Classification of Crude Oils and its Fractions on the Basis of Paraffinic, Naphthenic and Aromatics

Wedad H. Al-Dahhan^{*} and Shaymaa MA Mahmood Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-Iraq. *Corresponding author: dahan6262@gmail.com

Abstract

The ratios of crude oils hydrocarbons vary according to its origin. Two types of crude oil (A&B) were selected from Dura refinery which was extracted from Basra oil fields. These samples were tested according to physical properties: density, Specific gravity, API gravity, Pour Point, Kw factor and Correlation Index. Results show that crude oil (A) heavier than (B) due to higher density; pour point and lowers (API). Crude oil (A) shows it has more aromatic compounds than the crude oil (B) according to its higher (Kw) and lower (CI) values or (B) contain more paraffinic compounds than (A) for the same reasons. Atmospheric distillation process was done according to ASTM 2892 method for the two selected crude oils. Fractions obtains were tested according to physical properties: density, Aniline Point, API gravity, Kw factor and Correlation Index. The nature of the ingredients for petroleum fractions derived from distillation of the crude oil samples can be classified on the basis of the Paraffinic, naphthenic or aromatic content, depending on the results obtained from distillation which confirm the findings stated above for crude oil. Fourier Transform Infrared Analysis was carried out for crude oils atmospheric fractions to identify the components in terms of being paraffinic, naphthenic or aromatics. Results refers to the same ingredients for crude oil B for the paraffinic and naphthenic components as in crude oil A but the main difference here is the disappearance of the bands for aromatics C-H stretching occur above 3000 cm⁻¹ for crude oil B which refers that this crude has less aromatic compounds than crude oil A. These results have been confirmed through ultraviolet tests. [DOI: 10.22401/ANJS.22.3.05]

Keywords: Crude oil, Distillation, FT-IR, Ultraviolet.

1-Introduction

Crude oil mainly contains hydrocarbons with a small proportion of other chemical compounds that can contain nitrogen, oxygen or sulphur and can contain elements such as iron, nickel, copper and palladium [1]. These components directly affect refining processes as well as the methods of analysis adopted [2].

The ratios of crude oils hydrocarbons vary according to its origin. The distribution of hydrocarbons to different types of crude oil depends on the petroleum reservoirs. The chemical and physical properties of this permeability will vary according to the different origins [3].

The most important and most common hydrocarbons in crude oil are the straight and branched alkanes (called paraffins), cycloalkanes (called naphthenes), aromatic hydrocarbons and the most complex chemical substances, such as the asphaltic ingredients, 800-2500[4]. its molecular weight is Hydrocarbons have a range of (15-60%) for paraffins, (30-60%) for naphthenes, (3-30%) for aromatics and the remainder is asphaltics [5].

Crude oil with low carbon, high hydrogen and high API (American Petroleum Institute) is rich in paraffins and produces large quantities of gasoline and light petroleum products, but oil with a large carbon, low hydrogen and a low API rich in animates, the first oil is called light oil and the second is called heavy oil [6]. Crude oil can be classified on the basis of the nature of its main hydrocarbons components as paraffinic, naphthenic or aromatic. The ratios of these ingredients vary in oil fractions resulting from crude oil distillation [7].

This work aims to identify two types of crude oil and its fractions on the basis of Paraffinic, Naphthenic and Aromatics using physical properties and spectrophotometric analysis.

2. Experimental

2.1. API (**American Petroleum Institute**) API gravity used to specify the specific gravity

(SG) of the crude oil as API = (141.5/SG) - 131.5. SG is the specific gravity which is defined as the ratio of the density of the crude oil to the density of water at 15.6 °C (60 °F) for both. The API gravity classification illustrated in Table 1[8].

Table (1)The API gravity classification.

API gravity	Description
less than 10	very heavy crudes
between 10 and 30	heavy crudes
between 30 and 40	medium crudes
above 40	light crudes

Density and specific gravity at a temperature of 20°C was determined according to ASTM 1217.

2.2. Crude oil classification by characterization factor

Since then, oil factories have been willing to draw up classifications based on practical mathematical bases for classifying the identity of hydrocarbons in crude oil, Watson "characterization factor" (Kw) is one of the oldest indicators used to categorize the identity of crude oil[9]. Equation (1) illustrates how to calculate (Kw) and correlation index (CI) as shown in equation (2) [10].

 $Kw= (TB)^{1/3} /G$ (1) CI= 87552/TB +473.7 G - 456.8 (2)

(TB) is the average boiling point in degrees Rankine ($^{\circ}F+460$)

(G) is the specific gravity $60^{\circ}/60^{\circ}F$.

