

RESULTS AND DISCUSSIONS

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Petroleum is a product whose composition varies due to its natural origins and to transportation and storage conditions. In some origins, petroleum comes from a variety of different oil fields that produce predominantly heavy petroleum.

The demand for high value petroleum products such as middle distillates, gasoline, and lube oils is increasing, while the demand for low value products such as fuel oil and residua based products is decreasing. Therefore, maximizing of liquid products yield from various processes and valorization residues is of immediate attention to refiners. At the same time environmental concerns have increased, resulting in more rigorous specifications for petroleum products, including fuel oils. These trends emphasized the importance of processes that convert the heavier oil fractions into lighter and more valuable clean products⁽¹¹⁸⁾. A number of technologies have been developed over the years for residual oil upgrading, which include process that are based on the carbon rejection route and hydrogen addition route⁽⁴⁸⁾.

Large proportions of crudes processed in oil refineries are set aside as distillation residue. At present these residue are of relatively little commercial value. More detailed structural characterizations are necessary before improved process routes to upgrade these materials can even be contemplated.

3.1. Physico-chemical Properties of the Residues and their Constituents:

Physico-chemical properties of the residues and their maltenes separated by different solvents have been determined using ASTM and/or IP standard methods. The results are given in Tables 2 and 5.

The Physico-chemical properties of the studied residues (Table 2) show that these residues are high in density, viscosity and pour point. The results also reveal that these residues have high contents of sulphur, nitrogen, nickel and vanadium.

The results of the physico-chemical properties of the maltenes (Table 5) show that the density and viscosity of the maltenes are less than that of the corresponding residues. The results are also revealing that the sulphur, nitrogen, nickel and vanadium contents in the maltenes are less than that of the corresponding residues. On the other hand, wax content in the maltenes is high than that in the residues. This indicates that the sulphur, nitrogen, nickel and vanadium elements are more concentrated in the asphaltenes, while the paraffinic compounds are concentrated in the maltenes.

The results of the physico-chemical properties of the maltenes also show that the sulphur, nitrogen, nickel and vanadium contents of the maltenes separated by ethyl acetate solvent are less than that of maltenes separated by *n*-heptane solvent, while the wax content has reverse trend

3.2. Composition of the Studied Vacuum Residues:

The two under studied residues were analyzed in order to know how much they contain saturates, aromatic, resins, and asphaltenes. The results are given in Table 3 and illustrated in figure 5 and 6. From Table-3 one can see the following:

- 1- The two Vacuum Residues (**VR**) contain high percentage of aromatics over both saturates and resins. The order of the percentage of the three components is as follows, whatever the solvent used: aromatics > resins > saturates.
- 2- The Vacuum Residue from Suez has high aromatic content than that in Alexandria Vacuum Residue. On the other hand, Alexandria Vacuum Residue has higher percentage of both saturates and resins over those in Suez one.

- 3- The asphaltenes content of Alexandria vacuum residue is higher than that of Suez vacuum residue.
- 4- In the two studied residues the yield of the asphaltenes separated by ethyl acetate solvent is higher than that separated by *n*-heptane solvent. This indicates that ethyl acetate is more efficient for the separation of the asphaltenes than *n*-heptane.

The data in Table-3 also shows the distribution of hydrocarbons as saturates (*n*-paraffins and cyclic compounds) and aromatics (mono-, di-, and poly). It is clear that *n*-heptane is less efficient for the separation of asphaltenes than *n*-pentane. On the other hand, *n*-heptane gives good results than ethyl acetate and *n*-pentane for the separation of Maltenes. These data are fully agreed with the data given by H. Alboudwarej and others ⁽⁶⁹⁾, who stated that if higher-carbon-number alkanes are used, less asphaltenes are separated.

3.3. Gas Chromatographic Analysis of the Separated Saturates:

The saturates separated from maltenes by different solvents were subjected to gas chromatographic analysis, and the data are shown in Table-7. From the Table-3 we can see that the saturates separated from maltenes of Alexandria vacuum residue, show higher percentage than that separated from Suez vacuum residue.

