

Article

Characterization Techniques Coupled with Mathematical Tools for Deepening Asphaltene Structure

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Abstract: Asphaltenes are the heavy fraction of fossil fuels, whose characterization remains a very difficult and challenging issue due to the still-persisting uncertainties about their structure and/or composition and molecular weight. Asphaltene components are highly condensed aromatic molecules having some heteroatoms and aliphatic functionalities. Their molecular weights distribution spans in a wide range, from hundreds to millions of mass units, depending on the diagnostic used, which is mainly due to the occurrence of self-aggregation. In the present work, mass spectrometry along with size exclusion chromatography and X-ray diffraction analysis have been applied to asphaltenes for giving some further insights into their molecular weight distribution and structural characteristics. Relatively small polycyclic aromatic hydrocarbons (PAHs) with a significant degree of aliphaticity were individuated by applying fast Fourier transform (FFT) and double bond equivalent (DBE) number analysis to the mass spectra. X-ray diffraction (XRD) confirmed some aliphaticity, showing peaks specific of aliphatic functionalities. Size exclusion chromatography indicated higher molecular weight, probably due to the aliphatic substituents. Mass spectrometry at high laser power enabled observing a downward shift of molecular masses corresponding to the loss of about 10 carbon atoms, suggesting the occurrence of aryl-linked core structures assumed to feature asphaltenes along with island and archipelago structures.

Keywords: asphaltenes; mass spectrometry; DBE; size exclusion chromatography; X-ray diffraction



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1. Introduction

The need to define peculiar classes of heavy liquid and solid fuels, such as asphaltenes, in operational terms, mainly related to their solubility/insolubility in certain solvents, is already in itself an index of their chemical and structural complexity. Specifically, asphaltenes are defined as a class of species insoluble in aliphatic hydrocarbons such as n-pentane or n-heptane and soluble in aromatics such as toluene and benzene [1]. When separated, asphaltenes come in the physical form of dark-brown-to-black friable solids, without a definite melting point, which foam, swell, and leave a carbonaceous residue upon heating [2]. The carbonization and degradation tendency as well as the enhancing effect of asphaltenes on rheological properties such as the viscosity of liquid fuels [3–5] have a negative impact on fuel processing technology and utilization, reducing the fuel economic value and causing undesirable effects to the industry using them. Their hindrance on the production and processing in the petroleum industry has required focusing fundamental and applicative research on physical and chemical characterization asphaltenes to understand how to separate asphaltenes from the petroleum before the refining processes or to obtain their “upgrading” to a less refractory (lighter) fraction (e.g., via catalytic cracking). Many of the results are reviewed in books devoted to the specific aim of asphaltenes analysis [1,2,6]. From a chemical point of view, asphaltenes are a mixture of organic species,

which are constituted mainly of carbon and hydrogen. The main components are heavy aromatic species substituted with aliphatic functionalities and/or inorganic elements such as oxygen, nitrogen, sulfur, and metals [7]. In the last decades, an intense debate has regarded in particular the determination of both the chemical composition and molecular weight (MW) of asphaltenes. Especially with regard to the MW, a wide range of molecular masses, from hundreds to millions of mass units, has been found in dependence on the method used [8,9].

In spite of the efforts and progresses so far done, there is still discussion about the MW and structural properties of asphaltene components [10–12]. The controversy and questions on asphaltene MW of the order of thousands or hundreds of mass units have been read in light of the “archipelago or island” molecular structure affecting the nature of the molecular interactions involved in asphaltene self-aggregation [9,11,13].

The present work is placed in this context aiming to give some insights on the MW and compositional features of asphaltenes by using laser desorption ionization time of flight mass spectrometry (LDI-TOFMS) at low and high laser power, employing mathematical methods, specially designed to address the complexity of the mass spectra. Size exclusion chromatography and X-ray diffraction have been also implemented as ancillary tools for asphaltene characterization.

2. Materials and Methods

Asphaltenes were separated from a #6 commercial heavy oil as the alkane (pentane)-insoluble/aromatic (toluene) soluble fraction by using the ASTM D2000-3 method.