Highly paraffin oils have K in the range 12.5 to 13.0 and cyclic (naphthene) oils have K in the range 10.5 to 12.5. The CI scale is based upon straight-chain paraffins having a CI value of (0) and benzene having a CI value of (100). The lower the CI value, the greater the concentration of paraffin hydrocarbons in the fraction, and higher the CI value, the greater the concentration of naphthenes and aromatics [11].

2.3. Aniline point

Aniline point can be defined as the lowest temperature possible to blend equal volumes from liquid petroleum fraction with aniline. The degree of aniline is important in the knowledge of the properties of the petroleum fractions which increases with molecular weight and carbon number increases. For equal number of carbon, aniline point increases for the largest proportion of the paraffin and decreases for aromatics present in petroleum fractions [10]. Therefore, the aniline point is an indicator that is highly related to the hydrocarbon types in petroleum fractions [12].The aniline point has been measured according to ASTM-D 611[7].

2.4. Crude oil distillation

Distillation under normal atmospheric pressure separates the ingredients of crude oil into oil derivatives with slightly different boiling points [13]. The distillation of crude oil or petroleum includes two types, first distillation under normal atmospheric pressure and the other under vacuum. In the first, it produces oil fractions called straight run products, the most important of which are the gasoline, kerosene and gas oil while vacuum distillation products include mainly vacuum gas oil (VGO) [14]. From distillation operations under normal atmospheric pressure, it is possible to obtain important data on the boiling points of the oil products against the volumes produced for those derivatives, through which the distillation curve can be drawn, the quantities of the gasoline, kerosene, gas oil and heavy residues within this stage [15]. Atmospheric distillation was done using the ASTM D 2892 method and at temperatures not exceeding 350°C to avoid thermal cracking within this stage [16]. Two samples of crude (A & B) recovered from Dura oil refinery. distillation has been carried out in distillation apparatus, according to ASTM-D 2892.The standard limits for crude oil atmospheric distillation fractions are: (32.2-104.4)°C for gasoline, (104.4-157)°C for naphtha, (157-232)°C for kerosene, (232-426)°C for gas oil and (>426 °C) for residuum (including asphalt) [17].

3. Results and Discussion

3.1. Properties of the selected crude oils **3.1.1.** Physical properties

It is important to get the main specifications of the crude oil samples under

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study before going into the specifications of the crude oil fractions of the two selected crude oils. Table (2) shows that crude oil (A) heavier than (B) due to higher density, pour point and lowers (API) (see section 2.1). Crude oil (A) shows it has more aromatic compounds than the crude oil (B) according to its higher (Kw) and lower (CI) values or (B) contain more paraffinic compounds than (A) for the same reasons (see section 2.2).

Table (2)Physical properties of the crude oils (A & B).

Crude Type	Density g/cm ³ (20 °C)	Density g/cm ³ (15.6 °C)	Specific gravity (15.6 °C)	API gravity	Pour Point (°C)	Kw Factor (°R)	Correlation Index(CI)
Α	0.84	0.85	0.85	34.97	-18	11.64	5.44
В	0.76	0.78	0.78	49.91	-25	11.92	< 0

3.1.2. Atmospheric Distillation Results

Atmospheric distillation process was done according to ASTM 2892 method. Results from distillation for crude oil (A) and (B) illustrated in Table (3 and 4) respectively and Fig.(1).

Cumulative Volume %	Boiling Point °C	Density g/cm ³ (20 °C)	Density g/cm ³ (15.6 °C)	Specific gravity (15.6 °C)	API gravity	Aniline point (°C)	Pour Point (°C)	Kw Factor (°R)	Correlati on Index (CI)	Fraction
First drop	107	-	-	-	-		-	-	-	ıta
5	151	0.71	0.73	0.73	62.33	58.9	-30.6	13.56	< 0	Naph
10	187	0.75	0.77	0.77	52.26	56.0	-28.1	12.85	< 0	ne
15	203	0.79	0.80	0.80	45.37	53.1	-25.0	12.37	< 0	rose
20	238	0.82	0.84	0.84	36.95	50.0	-21.1	11.78	1.07	Ke
25	281	0.86	0.89	0.89	27.48	48.2	-15.3	11.12	22.95	
30	295	0.89	0.90	0.90	25.72	40.9	-11.3	11.00	27.33	il
35	307	0.90	0.92	0.92	22.30	40.0	-9.6	10.76	36.08	as O
40	321	0.90	0.92	0.92	22.30	38.7	-6.7	10.76	36.08	Ű
45	332	0.93	0.95	0.95	17.44	38.0	-4.4	10.42	49.21	
50	346	0.93	0.95	0.95	17.44	35.3	-3.2	10.42	49.21	

Table (3)Crude oil (A) atmospheric distillation results.

