



Monitoring the liquid/liquid extraction of naphthenic acids in brazilian crude oil using electrospray ionization FT-ICR mass spectrometry (ESI FT-ICR MS)

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HIGHLIGHTS

- ▶ Non-continuum liquid–liquid extraction of naphthenic acids at different pHs from two crude oil samples.
- ▶ The residue and the acid fraction were characterized using ESI(–) FT-ICR MS, FTIR and sulfur analysis.
- ▶ We observe a decreasing TAN in the original oil with increasing pH (7 → 14), reaching a value of almost zero at pH 14.
- ▶ The most abundant naphthenic acids extracted are those with short alkyl chain lengths (<C₄₄) and DBE = 3–4.

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ABSTRACT

Although the term “naphthenic acids” was originally used to describe acids that contain naphthenic rings, today this term is used in a more general sense and refers to all cyclic, acyclic, and aromatic acids in crude oil. In crude oil, naphthenic acids exist as a complex mixture of compounds with broad polydispersity with respect to both molecular weight and structure. Recently, there has been increasing interest in acidic fractions in crude oil because of the corrosion problems that these compounds cause during oil refinery. This corrosion is associated with the total acid number (TAN). However, it has been argued that there is no clear correlation between the TAN and the level of corrosion. Herein, naphthenic acids were extracted from two crude oil samples (TAN = 4.95 and 3.19 mg KOH g⁻¹) using liquid/liquid extraction with alkaline solutions at three different pHs (pH 7, 10 and 14), thus evaluating the efficiency and selectivity among different acidic extraction methods to prevent future corrosion processes in petroleum industry such as regions of the refineries working. The original oil samples and their naphthenic acid fractions and residues (washed oil from the acidic extraction) were analyzed using negative-ion electrospray ionization (ESI) Fourier transform ion cyclotron mass spectrometry (FT-ICR MS) and Fourier transform infrared spectroscopy (FTIR). The TAN and sulfur content were also determined. We observe a decreasing TAN in the original oil with increasing pH (7 → 14), reaching a value of almost zero at pH 14. Consequently, an intense band at approximately 1700 cm⁻¹ was observed for the naphthenic acidic fraction. Fractions produced ESI(–)-FT-ICR MS spectra with average molecular weight distribution, M_w , and m/z values ranging from m/z 200–350 and $M_w = 270$ (for pH 7) to m/z 200–650 and $M_w = 390$ (for pH 14). Therefore, the acidic extraction method at pH 14 was more efficient and the ESI FT-ICR MS analysis reveals that the most abundant naphthenic acids are those with short alkyl chain lengths (<C₄₄) and DBE = 3–4. We associate these compounds as responsible for the TAN observed for the original oil.

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1. Introduction

The chemical composition of crude oil consists predominantly of hydrocarbon compounds such as naphthenes, paraffins, and aro-

matic hydrocarbons (~90%). The remainder (~10%) consists of polar compounds containing N, O, and S heteroatoms and metal atoms (only vanadium and nickel exist at concentrations >1 ppm) [1]. Despite the small percentage of polar compounds, approximately 20,000 polar organic compounds with different elemental compositions (C_xH_yN_nO_oS_s) have been found in crude oil [2]. These polar compounds sometimes cause problems during the production, refining and storage of petroleum. These problems include

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corrosion, the formation of emulsions, the poisoning of catalysts, coke formation, the development of poisonous and carcinogenic characteristics, and contamination. Oil consumption is continuously growing, creating demand to use the limited oil reservoirs and heavier fractions more efficiently. Therefore, it is important to know the composition of crude oils from different origins to optimize the refining processes.

Among the polar components of petroleum containing heteroatoms, naphthenic acids and phenols are the two most common oxygen-containing compound classes in crude oil. There are other minor acidic classes, such as aromatic, olefinic, hydroxyl, and dibasic acids [3]. Naphthenic acids are defined as carboxylic acids that include one or more saturated ring structures, with five- and six-membered rings being the most common. In addition to ring-containing acids, linear carboxylic acids are often included in the naphthenic acid class [4]. Naphthenic acids are known to be a significant source of corrosion in oil-refining equipment [5]. Corrosion

is associated with the total acid number (TAN), which is defined as the mass of potassium hydroxide (KOH) in milligrams required to neutralize 1 g of crude oil. However, it has been argued that there is no clear correlation between the TAN and the level of corrosion [6].

Crude oil contains both neutral and basic nitrogen compounds. Neutral nitrogen compounds include, for example, carbazoles, indoles, and pyrroles and correspond to less than 30% of all organic nitrogen compounds [7]. Basic nitrogen compounds include, for example, pyridine and quinoline derivatives. Nitrogen compounds are harmful in oil refining because they decrease the efficiency of catalytic processes and increase product instability during storage [8].

Recently, there has been growing interest in the chemical characterization of naphthenic acids and the acidic fractions of crude oils due to the problems that these components cause for the oil refinery business [9]. Naphthenic acids are predominantly found

Table 1
The TAN and sulfur content of the two crude oil samples and their respective residual oils.

| Sample | TAN (mg of KOH/g) | Reduction in the TAN (%) | Sulfur (%) |
|-------------------------|-------------------|--------------------------|------------|
| Crude oil I | 4.95 | 0 | 0.97 |
| Residual oil I – pH 7 | 3.79 | 23 | 0.93 |
| Residual oil I – pH 10 | 3.08 | 38 | 0.93 |
| Residual oil II – pH 14 | 0.40 | 92 | 0.71 |
| Crude oil II | 3.19 | 0 | 0.59 |
| Residual oil II – pH 7 | 2.27 | 29 | 0.59 |
| Residual oil II – pH 10 | 2.28 | 28 | 0.58 |
| Residual oil II – pH 14 | 0.46 | 85 | 0.51 |

