Effect of Salinity, Temperature, Water Content, and pH on the Microwave Demulsification of Crude Oil Emulsions[†]

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The main objective of this work is to investigate the effect of a set of crude oil emulsion variables, including pH and salt and water contents, upon the microwave demulsification process. A series of batch demulsification runs were carried out to evaluate the final emulsified water content of emulsion samples after the exposure to microwaves. Tests were performed at distinct heating temperatures, using water-in-heavy crude oil emulsion samples containing different salt and water contents and pH. Well-defined temperature programs were established to control the amount of energy applied to the emulsion and, ultimately, the viscosity. Higher microwave demulsification efficiencies were achieved for emulsions containing high water contents, except when high pH and salt contents were simultaneously involved.

1. Introduction

The complex nature of typical water-in-crude oil emulsions is one of the main difficulties for the development of adequate separation techniques in the petroleum industry. Despite the huge efforts that have been made in the last 30 years for the development of reliable and efficient demulsification techniques, most water-in-crude oil emulsions cannot be broken in short times. In fact, the demulsification operation constitutes a key process for removing water from crude oil in the production platforms and the refinery. In particular, demulsification stages are required at the desalting plants generally found in the refineries to remove water-soluble salts from the crude oil.

It has been recognized that crude oil emulsions are stabilized by rigid interfacial films on the surface of the dispersed water droplets that prevent the droplets from coalescing.[1] Surface-active species commonly found in the crude oil such as asphaltenes, resins, oil-soluble organic acids, solids, and waxes are among the materials constituting these interfacial films.[2] Because some of these substances contain ionizable groups, the water-phase pH can be expected to affect their ionization in the interfacial films, producing radical changes of the physical properties of the films and also the solubility of some polar organic compounds toward the water phase.[1] As a consequence, a number of demulsification techniques for water removal have been applied at the oil or petroleum industry, including chemical demulsification, gravity or centrifugal settling, pH adjustment, filtration, heat treatment, membrane separation, and electrostatic demulsification.[3] However, the demulsification of water-in-oil emulsions of highly viscous crude oils can be very laborious, introducing undesirable long time delays. Besides, there is the difficult task of relating crude oil emulsion properties (which can usually be evaluated in the lab, such as water contents (WCs), salinity, pH, asphaltene contents, and stability, among others) and the separation conditions (such as temperature, type and amount of demulsifier, residence time, and electric-field magnitude, among others), whose quantification is usually determined after time-consuming tests and calibrations.

For all of the reasons discussed above, it is therefore of interest to investigate alternative separation procedures able to demulsify water-in-highly viscous crude oils at short times that are inexpensive, easy to implement, without time-consuming calibrations, and widely applicable.

A lot of activity has been developed recently regarding the use of microwave irradiation for demulsification purposes.[4−9] This is because the microwave irradiation offers a clean, inexpensive, and convenient method of heating, which often results in higher yields and shorter reaction times.[10] It has been recognized that the acceleration of reactions by exposure to microwaves results from material−wave interactions, leading to thermal effects easily estimated by temperature measurements (the so-called dielectric heating) and specific effects (not purely

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thermal) generally associated with the selective absorption of microwave energy by polar molecules.[11] In particular, materials dissipate microwave energy by two main mechanisms: dipole rotation, which is related to the alignment of molecules that have permanent or induced dipoles with the electric-field component of the radiation, and ionic conduction, which refers to the migration of dissolved ions with the oscillating electric field.[12]

Concerning demulsification applications, it seems that Wolf[4] was the first to report the successful use of microwave irradiation for the separation of water-in-oil (W/O) emulsions. The work revealed that the microwave irradiation provides high efficiency in the breaking of W/O emulsions, when compared to other techniques involving conventional heating. Following this pioneering work, other interesting studies had been published aiming at the emulsion separation in short times (few minutes), looking at both O/W and W/O emulsions.[5-9] Fang et al.[5,6] compared the use of microwave heating with conventional heating for the separation of O/W emulsions at the lab scale and in the petroleum field. In their patent application, Nilsen et al.[7] proposed a method for separating W/O emulsions based on microwave heating and the use of specific frequency ranges in the microwave region. Chang and Chen[8] studied the demulsification of liquid-membrane emulsions by microwave irradiation, looking at the effects of salts and inorganic acids in the aqueous phase of W/O emulsions. According to this study, both the separation efficiency and demulsification rate are increased with the acid concentration and also with the electrolyte concentration (NaCl, KCl, NaNO$_3$, and Na$_2$SO$_4$) in dilute range (<0.5 M). Xia et al.[9] investigated the role of asphaltenes and resins on the stability of model water-in-kerosene emulsion during microwave demulsification tests. Their experimental results demonstrated that microwave irradiation can enhance the demulsification rate by an order of magnitude, when compared to conventional heating procedures.

