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## RESEARCH ARTICLE

### FINGERPRINTING OF EGYPTIAN ASPHALTENES USING X-RAY DIFFRACTION AND RAMAN SPECTROSCOPY

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#### ABSTRACT

Four Egyptian crude oil samples were collected from different oil fields located at Eastern and Western Deserts. Asphaltenes have been extracted and then characterized by X-ray diffraction and Raman spectroscopy. Different structural parameters were obtained from X-ray diffraction patterns and were compared with the Raman results. The Comparable results of both techniques indicated that asphaltenes which were extracted from El -Wahat crude oil samples (Western Desert) have the largest crystallite size and the smallest strains in directions perpendicular to (002) and (100) planes. These findings confirmed that El-Wahat crude oil is the youngest one among the other four studied crude oils. The influence of the different precipitating solvents on the asphaltenes has been studied. It was found that precipitating solvent has a great effect on the crystallinity of the studied samples; it was found that asphaltenes extracted by n-heptane is more crystalline than those extracted by n-pentane.

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## INTRODUCTION

Crude oil is one of the most important natural resources, hence it has a significant social and economic impact on modern human society. Because of its importance, a large body of work has been devoted to investigating the chemical compositions of crude oil (Kim *et al.*, 2015). Crude oil is a colloidal mixtures consisting of various fractions of saturated hydrocarbons, aromatics, resins and asphaltenes (Herod *et al.*, 2007). The asphaltenes fractions are considered to have the highest polarity and highest molecular weight among all the crude oil fractions (Vargas *et al.*, 2009). Asphaltenes are dark brown to black materials, they contain large fused aromatic rings, bearing long aliphatic substituents and saturates paraffin as straight branched compounds, metals and heteroatom are present as part of the ring system. The asphaltenes are considered to be repeating units of similar composition but at the same time they have major differences in the aromaticity. The structural characteristics of asphaltenes are very important

to refiners because it helps them in determining the percentage of the yields from the residual fraction of the crude oils, moreover it help in finding the operating parameters of the process units for deep conversion processes (Mushrush and Speight, 1995). The X-ray diffraction technique provides useful information about the macro- structures and the microstructures of different asphaltenes extracted from different crude oils, this extracted information are highly needed in identifying the aging of the crude oils from which the asphaltenes were extracted (Speight and Long 1996). X-Ray powder diffraction (XRD) method is also needed in identifying the aromaticity, the interlayer spacing, the interchain distance, the diameter of aromatic clusters perpendicular to the plane of the sheet, the diameter of aromatic sheets and the effective number of aromatic sheets associated with one stacked cluster. The asphaltenes fractions present in the petroleum crude oils are defined as the fraction which is insoluble in low boiling point paraffin hydrocarbons and soluble in carbon tetrachloride and benzene (Nellensteyn, 1924) On the other hand Pfeiffer (1950) defined asphaltenes as the fraction which is insoluble in n-heptane and soluble in toluene. However, recently asphaltenes are defined as the higher molecular weight solids which are soluble in aromatic

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solvents such as benzene and toluene and insoluble in paraffinic solvents (Ashoori *et al.*, 2010). Since the definition of asphaltenes is based on its solubility, then asphaltenes can be considered as a class of mixture compounds with different structures which have similar solubility properties rather than a pure substance with a well-defined molecular structure. Yen and Chilingarian (1994) were the first to characterize asphaltene by X-ray diffraction. For a discrete molecule with a simple structure, a macrostructures are sufficient to analyze and characterize the given molecule. For much complicated and bulked systems like asphaltenes, more information is also needed for better characterization. Ebert *et al.* (1983) presented some problems associated with the use of XRD. The results from the numerical simulation of the X-ray diffraction patterns illustrate specific difficulties in the beginning. But their study confirms that diffraction can distinguish between paraffinic, naphthenic and aromatic structures. X-ray diffraction studies of the four Saudi Arabia crude asphaltenes support the general concept of condensed aromatic sheets (having a tendency to stack) bearing naphthenic and alkyl systems on their periphery (Shirokoff *et al.*, 1997). The aromatic sheet structure of an asphaltene can also be characterized by X-rays diffraction patterns of the (002) and (100) peaks.

