

An evaluation of the aromaticity of asphaltenes using atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry – APPI(±)FT-ICR MS



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HIGHLIGHTS

- We evaluate the aromaticity of asphaltenes using APPI(±)FT-ICR MS.
- APPI(±)FT-ICR MS data were compared and discussed with aromaticity parameters obtained from elemental analyses and ¹H NMR.
- An inverse correlation was observed between aromaticity degree and the N and O concentrations.
- The slopes of DBE versus carbon number plots are direct indicative of variation of aromaticity.

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ABSTRACT

Asphaltene can be considered like the ‘bad guys’ when heavy petroleum are transported or upgraded. These compounds are not classified by their chemical structures but by the solubility class, that is defined as solubles in aromatic solvents, such as toluene, and insolubles in *n*-alkanes, such as *n*-heptane. Here, we analyze three crude oil samples (classified as extra-heavy, heavy and asphaltic having API degree of 17.3, 22.0 and 13.5, respectively) and their asphaltene by atmospheric pressure photoionization (APPI) coupled to Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) in positive and negative ionization modes, APPI(±)-FT-ICR MS. We apply the DBE (double bond equivalent) versus carbon number (CN) plots as the aim of to predict the aromaticity of crude oil and their asphaltene. Additionally, average molecular weight, M_w , heteroatomic-containing compounds profile and van Krevelen diagrams were constructed to visualize and interpret the MS data. MS data were compared and discussed with aromaticity parameters obtained from elemental analyses and ¹H NMR measurements. For three crude oils analyzed with different magnitude of the viscosities ($\text{III} > \text{II} > \text{I}$), the amount of the asphaltene extracted followed the behavior analogous ($7.63 \pm 0.65 \text{ wt\%}$; $2.23 \pm 0.25 \text{ wt\%}$; and $0.41 \pm 0.01 \text{ wt\%}$, respectively). The aromatic hydrogen content (H_{ar} , in molar%) was determined from ¹H NMR, where the heavier crude oil and its asphaltene ($H_{ar} = 4.90$ and 27.3 M\% , respectively) were slightly more aromatic than other. An inverse correlation was observed between H_{ar} values and the N and O concentrations determined from elemental analyses. For APPI(±)FT-ICR MS data, the values of M_w observed for asphaltene (m/z 200–650) were significantly distinct, being correlated with the physico-chemical characteristics of their parent crude oil. Using the concept of planar limited, the line generated by connecting maximum DBE values at given CN in the DBE versus carbon number plots, it was possible to extract the aromaticity degree from APPI FT-ICR MS data. The slopes of these lines determined by DBE/carbon number ratio were calculated by linear regression for protonated hydrocarbons (HC[H]) and basic nitrogen (N[H]) compounds classes. We observed an increase in slopes in function of an increasing of the H_{ar} values.

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1. Introduction

Asphaltene can be considered like the ‘bad guys’ when heavy petroleum is transported or upgraded [1]. Their precipitation represents a serious concern to the petroleum industry, requiring a

large capital investments for removal, prevention of deposit formation and researches funding designed to better clarify its chemical composition [2–5]. The process of deposit formation can be induced by variations from pressure, temperature, reservoir fluid composition, flow shear rate, surface characteristics, particle size to chemical interactions [2,6].

It is well-known that asphaltenes are the heaviest and most complex molecules of the crude oil [7]. These compounds are not classified by their chemical structure but by the solubility class, that is defined as compounds soluble in aromatic solvents, such as toluene, and insoluble in *n*-alkanes, such as *n*-heptane [2,8]. Several physicochemical properties of crude oil are affected by presence of high content of asphaltenes such as viscosity, emulsion stability, flow assurance problem, rheological properties and refraction index [4].

The asphaltenes can structurally be classified based on “island”-type structures (models of one aromatic core) or “archipelago”-type structures (models of multiple aromatic centers bridged by alkyl chains) [5,9] and have a high tendency to associate into larger aggregates [10,11]. Their stability in petroleum fluids can be disrupted by pressure drop or compositional changes, which lead to asphaltene precipitation and deposition in subsurface formations, wellbores, or transportation pipelines [4,5].

Successful prediction of asphaltene precipitation requires the understanding of mechanisms of asphaltene aggregation in terms of its composition. It is known that intermolecular forces play an important role on asphaltene aggregation [12]. Recently, a modified Yen model (also called Yen–Mullins model) stipulated that asphaltene nanoaggregates consist of less than 10 molecules stacked on top of each other. The aggregation stops beyond nanoaggregation; however, nanoaggregates can coagulate due to their high molar weight forming clusters of aggregates, which can eventually lead to flocculation. The driving force of aggregation is the π – π stacking or aromatic interactions from the aromatic core of asphaltenes, and the force limiting their aggregation is the steric hindrance caused by aliphatic side chains. Aromatic interactions occur due to electrostatic attraction between the negative π electron cloud and positive σ frame of aromatic rings [11,12]. Thus, a clear picture of the aromaticity degree or aromatic content of asphaltenes is a prerequisite to predict aggregation.

Usually, advanced NMR techniques can provide the degree of aromaticity, the average aromatic core number and the size distribution in asphaltene fraction. However, the NMR results provide the average molecular structures, being routinely found that more one structure might be compatible with a set of NMR data. For a successful prediction model, it is important to know the chemical composition of various compound classes, the carbon number distribution in each compound classes and the carbon center distribution for each carbon number. Among numerous analytical techniques for asphaltene characterization, atmospheric pressure photoionization (APPI) coupled to Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry provides the most extensive molecular characterization of nonpolar petroleum compounds. FT-ICR MS provides an unsurpassed mass resolution and mass accuracy, thus enabling, a molecular level analysis of complex petroleum mixtures and asphaltenes [13,14]. Accurate mass measurements [15,16] define a unique elemental composition ($C_cH_nN_pO_oS_s$) and DBE (double bond equivalent), facilitating material classification by heteroatom content and the degree of aromaticity [17–23]. APPI is well-suitable to characterize purely cycloalkane hydrocarbon and aromatic species, thiophenes, and furans that are inaccessible to electrospray ionization because the molecules are insufficiently basic or acidic to accept or lose a proton. APPI can positively charge these species to produce both radical cations $[M]^+$ and protonated molecules $[M+H]^+$ [24,25]. Specifically, APPI ionizes species that can either undergo direct ionization from

10 eV photons (aromatics, such as asphaltenes) to gas-phase proton transfer or charge exchange reactions.