2.1. Laser Desorption Ionization-Time of Flight Mass Spectrometry (LDI-TOFMS)

The asphaltene sample dissolved in N-methylpyrrolidinone (NMP) was deposited on a standard stainless steel plate and heated in an oven at about 100 °C for few minutes in order to evaporate the solvent. LDI-TOFMS spectra of asphaltenes were recorded on a SCIEX TOF/TOF™ 5800 System in positive reflectron mode, using a N₂-laser with the power varied from 40% up to 90% of its nominal value. Each spectrum represents the sum of 12,000 laser pulses from randomly chosen sample position spots. Matrices were not added, since asphaltenes, as well as in general aromatic materials, are able to absorb the laser beam ($\lambda = 337$ nm), acting as a self-matrix [14–16]. Fast Fourier transform (FFT) analysis was applied to the asphaltene spectra to compute the discrete Fourier transform (DFT) of repetitive signals. Origin software was used for data plotting and analysis. More details on the method as applied to mass spectra are reported in [17].

The double-bond equivalent (DBE) number, also called the degree of unsaturation, was calculated for asphaltenes from the structure of the chemicals, considering that each π bond or ring generates one DBE. If the compound contains the elements C, H, O, and N, the DBE for the general formula C_xH_yN_zO_n is calculated as follows [18]:

$$\text{DBE} = x - (y/2) + (z/2) + 1.$$

In this work, the DBE was determined for each mass peak considering the simplified formula for C_xH_y hydrocarbons: $\text{DBE} = x - (y/2) + 1$ by home-made software [19]. By plotting the DBE number and the relative intensity against the carbon number (CN), iso-abundance graphs were plotted using Origin software.

More details are reported in [19].

2.2. Size Exclusion Chromatography (SEC)

SEC analysis of asphaltenes was carried out on an HPLC system HP1050 series by elution with NMP on a PL-gel polystyrene–polydivinylbenzene individual-pore column (Polymer Laboratories Ltd., Church Stretton, UK, part no. PL1110-6525 particle size of 5 μm diameter and a pore dimension of 50 nm) for the MW determination in the 100–50,000 u range. The relation between retention times and molecular mass of polystyrenes has shown to be held also for aromatic standards (toluene, dicoronylene, paracyclophane, pyrene,

and a standard polycyclic aromatic hydrocarbon (PAH) mixture (Supelco EPA 525 PAH mix A)). The injection volume was 100 μL , and the analyses were performed at a constant temperature of 70 $^{\circ}\text{C}$ with a flow rate of 0.5 mL min^{-1} . The online detection of species eluted from the SEC column used a HP1050 UV–visible diode array detector (Hewlett-Packard, Palo Alto, CA, USA) that measured the absorbance signal at a fixed absorption wavelength (350 nm). A 100 ppm asphaltene solution in NMP was prepared.

2.3. X-ray Diffraction (XRD)

XRD spectra were acquired on a Bruker D2 II with a Cu cathode ($K\alpha_1$ 1.54 \AA , 30 kV at 10 W). A 2.5 $^{\circ}$ Soller slit with a 4 mm divergence slit and a 0.6 mm collector slit were used. A 1.5 mm Ni foil filter was used to remove the $K\beta$ ($\lambda = 1.392 \text{\AA}$) X-ray Cu spectral lines. Instrument resolution was 0.05 $^{\circ}$ 2 θ . A “zero background” silicon crystal sample holder, specially designed to minimize the background contribution, was used.

3. Results

The LDI-TOFMS mass spectrum of asphaltenes reported in Figure 1 is very complex as featured by a large number of peaks differing for only m/z 1 and distributed in a unique broad MW mode ranging from about m/z 200 and tailing up to 1000, with a peak maximum around m/z 550. Mathematical methods applied to mass spectra featured by a high number of peaks are helpful for extrapolating compositional features from such complex mass spectra.