The efficiency of the microwave radiation on the emulsion separation has been attributed to the following effects: (i) reduction of the viscosity of the continuous phase (oil) because of the increase of the temperature, which favors the water droplets contact,[5,7] (ii) reduction of the stability as a result of microwave-induced rotation of water molecules, which neutralizes the ζ potential of the dispersed droplets, besides breaking hydrogen bonds between water and surfactant molecules,[6] (iii) reduction of the thickness of the interfacial surfactant film because of the expansion of the dispersed phase caused by the increase of the internal pressure of the water droplets during microwave irradiation,[7,9] and (iv) reduction of the stability as a result of breaking hydrogen bonds between the surfactant molecules and the water molecules.[7]

All of these effects can be more or less favored depending upon the dielectric properties of the material, the emulsion composition, the size distribution of the dispersed phase of emulsion, and the operation conditions, including the temperature of heating and the frequency of the microwave radiation.[10,12,13] Particularly, additions of dissolved salts to the aqueous phase markedly affect the dielectric properties as electric conductivity increases, which may increase the dielectric heating.[10,13] This occurs mainly at low-frequency values, where

Table 1. Summary of Crude Oil Properties

crude oil properties	
density (deg of API)	19.1
WC (wt %)^a	0.76
asphaltene content (wt %)^b	2.95
viscosity at 30 °C (cP)	290
TAN (mg of KOH/g of crude oil)	1.32
salinity (mg of NaCl/L of crude oil)	279

^{a} WC means weight percentage of "water content" in the mixture. ^{b} Defined as the *n*-heptane-insoluble fraction from the oil.

the contribution of the conduction mechanism predominates in the dielectric heating.[14] Indeed, the droplet-size distribution (DSD) of the colloidal system can modify some emulsion properties, such as the emulsion viscosity, which in turn may influence the dielectric constant, the dielectric loss, and the penetration depth.[12,13] Because the dielectric heating is influenced by pH, viscosity, and salt content and WC, which in turn influence the crude oil emulsion stability, it is necessary to understand the relationship among those variables and the microwave demulsification performance.

The main objective of this work is to investigate the effect of a set of crude oil emulsion variables, including pH and salt content and WC, upon the microwave demulsification process. A series of batch demulsification runs were carried out to evaluate the final emulsified WC of emulsion samples after the exposure to microwaves. Tests were performed at distinct heating temperatures, using water-in-heavy crude oil emulsion samples containing different salt content and WC and pH. Well-defined temperature programs were established to control the amount of energy applied to the emulsion and, ultimately, the viscosity.

2. Experimental Section

2.1. Emulsion Preparation. Water-in-oil emulsions were prepared by homogenizing known amounts of a heavy crude oil (19.1 API gravity) and model brine solutions containing specified amounts of NaCl and NaOH, to adjust the salt contents and the pH of the aqueous phase in the emulsions. The NaOH solution consisted of 0.07 wt % NaOH in water. The characteristics of this oil are summarized in Table 1.

The asphaltene content was determined after recovering the *n*-heptane insoluble fraction from the oil, in accordance with the ASTM D-6560 test method.[15] The total acid number (TAN) was determined by potentiometric titration of the crude oil with alcoholic potassium hydroxide (KOH) solution, in accordance with the ASTM D-664 test method.[16] The WC of the crude oil was determined by the Karl Fischer (KF) reagent method, in accordance with ASTM D-1744 procedures.[17] The salinity of the crude oil was determined using the electrometric method, according to ASTM D-3230 procedures.[18] Note that the crude oil studied here is moderately acidic (as indicated by its TAN value) and possesses a significant salt content, as usually encountered in the inlet stream of a typical industrial desalting plant, which should reduce the water and salt content of the crude oil.