In 2006, Purcell et al. [24] have analyzed naphtho[2,3-*a*]pyrene and crude oil by APPI(\pm)-FT-ICR MS, where the results reveals that APPI(\pm) can produce protonated molecules, $[M+H]^+$, deprotonated molecules, $[M-H]^-$, and radical molecular ions, M^+ or M^- , consequently, producing mass spectra of ca. >12000 peaks, being that 63 species are identified for each nominal mass unit. In 2008, Qian et al. [26,27] demonstrated that APPI(+) provides soft ionization of Vanadyl porphyrins, sulfur-containing Vanadyl porphyrins [25] and Nickel porphyrins [26]. All were present in petroleum asphaltene, generating primarily molecular ions M^+ . The changes in hydrocarbon and sulfur classes during deep hydrotreatment processes were also observed, being successfully applied to identify and catalog diverse structures of Vanadyl porphyrins. In 2009, McKenna et al. [25] have analyzed Vanadyl porphyrins by APPI(+)-FT-ICR MS. Despite the rich literature related to asphaltenes characterization using APPI FT-ICR MS, there is few studies that correlate between the APPI FT-ICR MS data and other analytical techniques with of aim of predicting any physico-chemical properties. Here, we analyze three crude oil samples (classified as heavy, extra-heavy, and asphaltic oils) and their asphaltenes by APPI(\pm)-FT-ICR MS. We apply the concept of planar limits, defined as lines generated by connecting maximum DBE values at given carbon numbers in a plot of DBE versus carbon number as the aim of to predict the aromaticity of crude oil and their asphaltenes. We use the slopes of the lines determined by the DBE/carbon number ratios as indicative of degree of aromaticity. These data were compared and discussed with aromaticity parameters obtained from elemental analyses and 1H NMR spectrometry measurements.

2. Experimental

2.1. Reagents

Heptane and toluene (analytical grades with purity higher than 99.5%), were used for extraction procedure of asphaltenes and characterization by APPI(\pm)-FT-ICR MS, respectively. Both were supplied by Vetec Química Fina Ltda, Brazil. Ethylenediamine tetraacetic acid (EDTA), acetanilide, chromium(III) acetylacetonate ($Cr(acac)_3$), deuterated chloroform ($CDCl_3$) and tetramethylsilane (TMS) were purchased from Sigma–Aldrich Chemicals USA (purity of 99.8%) and used for elemental analysis (CHNSO) and 1H NMR measurements. All reagents were used as received.

2.2. Petroleum characterization and asphaltene fraction extraction

Three samples of crude oil (termed in crude oil I, II and III) were characterized according to the standards of the ASTM by Laboratory of Petroleum Characterization of Federal University of Espírito Santo (LabPetro/UFES-Brazil). A primary characterization was conducted to determine density (ASTM D5002–99), [28] API degree (ASTM D1298–99) [29], and kinematic viscosity (ASTM D7042–04) [30]. The characterization data obtained for three crude oils are describe in Table 1, thus classifying the crude oils I, II and III as heavy, extra-heavy and asphaltic oils, respectively [31].

Three different asphaltene samples were obtained from crude oils (I, II and III) by precipitation with *n*-heptane (30 mL g^{-1} of crude oil) and washed in a soxhlet system using the same solvent. The precipitated asphaltenes were filtered and solubilized with toluene. After, the solutions were evaporated to obtain asphaltene fraction samples (termed in asphaltene I, II and III) according to the ASTM 6560–00 [26]. The asphaltene extraction from different crude oils was done in triplicate and their total weight recovery

Table 1

Chemical and physical characterization of three crude oils used for asphaltene extraction [30].

	Crude oil I (heavy)	Crude oil II (extra-heavy)	Crude oil III (asphaltic)
API degree	22.0	17.3	13.5
Density 20 °C (g cm ⁻³)	0.9180	0.9469	0.9721
Viscosity 20 °C (mm ² s ⁻¹)	196.04	2406.1	82163
Viscosity 40 °C (mm ² s ⁻¹)	62.332	519.39	7384.2
Viscosity 50 °C (mm ² s ⁻¹)	34.496	279.14	2827.3

(wt%) are as follows: asphaltene I: 0.41 ± 0.01 wt%; asphaltene II: 2.23 ± 0.25 wt%; and asphaltene III: 7.63 ± 0.65 wt%.

2.3. Elemental analysis (C, H, N, S and O)

The content of carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) was carried out on a elemental analyzer LECO CHNS 932 and VT-900, Brazil. For C, H, N and S content analyses, helium and ultrapure oxygen (99.9999%) were used as carrier and burning gases, respectively; the oxidation temperature was 1100 °C. For O content analysis, ultra-pure helium (99.9999%) was used as carrier and burning gas, simultaneously, and the oxidation temperature was 1300 °C. The instrument was calibrated using EDTA and acetanilide. The C, H, N, S and O content was expressed in wt% and calculated from an average done in triplicate, Table 2.

2.4. ¹H nuclear magnetic resonance (¹H NMR)

¹H NMR spectra for crude oil I, II and III samples and their respective asphaltenes were performed on a Varian VNMRs 400 spectrometer, operating at 9.4 T using 5 mm broadband ¹H/X/D probe. ¹H NMR experiments were performed at 25 °C, using 20 mg of asphaltene diluted in 0.6 mL of deuterated chloroform. Tetramethylsilane (TMS) was used to reference the chemical shifts. A spectral width of 6410.3 Hz with a relaxation delay of 1.5 s and 512 scans was used. The relaxation agent Cr(Acac)₃ diluted in deuterated chloroform at 50 mM was also employed [31]. To obtain the structural parameters of crude oils and to correlate with physicochemical properties of asphaltenes, the degree of aromaticity (%) was determined through the integration of areas from 9.0 to 6.0 ppm regions for aromatic and from 4.0 to 0.0 ppm regions for the aliphatic hydrogens, sees in Table 3.

2.5. APPI(±)-FT-ICR MS

Mass analysis was performed on 9.4 T Q-FT-ICR MS hybrid (Solarix, Bruker Daltonics, Bremen, Germany) [20–22] equipped with commercially available APPI source set to operate over a mass region of *m/z* 200–1300. Briefly, FT-ICR mass spectra of crude oil I, II and III samples and their asphaltene fractions spectra were acquired using positive and negative ionization modes, APPI(±).

Table 2

CHNSO analyses (in wt%) for asphaltenes I, II and III samples.