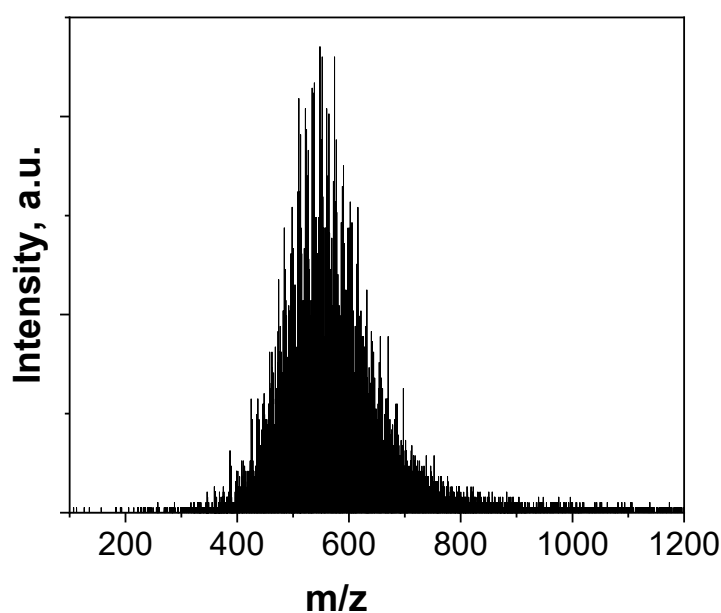


Figure 1. Laser desorption ionization- time of flight mass spectrometry (LDI-TOFMS) spectrum of asphaltenes using the laser at 40% nominal power.

As shown in Figure 2, applying the FFT analysis, the mass spectrum is reduced to a few peaks associated to main periodicities in MW distribution, which are indicative of the compositional features.

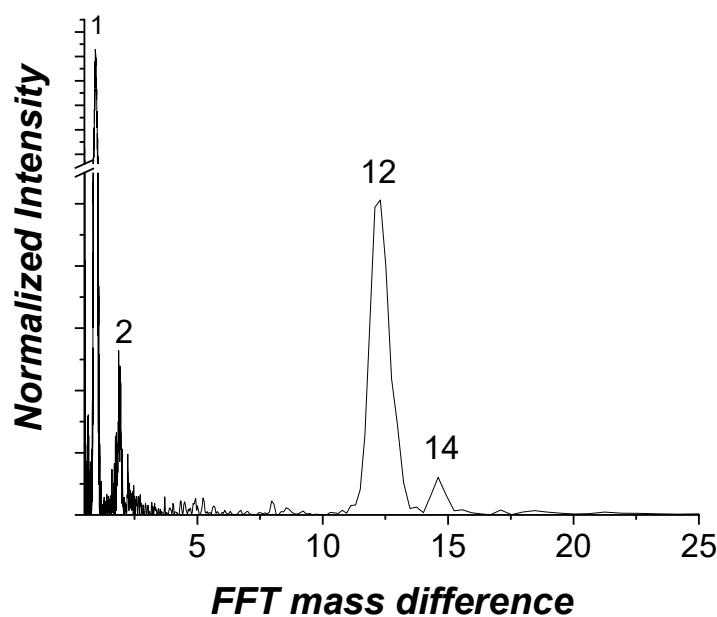


Figure 2. Mass periodicity evaluated by fast Fourier transform (FFT) of asphaltene LDI-TOFMS spectrum.

The main periodicity at m/z 12 of FFT profiles hints to a homologous series of aromatic carbon polymers with a different degree of unsaturation suggested by the presence of mass difference of m/z 1 (the prevalent FFT peak) and 2. Specifically, the periodicity at m/z 12 presents a large peak with a width at half height of m/z 1, which means some contribution of m/z 13. On the basis of infrared spectroscopic analysis performed in a previous work [20], the mass difference of 13 is arguably due not only to isotopic C13 contribution, but also to the presence of aliphatic groups (CH) bridging the building aromatic blocks of the molecules. Likewise, the smaller peak at m/z 14 suggests the presence of aliphatic (CH₂) and methyl groups (CH₃) located on and/or between the aromatic moieties, which is consistent with the quantitative infrared spectroscopic analysis [20]. Indeed, it is worth underlining that the infrared spectroscopic analysis has shown the high weight percentage of aliphatic hydrogen (higher than 6 wt%) and the very low contribution of aromatic hydrogen (less than 1 wt%), the latter one mainly present in form of three- and four-adjacent hydrogens located at the edge of the polyaromatic systems. These inferences hint to the presence of relatively long alkyl chains linked to small aromatic moieties [20]. The continuous increase in asphaltene MW in a small range (m/z 400–800) (Figure 1) and the absence of 24 mass difference periodicity (Figure 2), typical of large PAHs with an increasing number of carbon atoms [16,17,21], indicate that they are mainly constituted of relatively small aromatic moieties connected and/or substituted by aliphatic groups.

