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Comparative Study On The Crystallographic Form Of Hassi Messaoud Algerian Asphaltenes Using X-Ray Diffraction

DADA Saada [A, B], ABBAS Hadj Abbas [A, B], Abidi Saad Aissa [A]

[a] *Faculty of Hydrocarbons, Renewable Energies, Earth and Universe Sciences, University of Kasdi Merbah 30000 Ouargla, Algeria*
[b] *Sahara Geology Laboratory, University of Kasdi Merbah 30000 Ouargla, Algeria*
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Several constraints inhibit the production of crude oils, caused by precipitation and flocculation of asphaltenes, their treatment has shown that it is a matter constitutes complex hydrocarbon molecules that pose a difficulty during production, which requires great importance for the clarification of their molecular structure in hope of an improved treatment. The main goal of this work is to evaluate the crystallite parameters for eight asphaltene samples that are collected from different regions of the Hassi Messaoud field; the analysis of these samples is performed by a very powerful technique of X-ray diffraction (XRD) to know their structural characteristics.The different structural parameters were determined from the peaks of the gamma band (γ), the graphéne band (C = C) or (002), and the band (10) or (11) in the diffraction spectra of the respective samples. From the results obtained the values have been recorded concerning certain parameters tell that the distance between two aromatic leaves (d002 or d_m) which is in an interval of 4.24 Å until 4.53 Å, the distance between the saturated chains (d_γ or d_r) varies from 3.29 to 3.84 Å, plus the average height of the cluster perpendicular to the plain sheets (L_c), takes values from 13.77 Å to 37.06 Å, this height has an influence on the number of aromatic sheets in a cluster (M) which takes values from 4.91 Å to 11.38 Å. The diameter of the aromatic leaves (La) variable from 10.16 Å to 15.25 Å which is related to the number of aromatic cycles in the aromatic leaves (Ra = 3.80 – 5.72), other the number of carbon in the aromatic unit (C_{au} = 17.52 – 25.36) and finally aromaticity (f_a) depends on the area of the band Aγ and A002 these values are variable in an interval of 0.27 up to 0.59.

Key Words: Algerian asphaltenes, Flocculation, Oil recuperation, Hassi Messaoud, X-ray diffraction.

1. Introduction

Light oil is widely regarded as the primary energy source globally, and it is vital to the economies of many nations[1] .The heaviest molecular weight substances in crude oil are asphaltenes, which are also present along with saturates, aromatics, and resins that are soluble in toluene but insoluble in n-heptane[2-4].The presence of asphaltenes in oil causes substantial challenges during oil recovery which is a major worry in all the world’s oil fi elds[5-7].Different degrees of asphaltene precipitation were observed, including at the wellbore region, wellhead, separators, tubing, and safety valves[8].These asphaltene-related issues consequently result in large production losses and a sharp rise in operating expenses. Fundamental understanding of the microscopic and microscopic aggregation/deposition processes can also be gained by characterizing the chemical makeup and structure of the asphaltene molecules [9].One of the most effective methods for examining structural properties, particularly in asphaltenes, is X-ray diffraction (XRD)[10].This technique uses quantitative curves to assess the crystallite characteristics and molecular stacking of asphaltene aggregates [11-12]. X-ray diffraction is the technique that makes it possible to analyze the macrostructure of asphaltenes. Among the advantages of XRD are the ability to determine cell sizes, the separation between aromatic layers, aliphatic chains, etc. The XRD curve's asphaltenes peak's intensity and location determine the aforementioned criteria. This method can also be used to calculate aromaticity, the number of aromatic rings in aromatic sheets, the number of carbon atoms in an aromatic unit, and the number of aromatic sheets in a cluster [13-14].Bava et al.[15] proposed probable average structures for asphaltenes generated from three distinct Argentinean crude oils using XRD in conjunction with six additional techniques. The unstable asphaltenic oil from the Hassi Messaoud field was examined by the writers in [16,17]. A variety of methods, including XRD, Raman spectroscopy and ^{1}H and $^{13}CNMR$, were employed to determine the average molecule of Hassi Messaoud asphaltenes. Seven fused aromatic rings (FAR) and short aliphatic chains with up to six carbons were found to contribute to the aromaticity, which was predicted to range from 0.48 to 0.6 [16][18]. X-ray diffraction combined with solid state magnetic resonance (ss NMR) was utilized by Abbas et al. [19] to characterize the asphaltenes fractions. Their findings indicate that the primary causes of asphaltene instability are their high oxygen content and irregular compositional structures. X-ray diffraction (XRD) was employed by Mohamed Nahid Siddiqui et al. [20] to characterize Arabic asphaltenes from refineries in Kuwait (KW) and Ras Tanura (RT). The results of the XRD method were compared and analyzed in relation to the different types of asphaltenes and other fractions. The conclusion reached shows that the aging behavior of asphaltene's constituent parts is caused by the chemical makeup and source of the material.J. C. Akinnites et al. [21] studied five bitumen samples that were taken from oil sand outcrops in various parts of Nigeria. They used the X-ray diffraction (XRD) technique to determine the various structural parameters of the bitumen samples, which were derived from the peaks of the gamma band (γ), the graphene band (C = C) or (002), and band (10) or (11) in the diffraction spectra of the individual samples. For three of the samples, there were minor differences in the spacing between aliphatic chains and aromatic sheets, but the structural properties of the other two samples varied significantly. The work of Zahra Sadeghtabaghi et al. [22] was substantial, using XRD analysis of asphaltenes from various sources reveals that asphaltenes recovered from coal and asphalt have, respectively, the highest and lowest aromaticity values. Faisal S et al. [23] investigated the products of the heat breakdown of the n-heptane insoluble fractions that were precipitated and collected from three distinct vacuum residues. The macrostructure of the asphaltene molecule and the effect of thermal stresses on its structural characteristics were both made clear by X-ray diffraction (XRD) investigation. The findings showed that the degree of cracking had no discernible impact on the distances between aromatic layers (dm) and between aliphatic chains and naphthenic sheets ($d\gamma$).Bouhadda Y. et al. [24], The molecular structures of Hassi-Messaoud asphaltenes and their local order in the solid state are