Figures (11-15) show the gas chromatograms of the saturates separated from both vacuum residues by different solvents. The chromatograms indicate that the saturates are formed from the resolved components (*n*- and iso-paraffins), and the hump, which is the unresolved complex mixture of naphthenes. The *n*-paraffin distribution of all the saturates separated ranges from about C₂₀ to about C₄₀ in addition of some traces lighter than C₂₀ and higher than C₄₀.

As shown from Table-7, the maximum percentages of *n*-paraffins were separated using *n*-heptane (14.65 % from Alexandria vacuum residue and 13.7 % from Suez vacuum residue). The Table also shows that although ethyl acetate is

less efficient for the separation of *n*-paraffins, it is more efficient than *n*-Pentane which was used in the case of Alexandria vacuum residue only.

3.4. Infrared Studies

The usefulness of infrared spectroscopy lies not only in the detailed information which can be obtained for small molecules, but also, for organic molecules, in the rapid and fairly inexpensive technique it provides for deciding which functional groups are present in a molecule. It has some advantages over mass spectra and nuclear magnetic resonance (NMR), thus, compared with the former it has the advantages that it can be easily applied to no-volatile samples.

Compared to nuclear magnetic resonance, it possesses the ability to give information about all the atoms in the molecule, not just those nuclei with magnetic moments. In practice all the three techniques, and also the ultraviolet spectroscopy, can usually be used to complement each other in a complete diagnosis. Further, infrared spectroscopy does find applications not only for structure determination, but also can be employed for the rapid quantitative analysis of the components of a mixture.

Infrared absorption spectroscopy can be applied for the investigation of the structure of petroleum and its fractions including their functional groups⁽¹³⁰⁻¹³³⁾. The assignments of the vibration of the function groups, which give rise to their bands in the infrared spectra of the petroleum fractions, are summarized in Table 6.

In this work, the infrared spectra of the two vacuum residues, asphaltenes and maltenes, separated by different solvents, as well as the resins, aromatics and saturates that separated from maltenes by alumina column chromatography, have been measured using FT-IR spectroscopic technique. The residues, maltenes, asphaltenes and resins were measured using the KBr disk technique while the aromatics and saturates were measured in the pure state. The measured infrared spectra in the range $4000\text{ cm}^{-1} - 400\text{ cm}^{-1}$ are shown Figures 16-28. The wave-number positions and their corresponding absorbance intensities are shown in Tables (8 - 14).

The infrared spectra of the *n*-heptane and ethyl acetate asphaltenes separated from Suez and Alexandria Vacuum residues are shown in Figures (19 and 20), Table 9.

It is clear that low intensity bands in the region 3500 cm^{-1} – 3300 cm^{-1} , with maxima at 3446 cm^{-1} – 3421 cm^{-1} as appeared in the spectra of the Suez vacuum residue, while appeared with maxima at 3451 cm^{-1} – 3419 cm^{-1} in the spectra of Alexandria vacuum residue. These two bands indicate very low concentration of OH and NH groups, which are responsible for asphaltenes aggregation through hydrogen bonding ⁽¹³⁴⁾. The very weak bands around 3050 cm^{-1} and 3040 cm^{-1} , result from C-H stretching in aromatic rings. The spectra also reveal strong bands in the region around 3000 cm^{-1} and 2800 cm^{-1} , particularly two distinct bands at about 2920 cm^{-1} . These two bands result from the CH₂ asymmetric and symmetric stretching, respectively. A small peak at about 1693 cm^{-1} in the spectra of asphaltenes may indicate the presence of the carbonyl group (C=O) stretching. All the infrared spectra also show an intense, fairly sharp, band at about 1600 cm^{-1} – 1500 cm^{-1} , which is characteristic of the C=C stretching in aromatic rings. Another strong band observed was also observed around 1461 cm^{-1} – 1451 cm^{-1} , which is due to asymmetric deformation of methyl and methylene groups. A small band observed at about 1375 cm^{-1} might be attributed to methyl symmetric deformation. The band at about 1315 cm^{-1} – 1305 cm^{-1} is due to CH₂ wagging in long chain paraffins. The appearance of a weak band at 1035 cm^{-1} – 1020 cm^{-1} results from the aliphatic C-O, C-N and / or S=O stretching. A very weak band at about 935 cm^{-1} – 906 cm^{-1} may be due to the OH out-of-plane deformation. Three bands at 865 cm^{-1} – 855 cm^{-1} , 810 cm^{-1} and 740 cm^{-1} are weak and broad, and probably result from the out-of-plane deformation of CH in aromatic rings. A weak band at about 720 cm^{-1} , due to CH₂ rocking in long chains $\{-(\text{CH}_2)-\}$ where $n \geq 4$, is also present.