The aliphatic content of asphaltenes can be deduced also from the slope of the planar limit line (PLL), which is the line generated from the iso-abundance plot by connecting the maximum DBE numbers at given carbon numbers [22] on the iso-abundance plots of DBE number vs. carbon number. The DBE plot and the PLL are reported in Figure 3 (left) for asphaltene mass spectrum obtained at low laser power.

In Figure 3 (left), it can be seen that the PLL line has a slope of 0.704, which is lower with respect to the PLL slope for aromatic-rich samples such as the flame-formed organic carbon typically evaluated to be around 0.8 [21] and aromatic pitch (PLL slope = 0.798, [19,23]). The PLL slope of asphaltenes is even lower than that evaluated for an aliphatic pitch (PLL slope 0.717 [19,23]), confirming the higher aliphatic character of asphaltenes.

In addition, the width of the DBE distribution of asphaltenes reported in Figure 3 appears rather different with respect to that typically evaluated for flame-formed organic carbon [21] and also for practical hydrocarbon mixtures as fossil fuels [24], and aromatic (coal) pitches [19]. Specifically, a higher DBE width for asphaltenes indicates a larger variety of molecules, as previously observed for aliphatic (petroleum-derived) pitch [19].

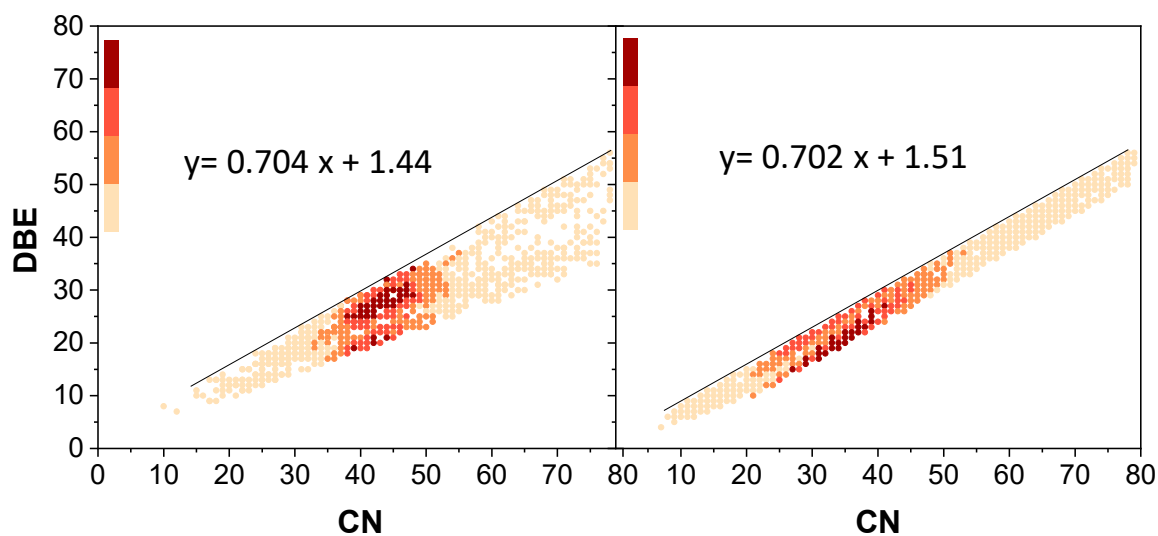


Figure 3. Iso-abundance plots of double bond equivalent (DBE) number vs. carbon number of asphaltenes at low laser power (40% of the nominal value) on the left panel and at high laser power (90% of the nominal value) on the right panel of the figure.