successfully characterized by the combination of Raman spectrometry and X-rays.Utilizing a three-peak approach to examine Raman spectra, the estimated dimension of the asphaltene molecular sheet La for the samples utilized in this investigation was between 11 and 17 Å. The X-ray analysis of sample DP45 yielded values of 17.5 Å for La and 28 Å for Lc, indicating the aggregates' vertical dimension. Dounya Behnous et al. conducted the characterization of asphaltenes obtained from crude oil deposits [25]. According to XRD and NMR analyses, asphaltene molecules have an aromatic between 0.55 and0.65, with roughly 7 fused rings to 3–4 carbon aliphatic chains. Researchers Y et al. [26] examined the Hassi Messaoud field's unstable asphaltene oil. An average Hassi Messaoud asphaltene molecule was defined by means of many techniques, including XRD. Based on seven fused aromatic rings (FAR) and short aliphatic chains with up to six carbons, the aromaticity has been calculated to be between 0.48 and 0.6. [27–28]. With an average of eight molecular stacks and a molar mass of 550 for the monomer, the molecular sheet size was determined to be between 11 and 17 Å. They proposed that the heteroatom concentration and the average diameter of the aromatic leaflet were responsible for the propensity to aggregate and flocculate. [27, 29].
This paper aims to compare the chemical structure and crystallographic form of Hassi-Messaoud asphaltene fractions collected at several critical points in the petroleum production process and at various geographical sites within the Hassi Messaoud Oil field, as detailed in Table 2. Our goal is to offer fresh perspectives on the intricate molecular underpinnings of asphaltene aggregation and to describe any potential compositional alterations that might arise from oil operations. X-ray diffraction analysis is an experimental technique used in this inquiry. The methodology is described in detail in section 2. The primary findings, which are detailed in Section 3, show that the dominant asphaltene crystallographic structure changes over the oil production process.

2. Experimental

2.1. Materials

An oil and deposit samples were obtained from Hassi Messaoud oil field and employed to extract the asphaltenes; n-heptane (99%) was used as solvent for asphaltenes extraction from Algerian light oil, the solvent was obtained from Sigma – Aldrich, Ontario, Canada and used as received.

2.2. Extraction of asphaltenes

The samples DA01,DA02 and DA03 were extracted from deposits that obtained from the Algerian Hassi Messaoud oil well at 2800m using were line technic, while the samples DA04,DA05,DA06, DA07 and DA08 were extracted from the crude oil of the same field (exact location of each sample was cited in the table1.). All asphaltenes fractions were exacted following the standard method ASTM D6560 (i. e, 1/40) deposits or oil/solvent ratio) [30]. The extraction process was carried out by adding n- heptane to the deposits or oil sample with an deposits or oil /solvent ratio of 1/40 (g/ml). The resulting mixture was heated to 80°C a flask. After that the mixture was sonicated for 45 min at room temperature for stabilization. The solution was then filtered using a 0.45μm pore diameter filter paper [31]. The precipitated asphaltene were washed with n-heptane at a ratio of 1/5 (g/ml) (O/S) in a Soxhlet apparatus until the filtrate because colorless. Finally the filtered asphaltene were dried overnight under vaccum at 80°C.