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(16) ASTM D-664. Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration.

(17) ASTM D-1744. Standard Test Method for Determination of Water in Liquid Petroleum Products by Karl Fischer Reagent.

(18) ASTM D-3230. Standard Test Method for Salts in Crude Oil (Electrometric Method).

The emulsion synthesis procedure involved two stages: a pre-emulsification stage and an emulsification stage. Prior to the pre-emulsification stage, the crude oil was shaken vigorously to ensure homogeneity before sampling. During the pre-emulsification stage, a known amount of water was added stepwise to the hydrocarbon phase, while the mixture was hand-shaken to completely incorporate the water, resulting in a pre-emulsion with a total volume of 300 mL. In the second stage, this mixture was homogenized using an Ultra-Turrax T-25 homogenizer fitted with a S25-25G dispersing tool (IKA). The ratio of water and crude oil in the mixture was varied to make up an emulsion with the desired value of WC (25, 35, or 45%). The homogenization conditions, such as the stirring frequency and the time of homogenization, were kept constant at 17 500 rpm and 10 min, respectively, to yield emulsions with similar DSDs.

2.2. Emulsion Characterizations. Emulsion properties such as DSD and WC were characterized before and after each test. The WC of the emulsions was determined by the KF reagent method, in accordance with ASTM D-1744 procedures.[17] The solvent used during the analysis was a mixture of dry methanol and chloroform (0.2%, v/v). For standardization of the KF reagent, distilled water was solubilized into the solvent cited before. A Metrohm KF titrator (model 836 Titrando) equipped with a double platinum electrode was employed during the water-content determination tests.

The DSD of emulsion samples was obtained with a Malvern Instrument Model 2000 Mastersizer particle-size analyzer based on the laser diffraction technique. The detection range of the instrument varies from 0.020 to 2000 μm. The apparatus is appropriated to perform measurements of systems with low concentrations in a transparent environment but also in slightly dark media. Because the emulsion samples used were dark and concentrated, a diluent was required. The main purpose of dilution is to avoid multiple scattering by getting the droplets far away from one another. The solutions were prepared by dispersing 5−10 drops of emulsion in 200 mL of a white mineral oil (EMCA 70, 19.3 cP, 25 °C) used as a diluent. This diluent has also been used by Petrobras during similar applications involving laser diffraction techniques. In a related effort, Ramalho and Oliveira[19] proposed a DSD analysis procedure for water-in-crude oil emulsions based on the use of a Malvern Mastersizer instrument and a similar white mineral oil. The reported DSD results using the laser diffraction analyzer were in very good agreement with microscopy analysis. In the current paper, the optical constants (refractive index, n, and absorption index, k) employed as internal parameters for the particle-size analyzer were $n = 1.33$ and $k = 0.1$ for the dispersed medium and $n = 1.467$ for the dispersing system.

For all water-in-oil emulsions synthesized in this study, the DSD results indicated bimodal distributions and median droplet sizes ranging from 3 to 60 μm. Similar DSD results were encountered by Petrobras during tests of emulsion generation at field conditions.[20] In that study, water-in-crude oil emulsions were generated in the flow lines during the production of oil with water injection, resulting in emulsions with fine droplets because of the presence of a choke valve and a centrifuge pump.

2.3. Microwave Demulsification Tests. The demulsification tests applying microwave irradiation were conducted using a commercial microwave reactor system (Anton Paar Synthos 3000). This instrument is equipped with two magnetrons able to provide 1400 W of continuous microwave power, a rotor system in which eight vessels with an 80 mL capacity can be inserted at one time, and magnetic stirrer for agitation of the sample in each vessel. Also, an infrared sensor placed on the rotor bottom enables us to assess the surface temperature of the vessel and an immersing temperature probe (gas bulb thermosensor) placed at one reference vessel can be applied to follow the temperature evolution of that sample during

tests. The vessels were 80 mL in capacity and made of quartz glass, resisting temperatures up to 300 °C and pressures up to 80 bar. The control system supplied with the instrument enables us to perform heating ramps with pressure and temperature conditions programmed prior to the run. A built-in forced-air cooling system allows for a fast cooling of the vessels.

