



Microwave demulsification of heavy crude oil emulsions: Analysis of acid species recovered in the aqueous phase



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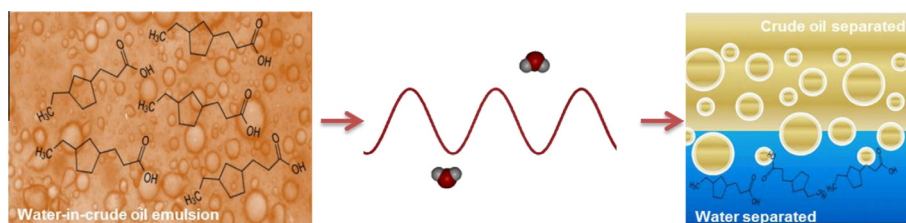
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HIGHLIGHTS

- We report the effect of microwaves and conventional heating on the crude oil.
- Microwaves allowed us to remove water and acidic compounds from the oil phase.
- Temperature and pH can be managed to alter the profile of acids recovered.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the application of microwave technology is investigated for breaking water-in-heavy crude oil emulsions focusing upon the identification of acidic species existing in the aqueous phase recovered by the microwave demulsification process. To accomplish this, a methodology for characterization of acidic species based on GC/qMS (gas chromatography coupled to mass spectrometry quadrupole type) has been developed. An experimental study was conducted to assess the effect of operating conditions, including the heating mode (microwaves/conventional heating), process time (30, 60 min), pH of the aqueous phase (pH = 2, 6, 10) and temperature (90, 120, 150 °C) over the migration of acidic species from the crude oil to the aqueous phase during the demulsification of a heavy crude oil. The most influential variable was the temperature, which favors the partitioning of a larger number of acidic species, including cyclic compounds of low molecular weight that were not extracted at low temperature. The microwave heating allowed a wider distribution profile of monocyclic and bicyclic acids than the conventional heating scheme. Changing the aqueous phase pH from acid to the alkaline range modifies the profile of acidic compounds from predominantly acyclic to monocyclic and bicyclic species.

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1. Introduction

The petroleum is a complex mixture composed of hydrocarbons and some heteroatoms such as nitrogen, oxygen and sulfur which contribute to acidity of the crude oil [1]. It has been recognized that

crude oils with higher total acid number (TAN) are potentially most toxic and corrosive, which may contribute to generate several complications on production and refinery operations. Among these acidic compounds, much attention has been done to naphthenic acids, which generally are defined by classical formula $C_nH_{2n+z}O_2$ [2–6]. Moreover, the acids behave like natural emulsifiers contributing to stabilize water-in-oil emulsions formed during the oil production [7–9]. Mostly, these compounds are found on the

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immature, biodegraded and heavy oils (viscous and high density) and also on wastewater [10]. Thus, one of the greatest challenges of the oil industry is to develop mechanisms to facilitate the separation of water-in-oil (W/O) emulsions and enhancing the removal of acidic species from the oily matrix. Although there are several methods to extract naphthenic acids, they still have economic and/or operational disadvantages [11].

The problems associated with stabilization of petroleum emulsions are multifaceted and strongly influenced by concentration of the natural emulsifiers and the recovery methods used in the production field [12]. The crude oil production is generally associated with produced water existing in the reservoir. Along the crude oil production, these phases are subjected to agitation and shearing, promoting the dispersion of one phase into another, resulting in highly stable emulsions [13]. Furthermore, the emulsification of water in oil is commonly employed to extract thin solids and salts from the oil in the refinery. The presence of natural emulsifiers in the crude oil, such as asphaltenes, resins, fine solids, naphthenic acids and other polar compounds, favors the formation of these emulsions as they tend to migrate to the water/oil interface to form a hard and viscoelastic film [14–19]. This film may act as a kind of barrier, preventing the droplets coalescence and consequently phase separation [20], making the destabilization of water-in-oil emulsions a very difficult task.

