

Characterization of Petroleum Crude Oils by Fourier Transform Infrared (FT-IR) and Gas Chromatography-Mass Spectrometry

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Abstract

We attempted to analyze light, medium, and heavy petroleum crude oils by Fourier transform infrared (FT-IR) and gas chromatographic mass spectrometry (GC-MS) so as to identify and quantify the various hydrocarbon group types and heteroatom-containing hydrocarbons. The results inferred that the crude oils studied have quite similar individual hydrocarbons but differ in hydrocarbon group types i.e. paraffinic, olefinic, naphthenic, and aromatic group types and carbon range products distributions. The RCP-I is dominated by C₁₁-C₁₃, while RCN-II and RCA-III by C₅-C₁₀ range hydrocarbons.

Keywords: Petroleum; Characterization; Spectroscopy; Chromatography; GC-MS

Introduction

Crude oil is a mixture of hydrocarbons that existed in the liquid phase in natural underground reservoirs and remains liquid at atmospheric pressure after passing through surface separating facilities [1]. Crude oil is naturally occurring material comprises of various hydrocarbons including paraffins, olefins, naphthenes, aromatic and heteroatom containing compounds as well as organometallic compounds of nickel and vanadium (porphyrins) [2]. Its composition/quality varies due to its origin and conditions to which it is exposed during

transportation and storage [3]. It is usually processed at a refinery to obtain useful products like gasoline, diesel, kerosine oil, lubricating oil feed stocks, furnace oil, bitumen/asphalt, etc. [4].

Major groups of compounds present in petroleum are saturated hydrocarbons (straight chained, branched and cyclic hydrocarbons), aromatic hydrocarbons, sulphur bearing compounds, resins and very large aromatic asphaltene compounds [5]. The concentration of different chemical components depends on the type of the crude oil. Light and medium crudes yield more

aliphatic/naphthenic components compared to heavy crude oil which yields more heavy compounds, such as aromatic structures, and a high concentration of asphaltenes and resins [6].

The phenomenal increase in global energy demand and depletion of conventional resources, combined with climate issues has urged careful and environment-friendly utilization of the proven crude oil reserves. Crude oils being high-cost commodities and valued feed streams for refining need careful characterization. Several attributes including cost, environmental impacts, and ability to produce light premium fuels are considered before recommending for refining. Its suitability for downstream processing is judged by detailed characterization [7]. However, owing to compositional complexity, its characterization and analysis is always considered as a challenging job [8].

Extensive studies focused on its characterization are available in the open literature including chromatographic, and spectroscopic methods [9-14]. Thermal methods can also be effective [15-17]. Elemental analysis of crude oil shows that it contains mainly carbon and hydrogen in the approximate ratio of six to one by weight [18]. The mixture of hydrocarbons is highly complex and the complexity increases with boiling range. The instrumental techniques of chromatography, ultraviolet and infrared spectroscopy together with mass spectrometry facilitate knowledge of the detailed hydrocarbon type composition of the complex crude oil. FTIR and GC-MS are considered as better techniques for petroleum characterization [19-21]. We illustrate the use of FTIR and GC-MS for detailed analysis of the three indigenous crude oils i.e. light, medium and heavy crude oils so as to know about their chemical compositions and heteroatom contents.

Experimental

Samples Collection and Physico-Chemical Characterization

Three indigenous crude oils were used in current investigation and coded as:

1. Light crude denoted as LC, Pariwali, oil field
2. Medium crude denoted as MC, Naspha oil field
3. Heavy crude denoted as HC, Turkawali oil field.

The as received oils were characterized by ASTM methods [22]. The properties determined were:

Physico-Chemical Properties:

1. Density; ASTM D 1480
2. API gravity; ASTM D 4052
3. Conradson carbon residue; ASTM D 189 – 05
4. kinematic viscosity; ASTM 445
5. pour point; ASTM D 97 – 05
6. flash point; ASTM D 93
7. aniline point; ASTM-D 611-04
8. Watson characterization constant.

Elemental Analysis

1. Determination of C, H, N, S and O. The elemental analysis was carried out by CHNS analyzer.

FTIR and GC-MS Characterization

A double beam FTIR spectrophotometer was used in this study. In a typical analysis, potassium bromide (KBr) pellets were prepared by using analytical grade KBr. A small drop of the test oil was applied to the prepared KBr disc. The GC-MS analysis was carried with a gas chromatograph coupled with MS analyzer (GC-MSQP2010 Shimadzu).