The standard procedure for demulsification runs involved the use of just two quartz glass vessels, each of them filled with 40 g of emulsion. These samples were stirred throughout the tests using the magnetic stirrer, to facilitate the contact among the water droplets in the emulsion. The total microwave irradiation time was set to 15 min for each test. During this irradiation time, the temperature was programmed to increase from ambient to the set-point value in 2 min, being kept at this value during the subsequent 13 min. In this way, the microwave power supplied by the instrument was automatically manipulated to ensure the temperature programmed for the samples during the heating ramp. After the irradiation time, samples were quenched by the cooling system during 10 min and their different phases formed during the demulsification test were characterized in terms of masses of both the resolved water and the remaining emulsion. KF analyses were performed to evaluate the unresolved WC in the remaining emulsion ("final WC" values). These final WC values could then be compared to the WC of the original emulsion sample to assess the demulsification efficiency of the microwave irradiation process. For those samples in which no distinguishable phase was formed, DSD and KF analyses were performed at different heights of the final emulsion sample to infer the extent of coalescence of the water droplets in the sample because of the microwave irradiation.

An experimental study was conducted to evaluate the effects of a set of operating variables on the demulsification performance. Several microwave irradiation demulsification runs were carried out at different heating temperatures (80, 95, and 130 °C), using water-in-oil emulsion samples containing different WCs (25, 35, and 45%), salt contents (0.0, 15 000, and 30 000 ppm) and pH (7, 9.5, and 12). It should be noted that salt contents around 30 000 ppm (or even higher) are easily encountered in the water present in the geologic formation and produced with the crude oil during the petroleum production in the field. On the other hand, the salt content of the aqueous phase is expected to vary during the desalting process in the refinery. As a consequence, the study of the salt content effect on the microwave demulsification can be helpful for breaking those emulsions generated during petroleum production and also during the desalting process. The pH values of the water phase chosen in this study were in the alkaline range, because most of the emulsions observed in the field contain additives that generally lead to a pH increase. The temperature levels were chosen with the objective of provoking changes of the viscosity of the continuous phase in the emulsion, considering a limit value of 130 °C to minimize sample vaporization and pressure variation. Table 2 summarizes the set of emulsion properties, temperature conditions, the applied energy, and the final WC of the resulting emulsion.

In particular, the microwave energy applied by the instrument in each test was calculated through the numerical integration of the applied power recorded by the instrument as a function of the time. The emulsion DSD was described by three moments of the distribution curve provided by the particle-size analyzer: the D(0.5), the D(0.9), and the D(4.3) that respectively represent the median droplet size, the droplet size for which 90% (v/v) of the water droplets have a lesser or equal size, and the volume-weighted mean.

3. Results and Discussion

3.1. Demulsification Test Repeatability. The repeatability of the demulsification tests using microwave irradiation was evaluated through the repetition of test T3. Thus, five experiments were carried out at the same conditions of heating temperature, emulsion WC, pH, and salinity of the aqueous phase. The procedure for preparing emulsion samples was kept between tests; however, some fluctuations were observed in

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Table 2. Emulsion and Aqueous Phase Properties, Operation Temperature, Applied Energy, and WC of the Final Emulsion for the Microwave Demulsification Tests

	initial emulsion properties				aqueous phase properties		operation condition		separation resolution
run	WC (%)	D(0.5) (μm)	D(0.9) (μm)	D(4.3) (μm)	salinity (mg of NaCl/L of water)	pH	temperature (°C)	energy (kJ)	final WC (%)
T1	25	6.1	15.3	7.2	0	7.0	80	303	24.9
T2	35	8.5	22.7	10.3	0	7.0	80	174	27.4
T3	45	3.5	16.7	7.3	0	7.0	80	143	17.0
T4	25	4.8	13.8	6.3	30 000	7.0	80	108	25.0
T5	35	10.1	24.8	11.4	30 000	7.0	80	64	28.7
T6	45	19.6	53.0	23.5	30 000	7.0	80	50	24.7
T7	45	22.5	62.4	26.9	15 000	7.0	80	61	23.6
T8	45	5.6	26.5	10.3	0	9.5	80	122	20.2
T9	45	15.3	42.1	23.4	30 000	9.5	80	47	28.5
T10	45	22.1	59.5	28.0	0	12.0	80	100	12.5
T11	45	21.4	53.1	24.9	0	12.0	80	97	14.1
T12	45	16.1	53.3	22.6	30 000	12.0	80	45	45.0
T13	45	13.5	45.1	17.8	30 000	12.0	80	48	45.0
T14	45	36.4	100.1	43.5	0	7.0	95	141	9.7
T15	45	20.6	64.0	26.9	0	7.0	95	156	8.2
T16	45	27.9	72.7	31.7	0	7.0	130	238	5.6
T17	45	16.9	59.5	24.3	0	7.0	130	255	2.6