Elemental analysis	Asphaltene I	Asphaltene II	Asphaltene III
Carbon (wt%)	79.33 ± 0.93	79.34 ± 0.44	88.37 ± 0.90
Hydrogen (wt%)	7.97 ± 0.30	7.52 ± 0.52	7.83 ± 0.55
Nitrogen (wt%)	1.89 ± 0.06	1.87 ± 0.06	1.60 ± 0.03
Oxygen (wt%)	4.19 ± 0.46	2.52 ± 0.28	1.35 ± 0.22
Sulfur (wt%)	6.63 ± 1.08	8.75 ± 0.74	0.80 ± 1.08
C/H atomic ratio	0.83	0.88	0.94
Total heteroatoms	12.70	13.14	3.80

The crude oil samples were diluted to ≈ 0.2 – 0.4 mg mL⁻¹ for crude oils and ≈ 0.5 – 1.0 mg mL⁻¹ for asphaltenes in toluene. After, they were sonicated for 5 min and directly infused at a flow rate of $10 \mu\text{L min}^{-1}$. The APPI(±) source conditions were as follows: nebulizer gas pressure of 2.0 bar, capillary voltage of 2–3 kV, transfer capillary temperature of 250 °C and Krypton photoionization lamp. The ions are accumulated in the hexapolar collision cell with time of 0.3 s followed by transport to the analyzer cell (ICR) through the multipole ion guide system (another hexapole). Each spectrum was acquired by accumulating 200 scans of time-domain transient signals in 4 mega-point time-domain data sets. The front and back trapping voltages in the ICR cell were -0.60 V and -0.65 V for APPI(–) and $+0.80$ V and $+0.85$ V for APPI(±), respectively. All mass spectra were externally calibrated using a NaTFA solution (*m/z* from 200 to 1200) after they were internally recalibrated using a set of the most abundant homologous alkylated compounds for each sample. A resolving power ($m/\Delta m_{50\%} \approx 500000$, in which $\Delta m_{50\%}$ is the full peak width at half-maximum peak height) of *m/z* 400 and a mass accuracy of <1 ppm provided unambiguous molecular formula assignments for singly charged molecular ions. Mass spectra were acquired and processed using a custom algorithm developed specifically for petroleum data processing, Composer software (Sierra Analytics, Modesto, CA, USA). DBE versus carbon number, heteroatomic-containing compounds profile and van Krevelen diagrams were constructed to visualize and interpret the MS data.

3. Results and discussion

3.1. CHNSO and ¹H NMR

Table 1 illustrates the API degree, density and the viscosity values (obtained at 20, 40 and 50 °C) of the three crude oils. Note that the magnitude of the viscosity of these crude oils in function of temperatures decreases in the follow order: III > II > I. On the other hand, the API decreases in an inverse order. Comparing the amount of the asphaltenes extracted with the API degree of the crude oils, we can observe that from crude oil III, lower API degree, was extracted a higher quantity of asphaltene (7.63 ± 0.65 wt%). On the other hand, from crude oil I, higher API degree, was extracted a lower quantity of asphaltene (0.41 ± 0.01 wt%). From crude oil II, intermediate API degree, an intermediate quantity of asphaltene (2.23 ± 0.25 wt%) was extracted.

Asphaltenes (I, II and III) were also characterized by CHNSO and ¹H NMR analyses, and the results are described in Tables 2 and 3. For CHNSO analyses, Table 2, a higher amount of N, O and S were observed for asphaltenes I and II, which show total heteroatomic concentrations of 12.70 and 13.14 wt%, respectively. These two asphaltenes were originated from the two lighter crude oils, API degree 22, and 17, respectively. In contrast, for asphaltene III was detected a higher carbon content (88.37 wt%) and C/H atomic ratio (0.94) [26].

Aromatic hydrogen content (*H_{ar}*, in molar%) of three crude oils and their respective asphaltenes are shown in Table 3. Note that the crude oil III and its asphaltene (*H_{ar}* = 4.90 and 27.3 M%, respec-

Table 3

Aromatic (H_{ar}) and aliphatic (H_{alk}) hydrogen content (molar%) obtained from 1H NMR spectra of crude oil I, II and III samples and their respective asphaltenes (asphaltene I, II and III).

Samples	Aromatic hydrogen, H_{ar} , 6.0–9.0 ppm region (molar%)	Aliphatic hydrogen, H_{alk} , 0.0–4.0 ppm region (molar%)
Crude oil I	3.89	96.11
Asphaltene I	7.40	92.60
Crude oil II	3.90	96.10
Asphaltene II	26.90	73.10
Crude oil III	4.90	95.10
Asphaltene III	27.30	72.70

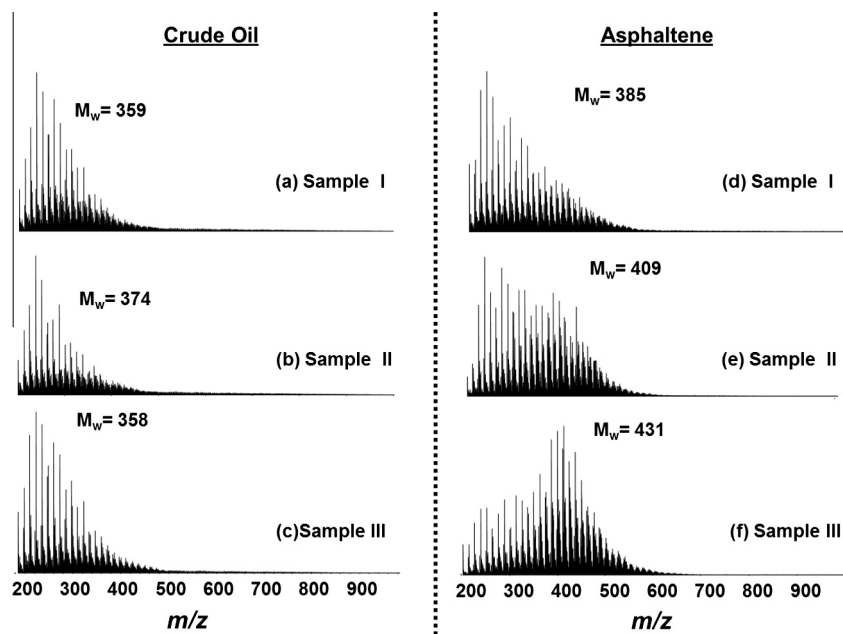


Fig. 1. APPI(+)-FT-ICR mass spectra of three crude oil samples (a–c) and their asphaltenes (d–f). Note that the M_w of asphaltenes increases in function of physico-chemical characteristics of their crude oil, varying in following order: III > II > I.