Moreover the diameter of the aromatic planar sheet ( $L_a$ ) and the height of the crystallite in the c-axis direction ( $L_c$ ) using Bragg's and Warren equations can be also estimated (Ungar *et al.*, 2002). Incorporation of X-ray diffraction (XRD) with Raman spectroscopy has been the most frequently used "twin techniques" for characterizing aromatic containing carbonaceous materials (Fauteux and Pegna, 2004). They characterize the aromatic portion of the molecules via different mechanisms. XRD determines all the structural parameters of the aliphatic and the aromatic sheets of asphaltene molecules (Darmstadt *et al.*, 2000). Raman spectroscopy on the other hand provides evidence of the molecular bond vibrations that are regulated by inter and intra molecular interactions. Moreover, Raman scattering carries information about the crystallinity (crystalline domain dimension) of aromatic compounds (Sadezky *et al.*, 2005). The aim of the present work is to use X-Ray powder diffraction and Raman techniques in order to evaluate the aromaticity, the interlayer spacing, the interchain distance, the diameter of aromatic clusters perpendicular to the plane of the sheet, the diameter of aromatic sheets, the effective number of aromatic sheets associated with one stacked cluster and finally to find the macro and micro structure of each samples. All these parameters are highly needed in identifying the structural characterization and aging of each asphaltene sample.

## Experimental

### Samples collection

Four samples of Egyptian crude oils were collected from four oil fields; Petrodra-15, Petrodra-24 and west Bakr samples were collected from the Eastern Desert, while El-Wahat samples were collected from the Western Desert (Fig.1). All the crude oils samples were centrifuged using 1500 rounds per minute (rpm) at 50°C, in order to separate emulsified water from the crude oil samples.



Fig. 1. Map of the study area

### Asphaltene Samples Preparation

All asphaltenes were separated from the crude oils according to IP 143/1993 (IP 1993) 300 ml of the crude oil was charged into a flask, closed with a cork carrying a thermometer. The flask was heated slowly up to 150°C and after the process is stopped, the residue is allowed to cool. A quantity of the residue is taken (2 gm) and dissolved in n-heptane (1 gm: 30 ml) which was refluxed for one hour, and then stored in dark overnight. The mixture was decanted onto filter paper (Whatman 42) and the residue in the flask was then transferred completely into the filter paper, using successive quantities of the solvent. The filter paper with its contents was placed in a soxhlet extractor and refluxed with the solvent until becoming colorless. The asphaltenes precipitated in the filter paper were then extracted by toluene. The solvent was distilled off and the asphaltenes were dried to a constant weight. The separated asphaltenes crystals were mortared into fine powders prior to measurements and then placed in the sample holder by back filling method.

### X-ray Diffraction

The X-ray diffraction (XRD) patterns were recorded by using PANalytical instrument, model X'Pert PRO with Cu-K $\alpha$  radiation. Asphaltene samples were recorded at d-spacing between 22.05-1.34 Å ( $2\theta = 4 - 90^\circ$ ). The instrument has vertical goniometer attached to a broad-focus X-ray tube with a copper target operating at 40 kV, 40 mA. Scan rate 0.01  $2\theta$  per second and with 10 second per step count time were employed. The scan type used is a step size scan.

### Raman Spectroscopy

Laser Raman spectroscopic examination was performed on different asphaltene samples, using Dispersive Raman spectrometer (BRUKER-SENTERRA, Germany) equipped with an integral microscope (Olympos). The excitation source was neodymium – doped yttrium aluminum garnet Nd/YAG laser (532 nm), focused with a 100 x long-local-length objective microscope and providing a power of 20 mW on the sample.

## RESULTS AND DISCUSSION

### Effect of the Precipitating Solvent

In order to investigate the influence of the type of precipitating solvent on the asphaltenes precipitation, two different solvents were tried for extracting asphaltenes from petrodara-15 sample. The results show that, the asphaltenes yields obtained by using higher carbon number solvents (n-heptane) are lower in contents, but at the same time higher in their degree of crystallinity than those precipitated from the lower carbon number solvent (n-pentane), this is shown in Fig. 2, it can be noticed also from this figure that the smaller peaks in the diffraction pattern of the n-heptane asphaltenes are very well developed and are more sharper than those of n-pentane asphaltenes. This indicates that the asphaltenes extracted by n-heptane is more crystalline than those extracted by n-pentane. The lowering in the yields of asphaltenes obtained by n-heptane is probably due to the fact that the solvent with higher carbon number maintains high molecular weight resins and low molecular weight asphaltenes in solution, consequently it precipitates smaller amounts of asphaltenes.