Table 1: extraction Location of each sample.

Samples	**Extrtacted from**
DA01	**Well 1** , Wereline 2800 m South Hassi Messaoud (HMD) from deposit
DA02	**Well 2**,Wereline2800m north HMD, from deposit
DA03	**Well 3,**HMD Center from deposit
DA04	**Well 4**, from oil, HMD
DA05	**Well 5**, From Oil, HMD
DA06	**Well 6** From Oil, HMD
DA07	**Well 7**, From OIL,HMD
DA08	**Well 8**, HMD

3. Methods

3.1. X-ray diffraction

X-ray diffraction (XRD) is a technique for characterizing crystallized materials, whether massive or in the form of powder or deposits. Since asphaltenes are crystalline and in powder form, it is preferable to introduce this technique (XRD) to know the crystallite parameters and structural characterizations. From the beginning, several bands appeared in the diagram such as band γ which indicates the distance between the aliphatic chains, the distance between the aromatic layers is relevant for the band of graphéne (band 002), plus two other bands of (10) and (11) are proportional to the size of their clusters. These four bands are generated respectively around 2θ = 20°, 25°, 40° and 80° with a reserve for the fourth band (11) is very low so it is undetectable [32,33-35,36]. Figure 1 shows these different bands

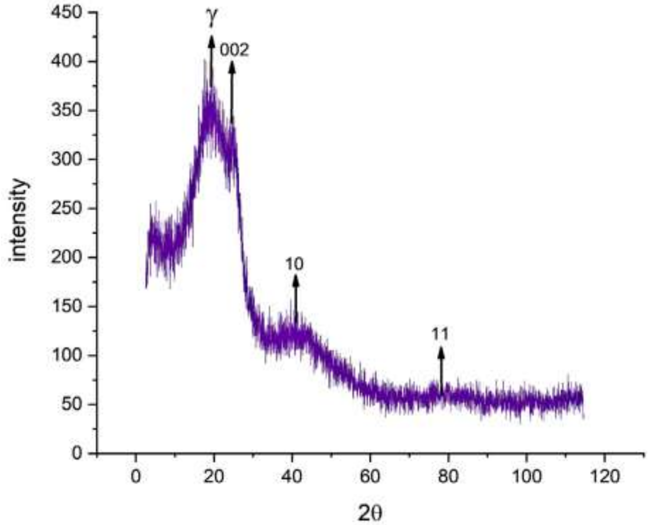


Figure 1. the positions of these bands[10].

Several crystallite parameters are drawn from these bands as the distance between two aromatic leaves (d002 or dm), distance between saturated chains (dγ or dr), average height of the cluster perpendicular to the plain sheets (Lc), diameter of the aromatic sheets (la), number of aromatic strips in a cluster (M), number of aromatic cycles in the aromatic strips (Ra), number of carbon in the aromatic unit (Cau) and aromaticity (fa) [32,37]. All these parameters are reported in Figure 3.

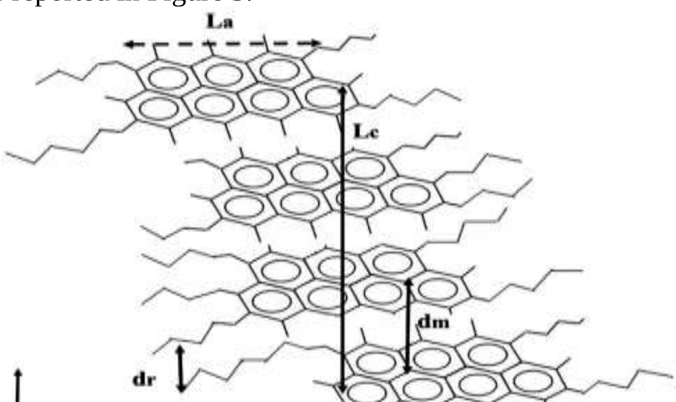


Figure 2. Hypothetical cross-section of asphaltene cluster [36].