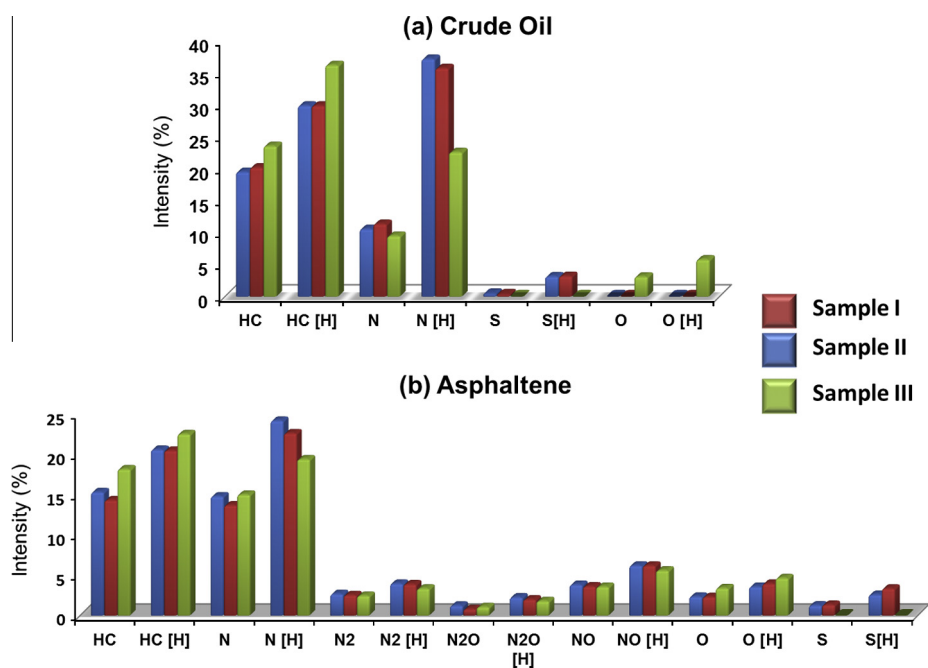


Fig. 2. Class distribution for (a) crude oil samples and (b) their asphaltene fractions obtained from APPI(+)-FT-ICR MS data.

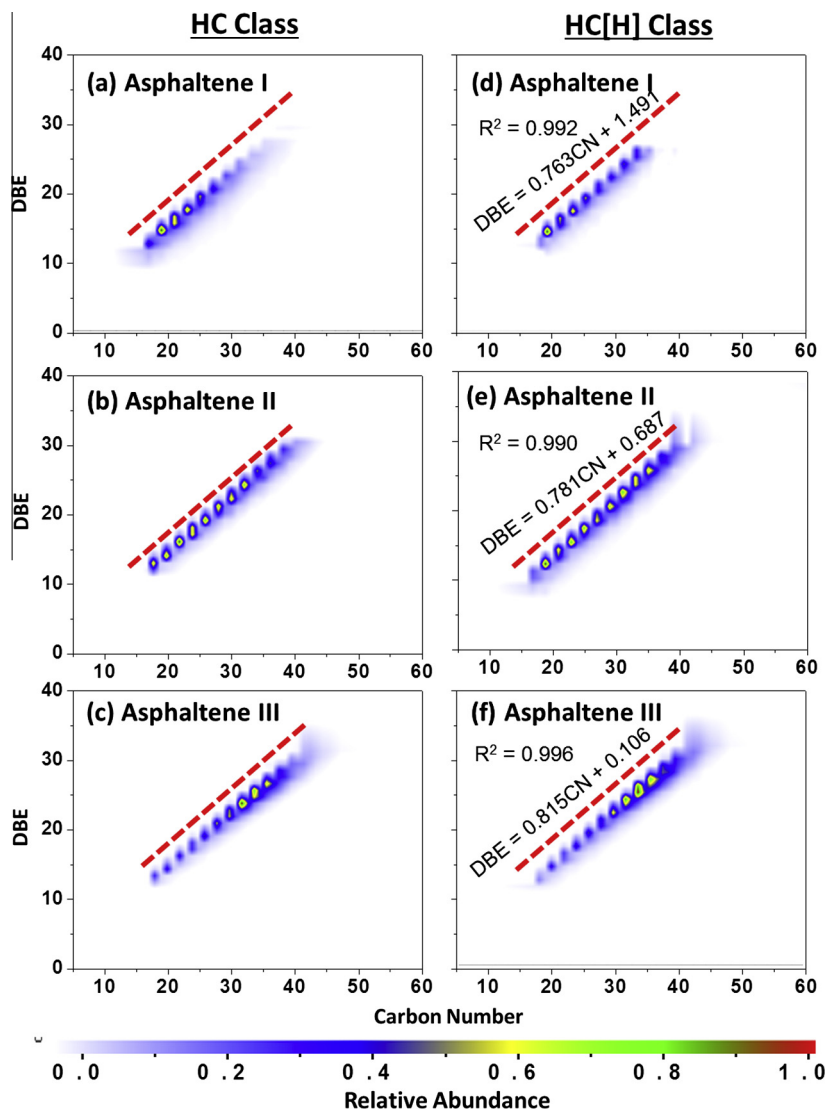


Fig. 3. DBE versus carbon number plots for hydrocarbon-containing compounds (HC (a–c) and HC[H] (d–f) classes) generated from APPI(+)-FT-ICR MS data of three asphaltene fraction samples.

tively) have higher H_{ar} concentration than the crude oil II and its asphaltene ($H_{ar} = 3.90$ and 26.90 M%). Alternatively, the asphaltene I is drastically different from others two, being more aliphatic ($H_{ar} = 7.40$ M%). Generally, an inverse correlation is observed between H_{ar} values and the N and O concentrations. Therefore, when the C/H atomic ratio and H_{ar} increases [asphaltene I (0.83 and 7.40) < asphaltene II (0.88 and 26.9) < asphaltene III (0.94 and 27.3)], a decrease in N and O concentrations is observed. In 2006, Castro [32] studied chemical composition of crude oil residues from distinct refineries using ^1H - and ^{13}C NMR, FTIR and elemental analysis. The average aromaticity index calculated (from nine samples) using ^1H NMR measurements was of ca. 26 M%, being similar to the observed for asphaltenes II and III.

Oliveira et al. [31] studied the relationship between the structural type (continental or archipelago) and aggregation properties of same asphaltene samples. The drastic difference in the H_{ar} values of asphaltene I ($H_{ar} = 7.40$ M%) in relation to other ($H_{ar} = 26.90$ and 27.30 M%), indicates a presence of highly condensed aromatic rings, thus suggesting, a continental-type structure for asphaltene I and archipelago-type structure for asphaltenes II and III.