Results and Discussion

Physico-Chemical Characterization

It is well documented elsewhere that the physical and chemical characteristics of a crude oil vary considerably with its composition [2]. The physico-chemical characterization of the crude oils under study was carried out. The values for different physicochemical parameters obtained for the oil samples were; densities (0.76, 0.85, and 0.94 g/cm³); API gravities (54, 35, 19); viscosities (10, 8, and 14 mm²/s); CCR (0.98, 0.92, and 0.98 % wt); pour point (-12, -14, and -16°C), flash point (96, 93, and 96°C) and Watson characterization constant (K) values (12, 11 and 10), for LC, MC and HC, respectively.

The elemental analysis were; C (85.44, 85.91 and 86.10 %), H (11.15, 11.30, and 11.55; O (1.85, 1.21, and 0.96), N (0.11, 0.14, and 0.15) and S (1.45, 1.44, and 1.24) for LC, MC and HC, respectively. It can be seen that the nitrogen and sulphur contents are mostly concentrated in the naphthenic and heavier fractions. The results indicate that the LC, MC, and HC oils have different physico-chemical properties agreed to the values of published data and are found to be light, medium and heavy crudes, respectively [4,23-25].

FTIR Results

Structural analysis of petroleum based products is performed to know about fraction recognition, combustion properties, and efficiency of fuel and quality inspections. It also influence the quality of the marketable products derived from crude products [26].

It has been reported elsewhere that crude oils which have similar physical properties but possess widely varying chemical compositions [27]. The absorption bands of aliphatic C-H bonds, with additional bands originating from groups containing aromatics, oxygen, sulfur, and nitrogen, usually dominate the spectra of crude oils [28]. The FTIR of the oils understudy was carried out. The results are discussed as under:

LC: The FTIR analysis of LC was performed. The data is given in Table 1. The clear larger size absorption peaks were observed at 2954 and 2822 cm^{-1} corresponded to the CH and CH_2 stretching vibrations. The other well developed bands centered at 1446 and 1419 cm^{-1} corresponded to the CH, CH_3 bending vibrations

(deformations) were also observed. A medium intensity peak appeared at 727 cm^{-1} showed CH_2 bending. Another medium intensity band at 1078 cm^{-1} observed evident the CH bending vibrations [29]. The appearance of these peaks reveals the paraffins characterized by CH, CH_2 and CH_3 vibrations. The results exhibited bands appearing at 852 and 1647 cm^{-1} due to CH bending and C=C stretching, respectively [30]. A medium peak exhibited at 1725 cm^{-1} is indicative of carbonyl compounds i.e. ketone. Similarly, a small band observed at 3550 cm^{-1} due to O-H bond stretching vibrations confirmed the alcoholic contents of the sample under study. It is clear from the results that the intensities of the bands appeared for paraffins were found to be high which reveals its high concentration in the sample under test. On the other hand band, the peaks observed for aromatics/olefins and oxygenated compounds have poor intensities which indicate their presence in low concentrations. It may be concluded from the results that the LC possess long chain paraffins as the major constituents and the aromatics/olefins and oxygenated compounds as the minor components.

Position (cm^{-1})	Intensity	Assigned configuration
727	Medium	CH_2 (bend) aliphatic
852	Weak	C-H (bend) aliphatic
1005	Weak	C-H (bend) aliphatic
1273	Medium	C-O(Stretch) Alcohol
1377	Strong	C-H (bend) aliphatic
1446	Strong	CH_3 (bend) aliphatic
1647	Weak	C = C (stretch) aromatic
1725	medium	C=O (stretch) ketone
2822	Strong	CH_2 (bend) aliphatic
2954	Strong	CH (bend) aliphatic

Table 1: FTIR analysis of LC: Major Absorption Peaks Observed.

MC: The FTIR analysis of MC was carried out and data have been presented in Table 2. Some distinct bands appeared at 2922 and 2852 cm^{-1} characterizing the CH and CH_2 stretching vibrations. Peaks observed at 1456 and 1377 cm^{-1} corresponded to the CH, CH_3 bending vibrations (deformations) were evident. A moderate intensity peak at 727 cm^{-1} indicated CH_2 bending while a peak at 1078 cm^{-1} showed CH bending vibrations. The observation of these bands implies the existence of

paraffins which evidence CH, CH_2 and CH_3 vibrations. The aromatics/olefins as constituent of the oil under test was ensured by the appearance of some medium intensity peaks centered at 790 and 1580 cm^{-1} due to CH bending and C=C stretching, respectively. A small peak exhibited at 1715 cm^{-1} corresponded to ketone as carbonyl compound. For alcoholic contents, a small intensity peak can be observed at 3525 cm^{-1} which is due to O-H bond stretching vibrations.