Table 3. Crude Oil and Emulsion Properties, Initial Temperature of the Sample, Applied Energy, and WC of the Final Emulsion for Five Repetitions of the Run T3

	crude oil	emulsion			operation condition		separation resolution
run	WC crude oil (%)	D(0.5) (μm)	D(0.9) (μm)	D(4.3) (μm)	initial temp. (°C)	energy (kJ)	final WC (%)
T3	0.76	3.5	16.7	7.3	30	143	17.0
T3_2	0.76	22.0	100.7	38.2	35	117	20.8
T3_3	0.76	38.3	86.3	40.8	39	115	21.6
T3_4	1.31	32.7	79.9	35.9	34	107	18.9
T3_5	1.31	42.3	102.2	46.3	31	104	21.5

emulsion DSD and also in the sample temperature. These properties are difficult to reproduce accurately, mainly when the composition of the system varies between tests. The fluctuations in these properties and the demulsification results (applied energy and final WC) can be observed in Table 3.

Because two demulsification runs (T3_4 and T3_5) were performed using emulsion samples prepared from a different lot of the crude oil, sharp differences were verified in the WC of the crude oil between lots. Changes of the WC in the crude oil generally lead to variations of the salt content in the crude oil; therefore, an increase in the WC may raise the salt amount per total volume of emulsion. Once the salt concentration influences the dielectric heating, the applied microwave energy is expected to decrease with the increase in the amount of salt in the total volume. This relationship between salt contents and dielectric heating may explain the sharp differences observed in the applied energy between crude oil lots.

Concerning the separation resolution in Table 3, slight differences were observed in the final WC values between tests. These differences seem to be related to the microwave energy applied in each test. Thus, for tests T3, T3_2, and T3_3, whose emulsions had been synthesized from the crude oil coming from the same lot, the final WC diminishes with the increase of the energy applied to the system. Similar results occurred for the tests T3_4 and T3_5, supporting the idea that an increase of the energy applied to a sample leads to an enhanced demulsification. As shown in Figure 1, the temperature profile during the entire demulsification process was essentially the same from run to run, which means that differences in the applied energy did not result in changes of temperatures, suggesting that different kinds of heating may have occurred for those emulsions. Such differences can be linked either to the changes in

the initial temperature of the sample, because lower initial temperatures require greater heating energies, or to the variations in the initial DSD of emulsions. Thus, it is possible that the size and number of water droplets influence the heating of the sample. According to Table 3, the increase in the applied energy is associated to a reduction in the median droplet size for tests T3, T3_2, and T3_3. This behavior is also observed for runs T3_4 and T3_5. Even though variations in the initial DSD of emulsions did exist, the range of variations was too narrow; thus, no noticeable improvement on the demulsification results was obtained exclusively because of a droplet size increase. As a final remark, the demulsification test repeatability presented here is governed by the amount of applied energy, which in turn depends upon the initial temperature of the sample. Therefore, the demulsification variance is expected to be reduced, if energy control had been performed during the runs. Additional studies are being conducted on our laboratories to account for the variance on the demulsification results, including a tighter control of conditions.

3.2. Influence of WC on Demulsification Efficiency. Because dielectric properties are influenced by medium composition, it is necessary to determine the relationship between these properties and the emulsion WC. This is especially important in demulsification processes, where WC variations are expected to occur. Besides, emulsion WC can also influence the coalescence efficiency during the demulsification process, leading to a reduced distance between droplets in the sample. This distance can be severely narrowed with the increase of the volume of the aqueous phase in the emulsion, raising the probability of collision between the droplets.