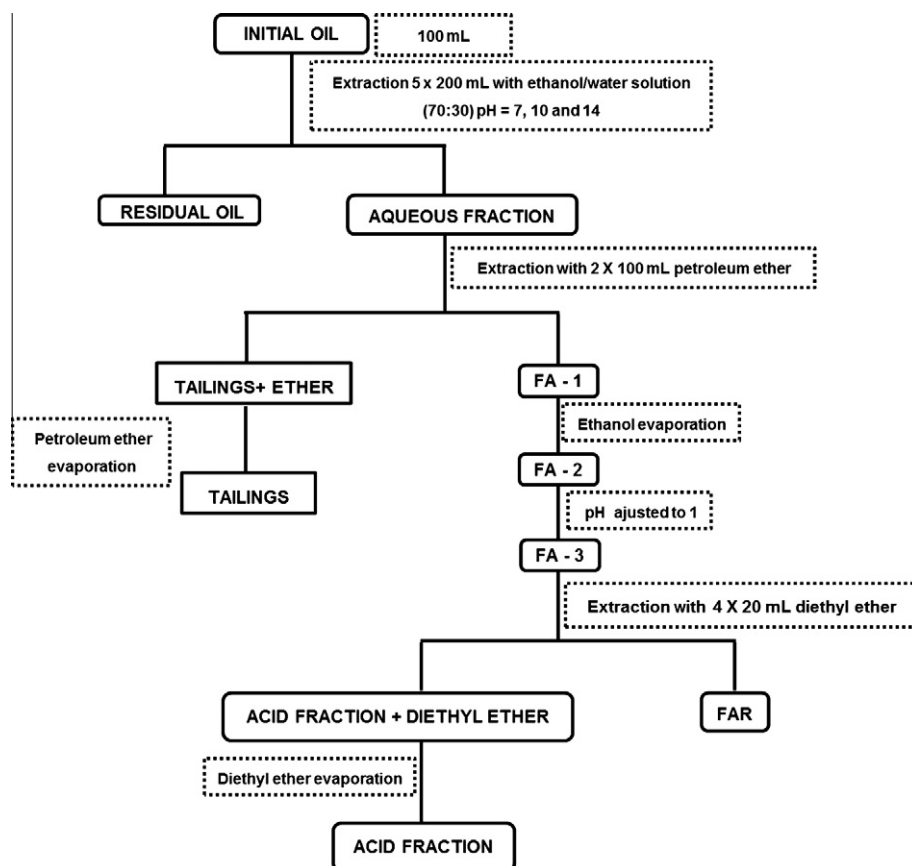


Fig. 1. Scheme of the liquid–liquid extraction of naphthenic acids. (FA – fraction acid, FAR – fraction acid residue).

in low mature heavy crude. Hence, they are assumed to be generated from the in-reservoir biodegradation of petroleum hydrocarbons. Naphthenic acids can be obtained from crude oils by extraction procedures such as liquid/liquid extraction with alkaline solutions and solid/liquid extraction or by ion exchange chromatography [9–11]. These isolated naphthenic acid fractions and other polar fractions have been examined by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance, and mass spectrometry (MS) [9,12]. However, most methods (with exception of MS) do not allow the determination of the elemental compositions of compounds. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) offers the highest available mass resolution, mass resolving power, and mass accuracy, enabling the analysis of complex petroleum mixtures on a molecular level [13]. High-resolution MS data have shown that it is possible to discriminate different compounds [14] because of the different ionization efficiencies of crude oil constituents [15].

The extraction and characterization of the acids compounds from crude oil is necessary in order to have clear information on the role of these acids. Herein, two acidic crude oil samples (TAN = 4.95 and 3.19 mg KOH g⁻¹, respectively) were submitted to a liquid/liquid extraction process modified [9] with alkaline solutions at three different pHs (pH 7, 10 and 14), yielding acidic fractions and residual oil samples. Both, acidic fractions and residual oil samples were analyzed using negative-ion electrospray ionization FT-ICR MS and FTIR. The sulfur (S) content and TAN also were determined. The main objective of this study is to evaluate the efficiency and selectivity of non-continuous liquid/liquid

extraction process in terms of TAN reduction, thus providing, a detailed characterization of chemical composition of acidic polar species in function of pHs of extraction (pH 7 → 14).

2. Experimental

2.1. Reagents

Ethanol, petroleum ether, diethyl ether, chloridric acid, HCl, anhydrous propan-2-ol, toluene and potassium hydroxide, KOH, (analytical grades with purity higher than 99.5%) were used for acidic extraction method and TAN measurements, being supplied by Vetec Química Fina Ltda., Brazil. Ammonium hydroxide, NH₄OH, and sodium trifluoroacetate, NaTFA, were purchased from Sigma-Aldrich Chemicals USA and used for ESI(-)-FT-ICR MS measurements. All reagents were used as received.

2.2. Acidic extraction

Two samples of crude oil (termed crude oil I and crude oil II; TAN > 3 mg KOH g⁻¹, Table 1) were submitted to an acidic extraction procedure according to the scheme shown in Fig. 1. Briefly, (i) 100 mL of crude oil was washed five times with 200 mL of a 70% (v/v) ethanol aqueous solution at pH 7, 10 or 14, producing an aqueous phase and a residual phase (termed the residual oil – pH 7, 10 and 14). The three aqueous phases from each wash were then extracted with two times 100 mL of (ii) petroleum ether (30–60 °C).