Depending on the positions, intensities, and zones of the bands detected in the asphaltene model, the calculations of these parameters make the following equations:

$$d_r = \frac{\lambda}{2 \sin \theta_\gamma} \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$d_m = \frac{\lambda}{2\sin\theta_{002}} \quad (2)$$

$$L_a = \frac{1.84\lambda}{\omega\cos\theta_{10}} \quad (3)$$

$$L_c = \frac{0.9\lambda}{\omega\cos\theta_{002}} \quad (4)$$

$$C_{au} = \frac{L_a + 1.23}{0.65} \quad (5)$$

$$R_a = \frac{L_a}{2.667} \quad (6)$$

$$M = \frac{L_c}{d_m} \quad (7)$$

$$f_a = \frac{A_{002}}{A_{002} + A_\gamma} \quad (8)$$

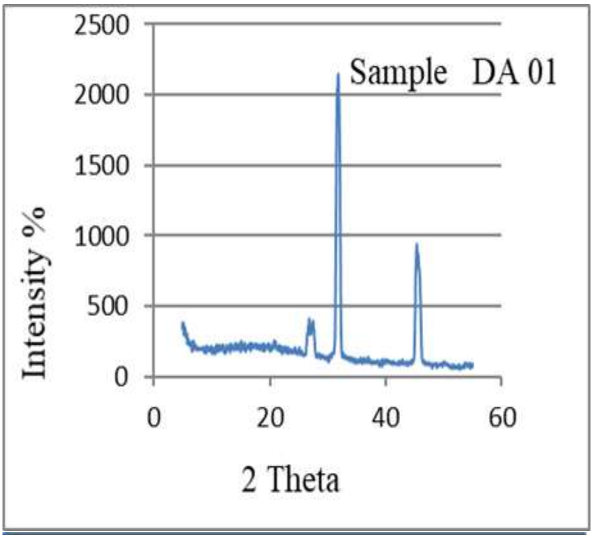
Where λ is the wavelength of the radiation applied, θ is the band angle, ω is the full width at mid-width of the associated band in the formula and A is the area under the peak [32,37]. Several researchers used the following equation to calculate M:

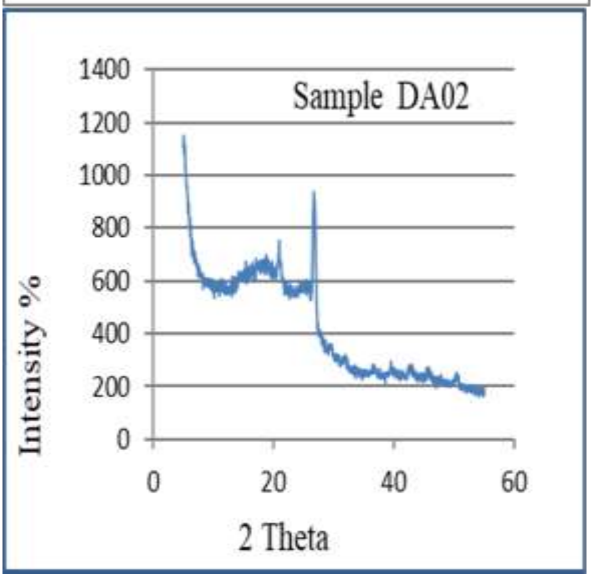
$$M = \frac{L_C}{d_m} + 1 \quad (9)$$

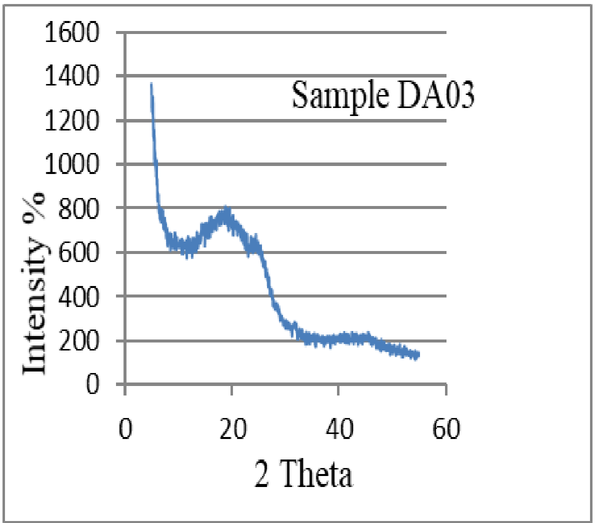
But it should be noted that in this article, all the quantities of M are calculated / recalculated based on an equation. (9).