Tests T1, T2, and T3 were conducted under similar experimental conditions but with different emulsion WC. According to Table 2, improved emulsion resolution was obtained for emulsions with greater initial WC. Thus, for test T1 (low WC), a negligible variation was detected for the WC after and before the demulsification test (25% before and 24.9% after). The greatest reduction in the WC was verified for test T3 (high WC), in which the WC diminished from 45 to 17.0%.

Similar results were obtained for tests T4, T5, and T6, whose emulsions were prepared with 25, 35, and 45% WC, respectively. The aqueous phase used in the emulsion preparation was a brine (NaCl) solution with a concentration of 30 000 ppm of NaCl. Concerning the demulsification results, no water separation was verified for T4 (25% WC). Conversely, the
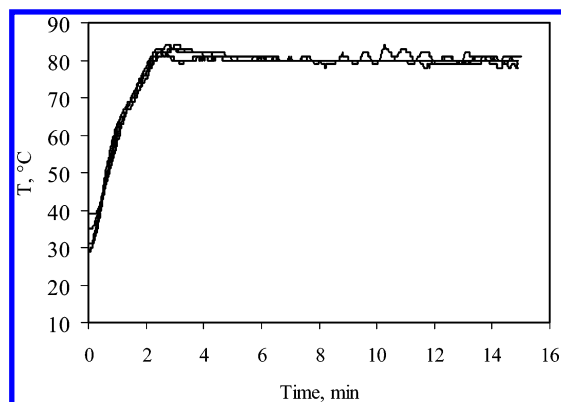
Figure 1. Temperature profiles during demulsification tests: five repetitions of the run T3.

Figure 2. Emulsion DSD before and after the demulsification process for test T4.

deepest reduction in the WC was reached in T6 (high WC), with the WC diminishing from 45 to 24.7%.

According to Figure 2, the DSD did change during the microwave demulsification process in T4. Although no free water was observed after this run, a coalescence process played a role during the demulsification, resulting in the formation of a new population of bigger droplets. As a consequence, the final emulsion presented a trimodal distribution of size of water droplets.

The DSD of the emulsion samples can also influence the efficiency of the demulsification process, once the coalescence rates and the sedimentation velocity of the droplets depend closely upon the diameter of the droplets.[3] However, because, in our experiments, the samples were stirred throughout the tests, the sedimentation velocity of droplets did not influence the demulsification results. The initial DSD of the emulsions did change between tests (see Table 2). Nevertheless, these changes in DSD do not seem to be enough to cause a clear effect on the demulsification performance. Considering the tests T1, T2, and T3, the emulsion used in test T3 (WC = 45%) had the lowest D(0.5) value; however, this test resulted in the highest free water amount. Conversely, for the tests T4, T5, and T6, the emulsion used in the test T6 (WC = 45%) had the highest D(0.5) value and provided the highest demulsification efficiency. Therefore, any DSD effect in the phase separation must be masked by a more predominant WC effect.

The emulsion composition effect on the dielectric heating can be inferred through the analysis of the results obtained for tests T1−T6. Thus, the lower the WCs in the emulsion sample, the greater the energy that might be applied to the sample will reach the set-point temperature. This effect is well-known, has been reported in the microwave literature,[10,12] and can be described mathematically through the so-called "dielectric heating equation"