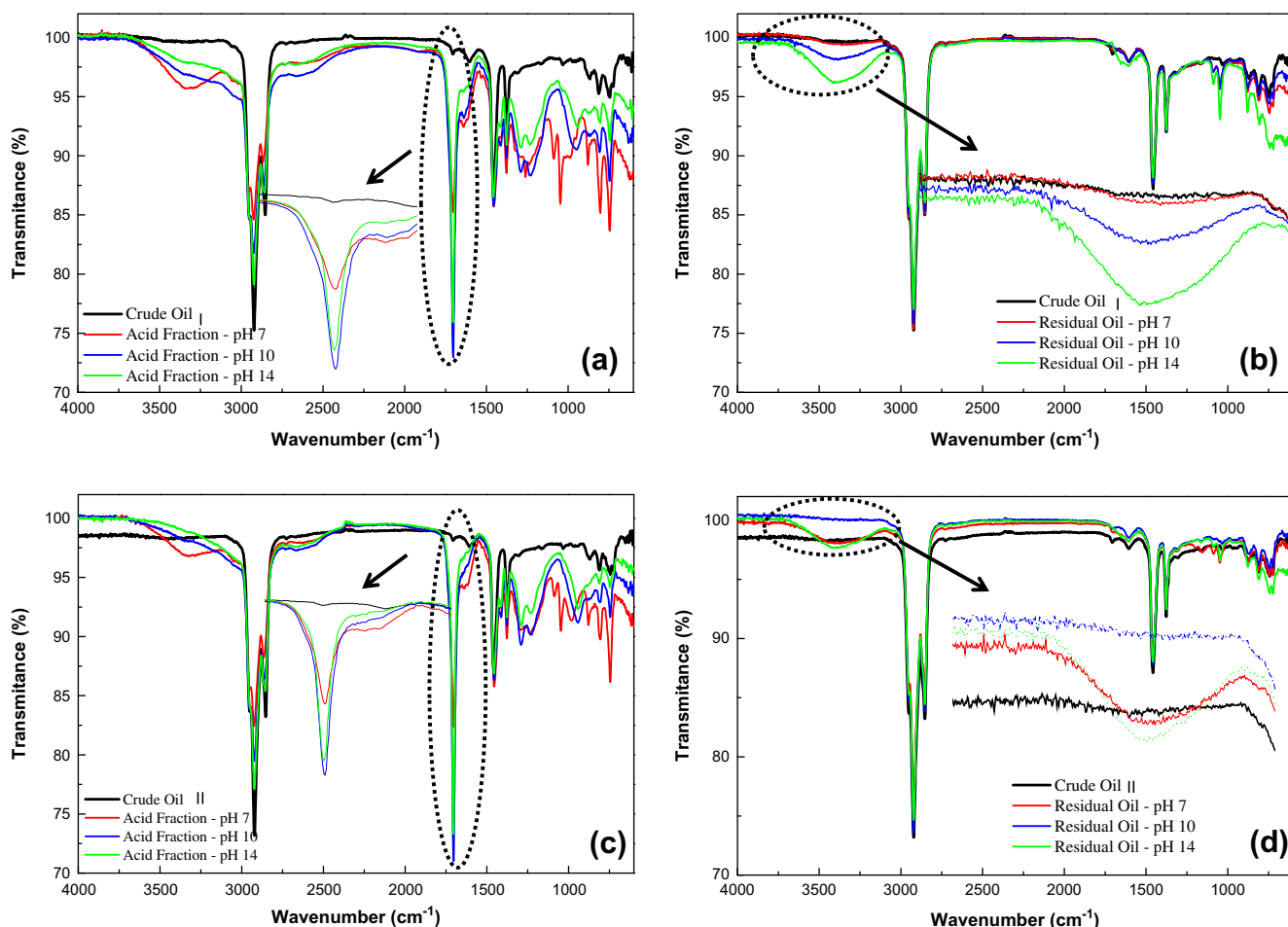


Fig. 2. FT-IR spectra of crude oil I and crude oil II and their respective acidic fractions (a and c) and residues (b and d).

The aqueous extracts were combined, and the ethanol was evaporated to prevent the formation of esters upon acidifying the solution in the next step. The pH was then adjusted to pH 1 (using a concentrated solution of HCl) before extraction with four times 100 mL of diethyl ether. The diethyl ether was then evaporated to obtain the polar acidic fraction (three acidic fractions termed acidic fraction – pH 7, acidic fraction – pH 10 and acidic fraction – pH 14). The acidic extraction method developed in this work was based on that of Hemmingsen et al. [9] The initial crude oils, residual oils and acidic fractions were subsequently analyzed by FT-IR and ESI(-)-FT-ICR MS. The TAN and S content were determined for the crude oils and residual oil samples.

2.3. Characterization

2.3.1. TAN

TAN measurements were performed according to the standard ASTM method (ASTM D664-09) using a potentiometer (Metrohm Analytical Instruments and Accessories, USA) with an accuracy of $\text{pH} \pm 0.003$. In 250 mL beakers, the crude oil samples (5.0 ± 0.5 g) and their respective residues (20 ± 2 g) were weighed, dissolved in 125 mL of water/anhydrous propan-2-ol/toluene (0.5/49.5/50% in volume), and then titrated, in duplicate, with a 0.1 mol L^{-1} alcoholic KOH solution. The results are expressed as milligrams of

potassium hydroxide per gram of sample required to titrate a sample in a specified solvent to a specified end point (see Table 1) [16].

2.4. Sulfur content

The sulfur content was determined according to the standard ASTM method [17] (ASTM D4294) using an SLFA-2800 energy dispersive X-ray fluorescence spectrometer from Horiba Scientific (New Jersey, USA). First, calibration curves were constructed, and parameters such as the linearity and limits of detection were obtained. The measurement time was 100 s. The sulfur contents of the crude oil and residue samples were determined in triplicate.

2.4.1. FTIR

For the FTIR studies, an ABB BOMEN IR (FTLA2000-102 model) coupled with a MIRacle attenuated total reflectance (ATR) accessory was used. Crude oil samples and their respective fractions and residues were placed under a single-reflection crystal plate, and a total of 16 scans were taken. The spectra were recorded from 4000 to 400 cm^{-1} in transmission mode with a resolution of 4 cm^{-1} . The background was performed in air, and background scans were acquired before each sample was analyzed. The ATR-FTIR spectra were acquired using GRAMS/AI software (Thermo Galactic).