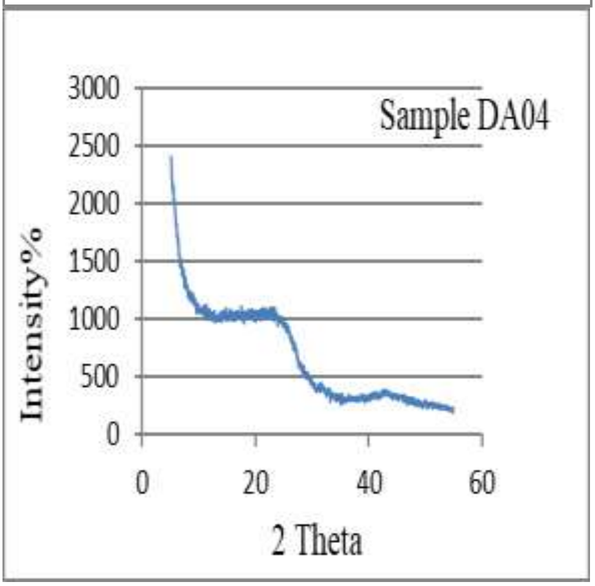
4. Results and discussion

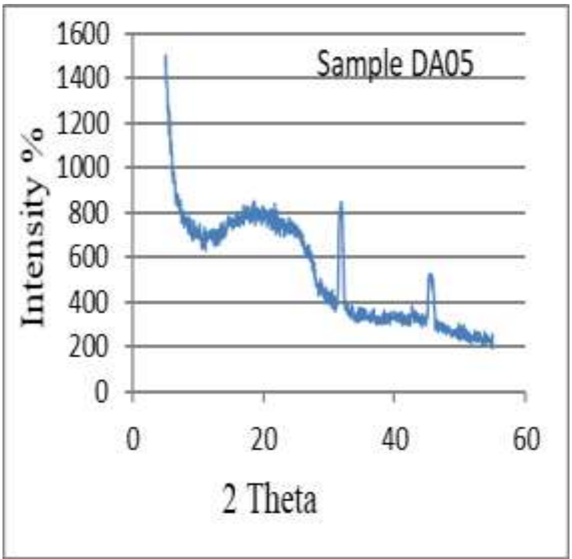
Figure 3 displays the X-ray diffraction patterns of the asphaltenes under study. As can be observed, the first sample D01's spectrum exhibits five distinct bands. Silicon oxide (SiO2) is indicated by a strong, crisp band (at 2 theta = 32). The aromatic structures are shown by two peaks, such as the (002) band at (at 2 theta = 32) (Yen et al. 1961). The last band (10) at 2 theta = 45.5 results from the aromatic structure's in-plane reflection in the X-ray pattern (Siddiqui et al. 2002). Similar peaks were noted by [8]for the Hassi-Messaoud asphaltenes from Algeria. Nevertheless, the bands at 2Theta=3 and 17 were difficulty indicated. By using the locations of observed peaks and their intensities, the XRD technique can offer structural characterizations of amorphous organic matter as well as crystallite characteristics. The distance between aromatic layers is relevant to the graphene band (002-band) in the XRD pattern of coals or asphenes, the distance between aliphatic chains correlates to the γ-band, and two additional bands of (10) and (11) are proportionate to the sizes of their clusters. Around 2 θ= 20 °, 25 °, 40 °, and 80 °, respectively, the γ, 002, (10) and (11) bands emerge. Note that the eleventh band is typically very weak and undetectable [10]. All previously examined samples D02 through D08 will be analyzed using the previously established rule.