$$p = 2\pi f \epsilon_0 \epsilon'' E^2 = \sigma E^2 \qquad (1)$$

where the power dissipated per unit volume (p) is related to the permittivity of free space (ϵ_0), the loss factor (ϵ''), the electric-field intensity (E), and its frequency (f). Because the electrical conductivity (σ) effects are usually included within the loss factor, it is evident from the equation above that the power dissipation is proportional to the electrical conductivity. As a consequence, the greater the WC in the emulsion, the greater will be the power dissipation per unit volume of the sample and thus the heating effect. In this sense, the required energy to raise the emulsion temperature up to 80 °C was 303 kJ for test T1 (with an emulsion WC of 25%) and 143 kJ for test T-3 (with an emulsion WC of 45%).
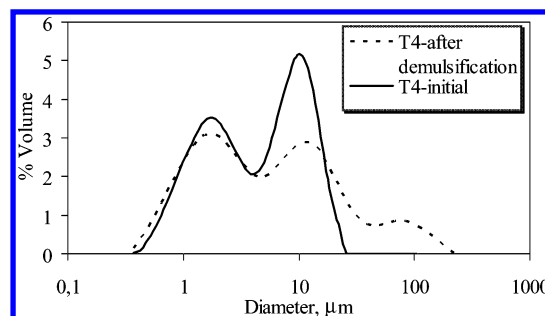
The previous results are of great interest for the desalting process of crude oils, where the emulsion WC may constitute an important operation variable during the process. A typical desalting plant involves six major steps, including separation by gravity settling, chemical injection, heating, addition of fresh or less salty water, mixing, and electrical coalescing.[21] The emulsion formed during the mixing process that enters into the desalting vessels may contain up to 10% WC. Industrial experience has shown that dehydration (or demulsification) efficiencies around 95−97% may be achieved during the desalting of crude oils similar to that studied here. Indeed, conventional heating is generally applied to reduce the crude oil viscosity and reach practical sedimentation rates. Consequently, improved demulsification rates may be achieved during the desalting process with the help of microwave irradiation that can be used in combination with the conventional process, to treat a fraction of the emulsion containing high WCs. According to the microwave demulsification results presented before, the increase of the WC of the emulsion fed into the "microwave desalter" may result in greater efficiencies and lower energy costs. Moreover, improved droplet contact (coalescence) may be attained during the demulsification process when sample stirring is performed. Demulsification tests using microwave irradiation carried out in the absence of agitation (these results are not included in this paper) with emulsions containing 45% WC did yield little emulsion resolution.

3.3. Influence of Salinity on Demulsification Efficiency. As discussed before, the dielectric heating is influenced by the salt content in the aqueous phase. It is also well-known that the existence of ionic species in the media enhance the heating efficiency of the mixture. Besides, the salt contents may also play a role over the interfacial properties of the emulsion and over its stability.[22−24] For all of these reasons, the influence of the salt content on the demulsification performance was studied. A set of experiments were conducted using brine solutions prepared with concentrations of 15 000 and 30 000 ppm of NaCl. The tests T3, T6, and T7 were performed using emulsions containing 45% WC and different salt contents in the aqueous phase. As reported in Table 2, the increase in the salt content leads to a reduction on the microwave energy required to raise the temperature up to the set point, resulting in a more efficient heating. As a consequence, because the energy applied to the emulsion is decreased, the reduction in the WC of the final emulsion because of the demulsification process tends to be quite limited. This reduction on the separation efficiency with

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the increase of the salt content (or ultimately of the ionic strength) could be explained by the reduction on the power applied by the microwave device. In this way, the microwave interaction with the polar species in the interfacial film is expected to be poorer, resulting in weaker perturbations of this interface and, then, in reduced coalescence rates. Additionally, changes of the salt content may modify the partitioning of the surfactant species[23] and may even form new phases (e.g., micelles)[25] or also affect the colloidal stability.

To better understand the impact of the ionic strength on the demulsification process, a set of experiments was carried out by varying the salt contents and the aqueous phase pH. Surely, the pH also influences the partitioning of the surfactant species between water and oil phases, the interfacial properties of the emulsion,[26,27] and may also modify the type of emulsion formed (W/O or O/W) when dealing with high WC levels. It is generally accepted that increasing the pH produces ionic surfactant species that favor the formation of stable O/W emulsions.[22] General references on the effect of the formulation of emulsion properties report that the emulsion stability finds its minimum at the so-called optimum formulation at which the surfactant affinity is the same for both water and oil phases.[28,29] In the case of a W/O emulsion, the surfactant exhibits more affinity for the oil phase (lipophilic type); hence, an increase of the medium hydrophilicity (as produced by an increase of pH) would decrease stability, whereas a decrease of hydrophilicity (as produced by an increase in salinity) would increase stability.[29,30]

3.4. Influence of pH on Demulsification Efficiency. Demulsification tests T8−T13 were carried out at different salt content and pH values. After the emulsion preparation, the nature of the emulsion, whether it was oil or water continuous, was determined by adding a droplet of the emulsion to the pure mineral oil phase or pure aqueous phase, according to the procedures described elsewhere.[22] All of the emulsions prepared here had been perfectly homogenized in the mineral oil, indicating that their nature was always W/O emulsions.