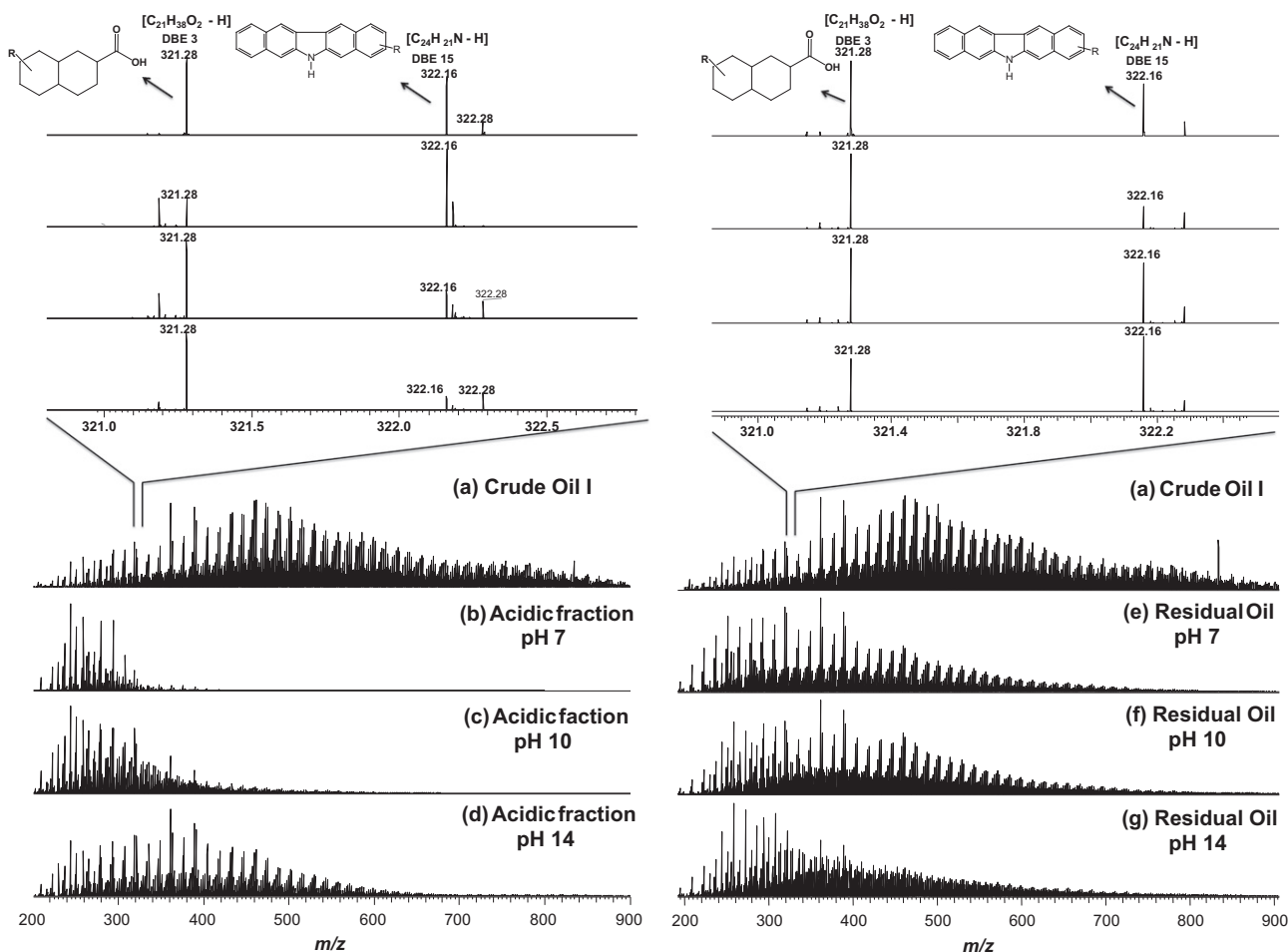


Fig. 3. ESI(-)-FT-ICR MS spectra of crude oil I (a) and its acidic fractions and residual oils when extracted at pH 7 (b and e), 10 (c and f) or 14 (d and g). The M_w distribution broadened and shifted to higher m/z values with increasing of. The insert shows the naphthenic acid and carbazole structures with their respective m/z and DBE values. The intensity of the $[\text{C}_{21}\text{H}_{38}\text{O}_2 - \text{H}]^-$ ion at m/z 321.28 increased for the acidic fractions and decreased for the residual oils as a function of pH (7 \rightarrow 14).

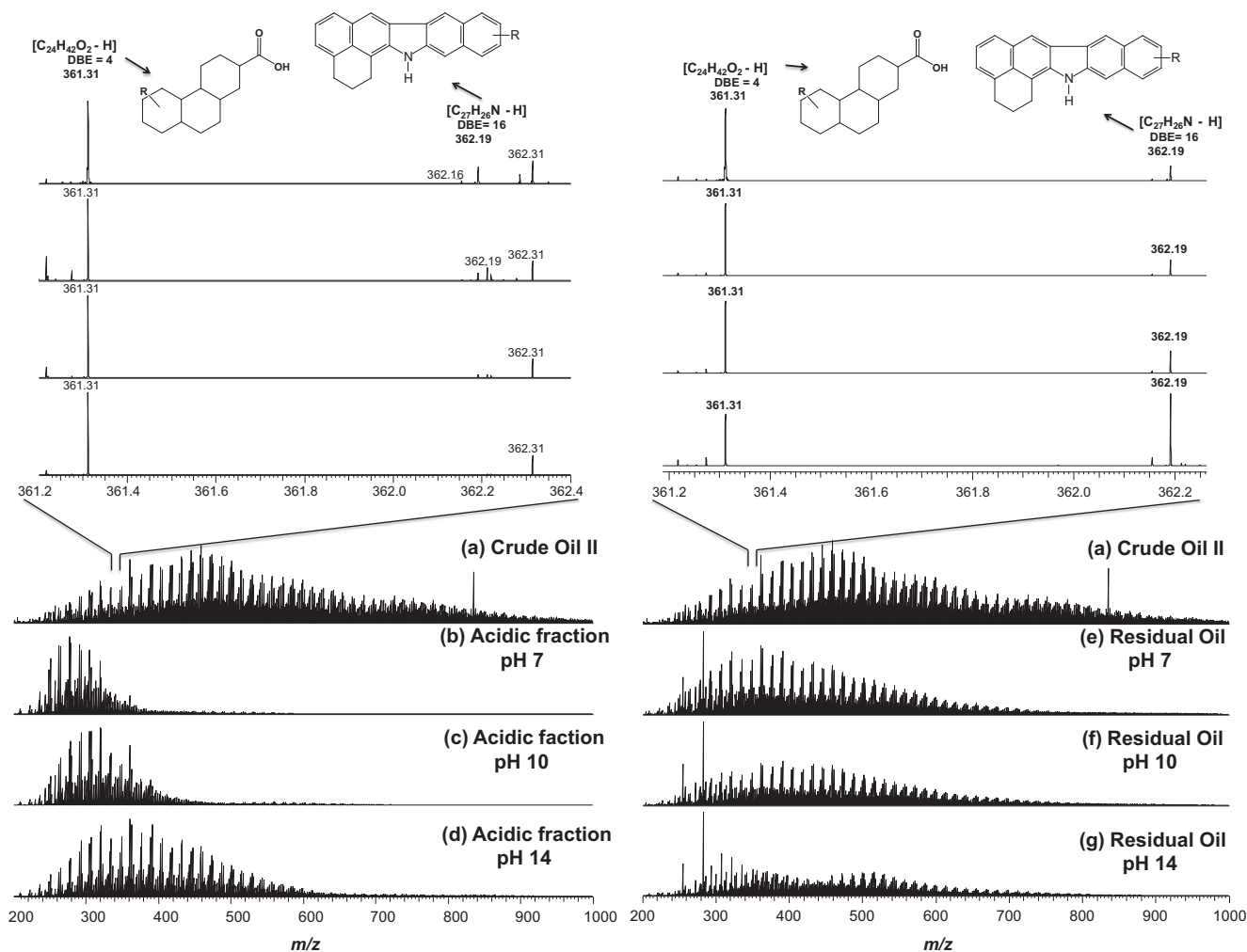


Fig. 4. ESI(–)-FT-ICR MS spectra of crude oil II (a) and its respective acid fractions and residual oils when extracted at pH 7 (b and e), 10 (c and f) or 14 (d and g). The M_w distribution broadened and shifted to higher m/z values with increasing pH. The insert shows the naphthenic acid and carbazole structures with their respective m/z and DBE values. The intensity of the $[C_{24}H_{42}O_2-H]^-$ ion at m/z 361.31 increased for the acidic fractions and decreased for the residual oils as a function of pH (7 → 14).