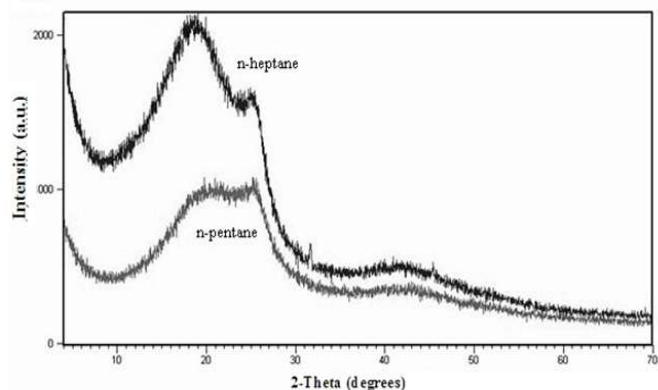


Fig. 2. X-ray diffraction patterns of n-heptane asphaltene and n-pentane asphaltene

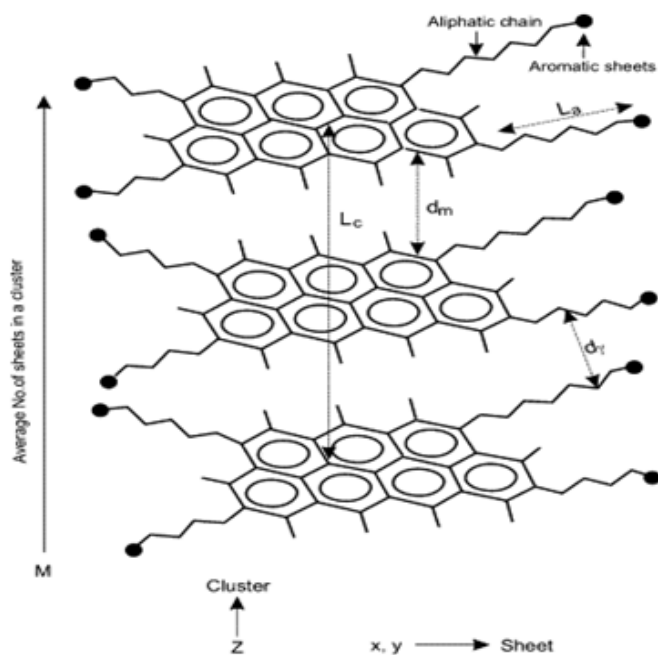


Fig. 3. The cross section of asphaltene cluster structure model

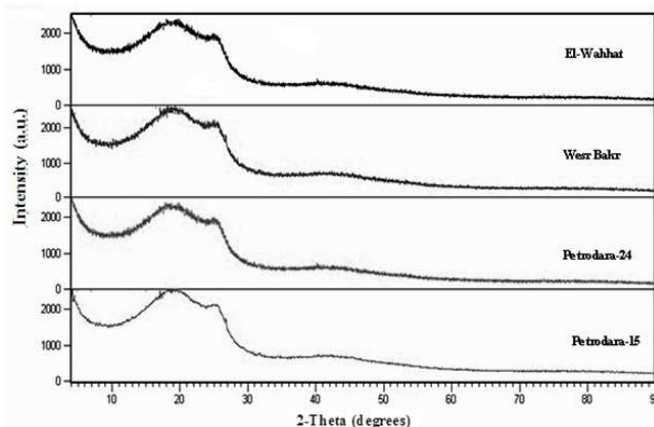


Fig. 4. X-ray diffraction patterns of the studied asphaltene samples

### Characterization of Different Petroleum Asphaltenes by X-ray Diffraction

The asphaltenes have been considered to be repeating units with similar composition. The sheets are stacked over each other along the c- axis of the hexagonal cell. The structural design of the arrangement of the sheets is shown in Fig.3 (Siddiqui *et al.*, 2002). The overlaying of the resultant X-ray diffraction patterns of the studied samples is shown in Fig.4. Generally, it can be easily noticed that all the asphaltene samples studied in this work show very similar XRD patterns.

### The Structural Parameters of the Different n-heptane Asphaltenes

Fig. 5 shows the diffraction pattern of n-heptanes asphaltene of sample (petrodara-15), from this figure different structural parameters were extracted; the inter-planar spacing ( $d$ ) of the two reflections (002) and (100), the angles  $2\theta$  ( $^\circ$ ), the integral breadths  $\beta$  ( $^\circ$ ), aromaticity  $f_a$ , distance between two aromatic sheets  $d_m$ , the average number of aromatic sheets  $M$  per one cluster, the average numbers of aromatic rings in one aromatic sheet  $R_a$ , the distance between two aliphatic chains or the distance between two saturated ring  $d_\gamma$  ( $\text{Å}$ ) for the ( $\gamma$ ) band. These parameters are listed together with the similar parameters obtained from the other studied samples in Table 2.