Several emulsion destabilization methods are available in the industry, including chemical treatment, gravity separation, centrifugation, filtration, heating, membrane separation and electrostatic treatment [21]. All of these methods, in combination or separately, are widely used in oil industry especially for processing of water-in-oil emulsions [22]. In order to ensure productivity gains, the improvement of existing techniques and the development of new ones focused on the emulsion processing are of great importance for the oil industry. In this context, microwave irradiation technology has appeared as an alternative process for emulsion separation [23]. Nevertheless, little has been done to evaluate the microwave effects on the partitioning of acidic species existing in the petroleum.

Microwave radiation provides a specific heating mode. The dielectric heating generated by microwaves is associated with the radiation interaction with matter at molecular level. Ionic conduction and dipole rotation provide greater microwave heating efficiency compared to conventional method. This advantage allowed its application in various areas such as organic and inorganic synthesis [24–33], processing of foods and biomass [34–41], processing of effluents, oil characterizations and in a number of other processes of interest for petroleum industry [22,42–49].

The microwave technology is also used to remove acidic components from petroleum. In general these studies evaluate the efficiency of the removal of acidic compounds with the variation in the TAN of specimen between before and after processing by microwave.

Lingzhao et al. [50] developed a study on separation of the naphthenic acids from the diesel fuel by microwave radiation. The authors explain that the microwave radiation causes a decrease in the zeta-potential and electric double layer in the W/O interface, thereby reducing the viscosity of diesel fuel, promoting acceleration of the separation of the naphthenic acids.

Huang et al. [51] conducted a study using microwave for removing naphthenic acids from petroleum distillates, oils and refined oils (lubricants). The optimum conditions for the refining process were as follows: S/O = 0.23:1, pressure of 0.11 MPa, radiation time 5 min (at constant pressure), the radiated power of 375 W and resting time of 25 min. Under these conditions, the acidity was reduced from 0.63 mg KOH/g to 0.0478 mg KOH/g, which was sufficient to meet the standard specifications.

Most recently, Mishra et al. [52] determined the efficiency of a laboratory scale microwave system on naphthenic acids degrada-

tion. These acids appear in process water used during petroleum refining and separation from oil sands. They analyzed the effects of TiO₂ catalyst and water source. The microwave radiation favored the catalytic decomposition of naphthenic acids and reduced its toxicity levels considerably.

In a related effort, Freitas et al. [53] described a pioneering method based on GC × GC (comprehensive two-dimensional gas chromatography) for the analysis of organic compounds extracted during microwave demulsification of water-in-crude oil emulsions. In particular, the characterization of polar organic compounds was performed using two analytical techniques: GC/qMS (gas chromatography coupled to mass spectrometry quadrupole type) and GC × GC/TOF-MS (gas chromatography coupled with comprehensive two-dimensional mass spectrometry flying time). These techniques allowed for the identification of a number of natural petroleum compounds that migrate to the water phase during the microwave demulsification process, as a function of temperature and irradiation period.

The objective of this work is to beyond what was done previously and to analyze whether the microwave irradiation process could favor the partitioning of acidic species from the oil phase to the aqueous phase during microwave demulsification runs. An experimental study was conducted to evaluate the effects of microwaves and conventional heating modes, residence time and pH, with the support of chromatographic techniques (GC/qMS).

2. Experimental section

2.1. Crude oil characterization

An experimental study was conducted to assess the demulsification performance of water-in-heavy crude oil emulsions prepared in the laboratory. A Brazilian crude oil was sampled in the petroleum field and used in this study. Table 1 presents its main characteristics and the techniques and standards used for analysis.

2.2. Emulsion synthesis

The emulsions were synthesized with crude oil mentioned in Section 2.1 and distilled water with distinct pH values (2, 6 and 10). Stable emulsions were generated by vigorous mixing of crude oil and water. An amount of water was added stepwise to the petroleum in accordance with previous studies, while the mixture was hand-shaken to completely incorporate water. This mixture was then homogenized using Ultra-Turrax T-25 homogenizer fitted with S25-25G dispersing tool (IKA) with stirring frequency at 6500 and 9000 rpm. The synthesized emulsions had water content between 35–39% and volumetric mean diameter of droplets ranging between 10 μm and 19 μm. This synthesis procedures were based on well-established techniques described previously [46].