2.4.2. ESI(–)-FT-ICR MS

Petroleum samples were analyzed by ESI(–)-FT-ICR MS. Briefly, each sample was diluted to $\approx 1.2 \text{ mg mL}^{-1}$ in 50:50 (v/v) toluene/methanol (containing 0.1% m/v of NH_4OH). The resulting solution was directly infused at a flow rate of $5 \mu\text{L min}^{-1}$ into the ESI source. The mass spectrometer (model 9.4 T Solarix, Bruker Daltonics, Bremen, Germany) was set to operate in negative ion mode (ESI(–)) over a mass range of m/z 200–2000. The ESI source conditions were as follows: nebulizer gas pressure of 0.5–1.0 bar, capillary voltage of 3–3.5 kV, and transfer capillary temperature of 250 °C. The ion accumulation time in the hexapole was 0.01 s and was followed by transport through a hexapole ion guide to the ICR cell. Each spectrum was acquired by accumulating 200 scans of time-domain transient signals in four mega-point time-domain data sets. The front and back trapping voltages in the ICR cell were -0.60 V and -0.65 V , respectively. All mass spectra were externally calibrated using a NaTFA (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 ($m/\Delta m_{50\%} \approx 530,000$, 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 the software package Compass Data Analysis

(Bruker Daltonics, Bremen, Germany). Using the Composer software (Sierra Analytics, Pasadena, CA, USA), the MS data were handled, and the elemental compositions of the compounds were determined by measuring the m/z values [18]. To help summarize, visualize, and interpret the MS data, three classical plots were constructed: (i) the distribution of heteroatom-containing compounds; (ii) a plot of the carbon number vs the double bond equivalents (DBE); (iii) and the DBE distributions for N1 and O2 species, where DBE is defined as the number of rings plus the number of double bonds in a molecular structure. The aromaticity of a petroleum component can be deduced directly from its DBE value according to the following equation:

$$\text{DBE} = c - h/2 + n/2 + 1 \quad (1)$$

where c , h , and n are the numbers of carbon, hydrogen, and nitrogen atoms, respectively, in the molecular formula.

3. Results and discussion

Table 1 shows the TANs for the two crude oil samples (I and II) and their respective residual oils (obtained from the original oil washed at different pHs: pH 7, 10 and 14, Fig. 1). First, the TANs for crude oil I and crude oil II were 4.95 and 3.19 mg KOH g^{-1} ,

respectively. Decreases in the TANs of both crude oils were observed with increasing pH, reaching values of almost zero at pH 14. Additionally, the TANs observed for the oils at washed pH 7 and 10 were closer. This behavior can be explained by a possible variation in the pH due to the hydrolysis processes that may occur during the extraction process, primarily at pH 10, because that no buffer was used during the first step of this process (Table 1). However, the acidic extraction process at pH 14 was more efficient for both crude oils, with reductions in the TAN of 92% and 85%, respectively.

For the sulfur content, the values remained constant from the crude oil to the residual oil at pH 7 and 10 ($S = 0.97 \rightarrow 0.91\%$ for crude oil I and $S = 0.59 \rightarrow 0.58\%$ for crude oil II; Table 1). A reduction of ~20–30% was observed only for the residual oil at pH 14. Given that sulfur species, such as thiols, have pKa values of approximately 10.5, this reduction is expected when performing the extraction procedure at $pH > 10$.

Fig. 2a–d shows the FT-IR spectra for the samples of crude oil I and crude oil II and their fractions (2a and c) and residual oils (2b and d). For the FTIR spectra of the crude oils, three main regions were identified: (i) 2923 cm^{-1} and 2853 cm^{-1} : asymmetric and symmetric C–H stretching, respectively, of CH_3 and CH_2 groups; (ii) 1452 cm^{-1} and 1376 cm^{-1} : CH_2 and CH_3 deformations (bending); and (iii) $900\text{--}700\text{ cm}^{-1}$: aromatic C–H deformation. All these vibration frequencies are typical of hydrocarbons [19,20]. In contrast, in the FTIR spectra corresponding to the acidic fractions (Fig. 2a and c), an intense band in the regions of 1700 cm^{-1} and 3380 cm^{-1} were observed due to the carbonyl (C=O), hydroxyl (OH) and amine groups (N–H) present in the heteroatom-containing compounds, which were primarily naphthenic acids, carbazoles and pyridines analogues [19–21]. However, with increasing pH (7 \rightarrow 14), a distinct behavior was observed for both bands: increasing and decreasing intensities were observed for the C=O and N–H groups, respectively (see the enlargement shown in Fig. 2a and c). This behavior is indicative of the increasing concentration of naphthenic acids in the acidic extracts, primarily at pH 10 and 14. For the residual oils, an increase in the concentration of nitrogen species was observed due to the removal of acidic groups from the original crude oil (see the enlargement of the region around 3380 cm^{-1} , Fig. 2b and d).

Fig. 3a–g shows the ESI(–)-FT-ICR MS spectra for crude oil I (3a) and its acidic fractions (3b–d) and residues (3e–g). Heteroatom-containing species were detected as deprotonated molecules, that are $[\text{M}-\text{H}]^-$ ions. For crude oil I (3a), an ESI(–)-FT-ICR MS spectrum with an m/z range from 200 to 900 and a maximum centered at m/z 460 was observed, corresponding primarily to naphthenic acids and carbazole analog species. For the acid fraction (3b–d), a lower average molecular weight distribution, M_w , was observed for each sample (m/z range: 200–700). Note that with increasing pH, the M_w distribution broadened and shifted to higher m/z values: pH 7: m/z 200–350 and $M_w = 270\text{ Da}$; pH 10: m/z 200–450 and $M_w = 300\text{ Da}$; and pH 14: m/z 200–650 and $M_w = 390\text{ Da}$. Therefore, low alkyl chain lengths acid species, m/z 200–650, are responsible by most TAN observed (from 85% to 92%).