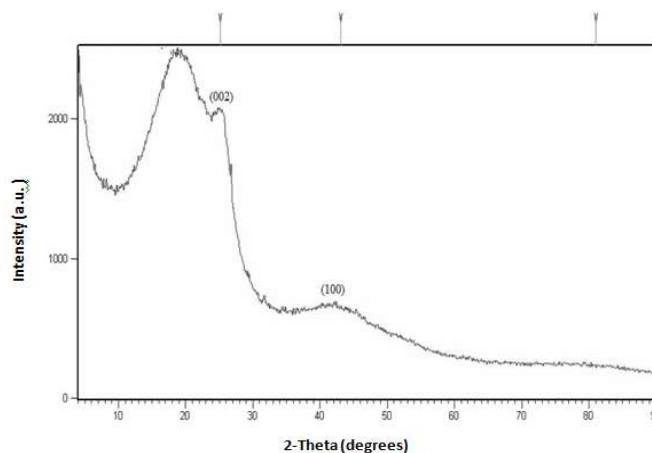


Fig. 5. The X-ray diffraction pattern and the peak positions of (002) and (100) planes of petrodara-15 asphaltene sample

**Table 1. Measured and calculated microstructure parameters of asphaltene samples**

Sample Name	2 $\theta$ (°)	Miller indices ( <i>hkl</i> )	Integral breadth $\beta$ (°)	Strain $\varepsilon \times 10^{-4}$	Crystallite size, D nm
Petrodra-15	25.133	(002)	2.3420	459	3.5
	42.725	(100)	6.87	767	1.2
Petrodra-24	25.016	(002)	2.4861	489	3.3
	43.414	(100)	7.37	809	1.2
West Bakr	25.155	(002)	2.5174	492	3.2
	43.126	(100)	7.67	847	1.1
El-Wahat	25.339	(002)	2.2565	438	3.6
	44.566	(100)	6.25	669	1.3

**Table 2. Calculated structural parameters of n-heptane asphaltenes obtained from XRD patterns of studied asphaltene samples**

Sample Name	$f_a$	$d_m$ , Å	$d_v$ , Å	M	$L_c$ , Å	$L_a$ , Å	$R_a$
Petrodra-15	0.21049	3.54	5.91	9.8	34.76	12.42	4.67
Petrodra-24	0.22415	3.56	5.92	9.2	32.74	11.6	4.36
West Bakr	0.23195	3.54	5.84	9.1	32.34	11.14	4.19
El-Wahat	0.2417	3.50	4.39	10.30	36.06	13.66	6.63

### Correlation Between the Structural Parameters and the Aging of Asphaltene

The analysis of the results obtained from Table 1 and 2, shows that the strains along the [100] direction in the four asphaltene samples are much larger than those along the [002] direction. This is an obvious result since the carbon aromatic sheets (graphene sheets) are well stacked over the top of each other along the c- axis, which reduce the strains tremendously along [002] direction, but on the contrary, the loose aliphatic chain in the [100] direction is playing a big role in inducing large strains along [100] direction.

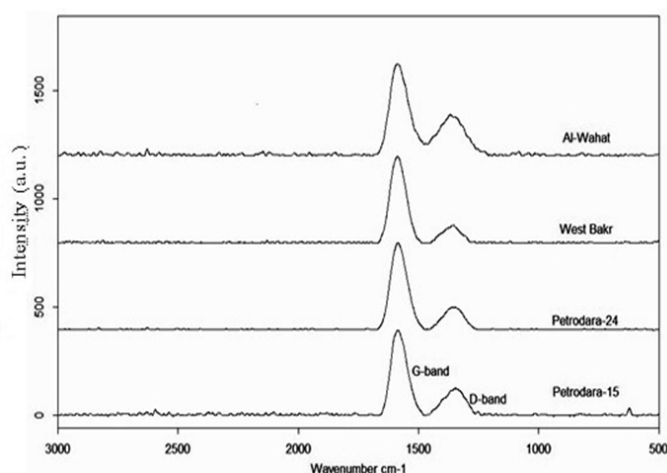
The distribution of the crystallite size and strains among the three asphaltene samples (Petrodra-15, Petrodra-24 and West Bakr) are more or less similar and the differences between them are not significant and they are within the experimental errors. On the other hand, El-Wahat asphaltene (Western Desert) showed the largest crystallite size and the smallest strains for the two corresponding reflections; (002) and (100) planes compared with other asphaltene samples of Eastern Desert.