Table 1
Main properties of the crude oil employed in this study.

Density (°API)	16.8	ASTM D-5002 [54]
Relative density (20/4 °C)	0.9506	ASTM D-5002 [54]
Water content (wt.%)	0.1450	ASTM D-1744 [55]
TAN (mgKOH/g crude oil)	3.35	ASTM D-664 [56]
Salinity [NaCl] (wt.%)	0.24	ASTM D-3230 [57]
<i>Hydrocarbons content (wt.%)</i>		
Saturated	44.8	
Aromatic	31.3	
Resins	21.6	
Asphaltenes	2.3	

2.3. Emulsion characterizations

After preparation, the emulsions were characterized with respect to water content (WC) and droplet size distribution (DSD). The WC of the crude oil was determined by the Karl Fischer (KF) reagent method, in accordance with ASTM D1744 procedure. A potentiometric titrator model 836 Titrando equipped with a double platinum electrode was employed for WC determination tests. The solvent used during the analysis was a mixture of dry methanol (Vetec, 99.8% purity) and chloroform (Vetec, 99.8% purity) in 3:1 molar ratio. The DSD was determined by laser diffraction using the Mastersizer 2000 Malvern.

2.4. Demulsification process

The microwave tests were performed using a commercial microwave reactor model Synthos 3000 from Anton Paar. This system is equipped with two magnetrons capable of providing 1400 W of power radiation in the 2.45 GHz frequency. The temperature was measured by temperature probe (gas bulb thermosensor) immersed in a reference vessel. This was used to follow the temperature evolution of that sample during tests. Furthermore, an infrared sensor placed on the rotor bottom allowed to assess the surface temperature of all 8 vessels. For this study just 4 vessels were used. Each of them was filled with 30 g of emulsion. Then experiments were performed at temperatures of 90 °C, 120 °C and 150 °C and process time of 30 and 60 min.

For comparison, additional tests were carried out with conventional heating using a thermostatic bath filled with water as heat transfer fluid. Thus one vessel described above was placed in a metal rack that enabled us to support the vessel into the bath. The tests were carried out at same times and temperatures of microwave processing.

The emulsions synthesized for this work presented high stability, with narrow droplet size distribution (10–19 µm), so that the free water formation with the breaking process by microwave and conventional heating was observed only with the addition of demulsifier agents. Such addition was carried out before the samples were sent to heating. Thereby, 20 µL of industrial typical demulsifier was added on 90 g of emulsion and mixed with the aforementioned homogenizer during 1 min at 9500 rpm frequency.

After the demulsification test, the separation extent was measured. Both free water and remaining emulsion were quantified through KF analysis. This way allowed us to compare the water content from original emulsion sample to assess the demulsification process efficiency.

2.5. Characterization of the aqueous phase

In order to study the processing effect on partitioning of acidic compounds between aqueous and oily phases previously emulsified, the free water formed after demulsification tests was collected. Water was subjected to solid phase extraction (SPE) in order to extract and concentrate analytes from aqueous phase into organic phase.

Due to its specific characteristics that provides both interactions with polar and a polar compounds, the cyanopropyl was chosen as stationary phase used in cartridges of 500 mg.

2.5.1. Sample preparation

To conditioning the extraction cartridge, 2 mL of dichloromethane and 2 mL of distilled water were employed. Then aqueous sample (10 mL) was added in cartridge aiming the retention of organic compounds. The elution was performed by 5 mL of dichloromethane initially and then 5 mL of methanol. After extraction step all samples were reduced to 0.5 mL, using a nitrogen flow.