The relatively low laser power value (40% of its nominal value) used for LDI-TOFMS measurements so far described was chosen in order to limit the fragmentation occurrence due to high laser power. Indeed, the almost complete absence of fragmentation is confirmed by the similarity of the LDI-TOFMS spectrum distribution (Figure 1) with the mass spectrum reported in Figure 4, which has been obtained on the same asphaltene sample with a softer ionization method, namely atmospheric pressure photoionization (APPI) [25]. Therefore, the chosen laser power represents a good compromise between asphaltene volatility and fragmentation [26]. However, in the present work, just the high laser power has been exploited for giving insights in the aliphatic/aromatic character of asphaltenes.

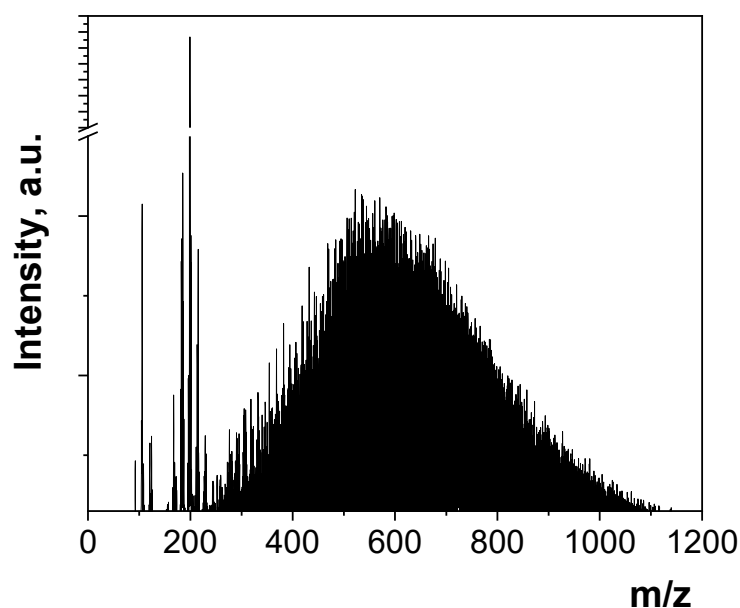


Figure 4. Atmospheric pressure photoionization mass spectrometry (APPI-MS) spectrum of asphaltenes (adapted from [25]).

In Figure 5, displaying the mass spectrum of asphaltenes at high laser power (90% of its nominal value), beside a higher signal intensity, it can be noticed that the high laser

power shifts the MW distribution to lower masses in the range from about m/z 150 up to 1000, with a maximum around m/z 400. It is arguable that the higher laser power causes the fragmentation in the aliphatic part of the asphaltene macromolecules, as previously found for aliphatic pitch composed of alky-substituted PAH oligomers [21]. The DBE plot of the spectrum measured in the high laser power conditions reported in the right part of Figure 3 puts better in evidence the shift to lower carbon number values of the more intense peaks (indicated with the darker colors) and the extension increase in the mass peak range. Specifically, at lower laser power, the CN range of the intense peaks lies between 38 and 50, whereas at high laser power, it lies between 28 and 40.

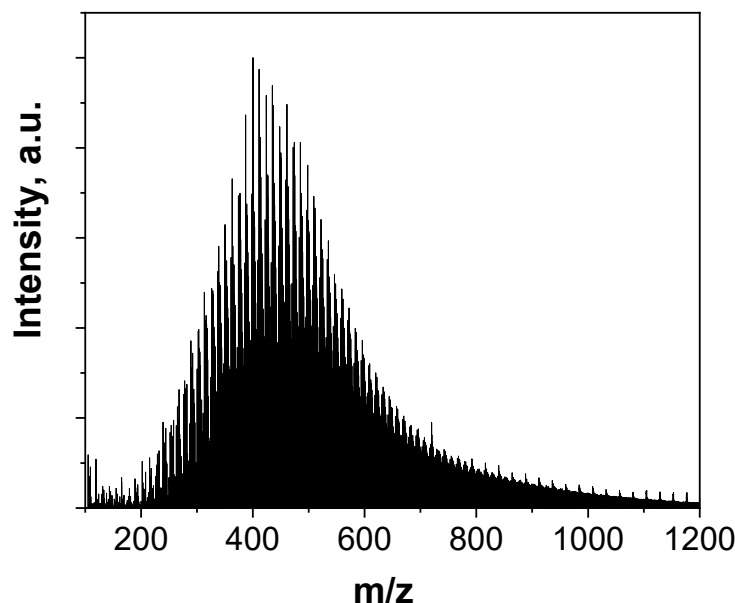


Figure 5. LDI-TOFMS of asphaltene at high laser power (90% of the nominal value).