This indicates that El-Wahat sample is the least deformed and accordingly it is the youngest among the other studied samples. Moreover El-Wahat asphaltene sample has the least distance between two aromatic sheets ( $d_m$ ), this means that the aromatic sheets are more stacked together and it means also that El-Wahat sample has the least foreign impurities inclusion between the aromatic sheets, i.e. the sample is not deformed by aging compared with the other asphaltene samples.

This was confirmed also by the presence of the highest number of aromatic sheets (M) per one cluster and the highest number of aromatic ring (R) found per one sheet, moreover the largest cluster diameter  $L_c$ , the largest aromatic sheet ( $L_a$ ), in addition El-Wahat asphaltene sample has also the smallest distance between two aliphatic chains ( $d_v$ ), compared with other studied asphaltene samples. All these specific parameters characterization leads to the conclusion that El-Wahat sample is the least deformed and aged among the studied asphaltene samples and accordingly El-Wahat asphaltene sample is the youngest among all other studied asphaltene samples and the other three crude oils are approximately of similar age.

### Dispersive Raman spectroscopy

The four asphaltene samples, which were extracted from different petroleum locations, and studied by X-ray diffraction, were also analyzed by Dispersive Raman Spectroscopy. Multiple Raman spectra were collected for the studied four samples at different places across the flat area of each sample. This technique is essential in order to examine the homogeneity of each studied sample and to obtain a realistic average spectrum. For all the selected places, the Raman spectra are visibly similar to each other as shown in Fig. 6. Two modes can easily be identified; the first mode occurs at a rather high frequency (around 1580  $\text{cm}^{-1}$ ) and is generally referred to as the G mode. This mode corresponds to the stretching vibration of the  $\text{sp}^2$  carbon atoms in the aromatic hexagonal sheet as well as those  $\text{sp}^2$  atoms in the chains. The sharp G mode peak suggests some order of the aromatic sheets in asphaltene samples. The second mode has a frequency around 1350  $\text{cm}^{-1}$ , this mode is referred to as the D1 mode. Physically, the D1 peak arises from the in-plane defects and the heteroatoms that initiate breathing vibration modes of the  $\text{sp}^2$  atoms in the rings (Jawhari 1995). In other words, it reflects the boundary of a crystalline-like structure, or in our case, the boundary of an asphaltene molecule.

**Fig. 6. Raman spectra of the studied asphaltene samples**

The above descriptions of the modes can only be adopted for qualitative analysis. A simple yet quantitative description linking the observed modes and the molecular structure was proposed by Tuinstra and Koenig (1970) through the intensity ratio between the G mode and the D1 mode. It has been largely adopted as an empirical relation. Tuinstra and Koenig showed that the integrated intensities (areas under the peak) of the D1 and G bands (respectively  $I_D$  and  $I_G$ ) are sensitive to size of aromatic sheet  $L_a$  according to the relation:

$$L_a = 4.4 I_G / I_D$$

The parameters extracted from the Raman spectra are given in Table 3. According to (Mapelli *et al.*, 1999) the G band frequency position should decrease upon increasing carbon sheet diameter, this suggestion coincides with data reported in Table 3. Also, the  $L_a$  values obtained from the Raman analysis is consistent with the results derived from X-ray diffraction.

**Table 3. Raman parameters of the asphaltene samples**

Sample Name	D1 band (cm <sup>-1</sup> )	G band (cm <sup>-1</sup> )	Size of aromatic sheet, $L_a$ (Å)
Petrodra-15	1348	1578	12.23
Petrodra-24	1351	1582	11.41
West Bakr	1352	1584	11.21
El-Wahat	1356	1574	13.31

## Conclusion

- Combination of Raman spectroscopy and X-ray spectrometry successfully characterizes the asphaltene molecular structures and gives approximately similar results.
- Asphaltene extracted by n-heptane is more crystalline than that extracted by n-pentane.
- The estimated asphaltene molecular sheet dimension (horizontal),  $L_a$ , was about in the range of 11–13 Å for the studied samples.
- The  $L_a$  values calculated from XRD and Raman spectroscopy are consistent with each other.
- Western Desert asphaltene crude oil has been registered to have the higher cluster diameter, largest crystal size and smallest strains along the direction perpendicular to (002) and (100) planes more than those present in Eastern Desert asphaltene.
- The specific parameters characterization indicates that El-Wahat sample is the least deformed sample and the least aged and accordingly El-Wahat asphaltene sample is the youngest among all the other studied samples.

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