The infrared spectra of *n*-heptane and ethyl acetate resins, illustrated in Figures 21 and 22 and the data are shown in Table 13, indicate that these resins

have nearly the same functional groups as present in asphaltenes. The spectra show broad bands of OH and NH in the region $3600\text{ cm}^{-1} - 3200\text{ cm}^{-1}$ with maxima at about 3419 cm^{-1} in Suez *n*-heptane resin and Alexandria *n*-heptane resin 3415 cm^{-1} or 3370 cm^{-1} . A weak band at $3051\text{ cm}^{-1} - 3018\text{ cm}^{-1}$ of CH stretching in aromatic rings, and two strong bands at about 2921 cm^{-1} and 2851 cm^{-1} of the CH₂ asymmetric and symmetric stretching, respectively. A weak band is assigned to the stretching in the carbonyl group at $1685\text{ cm}^{-1} - 1648\text{ cm}^{-1}$ [Alexandria resins ethyl acetate], or $1693\text{ cm}^{-1} - 1650\text{ cm}^{-1}$ [Alexandria resins *n*-heptane] and 1649 cm^{-1} in case of ethyl acetate Suez resins, while the band at about $1609\text{ cm}^{-1} - 1545\text{ cm}^{-1}$ is due to the stretching vibration of C=C aromatic rings. Bands at 1452 cm^{-1} , $1375\text{ cm}^{-1} - 1375\text{ cm}^{-1}$ and $1313\text{ cm}^{-1} - 1311\text{ cm}^{-1}$ are due to CH₂ plus CH₃ asymmetric deformation, CH₃ symmetric deformation and CH₂ wagging in long chain paraffins, respectively. The band of C-O, C-N or S=O stretching is present at about 1020 cm^{-1} , while that of the OH out-of-plane deformation band is at about $912\text{ cm}^{-1} - 914\text{ cm}^{-1}$. The CH aromatics out-of-plane deformation bands are at about $863-840\text{ cm}^{-1}$, $811-808\text{ cm}^{-1}$ and 745 cm^{-1} . The band of CH₂ rocking in long chains is also present at about 722 cm^{-1} .

Infrared spectra of the *n*-heptane and ethyl acetate aromatics, mono-aromatics, di-aromatics and poly-aromatics are shown in Figures 23, 24, 27 and 28 and the data are given in Tables 12 and 14. The OH and NH stretching are very weak above 3200 cm^{-1} with maxima at $3556\text{ cm}^{-1} - 3455\text{ cm}^{-1}$. The CH stretching in aromatic rings appear at about 3050 cm^{-1} , 3040 cm^{-1} and $3020\text{ cm}^{-1} - 3015\text{ cm}^{-1}$. There are very strong two bands at 2927 cm^{-1} and 2851 cm^{-1} , which are probably due to CH₂ asymmetric and CH₃ symmetric stretching, respectively. Two very weak bands appear only in the spectra of aromatics at about 2727 cm^{-1} and 1889 cm^{-1} , the first may represent CH stretching in aldehydes groups, while the second may be due to the overtones of Polycondensed aromatics. The C=O stretching in carbonyl groups is very weak and appears at $1700\text{ cm}^{-1} - 1654\text{ cm}^{-1}$. The C=C stretching in aromatic rings present as a weak band at about 1600 cm^{-1} .

in both Alexandria and Suez. The CH_2 plus CH_3 symmetric and CH_3 symmetric deformation bands at about 1462 cm^{-1} and 1376 cm^{-1} , respectively. These two bands are sharp and very strong and followed by a weak band at 1311 cm^{-1} – 1305 cm^{-1} due to the CH_2 wagging in long chain paraffins. The very weak band at about 1206 cm^{-1} – 1088 cm^{-1} is attributed to the $[-(\text{CH}_3)_2-\text{C}]$, while that at 1032 cm^{-1} – 1030 cm^{-1} may be due to C-O, C-N and / or S=O stretching. The CH in naphthenic rings is present as a very weak band at 960 cm^{-1} – 950 cm^{-1} . Three bands at 880 cm^{-1} , 865 cm^{-1} and 750 cm^{-1} represent the CH aromatic out-of-plane deformation. The CH_2 rocking in long chains, $[-(\text{CH}_2)_n-]$ where $n \geq 4$ is present at about 720 cm^{-1} .