3.2. APPI(+)-FT-ICR analysis

Fig. 1a–f displays the APPI(+)-FT-ICR mass spectra of crude oils (I, 1a, II, 1b, and III, 1c) and their respective asphaltenes (I, 1d, II, 1e, and III, 1f). For the crude oil samples, mass spectra have profile from m/z 200 to 500 with an M_w ¹ centered at approximately 359 (sample 1), 374 (sample 2) and 358 (sample 3) (Fig. 1a–c). Generally, these values are similar and cannot be used to predict any additional physico-chemical properties of crude oil such as density (or API degree), viscosity (Table 1) and total asphaltenes fraction recovery. Differently, the values of M_w observed for asphaltenes fractions (m/z 200–650) are significantly distinct and correlate with the physico-chemical characteristics of their parent crude oil. Note that the crude oil III has the higher value of the viscosity, lower API degree, (Table 1), and its asphaltene has the higher M_w value, 431 Da. In contrast, the crude oil I has the lower value of the viscosity, higher API degree and its asphaltene shows the lower value M_w , 385 Da.

Some papers have also been reported in the characterization of

¹ M_w was obtained from the petroleum data processing using Composer software, where 90% signals were assigned.

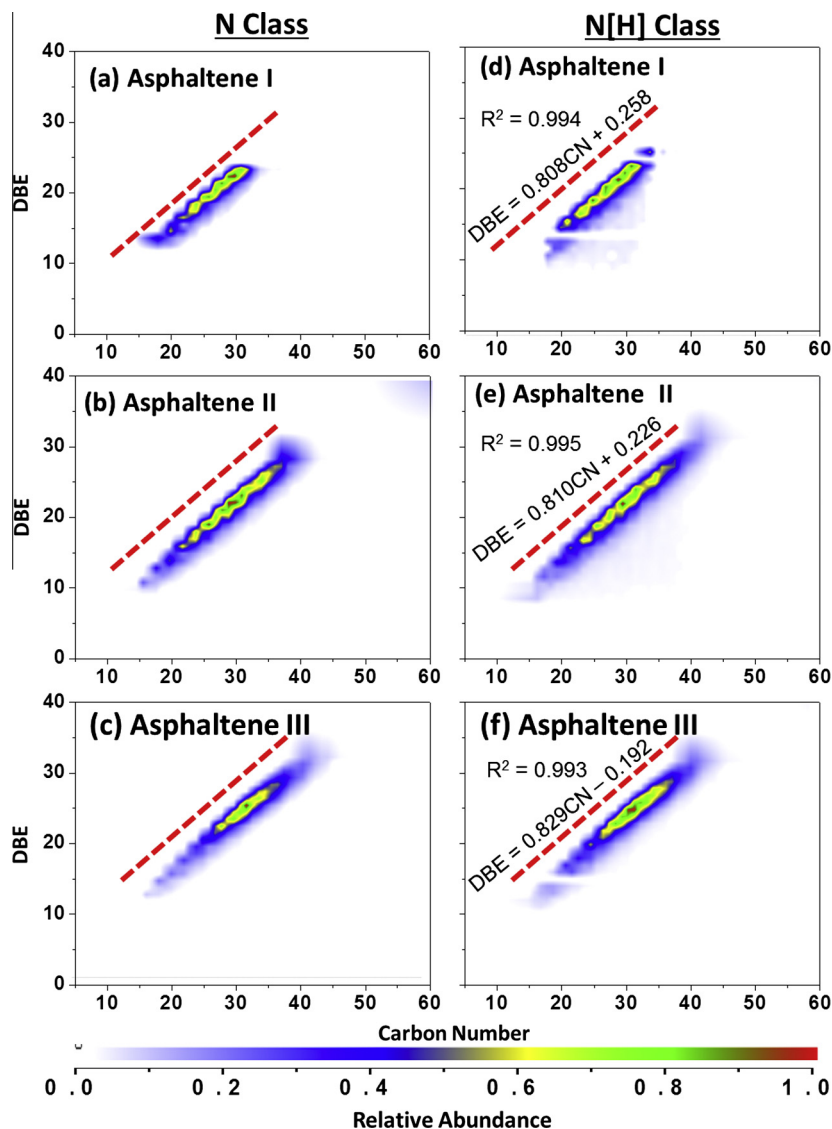


Fig. 4. DBE versus carbon number plots for nitrogen-containing compounds (N (a–c) and N[H] (d–f) classes) generated from APPI(+)-FT-ICR MS data of three asphaltene fraction samples.

asphaltene fraction using APPI(+) [33,34]. In 2011, Tachon et al. [33] isolated and characterized organic compounds from SARA fractions of bitumen using hybrid mass spectrometry, APPI(+)-Qq-TOF-MS. The fraction precipitated in heptane (ca. 13 wt%) showed a M_w of 500 Da. In 2012, Cho et al. [34] also observed similar results in compositional speciation of heavy oil products using a 15 T APPI(+)-FT-ICR MS, where $M_w > 600$ Da has been observed. In contrast to the results reported, our group has analyzed previously other Brazilian asphaltene fraction samples from original crude oil samples with API degree ranging from 13 to 31. In all cases, $M_w < 500$ Da has even been observed for FT-ICR MS in the positive ion acquisition mode. Like the M_w is a key parameter of Perturbed-Chain version of Statistical Associating Fluid Theory (SAFT) equation of state, these values can be applied to model asphaltenes phase behavior in crude oil [35].

Fig. 2a and b illustrates the polar and nonpolar compounds class distribution according to counts of assigned molecular formulas from APPI(+)-FT-ICR MS data for (2a) crude oil samples and (2b) their asphaltene fractions. APPI(+) promoted ionization via two mechanisms, protonation and electron transfer, producing $[M+H]^+$ and M^+ ions. Consequently, the classes observed were

identified as protonated or deprotonated, $CLASS[H]^2$, and radical, $CLASS^+$. Fig. 2. APPI(+) assesses selectively the nonpolar compounds such as hydrocarbons (HC and HC[H] classes) and basic nitrogen compounds (N and N[H] classes), as well as multiheteroatomic compounds (N_2 , $N_2[H]$, N_2O , $N_2O[H]$, NO, NO[H], O, O[H], S and S[H] classes). For crude oils I and II and their asphaltenes (I and II), a higher abundance of heteroatomic species is observed, Fig. 2a and b, respectively. These results correlated with the high heteroatomic concentrations observed for asphaltenes I and II (12.70 and 13.14 wt%, respectively), Table 2.

Figs. 3 and 4 presents the DBE versus the carbon numbers (CN) plots for the most abundant classes detected, HC and HC[H] classes, Fig. 3; and N and N[H] classes, Fig. 4 of asphaltene fraction samples. In all cases, for each value of DBE analyzed, a little amplitude of compounds, represented by CN, was observed. This provides a chemical imaging in form of a 45° line between the axes CN and DBE. Therefore, this is an indicative that these compounds

² $CLASS[H]$ is used to design ions classes identified in protonated or deprotonated form, whereas $CLASS^+$, is used to design ions classes identified in molecular ion form, M^+ .