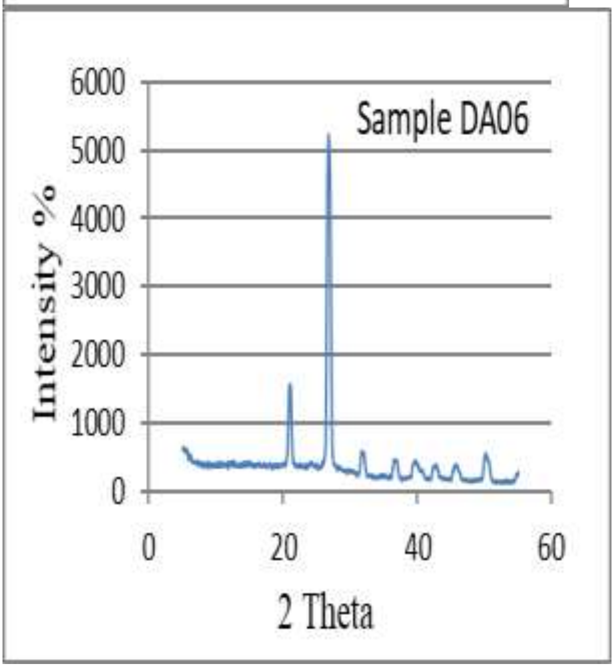

Sample DA 01
Intensity %
2 Theta
2500
2000
1500
1000
500
0
0
20
40
60


Sample DA02
Intensity %
2 Theta
1400
1200
1000
800
600
400
200
0
0
20
40
60


Sample DA03
Intensity %
2 Theta
1600
1400
1200
1000
800
600
400
200
0
0
20
40
60


Sample DA04
Intensity%
2 Theta
3000
2500
2000
1500
1000
500
0
0
20
40
60


Sample DA05
1600
1400
1200
1000
800
600
400
200
0
Intensity %
0
20
40
60
2 Theta


Sample DA06
6000
5000
4000
3000
2000
1000
0
Intensity %
0
20
40
60
2 Theta

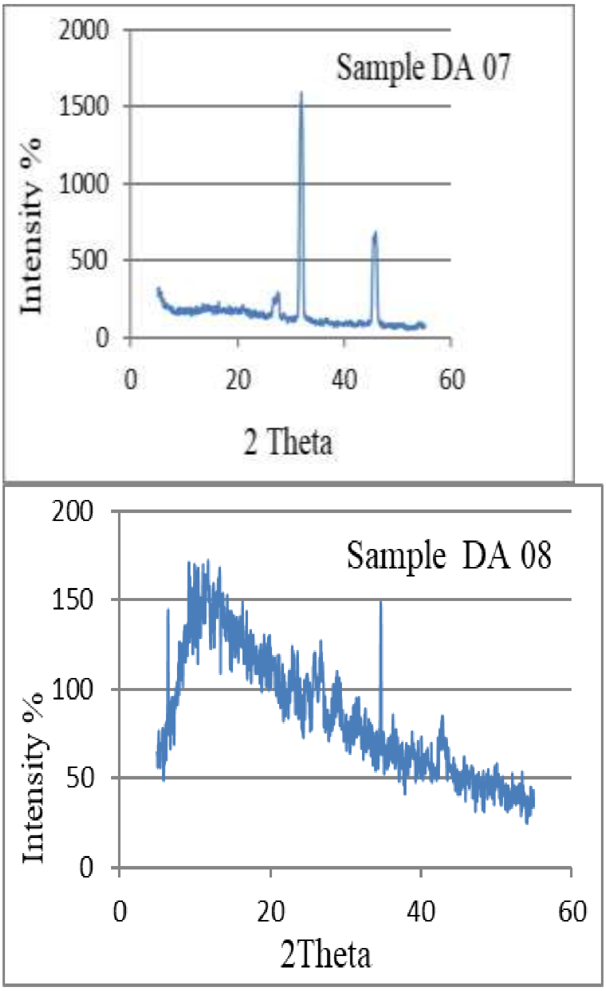


Figure 3. X-ray diffraction of studied Asphaltenes samples.

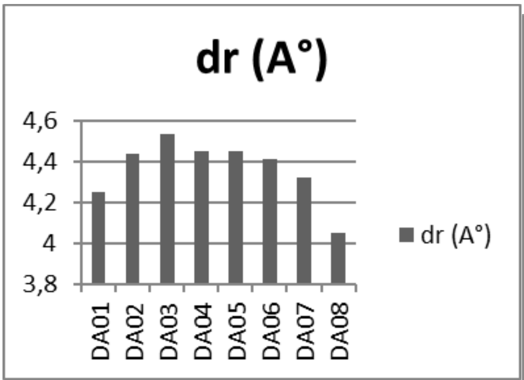
X-ray diffraction, concerns the internal structure of crystalline solids are detected, hence this structure can vary according to the type of bond and the geometric arrangement of atoms or molecules in the solid. For diffraction to occur in a crystal in which atoms are arranged in planes, the wavelength of the incident radiation must be of the same order as the atomic spatial distances between the crystallographic planes.
The studied samples were extracted from different areas of the Hassi Messaoud field are analyzed by X-rays (DRX), the results given in the form of DATA. Using OriginPro2016 software then transformed to diffractogram I= f(2θ). The obtained curves show peaks qualitatively at main characteristic bands, gamma band (γ), band 002 and band 10. Each sample has its own diffractogram that allows the different bands to be removed, and then calculate the different values of the crystallinity parameters for each sample that are present in Table 2.

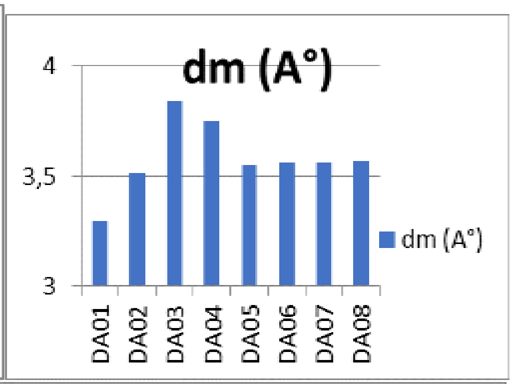
Table 2: different value of all structural parameters of asphaltene from eight samples.