The infrared spectra of the saturate, which were separated from the maltenes by alumina column chromatography, are shown in Figures 25 and 26 and the data are present in Tables 11. The spectra show very weak broad bands of the OH and NH stretching at about 3100 cm^{-1} and higher. The CH_3 asymmetric, CH_3 symmetric, and CH_2 symmetric, stretching vibrations in aliphatic appear as three very strong bands at 2958 cm^{-1} – 2854 cm^{-1} , 2927 cm^{-1} – 2917 cm^{-1} and 2854 cm^{-1} , respectively. The C=C stretching in aromatics is present as a weak band at 1606 cm^{-1} – 1503 cm^{-1} indicating that the saturates contain very small amounts of aromatics.

Strong bands at nearly 1460 cm^{-1} and 1375 cm^{-1} may be attributed to methyl symmetric deformation (scissoring). A very weak band at 1305 cm^{-1} assigned to symmetric wagging of methylene groups in long chain paraffins. The 1038 cm^{-1} very weak band may be due to C-O, C-N and S=O stretching vibrations.

The presence of two very weak bands at about 890 cm^{-1} – 793 cm^{-1} may be assigned to the out-of-plane deformation of C-H in aromatics. These bands, as well as the band of C=C stretching in aromatics at about 1600 cm^{-1} indicate, also, the presence of very small amounts of aromatic in the separated saturates. The two strong bands at about 730 cm^{-1} may be due to the rocking of methylene groups in long chain paraffins that having four $[\text{CH}_2]$ groups or more.

Some ratios calculated from peak heights of selected infrared bands allow for better comparison of the spectra. The ratio of absorbance of CH₃ symmetric deformation at 1375 cm⁻¹ to that of CH₂ + CH₃ symmetric deformation at 1460 cm⁻¹, i.e., A_{1375}/A_{1460} is measure of the degree of branching and the ratio of CH₂ rocking at 720 cm⁻¹ to CH₂ + CH₃ or CH₃ symmetric deformation, i.e., A_{720}/A_{1460} or A_{720}/A_{1375} is measure of the chain length⁽¹³⁵⁾. The degree of substitution in aromatic structure is measured from the ratio of absorbance of CH aromatic out-of-plane deformation two/three- or four adjacent hydrogen atoms, at 810 or 750 cm⁻¹, respectively, to that of one free hydrogen atom at 870 cm⁻¹⁽¹³⁶⁾, i.e., A_{810}/A_{870} or A_{750}/A_{870} .

The degree of branching, chain length and the substitution degree in aromatic structures have been determined for asphaltenes, resins and aromatics. The results are given in Table 15. The results show that the degree of branching in asphaltenes separated by *n*-heptane solvents from both Alexandria and Suez residues is more than that separated by ethyl acetate, while the chain length of *n*-heptane asphaltenes is less than that of ethyl acetate asphaltenes. The degree of branching of the resins and aromatics separated by *n*-heptane is less than that of those separated by ethyl acetate and the chain length of *n*-heptane resin and aromatic is more longer than that of ethyl acetate resin and aromatics. The results also reveal that the ratios of A_{810}/A_{870} or A_{750}/A_{870} in the asphaltenes separated by *n*-heptane are higher than that asphaltenes separated by ethyl acetate. This indicates that the degree of substitution in the aromatics system of the *n*-heptane asphaltenes is less than that of ethyl acetate asphaltenes. On the other hand, the degree of substitution in the aromatics system of *n*-heptane resins and aromatics is higher than that of ethyl acetate resins and aromatics.

3.5. Ultraviolet Studies:

Ultraviolet spectroscopy is generally employed to study the presence of total, mono-, di- and poly-aromatics in crude petroleum and its fractions.