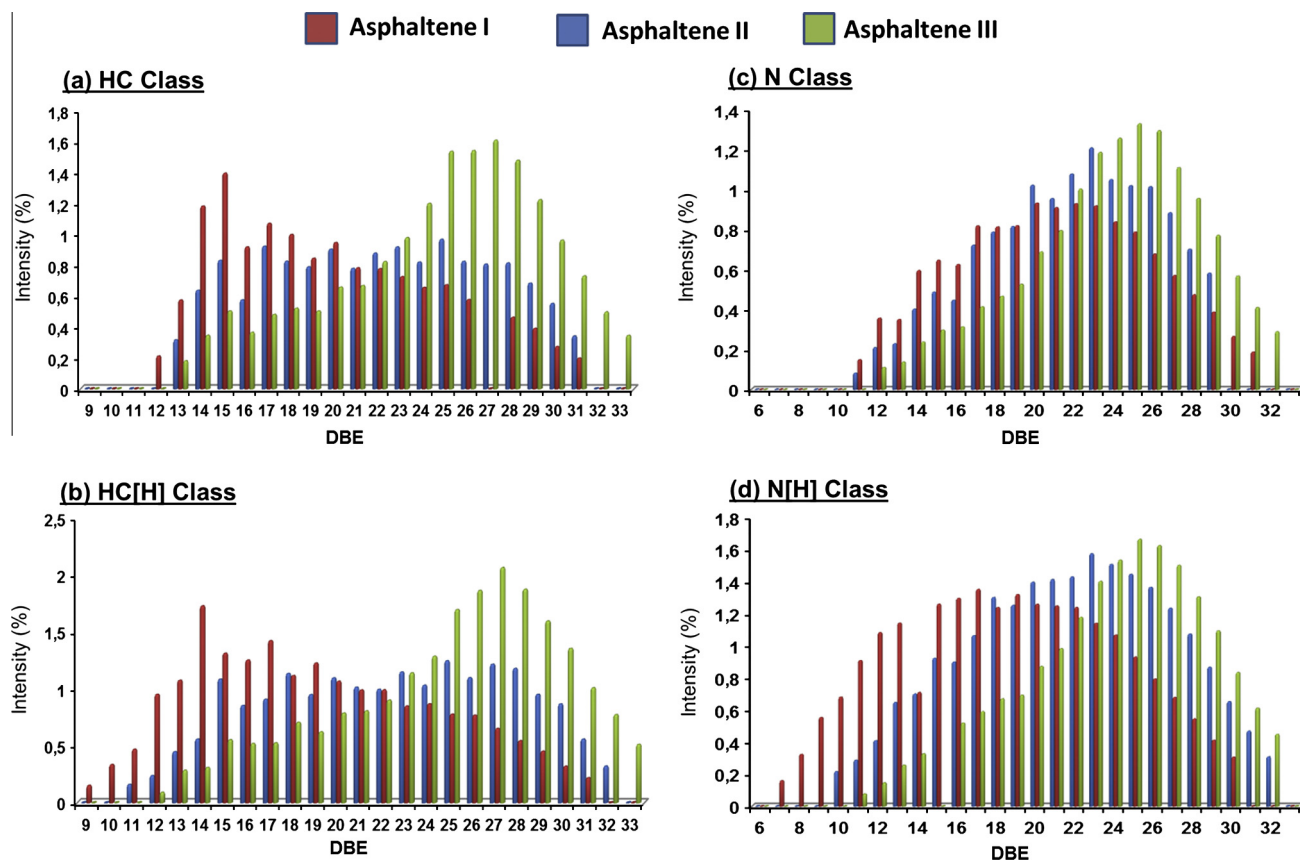


Fig. 5. Relative abundances for HC (a), HC[H] (b), N (c) and N[H] (d) compound classes from APPI(+)-FT-ICR mass spectra of three asphaltene fraction samples.

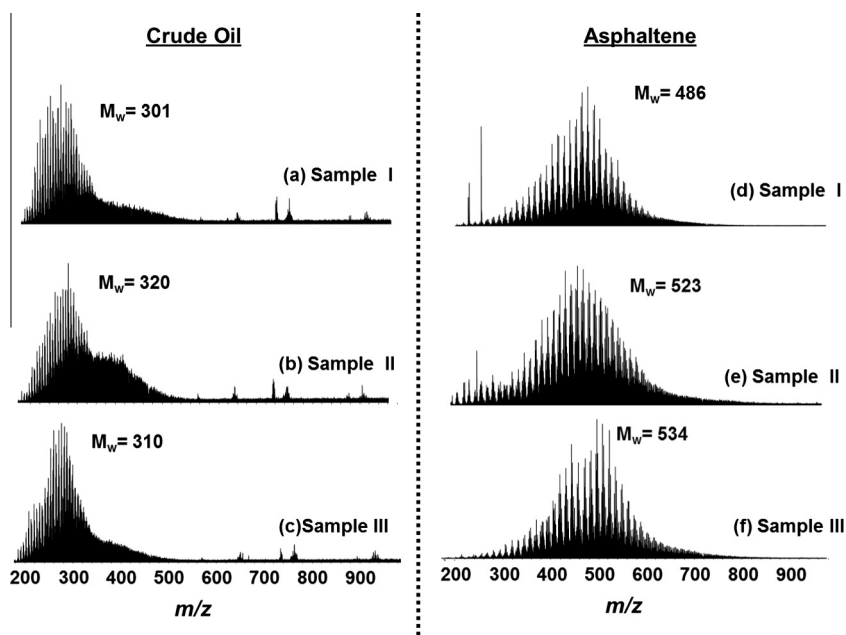


Fig. 6. APPI(-)-FT-ICR mass spectra of three crude oil samples (a–c) and their asphaltenes (d–f). Note that the M_w of asphaltene increases in following order: III > II > I.

do not exhibit large alkyl chains, being composed primarily of aromatic rings (\geq three aromatic rings). For nonpolar compounds, APPI(+) reveals CN ranging from C_{15} to C_{45} and DBE ranging from 10 to 35, where a higher amplitude of aromatic compounds are presents for asphaltene II (Fig. 3b and e) and III (Fig. 3c and f).

These results corroborate with CHNSO and 1H NMR analyses, where they presented higher C/H atomic ratio (0.88 and 0.94) and aromatic hydrogen content (H_{ar} = 26.9 and 27.3 M%), Tables 2 and 3, respectively.