Cumulative Volume %	Boiling Point (°C)	Density g/cm ³ (20 °C)	Density g/cm3 (15.6 °C)	Specific gravity (15.6 °C)	API Gravity	Aniline point (°C)	Pour Point (°C)	Kw Factor (°R)	Correlation Index (CI)	Fraction
First drop	67	-	-	-	-	-	-	-	-	e l
5	93	0.63	0.65	0.65	86.19	69.0	-50.0	14.30	< 0	olin
10	119	0.65	0.67	0.67	79.69	65.2	-47.9	13.88	< 0	Gas
15	132	0.69	0.70	0.70	70.64	61.6	-45.6	13.28	< 0	tha
20	143	0.71	0.72	0.72	65.02	58.3	-41.2	12.91	< 0	Vapł
25	168	0.73	0.75	0.75	57.16	58.0	-35.0	12.40	< 0	Z
30	180	0.77	0.80	0.80	45.37	53.2	-30.6	11.62	1.00	ne
35	210	0.81	0.81	0.81	43.19	44.3	-27.3	11.48	5.53	rose
40	232	0.81	0.82	0.82	41.06	41.6	-26.3	11.34	9.91	Ke
45	241	0.83	0.85	0.85	34.97	39.1	-19.8	10.94	23.04	as II
50	265	0.85	0.87	0.87	31.14	36.2	-11.1	10.68	31.79	Q. Q.

Table (4)Crude oil (B) atmospheric distillation results.



Fig.(1): Distillation curve for crude oil samples (A & B).

 Table (5)

 Straight run crude oil fractions from crude oils distillation curve.

Fractions	Gasoline	Naphtha	Kerosene	Gas oil			
Crude Oil	Volume Percent Distilled						
Α	-	5	13	32			
В	7	16	20	7			

3.1.3. Physical properties analysis along atmospheric distillation products

The nature of the ingredients for petroleum fractions derived from distillation of the crude oil samples can be classified on the basis of the Paraffinic, naphthenic or aromatic content, depending on the results obtained from distillation (see section 2.4) and some of the physical properties listed in the section 2.1, 2 and 3. These classifications can be summarized in Table (6) for fractions derived from crude oil (A) and the Table (7) for fractions derived from crude oil (B).

Table (6)						
Physical properties analysis along crude oil type (A) atmospheric distillation products.						

Physical Properties Fraction	API gravity	Aniline Point	Kw Factor (°R)	Correlation Index(CI)
Gasoline	-	-	-	-
Naphtha	low Specific gravity, high API, light fraction	High temperature low aromatic, high paraffinic compounds	High value (13.56) so, the fraction consider as paraffinic	The value is zero, the fraction consider as paraffinic
Kerosene	low Specific gravity, high API, lighter than gas oil, heavier than naphtha Iow Specific (52.26-36.95)°C It has highly percent of paraffinic compounds		High value(12.73- 11.78) so, the fraction consider as paraffinic	The value ranged between zero and (1.07), the fraction consider as paraffinic
Gas Oil	Heaviest atmospheric distillation fraction, has low API	The temperature decreases as aromatic % increases. so, this fraction consider as it is aromatic rather than it is paraffinic	The value decreases between (11.12- 10.42). so, the fraction consider as naphthenic to aromatic rather than paraffinic	The value increases from (22.95) to (49.21). so, paraffinic compounds decreases in this fraction with increasing naphthens and aromatics

Table (7)

Physical properties analysis along crude oil type (B) atmospheric distillation products.

Physical Properties Fraction	API gravity	Aniline Point	Kw Factor (°R)	Correlation Index(CI)
Gasoline	lowest Specific gravity, highest API, lighter fraction	Highest temperature, very low aromatics, highest paraffinic compounds	Highest value (14.30) so, the fraction consider as paraffinic	The value is zero ,the fraction consider as paraffinic
Naphtha	low Specific gravity, high API, light fraction	High temperature low aromatics, high paraffinic compounds	High value (13.56) so, the fraction consider as paraffinic	The value is zero ,the fraction consider as paraffinic
Kerosene	Specific gravity, API shows it is liter than gas oil, heavier than naphtha	Temperature range (53.2-39.11)°C shows decrease in paraffinic compounds with increasing of naphthenic and aromatic compounds	High value(13.28- 12.91) so, the fraction consider as paraffinic	The value ranged between zero and (23.04), the fraction consider as paraffinic with lower naphthenic content
Gas Oil	Heaviest atmospheric distillation fraction, has low API	The temperature decreases as aromatic % increases. so, this fraction consider as it is naphthenic or aromatic rather than it is paraffinic	The value decreases to (10.68) so, the fraction consider as low naphthenic to high aromatic and very low paraffinic compounds	The value increases from (23.04) to (31.79). so, paraffinic compounds highly decreases in this fraction with increasing naphthens and aromatics

All the specifications in the tables and their scientific analyses confirm the findings in the section (3.1.1), although the description of the oil derivatives represents about half of the

amount of crude oil at distillation as indicated in the Tables (5 and 6), which indicate that the product ratio is 50%.