The shift of only 10 carbon atoms is rather low with respect to an aliphatic pitch (about 30 [21]), which is more compatible with the breakup of aryl bonds linking small aromatic moieties, thus supporting the presence of a third class of structures recently termed as “aryl-linked core structures” and postulated to be present in asphaltene along with the “archipelago” (small aromatic moieties linked by aliphatic chains) and “island” (aromatic core with lateral aliphatic chains) structures [11]. The “aryl-linked core structure” has been defined as constituted of adjacent aromatic rings directly bonded together but without sharing a common bond in a ring, therefore presenting a single, contiguous sp^2 -hybridized carbon network containing one or more aryl groups.

SEC analysis is another way that has been used to evaluate the MW range of asphaltene [27]. In comparison to the LDI-TOFMS spectrum, the SEC profile of asphaltene reported in Figure 6 shows a peak in a wider MW range (300–4000 u), as already found for other complex carbon materials [28].

A peak in the region around 10,000 u is also shown, which is ascribable to aggregates formed as a consequence of the occurrence of supramolecular aggregation [29] which is an effect that greatly complicates the asphaltene chemistry, making it difficult to distinguish between covalent and non-covalent bonds [8,9].

The difference in the MW distribution of asphaltene is well evidenced by comparing the number-average molecular weight (M_n) evaluated on their LDI-TOFMS and SEC profiles.

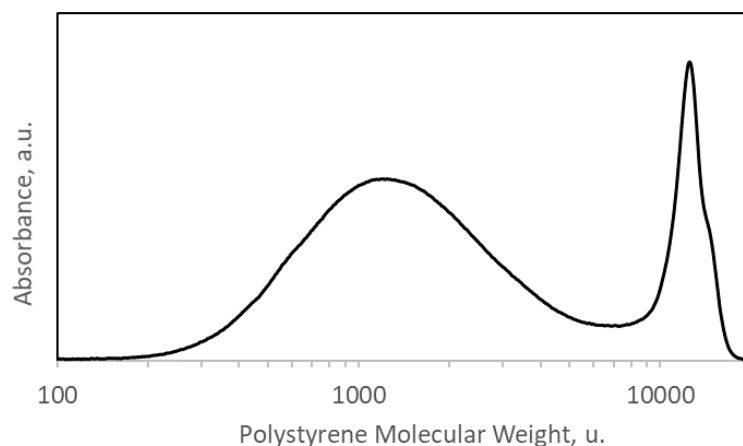


Figure 6. Molecular weight distribution measured by size exclusion chromatography (SEC) of asphaltenes at 350 nm absorbance wavelength for the detection.

The M_n has been evaluated in the 150–4000 u range, assuming the intensity of the mass spectrometric and SEC signals proportional to concentration through the formula [28]:

$$M_n = \frac{\sum_i I_i MW_i}{\sum_i I_i}$$

where I_i is the signal intensity and MW_i represents the MW for each point i of the SEC profile and mass spectrum.

The weight-average molecular weight (M_w) is calculated through the formula:

$$M_w = \frac{\sum_i I_i (MW)_i^2}{\sum_i I_i MW_i}$$

The M_n value obtained by LDI-TOFMS for asphaltenes by LDI-TOFMS is 569 ± 24 u, which is significantly different and lower in comparison with the M_n evaluated from the SEC profiles (measured at 350 nm), which is 1560 ± 62 u. The smaller M_n values measured by LDI-TOFMS can be due to the different MS detector responses to low and high-MW components. In fact, an intrinsic limitation of the LDI-TOFMS technique applied to blends of low- and high-MW species is the predominance of the signals of the high-volatile low-MW species, obscuring the high-MW species detection [28].