It is well known that saturates have no significant absorption bands in the ultraviolet or visible spectroscopy. Therefore, the ultraviolet–visible spectroscopy is generally employed for the detection of aromatics⁽¹³⁷⁾. On addition to the well defined amounts; of energy to increase its vibrational and rotational energy, a molecule can also absorb some energy to increase the energy of its electrons. The energy changes involved are considerably greater than those involved in vibrational and rotational energy changes and correspond to radiation in the ultraviolet ($\lambda = 200\text{--}400\text{ nm}$) and visible ($\lambda = 400\text{--}750\text{ nm}$).

In our study, the two understudied vacuum residues and their constituents were subjected to ultraviolet / visible study. The data are given in Tables 16 and 17 and the spectra are shown in Figures 29 and 30. From the two Tables, one can see the presence of two prominent bands, one sharp band at the range between about 230 nm to 235 nm, which mainly correspond to the diaromatics, and the other band is strong and appears at about 255 nm, which generally shifted towards higher wavelengths, 256.0 nm – 257.5 nm, as shown by Suez vacuum residue, Table-16, and 254.5 nm – 257.5 nm, as shown by Alexandria vacuum residue, Table-17.

A third band was reported at about 191 nm. This band sometimes shifted to higher wavelength, 191 nm – 198 nm, in the case of the two vacuum residues. Generally the absorption coefficient (α) is higher at λ_2 and λ_3 , corresponding to di-aromatics and poly-aromatics respectively, but it is lower in the case of λ_1 , which is corresponding to the mono-aromatics.

As shown from the two Tables, mono-aromatics, which were separated by asilica gel column chromatography, reveals three wavelengths at 195 nm (*of intensity coefficient 57.59*), 232 nm (*of intensity coefficient 43.95*), and 257 nm (*of intensity coefficient 40.13*) in the case of Suez vacuum residue, but in the case of the Alexandria vacuum residue, these three bands are shown at 194 nm

(of intensity coefficient 130.68), 231 nm (of intensity coefficient 68.92), and 256 nm (of intensity coefficient 51.78), respectively. The intensities of these bands indicate that mono aromatics separated by column chromatography still contain some traces of both Diaromatics and polyaromatics.

The same is observed in the case of Diaromatics and polyaromatics. The Diaromatics reveals three bands at 191 nm (of intensity coefficient 36.19), 231 nm, (of intensity coefficient 103.0), and 256 nm, (of intensity coefficient 98.16) in the case of Suez vacuum residue. On the other hand, Alexandria vacuum residue reveals corresponding three bands at 194 nm (of intensity coefficient 48.41), 229.5 nm, (of intensity coefficient 175.18), and 257.5 nm, (of intensity coefficient 96.81).

The polyaromatics also reveals three absorption bands at 197.5 nm, (of intensity coefficient 29.79), 229.5 nm, (of intensity coefficient 76.49), and 256.5 nm, (of intensity coefficient 109.76), as shown by Suez vacuum residue. These bands revealed by Alexandria vacuum residue at 193.5 nm, (of intensity coefficient 49.43), 231 nm, (of intensity coefficient 72.42), and 256 nm, (of intensity coefficient 125.72).

The above results indicate that the aromatic constituents of the petroleum vacuum residue contain a complex mixture of mono-, di-, and polyaromatics that affect the efficiency of silica gel column chromatography, and therefore, the separated monoaromatics, diaromatics, and polyaromatics each of them contains a trace amount of the two others.

3.6. Elemental Distribution:

Usually, crude oils typically contain trace amounts of metals and nonmetals. Of the nonmetals, sulfur and nitrogen are the most common; vanadium and nickel are the most common metals. Usually these elements are present in the form of oil soluble salts. The nonmetal sulfur is the only one which may occur in the elemental state. In conventional refining processes these elements become concentrated in the residual fractions.

Mohammed and Saeed ⁽¹²⁷⁾, the physical, chemical and catalytic treatment processes that carried out for the removal of vanadium and nickel which are mostly concentrated in the vacuum residues, specifically in the asphaltenes.

The distribution of the sulphur and nitrogen in the residues among their asphaltenes and maltenes and the distribution of the nickel and vanadium in the residues among their asphaltenes and resins are given in Table 4 and illustrated in Figures 7–10.