3.1.4 Fourier Transform Infrared Analysis

chromatography (GC). Gas gas chromatography/mass spectroscopy (GCMS), liquid chromatography (LC) and thin layer chromatography (TLC), however, these technologies need time to run, sample preparation and have high cost. Easy and cheap technologies are needed which can be operated on the work site [18]. FT-IR spectroscopy is one of important the ancient that well determined experimental techniques [19].

Spectral techniques like infrared spectroscopy ultraviolet, mass spectrometry, nuclear magnetic resonance spectroscopy and emission spectroscopy were used extensively in crude oil analysis [20]. It is possible to say technique can give qualitative infrared information rather than quantitative [21]. Bruker FT-IR Spectrophotometer module (Alpha) was used to analyze crude oil fractions which were obtained from the selected crude oil samples by atmospheric distillation. Figures (2 and 3) illustrate FTIR spectrum for crude oil atmospheric distillation products for crude oil A and B respectively. Paraffins in Fig.(2), CH₃ groups have C-H stretching bands at 2956 and 2872 cm⁻¹, while CH₂ groups have frequency at 2922. Other characteristic bands for paraffins are the asymmetric scissoring bending vibrations for CH₃ at 1374 cm⁻¹ and a symmetric one at or near 1459 cm⁻¹. Paraffins that have seven carbon atoms or more also exhibit a rocking vibrational band at 730 cm⁻¹. Olefins give weak C-H stretching bands above 3000 cm⁻¹. Aromatic C-H stretching bands occur at the 3021 cm⁻¹, while in-plane and outof-plane bending bands appear in 1300-1000 and 900-675 cm⁻¹ sectors respectively. For aromatic compounds the later bands are the most informative bands. Based on the same findings in Fig.(4) for crude oil A, Fig.(3) refers to the same ingredients for crude oil B for the paraffinic and naphthenic components as in crude oil A but the main difference here is the disappearance of the bands for aromatics C-H stretching occur above 3000 cm⁻¹ for crude oil B [22]. we can conclude that crude oil A contain more aromatic compounds than crude oil B which confirms the same conclusions in the physical tests for crude oil

samples and their atmospheric distillation products.



Fig.(2): FTIR spectrum for crude oil atmospheric distillation products for crude oil A.



Fig.(3): FTIR spectrum for crude oil atmospheric distillation products for crude oil B.

3.1.5 Ultraviolet Analysis for Crude Oil Fractions

Routine tests of oil fractions need quick and cheap analysis methods considering that mass spectrometry is, however, used only for research applications [23]. Ultraviolet spectroscopy is a low cost technique used for monitoring some properties of petroleum products such as the aromatics content in some petroleum fractions [24]. These types of applications based on the strong absorption of ultraviolet radiation by aromatic compounds due to the occurrence of conjugated electrons their structure [25]. It should be mentioned that in the literature there are very few applications of ultraviolet spectroscopy of petroleum fractions. The ultraviolet spectra were obtained in a Hewlett Packard 8453 instrument. The solvent used was spectroscopic grade normal hexane. The thickness of the cells used was 1 mm.

It is clear that both types of crude oil atmospheric distillation products A and B contains aromatic compounds illustrates in the region (230-270) nm, but type A contains more of these aromatic hydrocarbons. This confirms the previous results in the physical analysis and FTIR Analysis.

4.Conclusion

hydrocarbons present The in crude petroleum are classified into three general types: paraffinic, naphthenic and aromatics. Although two samples of crude oil and its fractions were analyzed in this research, but the indication of being considering the type of crude oil as paraffinic or aromatic was clearly defined. Crude oil (A) shows it has more aromatic compounds than the crude oil (B) according to its higher (Kw) and lower (CI) values or (B) contain more paraffinic compounds than (A) for the same reasons. Fourier transform infrared and ultraviolet analysis were carried out to determine the main components in crude oil fractions for the selected crudes .Results obtains confirms the previous results in the physical analysis.

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