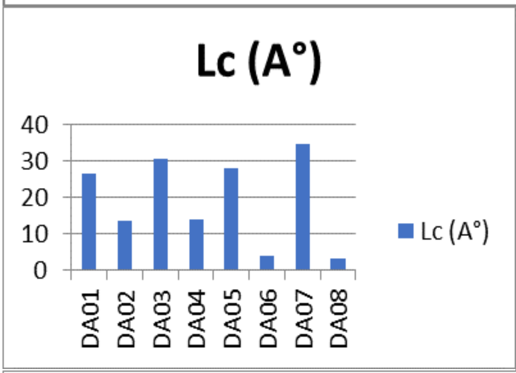
Samples	dr (Å)	dm (Å)	Lc (Å)	M (Å)	La (Å)	Cau (Å)	Ra (Å)	fa
DA01	4.250	3.298	26.568	9.055	/	/	/	0.42
D02	4.437	3.513	13.77	4.91	12.667	21.38	4.749	0.27
D03	4.536	3.845	30.50	9.036	10.162	17.52	3.81	0.598
D04	4.450	3.750	14.198	4.78	10.3	17.32	3.76	0.1577
D05	4.450	3.550	28.203	8.944	15.256	25.36	5.72	0.8473
D06	4.409	3.562	4.05	2.13	3.12	6.692	1.169	0.4688
D07	4.320	3.562	34.67	10.73	10.51	18.06	3.94	0.38
D08	04.05	3.569	3.155	1.88	20.08	32.73	7.573	0.3226

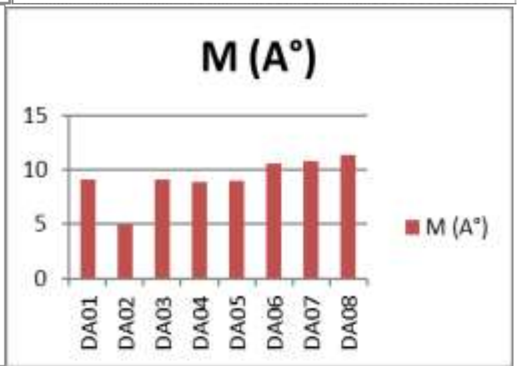
According to Table 2,Figure 2 and 4, shown from the beginning, the first remark observed concerns the DA01 sample. There were no values for La, Cau, and Ra. But as regards the other structural parameters of all the samples, the results indicate that the average distance of the layers between the aromatic leaves (dm) measures between 3.298 Å and 3.845 Å with higher and lower values was recorded at the samples DA08 and D01 respectively. Confirmed that the first sample DA01 have a shortdistance between two aromatic leaves. The average distance between the aliphatic chains (dr) is between 4.05 Å and 4.36 Å, while the average diameter of the cluster (Lc) is between 4.05 and 34.67 Å, indicated that the sample DA07 have a higher average height of the cluster perpendicular to the plain sheets in comparison with the remaining samples. The average number of aromatic leaves per stack (M) is between 1.88 Å and 10.73 Å. The important value of average diameter of the cluster (La) was recorded in the sample D08 while the remaining values were between 3.12 Å and 15.256 Å. For other parameters that are related to La such as Cau and Ra, they ranged from 6.692 Å to 32.73 Å and 3.76 Å to 7.573 Å respectively.However, the final sample, D08, had a large number of carbons per aromatic structure, or Cau (32.73 atoms).The results presented in the literature (Andersen et al. 2005; Bava et al. 2019; Abbas et al.) are consistent with these findings. Furthermore, a Gaussian technique was used to fit the aromaticity (fa), which was determined by dividing the regions of the (002) and the sum of the (002) and c bands. According to the data, the aromaticity (fa) of the investigated samples falls within the same range; however, the fifth asphaltene sample has a somewhat higher value (0.8473) than the other samples.

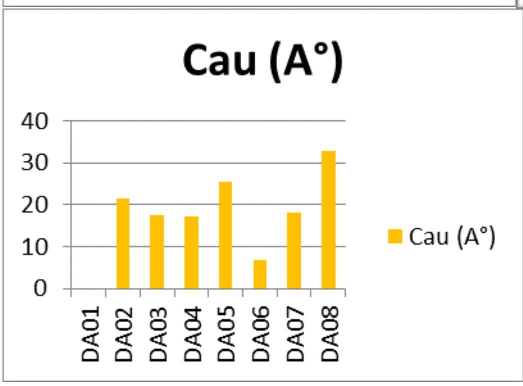
According to Yen et al. (1961)[8], the aromaticity value decreases as the value of (fa) decreases. This could therefore account for the long-term presence of aromatic rings in the crystalline portion of the fifth asphaltene sample. Even though the entire asphaltenes structure's crystal line section is the only part of the X-ray analysis.