Looking in Table- 4, one can see that sulfur is concentrated in Asphaltenes, whatever the solvent used. The Alexandria residue contains the highest amount of sulfur, as present in Asphaltenes, over that of Suez vacuum residue. Alexandria vacuum residue contains 3.83 wt % and 3.65 wt % sulfur as separated using *n*-heptane and ethyl acetate respectively, while the corresponding values in Suez vacuum residue are 3.12 and 2.99, respectively.

On the other hand, the percentage of nitrogen is (0.44 wt %) in the Suez vacuum residue; it is 0.97 wt % and 0.92 wt % as separated by *n*-heptane and ethyl acetate, respectively. In the same time, Alexandria vacuum residue shows higher percentages of nitrogen, they are 2.37 wt % and 2.27 wt % also as separated by *n*-heptane and ethyl acetate, respectively.

Concerning the distribution of sulphur between asphaltenes and maltenes separated by *n*-heptane and ethyl acetate solvents (Table 4 & Figure 7), it is clear that asphaltenes separated by *n*-heptane contain 0.31wt % and 0.24 wt % of the

total sulphur of Alexandria residue (3.09 wt %) and Suez residue (2.89 wt %), respectively and asphaltenes separated by ethyl acetate contain 0.61 wt % and 0.48 wt % of the total sulphur of Alexandria residue and Suez residue, respectively.

Considering the distribution of nitrogen between asphaltenes and maltenes separated by *n*-heptane and ethyl acetate solvents (Table 4 & Figure 8), it is clear that asphaltenes separated by *n*-heptane contain 0.19 wt % and 0.07 wt % of the total nitrogen of Alexandria residue (0.65 wt %) and Suez residue (0.44 wt %), respectively and asphaltenes separated by ethyl acetate contain 0.38 wt % and 0.15 wt % of the total nitrogen of Alexandria residue and Suez residue, respectively.

Vanadium and nickel contents in our studied samples were determined through the sulphuric acid ashing, dissolution in dilute hydrochloric acid and successive measurement using Inductively coupled plasma-atomic emission spectroscopic technique. The results given in Table-4 indicate that the quantity of the two elements separated is highly affected by the solvent used for separation.

The corresponding values of nickel and vanadium contents in the resins are so much lower than that in asphaltenes, but the Suez vacuum residue contains higher amounts over Alexandria vacuum residue.

Among the solvent used, *n*-heptane gave the best results in the case of the two vacuum residues used. *n*-heptane gave 458.91 ppm and 571.89 ppm nickel in case Alexandria and Suez vacuum residues respectively, while ethyl acetate gave corresponding values as 382.69 ppm and 421.45 ppm, respectively.

The results of vanadium show the same order. Ethyl acetate gave lower vanadium than *n*-heptane. The data obtained from *n*-heptane are 617.26 ppm and 857.56 ppm from Alexandria and Suez vacuum residues respectively, while ethyl acetate gave corresponding values as 469.54 ppm and 616.40 ppm, respectively.

The importance of the metal analysis in the heavy petroleum residues is to decide which suitable catalytic process must be used to upgrade such heavy

fractions. Another important point is the effect of heavy metals on the efficiency of the catalyst used, they not only contaminate the products, their chelates cause poisoning and fouling the catalyst and corrode the equipments.

Regarding the nickel and vanadium distribution between asphaltenes and resins (Table 4 & Figures 9 and 10), the Alexandria *n*-heptane asphaltens contain 37.22 ppm nickel and 50.06 ppm vanadium and Alexandria ethyl acetate asphaltens contain 63.79 ppm nickel and 78.27 ppm vanadium of the total nickel (89.94 ppm) and vanadium (118.23 ppm) of Alexandria residue. The corresponding values of the Suez asphaltenes 43.75 ppm nickel and 65.60 ppm vanadium and 67.97 ppm nickel and 99.42 ppm vanadium of the total nickel (113.45 ppm) and vanadium (145.23 ppm) of the Suez residue. This indicates that ethyl acetate solvent more efficient for removal the sulphur, nitrogen, nickel and vanadium elements from the vacuum residue than *n*-heptane solvent.