Position (cm ⁻¹)	Intensity	Assigned configuration
727	Medium	CH ₂ (bend) aliphatic
790	Weak	C-H (bend) aliphatic
1078	Weak	C-H (bend) aliphatic
1155	Medium	C-O(Stretch) Alcohol
1377	Strong	C-H (bend) aliphatic
1456	Strong	CH ₃ (bend) aliphatic
1580	Weak	C = C (stretch) aromatic
1715	medium	C=O (stretch) ketone
2852	Strong	CH ₂ (bend) aliphatic
2922	Strong	CH (bend) aliphatic

Table 2: FTIR analysis of MC: Major Absorption Peaks Observed.

HC: The results of FTIR analysis of HC are compiled in Table 3. Some strong intensity bands were observed at 2922 and 2852 cm⁻¹ which indicate the CH and CH₂ stretching vibrations. Few peaks noticed at 1456 and 1373 cm⁻¹ corresponded to the CH, CH₃ bending vibrations (deformations). A medium intensity band at 740 cm⁻¹ revealed CH₂ bending and another medium intensity peak at 1078 cm⁻¹ show CH bending vibrations. The appearance of these peaks indicates the presence of paraffins which represent CH, CH₂ and CH₃ vibrations. The aromatics/olefins contents of the oil under test was verified by the appearance of some medium intensity peaks centered at 795 and 1584 cm⁻¹ which can be

attributed to CH bending and C=C stretching, respectively. At 1715 cm⁻¹, a small peak evidenced the presence of ketone. A band at 3525 cm⁻¹ due O-H bond stretching vibrations can be seen which evident the presence of oxygenates. The results revealed some larger intensity bands characterized the paraffin content in high concentration of the oils. Conversely, the smaller intensity peaks for aromatics/olefins and oxygenate content accounted for their low concentration. Thus, it may be inferred that the crude under study contained long chain paraffins as the major components and the aromatics/olefins and oxygenate as the least concentrated components.

Position (cm ⁻¹)	Intensity	Assigned configuration
740	Medium	CH ₂ (bend) aliphatic
767	Weak	C-H (bend) aliphatic
1081	Weak	C-H (bend) aliphatic
1168	Medium	C-O(Stretch) Alcohol
1373	Strong	C-H (bend) aliphatic
1456	Strong	CH ₃ (bend) aliphatic
1586	Weak	C = C (stretch) aromatic
1718	medium	C=O (stretch) ketone
2851	Strong	CH ₂ (bend) aliphatic
2920	Strong	CH (bend) aliphatic

Table 3: FTIR analysis of HC: Major Absorption Peaks Observed.

GC -MS Results

The chemical and physical properties of petroleum are directly related to its chemical composition, which determines its market value [31]. The GC-MS distinguishes and characterizes crude oil sample according to their compound classes [32]. The chemical compositions in terms of paraffins, naphthenes, aromatics, oxygenates and olefins (PNAOO) of the three

crudes were studied by GC-MS. The data was used to calculate the paraffins, olefins, naphthenes, aromatics, sulfur and nitrogen containing hydrocarbon group types. The paraffinic hydrocarbons identified in the LC included mono, di, tri and tetraalkylparaffines ranging from hexane to octacosane, triacontane and tetratriacontane. Among the naphthenes, the major compounds identified were found to be mostly mono, di and tri alkyl cyclohexanes.

Very few olefins recognized to be present included 2,3,4-trimethyl-2-pentene, 11-chloro-1-undecene. The aromatics compounds verified in the crude oil mostly included alkyl derivatives of benzene. Some oxygenated hydrocarbons were also present which included alcohol and ketonic derivatives of paraffinic and aromatic hydrocarbons.

The GC-MS data of MC reveal similar results as obtained for LC. Compared with the main NIST library, most of the paraffins verified were found to be polyalkyl derivative of aliphatic hydrocarbons with carbon atoms from 6 to as high as 30 per molecule. Abundantly occurring paraffins were alkylated, hexane, heptane, octane, nonane and decane. The naphthenic hydrocarbon identified commonly mono, di or tri alkylcyclohexane. Among the olefins, the specific compounds identified were found to be 2, 3, 4-trimethyl-2-pentene, 11-chloro-1-undecene. The aromatics identified were solely the alkyl benzene derivatives. A number of largely occurring of oxygenates, including hydroxy and ketonic compounds were also identified.