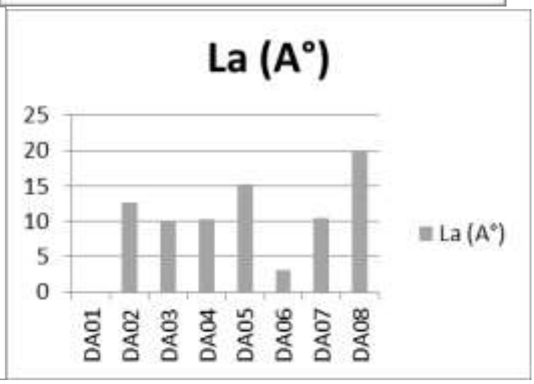

dr (A°)
4,6
4,4
4,2
4
3,8
DA01 DA02 DA03 DA04 DA05 DA06 DA07 DA08
dr (A°)


dm (A°)
4
3,5
3
DA01 DA02 DA03 DA04 DA05 DA06 DA07 DA08
dm (A°)


Lc (A°)
40
30
20
10
0
DA01 DA02 DA03 DA04 DA05 DA06 DA07 DA08
Lc (A°)


M (A°)
15
10
5
0
DA01 DA02 DA03 DA04 DA05 DA06 DA07 DA08
M (A°)


Cau (A°)
40
30
20
10
0
DA01 DA02 DA03 DA04 DA05 DA06 DA07 DA08
Cau (A°)


La (A°)
25
20
15
10
5
0
DA01 DA02 DA03 DA04 DA05 DA06 DA07 DA08
La (A°)

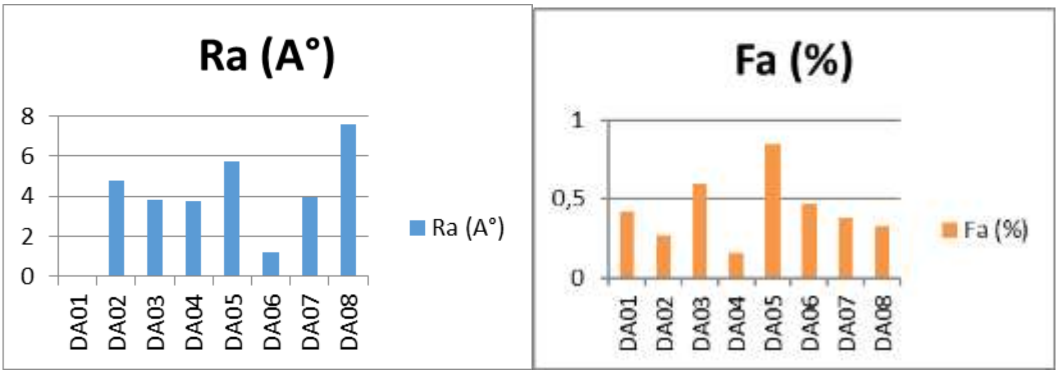


Fig 4. Average values of crystallite parameters for every category.

5. Conclusion

This work reports an experimental study of the structural parameters of eight asphaltene samples extracted from Algerian light oil collected from different regions of the Hassi Messaoud field. These samples were taken from crude deposits formed after its precipitation. For this, it is essential to use the technique of X-ray diffraction (DRX). This method is a non-destructive technique for the characterization of candidate samples. Through experiments, we can know the differences in structural parameters.

The XRD diagrams show the presence of gamma band (γ), graphéne band (C = C) or (002), and band (10) or (11) peaks in the respective sample diffraction spectra.

Analysis by X-ray diffraction (XRD) of the eight Algerian crude asphaltene samples from the Hassi Messaoud field from different locations shows that the highest aromaticity values are distinguished for DA05-DA03 samples (50%), between 50% to 30% for samples DA06-DA01-DA07-DA08 and the rest of the samples, the aromaticity values are less than 30%. This concerns the dm and dr distances for all almost identical samples. For the average height of the cluster perpendicular to the single sheets, the Lc are divided into two categories, the first (20 Å) corresponding to the samples DA07-DA03-DA05-DA01 and the samples DA02-DA04-DA06-DA08, the aromatic leaves with the largest diameter for DA08-DA05-DA02-DA07-DA04-DA03, the lowest value for DA05-DA01. The Cau and Ra, with similar classifications DA08-DA05-DA02-DA07-DA03-DA04-DA06, from which the classification decreases with the sample number, and finally, the number of aromatic leaves in clusters is divided into three classes. The most numerous belong to the samples DA07-DA01-DA03-DA05, the means for DA02-DA04, and the weak ones for DA06-DA08.

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