2.5.2. Derivatization

Extracts from the aqueous phase were derivatized in order to generate compounds which can be properly detected by chromatographic techniques. The sample derivatization was carried out adding *n*-methyl-*n*-(*tert*-butyldimethylsilyl) trifluoroacetamide (BDMSTFA) on inert atmosphere and 1:5 ratio in volume between sample and derivatizing. After, the system was heated in water bath at 60 °C and 15 min. The purpose of derivatization was to ensure ester formation from the acids present in processed water. After heating, vapor excess was eliminated and the sample conditioned in 500 µL of dichloromethane bi-distilled and forwarded to chromatography analysis.

2.5.3. Chromatographic analysis

The chromatographic analysis was performed by GC/qMS (gas chromatography with quadrupole mass spectrometric detection) with split/splitless injector, a Shimadzu 17, using the electron impact ionization method (EI) with ionization energy 70 eV. The capillary column used was an OV-5 (methyl silicone with 5% phenyl groups) with 0.32 mm internal diameter, 0.10 µm thick of stationary phase and 30 m long. The analysis parameters can be found in Table 2. The compound identification was carried out by comparing with compounds from NIST mass spectra library.

The GC/qMS (gas chromatography coupled to mass spectrometry quadrupole type) and GC × GC/TOF-MS (gas chromatography coupled with comprehensive two-dimensional mass spectrometry flying time) afford great robustness. Nevertheless, precision and accuracy of results depends on the measurement parameters, whose selection is left to the judgement of the analyst [58]. Thus, the analysis parameters used in this work can be found in Table 2.

2.5.4. Data analysis

Semi-quantitative GC analysis in SCAN mode was carried out in acids extracted from the heating tests, to identify linear and naphthenic acids by mass spectrum of compounds. After this step, a study was performed based on empirical formula of naphthenic acids $C_nH_{2n+z}O_2$ for obtaining the numbers of carbon atoms (*n*) and the number of hydrogen atoms lost in the structural cyclization (*z*) [60]. The number of rings present in structure is obtained by number *z* divided per two. Thereby, *z* is equal to 0 for saturated acyclic compounds, 2 for monocyclic compounds, 4 for bicyclic, 6 for tricyclic and so on [58,60]. The intensity of ion $[M-57]^+$ was considered of each identified compound in samples in order to find the acidic species distribution. The quantification was carried out by area normalization according to a previous work [59].

3. Results and discussion

3.1. Demulsification tests

In order to assess the processing effect on partitioning of acidic species in water-in-oil emulsions, demulsification assays were performed under different experimental conditions. Table 3 presents the values of water content (WC) and droplet size distribution

Table 2
Operation conditions of chromatographic analysis.

Parameters	GC/qMS
Injector and detector temperature	280 °C and 300 °C
Injected volume	1 µL
Injection mode	Splitless
Mobile phase flow rate	1.5 mL/min
Oven temperature ramp	75 °C (10 min) – 2 °C/min – 200 °C (10 min) – 280 °C (15 min)

Table 3
Parameters of emulsions and demulsification tests.

Test	Initial emulsion properties			Aqueous phase properties		Operation condition		
	WC ^a (%)	D(4,3) ^b (μm)	D(0,5) ^b (μm)	pH	Salinity [NaCl] g/L	Temperature (°C)	Time (min)	Remarks
T1	35.9	13.6	10.7	6	50	90	30	Conventional heating
T2	34.8	12.1	8.7	6	50	90	60	Conventional heating
T3	35.6	19.0	12.7	6	50	90	30	Microwave heating with ramp similar to the conventional method
T4	36.2	12.6	10.3	6	50	90	30	Microwave heating
T5	37.8	12.6	10.3	6	50	90	60	Microwave heating
T6	37.4	12.4	10.8	6	50	120	30	Microwave heating
T7	37.5	12.7	10.5	6	50	120	60	Microwave heating
T8	37.7	12.5	10.4	6	50	120	30	Microwave heating
T9	37.4	12.9	10.8	6	50	150	30	Microwave heating
T10	36.0	10.8	6.5	2	50	120	30	Microwave heating
T11	36.6	13.5	11.7	10	50	120	30	Microwave heating

^a Average of two measurements.

