refining process. On-land area petroleum or petroleum spills have the potential to introduce hazardous heavy metals into water bodies and soils, which will threaten the surrounding ecosystem.

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Declarations

Conflict of interest. There are no competing or conflicts of interest to declare.

References

1. Speight JG. The Chemistry and Technology of Petroleum. 5 ed. Boca Raton, FL, USA: CRC Press; 2014. p. 953.
2. Yang W, Gao Y, Casey JF. Determination of trace elements in crude oils and fuel oils: a comprehensive review and new data. Solution Chem Adv Res Appl. 2018:159-205.
3. Coker AK. Petroleum Refining Design and Applications Handbook. Hoboken, USA: John Wiley & Sons; 2018.
4. Merdrignac I, Espinat D. Physicochemical characterization of petroleum fractions: the state of the art. Oil Gas Sci and Technol-Revue de l'IFP. 2007;62(1):7-32.
5. Rezaee S, Doherty R, Tavakkoli M, Vargas FM. Improved chromatographic technique for crude oil maltene fractionation. Energy Fuel. 2019;33(2):708-13.
6. Riazi M. Characterization and properties of petroleum fractions. 1 ed. West Conshohocken, USA: ASTM international; 2005.
7. Sampaio FXA, Garcia KS, de Souza Queiroz AF, Machado ME. Determination of organic sulfur markers in crude oils by gas chromatography triple quadrupole mass spectrometry. Fuel Process Technol. 2021;217:106813.
8. Müller ALH, Picoloto RS, de Azevedo Mello P, Ferrão MF, dos Santos MdFP, Guimarães RCL, et al. Total sulfur determination in residues of crude oil distillation using FT-IR/ATR and variable selection methods. Spectrochim Acta Part A. 2012;89:82-7.
9. Rakhmatullin I, Efimov S, Tyurin V, Al-Muntaser A, Klimovitskii A, Varfolomeev M, et al. Application of high resolution NMR (1H and 13C) and FTIR spectroscopy for characterization of light and heavy crude oils. J Pet Sci Eng. 2018;168:256-62.
10. Duarte LM, Filgueiras PR, Silva SR, Dias JC, Oliveira LM, Castro EV, et al. Determination of some physicochemical properties in Brazilian crude oil by 1H NMR spectroscopy associated to chemometric approach. Fuel. 2016;181:660-9.
11. Shehata AB, Mohamed GG, Gab-Allah MA. Simple Spectrophotometric Method for Determination of Iron in Crude Oil. Pet Chem. 2017;57:1007–11.
12. Terra LA, Filgueiras PR, Tose LV, Romao W, de Castro EV, de Oliveira LM, et al. Laser desorption ionization FT-ICR mass spectrometry and CARSPLS for predicting basic nitrogen and aromatics contents in crude oils. Fuel. 2015;160:274-81.
13. Woods J, J K, Kingston D, Kotlyar L, Sparks B, McCracken T. Canadian Crudes: A Comparative Study of SARA Fractions from a Modified HPLC Separation Technique. Oil Gas Sci Technol. 2008;63(1):151-63
14. Speight JG. Asphaltene and the structure of petroleum. Petroleum Chemistry and Refining. Newy York: Marcel Dekker; 1998. p. 103-20.
15. Alizadeh S, Fazelipour F, Mousavi SM, Mansourian R, Qajar J. A comparative experimental evaluation of the performance of additive compounds for inhibition of asphaltene precipitation from crude oil. Energ Source Part A. 2021:1-19.
16. Milner O, Glass J, Kirchner J, Yurick A. Determination of trace metals in crudes and other petroleum oils. Anal Chem. 1952;24(11):1728-32.
17. Poirier L, Nelson J, Leong D, Berhane L, Hajdu P, Lopez-Linare F. Application of ICP-MS and ICP-OES on the Determination of Nickel, Vanadium, Iron, and Calcium in Petroleum Crude Oils via Direct Dilution. Energy Fuel. 2017;30(5):3783–90.
18. Sugiyama I, Williams-Jones A. An approach to determining nickel, vanadium and other metal concentrations in crude oil. Anal Chim Acta. 2018;1002:18-25.
19. Doyle A, Saavedra A, Tristao M, Aucelio R. Determination of S, Ca, Fe, Ni and V in crude oil by energy dispersive X-ray fluorescence spectrometry using direct sampling on paper substrate. Fuel. 2015;162:39-46.

20. Zahraei A, Arisz PW, van Bavel AP, Heeren RM. Evaluation of Thin-Layer Chromatography–Laser Desorption Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometric Imaging for Visualization of Crude Oil Interactions. Energy Fuel. 2018;32(7):7347-57.
21. Van Nes K, Van Westen HA. Aspects of the constitution of mineral oils. New York: Elsevier Publishing Company; 1951. 484 p.
22. Lynch TR. Process chemistry of lubricant base stocks. 1 ed. Boca Raton, FL, USA: CRC Press; 2007. 392 p.
23. International A. ASTM D3238-17a, Standard Test Method for Calculation of Carbon Distribution and Structural Group Analysis of Petroleum Oils by the n-d-M Method. 2017;5(Reapproved 2000):1-2.
24. Keseler MG, Lee BI. Improve prediction of enthalpy of fraction. Hydrocarbon Process. 1976;55:153-8.
25. Rodrigues ÉV, Silva SR, Romão W, Castro EV, Filgueiras P. Determination of crude oil physicochemical properties by high-temperature gas chromatography associated with multivariate calibration. Fuel. 2018;220:389-95.
26. Abou El Lei IM, Triki NM, Mezughi KM. Characterization of Pure and Undefined Petroleum Fractions of Messla and Sarir Crude Oils of Libya Using Correlation Models. Int J Sci res Sci Technol. 2020.
27. Ahmed RA, Karim AR, Jamel SM, Hamma-Saeed VS, Hussein BQ. Physical properties as indication for chemical composition of petroleum fraction of Hassira and Khurmala crude oil. Int J Eng Appl Sci. 2016;3(9):21-6.
28. Doryani H, Malayeri M, Riazi M. Visualization of asphaltene precipitation and deposition in a uniformly patterned glass micromodel. Fuel. 2016;182:613-22.
29. Ok S, Mahmoodinia M, Rajasekaran N, Sabti MA, Lervik A, van Erp TS, et al. Molecular structure and solubility determination of asphaltenes. Energy Fuel. 2019;33(9):8259-70.
30. Mohialdeen IM, Fatah SS, Abdula RA, Hakimi MH, Abdullah WH, Khanaqa PA, et al. Stratigraphic Correlation and Source Rock Characteristics of the Baluti Formation from Selected Wells in the Zagros Fold Belt, Kurdistan Region, Northern Iraq. J Pet Geol. 2022;45(1):29-56.
31. Simo SM, Naman SA, Ahmed KR, editors. Investigate the Carbon distribution and Structural Group Composition of Two Kurdistan Crude Oils (T-21A & PF2) and Their Fractions. 2018 International Conference on Advanced Science and Engineering (ICOASE); 2018: IEEE.
32. Ahmed BS. Desulfurization of Light and Heavy Gas Oil from Crudes of Kurdistan Region-Iraq by Oxidation, Solvent Extraction and Adsorption.: Sulaimani University; 2017.
33. Abdul-Karim MA-H, G. AH, Khaliq KHA. The Relationships betweenthe Physical andChemical Properties ofNarrow Fractions Distilled From Mixed Kirkuk and Sharki-Baghdad Crude Oils. Iraqi Journal of Chemical and Petroleum Engineering. 2008;9(2):1-8.