Using the concept of planar limited, a line was generated from connecting maximum DBE values at given CN in the DBE versus carbon number plots, possibiliting to extract the aromaticity degree from APPI FT-ICR MS data. This degree was obtained from the slopes of the lines determined by DBE/carbon number ratio. The slopes of these lines were calculated by linear regression and the value for protonated classes, HC[H] and N[H], that are shown in Figs. 3d–f and 4d–f, respectively. Note that the inclination of line or slope increases as function of an increase in the H_{ar} values.

Similar to Fig. 3, Fig. 4 shows DBE versus CN plots for nitrogen-containing compounds, N (4a–c) and N[H] (4d–f) classes, where again, short alkyl chains compounds, mainly composed by more than three aromatic rings, were detected. High abundant compounds show CN ranging from C_{20} to C_{35} and DBE from 10 to 25 for Asphaltene I, whereas these values range for Asphaltene III from C_{30} to C_{35} and DBE from 20 to 27.

Fig. 5 is a DBE relative abundance distributions of HC, HC [H] and N, N[H] classes of three asphaltene samples. These DBE distributions expose major differences in aromaticity distribution of the asphaltene I, II and III. Generally, the samples show a progressive shifts to a higher DBE in function of increasing the H_{ar} values. The increase in aromaticity is mainly due to a change in the distribution of the species in compositional space toward higher DBE values. Asphaltene III is more aromatic, which the abundance maximum is centered on average at DBE = 27 for HC and HC[H] classes, (Fig. 5a and b) and at DBE = 25 for N and N[H] classes (Fig. 5a–d). As expected, asphaltene I is the less aromatic, having the abundance maximum on average at DBE = 14 for HC and HC[H] classes, Fig. 5a and b; and DBE = 20 for N and N[H] classes, Fig. 5c and d.

3.3. APPI(–)FT-ICR mass spectra and diagrams

Fig. 6a–f displays the APPI(–)FT-ICR mass spectra of crude oils (I, 6a, II, 6b, and III, 6c) and their respective asphaltene fractions (I, 6d, II, 6e, and III, 6f). For the crude oils, mass spectra have profile from m/z 200 to 550 with M_w centered at approximately 301 (sample1), 320 (sample 2) and 310 (sample 3), respectively (Fig. 6a–c),

being similar to APPI(+), Fig. 1a–c. As expected, for asphaltene samples, the M_w values are pointedly different varying from m/z 486 (asphaltene I) to 534 (asphaltene III). However, the M_w values provided from negative ion mode are higher than observed for positive ion mode. This can be associated with APPI(–) does not assess non-polar compounds such as hydrocarbons (HC and HC[H] classes), but mainly nitrogen- and oxygen-containing compounds: N, N[H], N_2 , N_2 [H], N_2O , N_2O [H], N_2O_2 , N_2O_2 [H], NO, NO[H], NO_2 , NO_2 [H], O, O[H], O_2 and O_2 [H] classes, Fig. 7a and b.

Fig. 7a and b illustrates the distribution of compound classes obtained from APPI(–)FT-ICR MS for crude oils (Fig. 7a) and their asphaltenes (Fig. 7b). Similar to APPI(+), Fig. 2, two ionization mechanisms are also acting: proton abstraction and electron transfer resulting in two different ions for the same compounds: $[M-H]^-$ and M^- . Consequently, the classes are duplicated and identified as CLASS $^-$ (for M^- ions) and CLASS[H] $^-$ (for $[M-H]^-$ ions). Generally, the most abundant classes identified for crude oils are: N[H] > NO[H] > O_2 [H] > N_2 [H] > and N. For asphaltene samples, the most abundant classes identified are in following order: NO[H] > N[H] > N_2O [H] > N > NO > N_2O . Asphaltene III differs from other presenting low abundance nitrogen-containing compounds species (N, N[H], N_2 , N_2 [H], N_2O [H] and NO[H] classes). These results are corroborating with CNHSO and 1H NMR data, Tables 2 and 3, respectively.

Klein et al. [14] used the ESI(–)FT-ICR MS to characterize two geographically different crude oils and their corresponding asphaltene deposits. They find that the crude oil deposits contain higher aromatic character (more unsaturated) and are enriched in oxygenated species as well as multiple heteroatom classes compared to their crude oil counterpart. Similar to our work, the same inversion of intensity was observed for majority species (N[H] \rightarrow NO[H]) when compare to the data obtained from crude oils to their asphaltenes deposits.

The van Krevelen diagram is another important graphical tool that was first employed by Kim et al. [36] to distinguish condensed hydrocarbons from lipids and other components using FTI-CR mass spectrometry. van Krevelen diagrams consist of

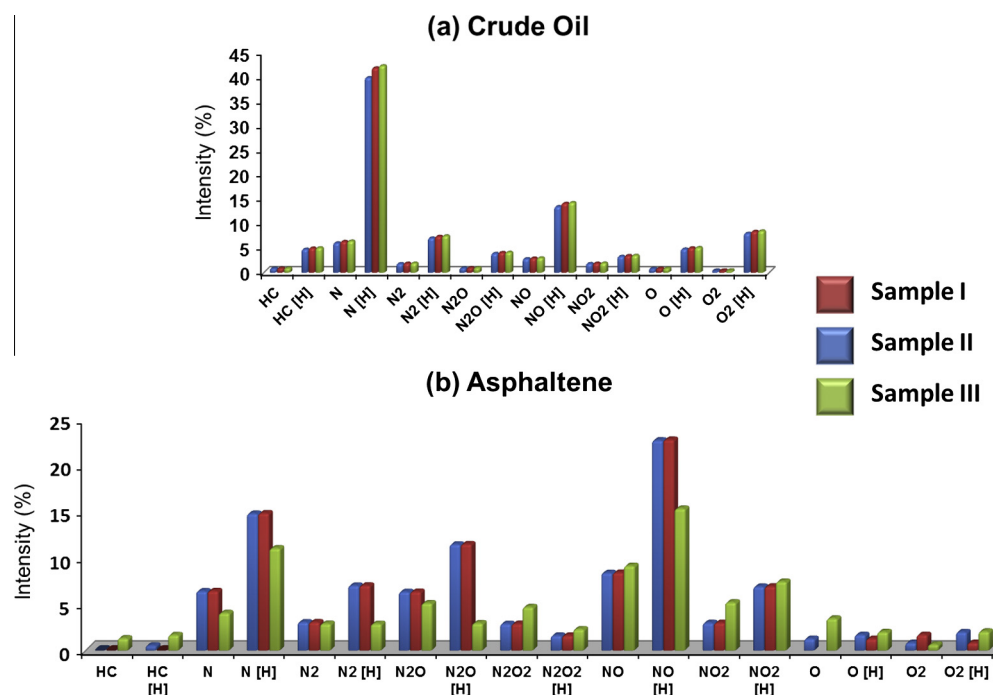


Fig. 7. Class distribution for (a) crude oil samples and (b) their asphaltene fractions obtained from APPI(–)FT-ICR MS data.