^b Average of three measurements.

(DSD) for samples in different assays. The variations observed in these two properties for emulsions synthesized from same methodology are those typically found in this synthesis procedure. Details about that variation can be found in Fortuny et al. [46].

The heating profiles of emulsions obtained by microwave radiation and conventional heating are shown to be distinct. Fig. 1 presents the temperature versus time for assays conducted in microwave reactor and conventional heating method, with temperature of 90 °C. As can be seen, the higher heating rate is achieved in microwave heating method.

3.2. Chromatographic analysis

The results presented in this work take into account cyclic and acyclic acids present in aqueous phase studied. A typical diagram was obtained by the GC/qMS for organic extract of aqueous phase separated from emulsion sample, after extraction and derivatization listed in Section 2.5.

The acids identified are represented by C_n symbol, indicating the number of carbon atoms in molecular chain of the compound and z symbol representing the hydrogen deficiency. Those chromatograms allowed us to deduce that eluting process of acidic compounds extracted drain off acyclic compounds and cyclic compounds with Z = -2 and Z = -4.

3.2.1. Semi-quantitative analysis

In order to analyze the influence of test parameters and properties of aqueous phase in partitioning of acidic species, a semi-quantitative analysis of the compounds was carried out. The acids were identified tentatively by gas chromatography with mass spectrometer (GC/qMS) using the single ion monitoring (SIM) mode. The quantification was performed in accordance with the method developed by Holowenko et al. [60] in which each ion represents a family of acidic compounds. To each acid family exists a corresponding area (AAc) and the summation of areas (SAc) of every family is equivalent to the full acids compounds present in the sample. The area normalization based on the following equation is:

$$\%acids = \frac{(AAc \times 100)}{SAc} \quad (1)$$

where AAc is the area of acidic compound of each family present in the sample; SAc is the summation of acidic compound areas existing in the sample.

The equation represents the acidic specie intensity (%) or the distribution of the acids family in water sample after the acids partitioning induced by the microwave heating process.

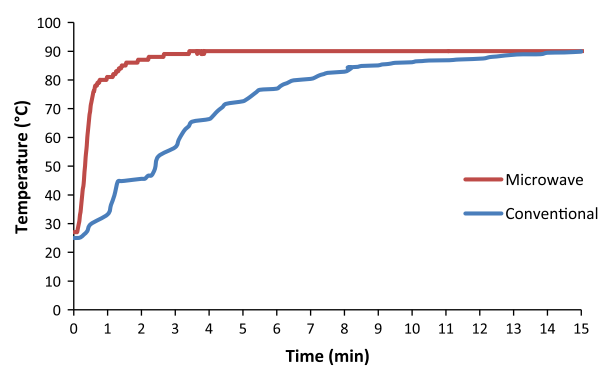


Fig. 1. Temperature versus time for test conducted by microwave radiation (T4) and conventional heating method (T1) at temperature of 90 °C.

3.2.1.1. Heating mode effect. The distinct heating profiles verified in two heating modes used stimulated us to study the influence of these differences in the partitioning of acidic species. This way, tests were performed under conventional heating mode at 90 °C (T1), and under microwave heating mode at the same temperature (T4). Nevertheless, in order to get a clearer picture of the heating effects, a microwave irradiation test was conducted under controlled heating rate to mimic the heating profile of the conventional heating method (T3). Fig. 2 presents the test in which the microwave heating mode reproduces the heating profile typically observed for the conventional method (slow case) in comparison with its typical heating rate shown in Fig. 1 (fast case).

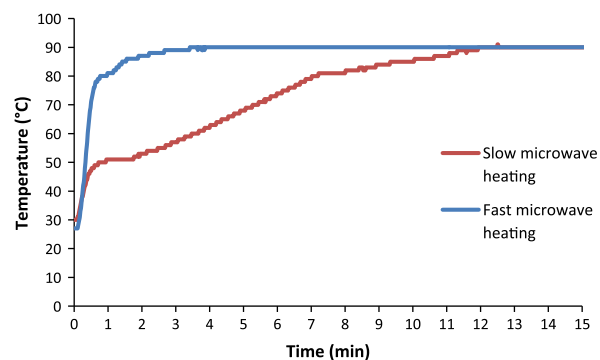


Fig. 2. Different heating rate in microwave irradiation tests. Slow microwave heating – T3, fast microwave heating – T4.