As consequence of the removal of naphthenic acid species from crude oil, a decreasing in the M_w was observed in the mass spectra for the residual oils (Fig. 3e–g). The enlarged area around m/z 321 (Fig. 3a–g) highlights the selectivity of the extraction of acid species. The relative intensity of the $[\text{C}_{21}\text{H}_{38}\text{O}_2-\text{H}]^-$ ion, which has an m/z of 321.28, increased for the acidic fractions and decreased for the residual oils as a function of pH. Similar to the TAN and FTIR results, the ESI(–)-FT-ICR MS spectrum also demonstrated that the extraction process at pH 14 was more efficient and selective.

In 2006, Hemmingsen et al. [9] studied the molecular composition of different acidic fractions produced from a North Sea acidic crude oil ($\text{NAT} = 2.9\text{ mg of KOH g}^{-1}$). Their FT-ICR MS results

showed that 90% of the acidic compounds consisted of carboxylic acids with molecular weights in the range 300–800 Da and a DBE = 3 being the most abundant. Therefore, their results agree with the results obtained in this work. The main difference is related to the MS spectra for the residual oil samples, where the species distributed in the range of m/z 600–900 corresponded to an asphaltene fraction in the oil washed at pH 14. This difference is due to the continuous acidic extraction process, in which the same residual oil was washed consecutively with aqueous ethanol solutions at pH 7, 10 and 14.

Similar ESI(–)-FT-ICR MS results were also obtained for another crude oil sample (crude oil II, Fig. 4a–g), thus confirming the continuous extraction of the same compound types at each pH evaluated. Note that the Figs. 3a and 4a were duplicated in order to compare changes such as M_w and polar species between crude oils and their acidic fraction and residual oils.

In 2012, Freitas et al. [18] studied the correlation between the composition of heavy distillation cuts and the corrosion process. The cuts presented boiling temperatures lower than $315\text{ }^\circ\text{C}$ and TAN values changes from 0.47 to 1.83 mg g^{-1} . According to the results of ESI(–)-FT-ICR MS, naphthenic acid species were only detected in the seven cuts studied, with $m/z < 300$ and DBE values ranging from 2 to 4. The relative abundance of heavy naphthenic acids and the TAN increase with distillation cut temperature. This information correlated with the corrosion mechanism for AISI 1020 steel in the heavy oil and distillation cuts, where the corrosion is evident in oil cuts being characterized as alveolar and pitting. In 2007, Silva and Senna [22] have also demonstrated that the reduction of the TAN from light petroleum cuts affected directly the

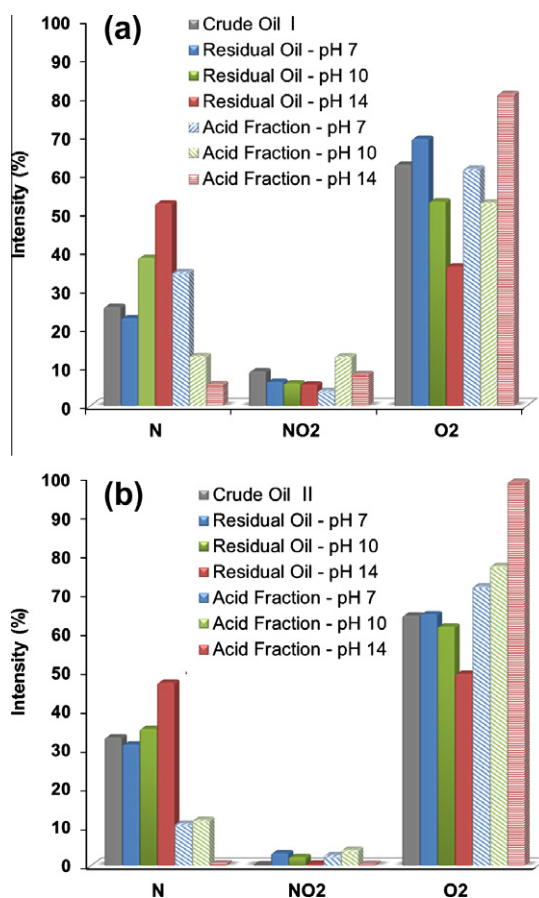


Fig. 5. Heteroatom-containing compound class distribution for crude oil I (5a) and II (5b) and their acid and residue fractions at pH 7, 10 and 14.