The M_w of asphaltenes evaluated by LDI-TOFMS and SEC are 587 and 2789 u, respectively. Thus, the polydispersity index (PDI), calculated as ratio between M_w and M_n is 1.03 for LDI-TOFMS and 1.79 for SEC, confirming quantitatively the much larger distribution observed by SEC. This is a larger difference with respect to those found for much less aliphatic carbon mixtures as aromatic pitches [28], hinting to a strong effect of aliphaticity on SEC elution and consequently on the related MW determination. This effect will be the subject of further study.

XRD has been also applied as additional diagnostic tool of asphaltene features. The diffractogram reported in Figure 7 shows two main peaks attributable to the (002) reflection of graphite and the γ band. The (002) reflection is located at 25° , which shifted with respect to the graphite value (26°), and it is very weak and diffuse compared with that of graphite, as typically occurs for amorphous materials [30]. Moreover, the γ band is not simply a shoulder of the (002) peak, as generally found in amorphous-like carbon material [31], but it is comparable with the (002) peak in form of a distinct broad peak that has been ascribed to aliphatic content [30]. The two very sharp peaks superimposed on the broad asphaltene pattern are typical of aliphatic chains, as verified in the present work by comparison with the XRD spectrum of paraffinic wax. This finding is in agreement with previous work [32], where similar peaks in the XRD spectrum of asphaltenes were attributed to free long-chain

alkanes co-precipitated with asphaltenes. However, whether they are attributable to free alkanes or to alkyl chains linked to the aromatic structure of asphaltenes, requires further work. Otherwise, the paraffinic wax spectrum here measured does not present any γ band, neither as a shoulder nor as a peak, supporting that it was instead due to the aliphatic chains embedded in the asphaltenes structure.

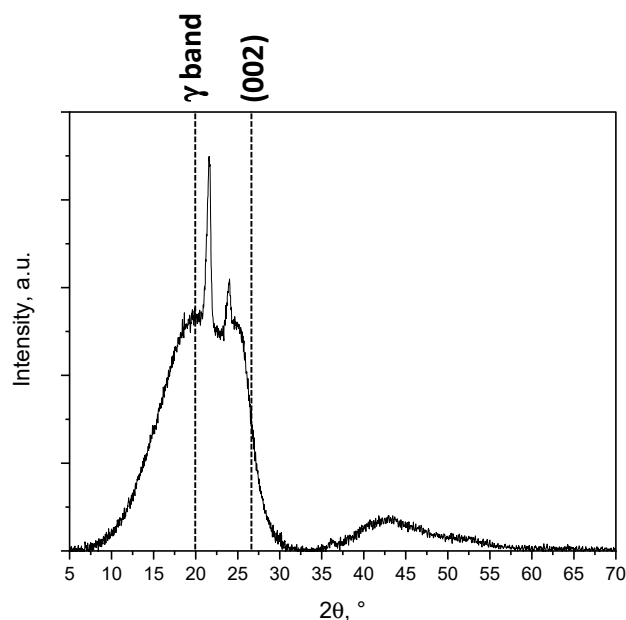


Figure 7. X-ray diffraction (XRD) patterns of asphaltenes, with indication of the positions of main peaks: (002) graphite reflection and the γ band.

4. Final Remarks

The paper reports the results on asphaltene features obtained by LDI-TOFMS along with XRD and SEC analysis. On the basis of FFT and DBE mass spectra analysis, it was inferred that asphaltenes are composed of relatively small aromatic moieties linked and/or substituted by aliphatic chains, with MW extending up to about m/z 1000. In addition to the aliphatic substitution, the application of high laser power, downshifting the MS distribution of about 10 carbon atoms, was found to have an effect on the asphaltene mass spectrum traceable to the so-called aryl-linked core structure recently postulated as an additional structure to the “island” and “archipelago” structures featuring asphaltenes. SEC also showed a similar continuous MW distribution of species but shifted toward higher MW values. Future work will be addressed to study the nature and the effect of aliphaticity on the MW as evaluated by SEC.

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