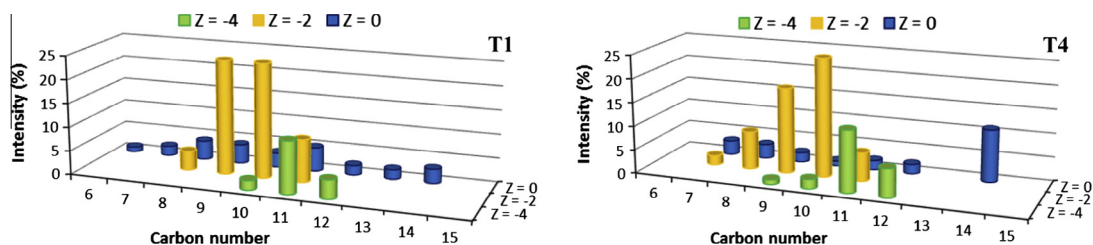


Fig. 3. Partitioning of acidic species after breaking emulsions through conventional heating (left) and microwave irradiation (right).

Based on the acids distribution shown in Fig. 3, one can verify that cyclic acids are present in greater proportion (77%) than acyclic acids (23%). In test T1 it was found approximately 55% of monocyclic acids with 9, 10 and 11 carbons in the molecular chain. Bicyclic acids with 10, 11 and 12 carbons atoms also were found. The other compounds represent acyclic acids with carbons number ranging from 6 to 14. The aqueous phases recovered from T4, the test which corresponds to a standard assay via microwave irradiation, showed differences in relation to the cyclic compounds profile. In this test, it can be verified an intensity change in compounds partitioned. Besides, one can observe the presence of bicyclic acids and monocyclic with 9 and 7 carbon atoms, respectively. Acyclic compounds such as C₆ and C₁₃ were not identified.

It was noted that microwave processing allowed the partitioning of monocyclic among 7 and 11 carbon atoms and bicyclic acid among 9 and 12 carbon atoms, respectively. This qualitative result may be indicative of the differential effect of microwaves on the partitioning of certain species. A possible explanation for this effect is related to the fact that microwave irradiation provides a volumetric heating of the reaction medium, with possible formation of hot spots which induce rapid species diffusion. On the other hand, the conventional heating produces a slow and superficial heating with lower impact on the species diffusion [61,46]. Perhaps this peculiarity of microwave irradiation favors a specific partitioning of some polar species.

3.2.1.2. Process time effect. Similar tests carried out with distinct process times (T1, T2; T4, T5; and T6, T7) were compared as to structure of acidic species in the aqueous phase recovered. Acyclic acids are present in greater range of carbon number (from C₆ to C₁₅) than cyclic acids, fact common to the other variables studied.

The test T4, performed at lower time (30 min), presented greater presence (70%) of compounds with medium molecular weight, between C₉ and C₁₁. In the test carried out at higher time (60 min), T5, the distribution of carbon atoms favored the partitioning of compounds with lower molecular weight, C₆ and C₇.

3.2.1.3. Temperature effect. The temperature effect was analyzed in heating microwave. The partitioning of acidic species was studied in three different temperatures 90 °C (T4), 120 °C (T6) and 150 °C (T9). In these tests, a distinct distribution of medium molecular weight compounds was obtained. The test conducted at lower temperature yielded acyclic compounds C₇ to C₁₄ (except C₁₃). Monocyclic and bicyclic acids with carbon atoms varying from 7 to 11 and 9 to 12, respectively, were also found. It should be noted that compounds C₉ and C₁₀ with Z = -2 and C₁₁ with Z = -4 presented intensity greater than 10%. In contrast to T4, the test performed at medium temperature yielded acyclic acids with 6 and 15 carbons atoms. Regarding cyclic compounds, as shown in Fig. 4, species including C₆ to C₁₄ (except C₁₃) monocyclic and C₁₀ to C₁₃ bicyclic were detected. The test carried out at higher temperature presented a regular distribution of acyclic compounds with carbon atoms range varying from 6 to 15. The main difference was the intensity of major cyclic compounds, which was essentially concentrated around 15%.