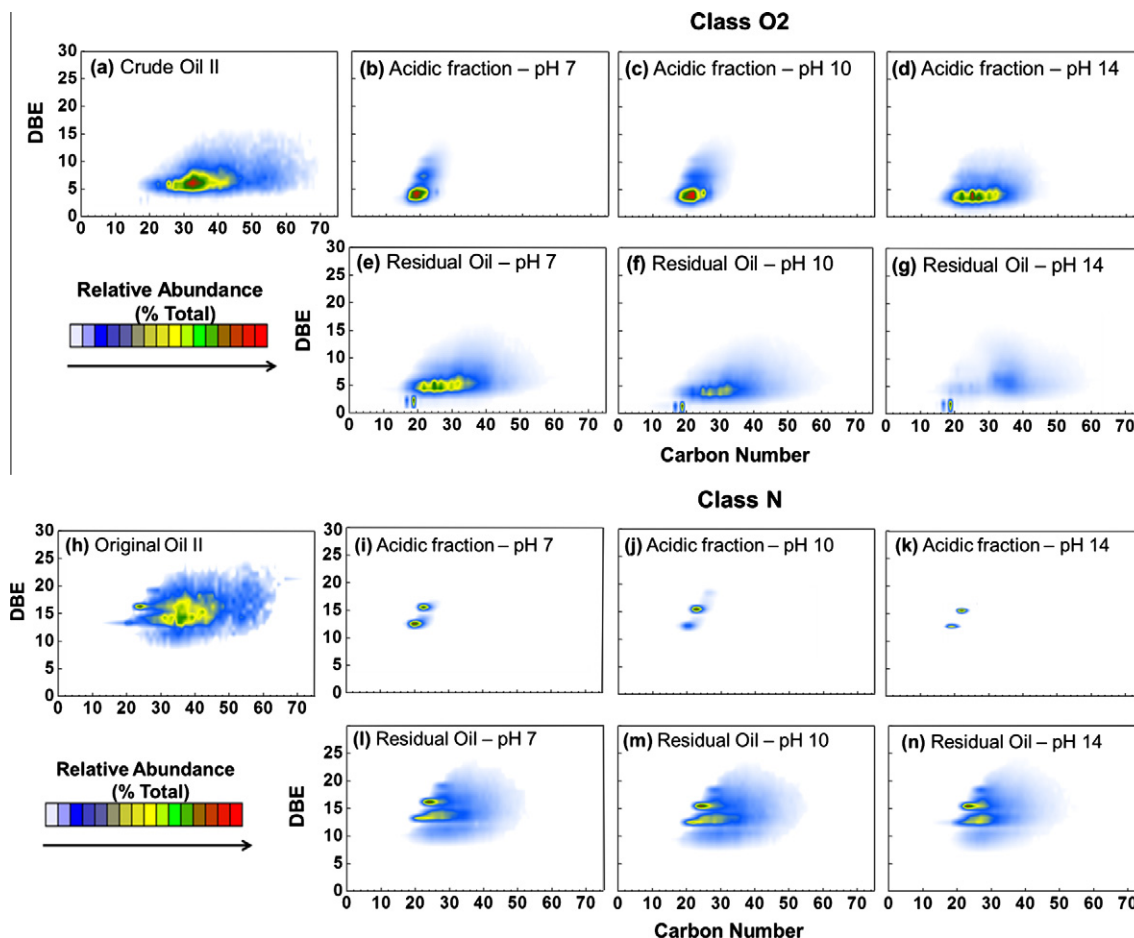


Fig. 6. Plot of the DBE vs the carbon number for the O_2 and N classes of crude oil II (a and h) and their acid extracts (b–d and i–k) and residues (e–g and l–n) at pHs 7, 10 and 14. The maximum carbon number decreased from $\approx C_{32}$ (crude oil, 6a) to $\approx C_{25}$ (acid fraction obtained at pH 14, 6g) for the O_2 class. Generally, carbazole species (N class) were negligible in the acid extracts, being present in high abundance only in the original oil and residues, in which the carbon number ranged from C_{16} – C_{64} (6h) to C_{18} – C_{52} (6l, m, n).

reduction in corrosion yields. Therefore, the liquid/liquid extraction method can be applied to prevent corrosion process in regions of the refineries working at temperatures above 100.0°C , since that the most acid species are obtained from acidic fractions ($M_w = 270$ – 390 and m/z 200–650), thus covering, all acid species detected from heavy distillation cuts as reported by Freitas et al. [18]. In general, it is always important to be careful in the correlation between the TAN and the corrosion process. The corrosion mechanism of naphthenic acids has not been fully elucidated, being known that the corrosive nature of oil is not directly related to the TAN but to the presence of a specific group of acids and sulfur compounds present in oil [18,23].

Generally, petroleum samples have chemical compositions that differ significantly from one another [24]. One way to display the similarities or differences between the signal patterns of crude oil samples is to construct certain types of plots, such as plots of the relative abundances of different classes of compounds and of the DBE vs the carbon number.

In the present study, for the class profile diagrams, the relative abundance was calculated by summing the peak magnitudes for all ions of each class and dividing by the summed peak magnitudes for ions of all assigned masses. The relative intensity of N, NO_2 and O_2 compounds present in the crude oils and their fractions are presented in Fig. 5a and b. For both oils, the O_2 compounds class was the most abundant class. The N class was the second most abundant, followed by the NO_2 class.

It should be noted that the relative abundance of O_2 compounds increased after the acid extraction process (pH 7 \rightarrow 14) from $\sim 63\%$ to $\sim 81\%$ for crude I (Fig. 5a) and from ~ 64 to $\sim 99\%$ for crude oil II (Fig. 5b) (compare the histograms for the original oil and the acidic extracts). Consequently, a decrease in the relative abundance of the O_2 class was observed for the residual samples, with decreases from $\sim 63\%$ to $\sim 36\%$ for crude oil I (5a) and from $\sim 64\%$ to $\sim 49\%$ for crude oil II (Fig. 5b). This result clearly indicates the greater efficiency of the extraction process in alkaline media with increasing pH.

Plots of the DBE vs the carbon numbers have proven to be useful tools for the differentiation of complex organic mixtures based on chemical composition. It has been shown that these plots allow the presentation of all signals from a specific class in a simple and feasible way [25,26]. For this reason, to qualitatively compare the crude oils and their acid fractions, DBE vs carbon number plots were generated, showing the distribution of all components from a specific class. Each line in the diagram represents a homologous series with a specific DBE value; each line differs by one CH_2 unit. To simplify the discussion and allow the better understanding of the changes in the profiles of different compound classes, we will focus this discussion on the data obtained for crude oil II and its respective acidic and residue fractions (Fig. 6).

Fig. 6a–n show plots of the DBE vs the carbon number for the O_2 and N classes of crude oil II (a and h) and their acidic (b–d and i–k) and residue fractions (e–g and l–n). For the O_2 class, there were