From the GC-MS data of HC, the major paraffins verified were found to be alkylated aliphatic hydrocarbons containing 7 to as high as 30 carbon atoms per molecules. Mostly these compounds included alkyl derivatives of hexane, heptane, octane, nonane, decane, eicosane, heneicosane, docosane, tricosane, tetracosane, pentacosane, hexacosane, octacosane and triacontane. The naphthenes confirmed were found to be di and tri alkyl cyclohexane. Among the olefins the specific compounds identified were found to be 2,3,4-trimethyl-2-pentene, 11-chloro-1-undecene. The aromatics identified

were; sec-butyl benzene, 1-methyl, 2-propyl benzene, 1-4-diethyl benzene, butane, 2-phenyl, 3-hydroxy, 4-cyano, (1, 1-dimethyl propyl benzene), (3, 3-dimethyl butyl) benzene. The oxygenates triasterianone, 3, 3-dimethyl 2-hexane-one, 2-butyl octanol. In case of original HC, the concentrations of paraffins, naphthenes, aromatic, oxygenates and olefins were found.

The relative abundance of the hydrocarbons types were calculated. The results of LC are provided in Table 4. The proportions of the paraffins, naphthenes, aromatic, oxygenates and olefins were found to be 85.67, 6.13, 6.16, 1.43 and 0.73 %, respectively. The carbon range hydrocarbons were found to be C₅-C₁₀, C₁₁-C₁₃, C₁₄-C₁₈ and C₅-C₁₀ in concentration of 25.26, 58.81, 6.21 and 9.72 %, respectively (Table 5). The relative abundance of hydrocarbons types i.e. paraffins, olefins, naphthenes and aromatics were calculated in case of MC. The results are provided in Table 4. The proportions of paraffins, naphthenes, aromatic, oxygenates and olefins were found to be 63.45, 26.20, 7.00, 2.70 and 0.90 %, respectively. The different carbon range hydrocarbons determined were C₅-C₁₀, C₁₁-C₁₃, C₁₄-C₁₈ and C₁₉-C_n in concentrations of 74.40, 16.92, 4.63 and 4.07 %, respectively. The distribution of the different hydrocarbons range compounds calculated from GC-MS data determined in case of HC is given in Table 4. The concentrations of paraffins, naphthenes, aromatic, oxygenates and olefins were found to be 64.52, 14.67, 7.59, 2.70 and 12.08 and 1.14 %, respectively. The different carbon range hydrocarbons were i.e. C₅-C₁₀ (61.52 %), C₁₁-C₁₃ (18.69), C₁₄-C₁₈ (8.12 %) and C₁₉-C_n (11.67) as per results compiled in the Table 5.

Concentration (wt%)					
	Paraffins	Naphthenes	Aromatics	Oxygenates	Olefins
Sample					
LC	85.67	6.23	6.26	1.53	0.73
MC	63.45	26.02	7	2.71	0.9
HC	64.52	14.67	7.59	12.08	1.14

Table 4: Hydrocarbon group types distribution determined in LC, MC and HC.

Concentration (wt%)				
	C ₅ -C ₁₀	C ₁₁ -C ₁₃	C ₁₄ -C ₁₈	C ₁₉ -C _n
Sample				
LC	25.26	58.81	6.21	9.72
MC	74.4	16.92	4.63	4.07
HC	61.52	18.69	8.12	11.67

Table 5: Carbon Number Distribution determined in LC, MC and HC.

It is inferred from the results that all of the three crude oils studied have quite similar chemical compositions in terms of various individual hydrocarbons. However, they differ in paraffinic, olefinic, naphthenic, and aromatic group types with varying carbon range distributions. The relative abundance of saturated hydrocarbons suggests that the oils are predominantly aliphatic. LC is dominated by C₁₁-C₁₃, MC by C₅-C₁₀ while HC also by C₅-C₁₀.

Conclusions

The study concludes that the three crude oils have almost similar individual hydrocarbons. However, they differ in hydrocarbon group types i.e. paraffinic, olefinic, naphthenic, and aromatic group types. The carbon range products distributions revealed that LC-I being light crude is dominated by C₁₁-C₁₃, while MC and HC, being middle and heavy crudes, respectively, are dominated by C₅-C₁₀ range hydrocarbons.

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