The emulsion heating using conventional thermal processes is done by classical mechanisms of heat transfer, principally by conduction and convection. It is expected that the temperature increase may intensify these mechanisms, and ultimately enhance the specie diffusion rates both within the continuous phase of the emulsion as in the interface, thus favoring the partitioning of species. Also in microwave heating mode, a higher partitioning

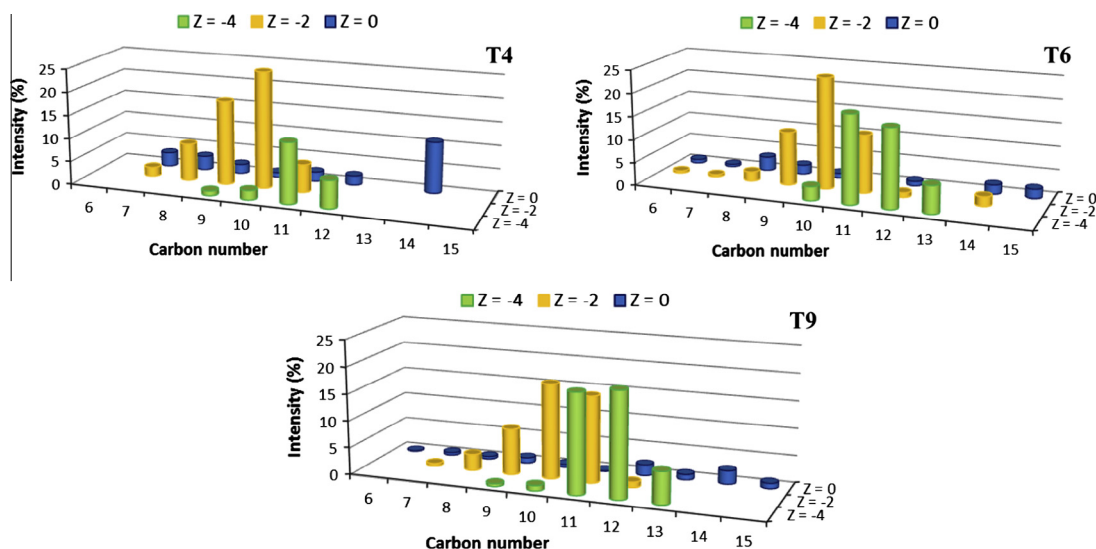


Fig. 4. Partitioning of acidic species after breaking emulsions in assays via microwave heating at temperature 90 °C (top left), 120 °C (top right) and 150 °C (down).