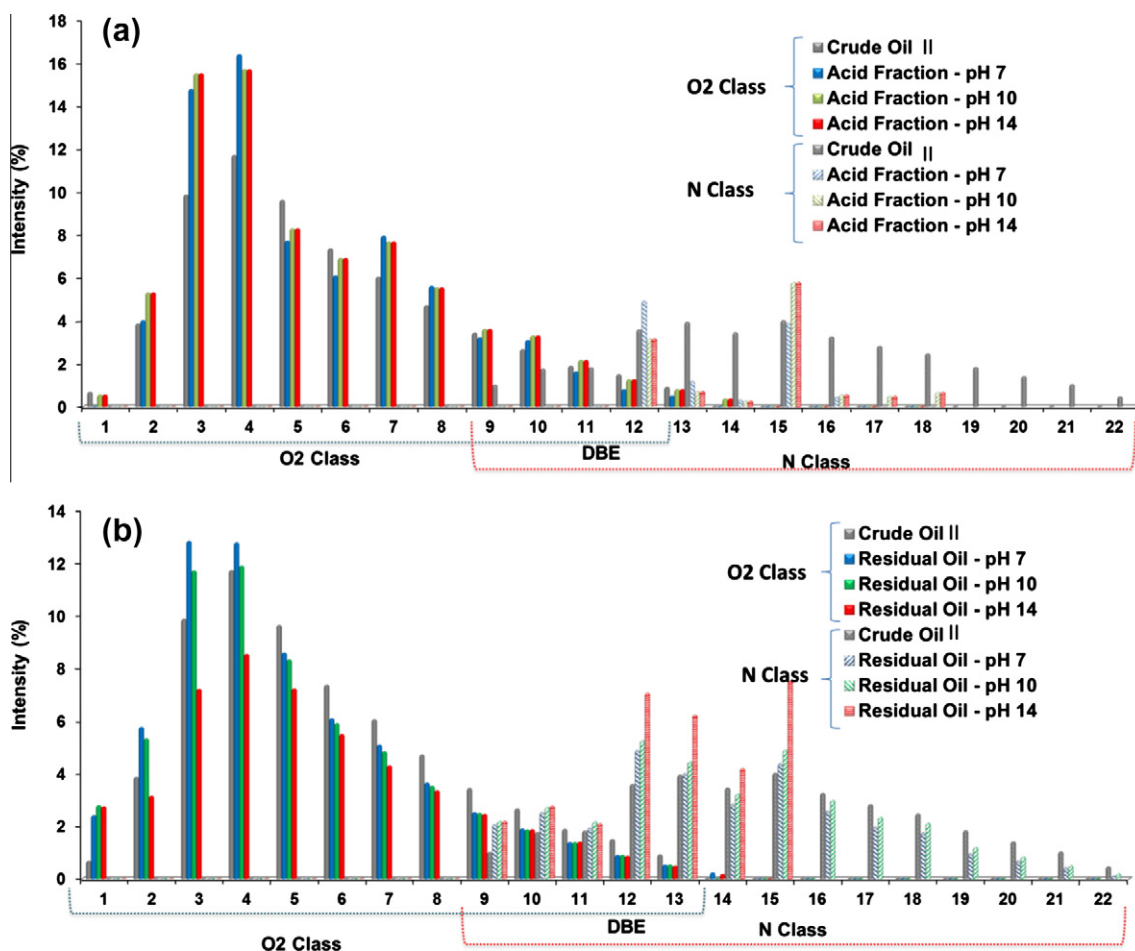


Fig. 7. Relative abundances of the O₂ and N compound classes in the ESI(-)-FT-ICR MS spectra of crude oil II and its (a) acid and (b) residue fractions produced at pH 7, 10 and 14. Naphthenic acids with DBEs of 2, 3, 4, 7 and 8 were the main carbon compounds removed from the original oil (7a).

compounds with DBEs ranging from 2 to 15 and carbon numbers ranging from C₁₆ to C₆₈, with the most abundant compounds being C₃₂ with a DBE of 4. The most abundant O₂ compounds were mainly composed of three naphthenic rings, in agreement with the results reported by Schaub et al. [27]. A notable difference among the acidic fractions was observed when the O₂ class was analyzed. For this class, the DBE and carbon distributions increases as a function of pH (pH 7 → 14, Fig. 6a–n). Initially, acid fraction – pH 7 contained a series of compounds with DBEs ranging from 1 to 10 Fig. 6b, including compounds with a narrow carbon distribution (from C₁₂ to C₃₈). However, for acid fraction – pH 14, Fig. 6d, a wide DBE distribution is observed, containing compounds with carbon distribution from C₁₂ to C₄₈. It is noteworthy that, at high pH, the extraction process remove majority a large amount of O₂ compounds due to the deprotonating mechanism that occurs within this pH range.

It is well-known that carboxylic acids exhibit strong acidities because of their abilities to form resonance hybrids. The equal distribution of the negative charge between the two oxygen atoms significantly reduces their attraction to a charged proton. Due to their complex chemical composition, naphthenic acids exhibit relatively considerable variation in their acidity. The calculated pK_a values for most naphthenic acids range from 3.0 to 20.0. This value is influenced by the hydrocarbon structure: cyclic vs acyclic and saturated vs aromatic rings. For aromatic structures, the pK_a substantially increases up to 1.0 unit. For saturated cyclic and acyclic structures, the magnitude of the change in acidity is reduced on the order of ~0.2–0.4 units, primarily due to the effects of steric

hindrance [11,12a]. This conclusion indicates that aromatic naphthenic acid species are mainly detected when higher pH values are used during extraction.

Fig. 6e–g shows the distribution of N compounds for crude oil II. Generally, the range of DBEs was notably higher and wider for the residue fractions than the acid fractions, with DBEs ranging from 9 to 24 and carbon numbers ranging from C₁₆ to C₆₄. These results are in good agreement with the acidity of N-containing compounds such as benzocarbazoles (DBE = 12) and dibenzocarbazoles (DBE = 15), which have high pK_a values and fully aromatic structures [28]. The results obtained for crude oil I are presented in the Supplementary material (Fig. S1).

Fig. 7 shows the relative abundance distributions for the O₂ and N compound classes in crude oil II and its acidic (7a) and residue (7b) fractions prepared at pH 7, 10 and 14. Naphthenic acids with DBEs of 2, 3, 4, 7 and 8 were primary compounds removed from the original oil (Fig. 7a). Consequently, an increase in the relative abundance distribution of the N class was observed for the residue samples (mainly with DBE = 12–15, Fig. 7b). The results for crude oil I are presented in Fig. S2 (Supplementary material).

4. Conclusion

A method for the liquid–liquid extraction of naphthenic acids in alkaline solutions has been adapted and was applied to two acidic crude oil samples (TAN = 4.95 and 3.19 mg KOH g⁻¹). We observe a decreasing TAN in the original oil with increasing pH (7 → 14),

reaching values of almost zero at pH 14. Additionally, the TANs observed for the oils washed at pH 7 and 10 were closer due to the variation in the pH during the extraction process, especially at pH 10. Therefore, the extraction process in alkaline solution at pH 14 was most efficient for both crude oils, which exhibited reductions in the TAN of 92% and 85%, respectively. In the FTIR spectra, an intense band in the region of 1700 cm^{-1} was observed for the naphthenic acidic fractions, indicating that there was an increasing concentration of acid species, primarily at pHs 10 and 14. For the residual oils, an increase in the concentration of nitrogen species (3380 cm^{-1}) was observed due to the removal of acidic groups from the original crude oil. The primary acid species responsible for the variation in the TAN were identified based on the ESI(–)-FT-ICR MS spectra. These acid species exhibited average molecular weight distribution, M_w , and m/z values from m/z 200–350 and $M_w = 270\text{ Da}$ (at pH 7) to m/z 200–650 and $M_w = 390\text{ Da}$ (at pH 14), with a maximum alkyl chain length of C_{44} and a high abundance of DBE = 4. This result suggested a structure that includes one carboxylic group and three naphthenic rings. In addition to the high abundance of acidic polar species (O_2 class), other species were also found in lower abundances, including N-containing compounds and NO_2 compounds.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2013.02.007>.

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