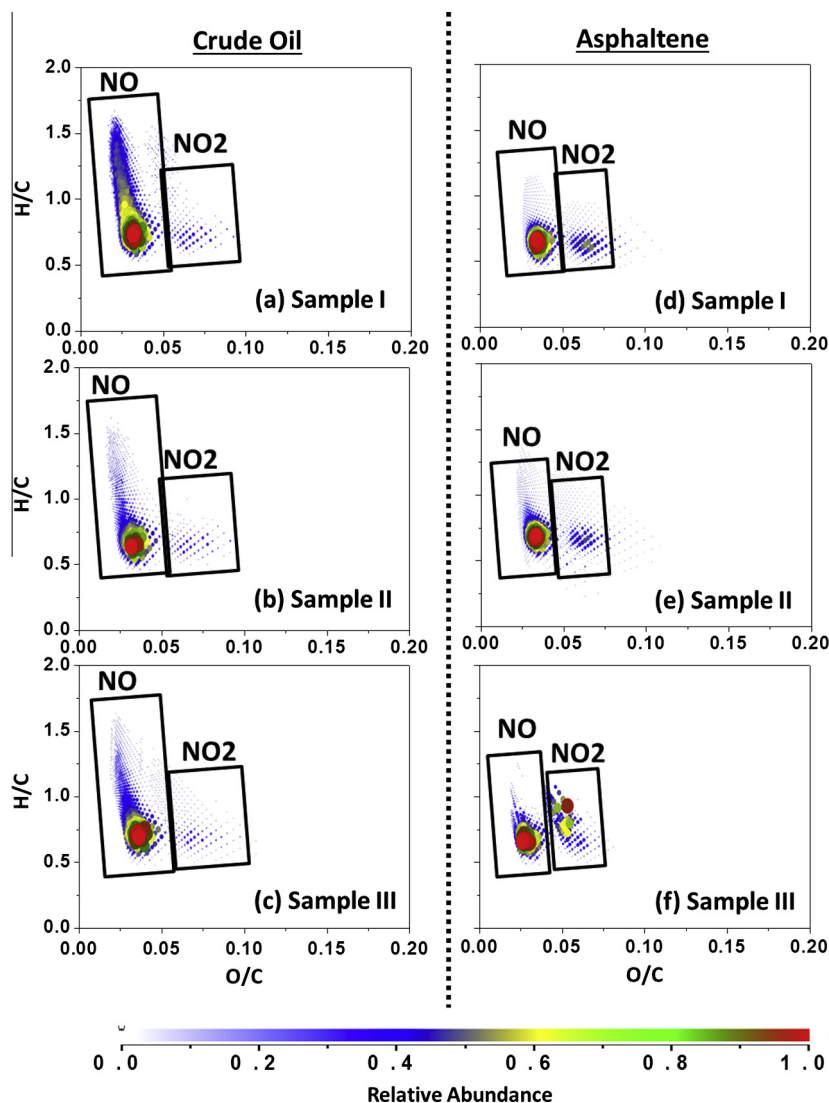


Fig. 8. van Krevelen diagrams for N_xO_y -containing species generated from APPI(–)FT-ICR MS data of crude oil (a–c) and asphaltene (d–f) samples.

iso-abundance contours as a function of the H/C ratio and O/C ratio for each compound containing the relevant atoms. In a van Krevelen diagram, the heteroatom classes were plotted separately on the x- (e.g., O/C ratio distinguished classes with different numbers of O atoms) and y-axes (the DBE difference was spread out along the H/C ratio). The homologous alkylation series was composed of compounds that contained the same number of rings plus double bonds, as well as the same heteroatom; different numbers of CH_2 groups appeared as diagonals. The van Krevelen plot facilitates the visual separation of heteroatom classes, DBE types, and alkylation patterns.

For the N_xO_y compounds, Fig. 8a–f, the APPI(–) accesses a range of compounds such as NO and NO_2 . In all cases, the most abundant compounds on average are centered in an H/C of ~ 0.7 , thus corroborating, with highly aromatic compounds. Fig. 8a–c displays the compound distribution for NO and NO_2 classes for crude oils samples. Note that for the NO class, greater amplitude of compounds was detected with H/C ratio varying from 0.5 to 1.75 with maximum centered at 0.7. In contrast, the NO_2 class showed lower amplitude of compounds detected with H/C ratio ranging from 0.5 to 1.25 with maximum also centered at 0.7.

4. Conclusion

APPI FT-ICR MS technique shows powerful tool in analyses of bulk property of crude oils and their asphaltenes, providing chemical information on a molecular level, thus defining a unique elemental composition ($C_cH_hN_nO_oS_s$) and DBE, facilitating material classification by heteroatom content and the degree of aromatic. Here, APPI(±)FT-ICR MS was successfully applied in three crude oils characterization (classified as heavy, extra-heavy and asphaltic having API degree of 22.0, 17.3 and 13.5, respectively) and their respective asphaltenes.

MS data were compared and discussed with aromaticity parameters obtained from elemental analyses and 1H NMR measurements. For three crude oils analyzed with magnitude of the viscosity different (III > II > I), the amount of the extracted asphaltene observed followed the behavior analogous (7.63 ± 0.65 wt%; 2.23 ± 0.25 wt%; and 0.41 ± 0.01 wt%, respectively). The aromatic hydrogen content (H_{ar} , in molar%) was determined from 1H NMR, where the crude oil III and its asphaltene ($H_{ar} = 4.90$ and 27.3 M%, respectively) were slightly more aromatic than the crude oil I and its asphaltene ($H_{ar} = 3.90$ and 26.90 M%). An inverse relation was observed between H_{ar} values and the N and O

concentrations determined from elemental analyses. The values of M_w observed for asphaltene fractions (m/z 200–650) from AP-PI(\pm)FT-ICR MS data, were significantly distinct, being correlated with the physico-chemical characteristics of their parent crude oil. Using the concept of planar limited, the line generated by connecting maximum DBE values at given CN in the DBE *versus* carbon number plots, we extracted the aromaticity degree also from APPI FT-ICR MS data. The slopes of these line were calculated by linear regression for protonated hydrocarbons (HC[H]) and basic nitrogen (N[H]) compounds classes: the slopes increase as H_{ar} values increase.

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