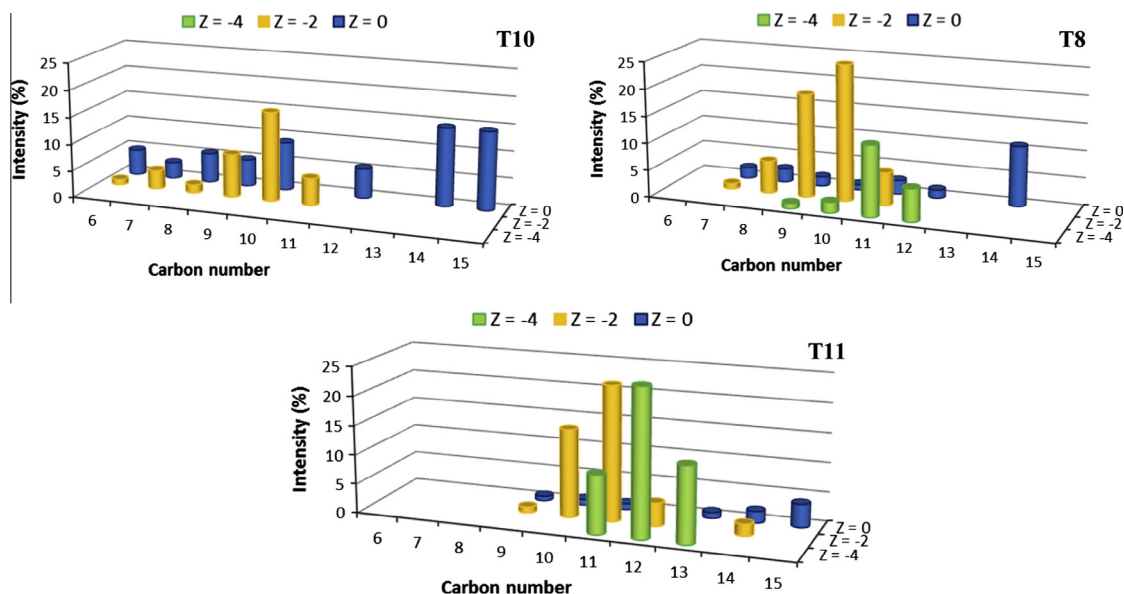


Fig. 5. Partitioning of acidic species after breaking emulsions in assays via microwave heating and pH of aqueous phase acidic (top left), neutral (top right) and alkaline (down).

of cyclic compounds was obtained at highest temperatures. The increase in temperature might reduce the viscosity of hard film formed by natural surfactants. Thus, the mobility of compounds at the oil–water interface may be improved, and a consequent migration of acids compounds from the interface to the aqueous phase is likely to occur.

3.2.1.4. Effect of phase aqueous pH. In many traditional processes in the petroleum industry, the variable pH is commonly manipulated in order to obtain operational advantages, as in the case of crude oil demulsification [46]. To study the influence of this variable, tests were performed in aqueous phases with different pHs (pH = 2, 6 and 10).

The tests yielded distinct acidic compounds distribution (Fig. 5). In test at acidic pH (T10) the carbon distribution focused on acyclic and monocyclic compounds of low and medium molecular weights. Special attention can be done to C_{14} and C_{15} with $Z = 0$ and C_{10} with $Z = -2$. These species presented intensity around 15%. The test with alkaline pH (T11) resulted in compounds with carbon atoms ranging from 9 to 15. In the T8, which involved neutral pH, there was a greater uniformity distribution of compounds, if compared to T10 and T11.

Test T10 was the only case for which the partitioning of bicyclic acids has not been detected. In spite of that, test T11 yielded a high partitioning of bicyclic and monocyclic with a lower range of carbon atoms number. In this same test, compounds C_6 to C_8 were not detected. Nevertheless the cyclic compounds intensity verified in T11 was higher than in T8. Therefore, according to Fig. 5, both the neutral and alkaline pH of the aqueous phase favored the partitioning of cyclic acids in greater proportion than the acidic pH.

4. Conclusions

The identification of acidic species existing in the water phase extracted from the crude oil during the demulsification process induced by microwaves or conventional heating was performed. The results of this work show that specific acidic compounds may migrate from the crude oil to the water phase, depending on the operation variables of the demulsification process, including the

heating mode (microwaves/conventional heating), process time, temperature and aqueous phase pH.

The microwave heating allowed a wider distribution profile of monocyclic and bicyclic acids than the conventional heating scheme. The temperature increase favors a most regular distribution of compounds with larger range of carbon atoms. The aqueous phase pH variation from acidic to alkaline modifies the profile of acidic compounds from predominantly acyclic to monocyclic and bicyclic.

The partitioning of the acidic species between aqueous and oil phases induced by microwave irradiation is still in its early stages of development. Nevertheless, this technology is promising and merits further studies toward the application of microwaves as a tool to simultaneously achieve two highly relevant targets: the separation of emulsions and the removal of acids existing in the oil phase.

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