Once the increase of the pH of the emulsion was accomplished by raising the NaOH concentration in the system and the addition of electrolytes in the aqueous phase favored the dielectric heating, the experiments involving emulsion with higher pH values (9.5 and 12.0) required lower energy levels to reach the same temperature set point. Besides, experiments carried out at pH 9.5 yielded final WC values comparable to those obtained by the experiments conducted at pH 7.0. When the demulsification results at these pH values (7.0 and 9.5) were confronted in the presence of 30 000 ppm of NaCl (see tests T6 and T9 in Table 2), a slight increase of the demulsification efficiency is verified for the emulsion at pH 7.0. However, as discussed before, this slight difference on the final WC may be due to the reduction in the energy applied during the experiment at higher pH.

Experiments carried out at pH 12.0 were run in duplicates and yielded final WC results quite different from those obtained by tests conducted at lower pH values. Considering emulsions at pH 12.0 and exempt of salts (tests T10 and T11), the total energy applied during the demulsification process was lower
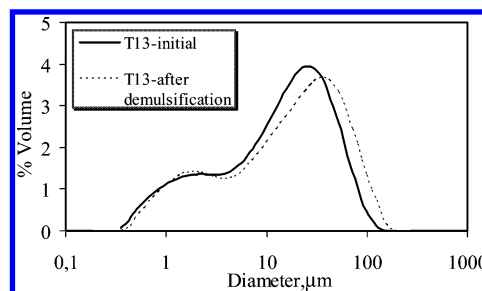

Figure 3. Emulsion DSD before and after the demulsification process for test T13.

than in the experiments using emulsions with pH 7.0 or 9.5. Despite this lower energy input, these tests at pH 12 provided highly efficient demulsification, which can be explained by the reduced stability of W/O emulsions with the increase of the pH, as discussed in section 3.3, and the microwave effects were apparently independent from that. Indeed, it should be pointed out that the resolved water obtained with these tests at pH 12 were very different from those obtained with tests run at other conditions, looking dirty and opaque, suggesting that a sort of micellization in the aqueous phase played a role, and then, portions of the oil remained dissolved in the aqueous phase. For industrial purposes, this situation may be avoided once it may increase the volume of oily water sent to the treatment facilities.

Conversely, no free water was observed after the demulsification tests were performed with emulsions at pH 12 containing 30 000 ppm of NaCl (see tests T12 and T13 in Table 2). Besides, DSD results for these tests revealed that the DSD curves before and after each demulsification run were essentially kept constant. Figure 3 shows the DSD results for T13. Note that, although these runs involved low-energy levels, some separation or coalescence would be expected to happen, as occurred for the test T9, which was conducted at pH 9.5 but had comparable energy levels and the same initial WC, DSD, and salt contents. These results suggested that the NaCl species at that higher pH might contribute to render improved stability to the water droplets in the emulsion.

3.5. Influence of Temperature on the Demulsification Efficiency. To assess the effect of the temperature (and ultimately the viscosity) on the demulsification performance, a series of experiments were conducted with similar emulsions at different temperature set points, such as 80 °C (T3), 95 °C (T14 and T15), and 130 °C (T16 and T17). When the final WC of the emulsions after the demulsification is compared (Table 2), one can infer a straight relationship between the demulsification efficiency and the temperature. Experiments conducted at the highest temperature yielded a huge reduction in the final WC, from 45 to 2.6% in the test T17 and from 45 to 5.6% in T16, which represents demulsification efficiencies of about 94 and 87%, respectively, not too far from the demulsification efficiencies observed during actual desalting plants, as described in section 3.2. When these latter tests were confronted with run T1, which involved the highest applied energy amount and negligible separation, note that the demulsification is not guaranteed by intense energy application solely. Finally, one should consider that, at enhanced temperatures, besides reducing the viscosity, higher levels of applied energy are required, contributing to an improved demulsification performance. Therefore, both the viscosity reduction effect and the enhanced energy should contribute toward the increase of demulsification efficiency. Again, even though the same experimental conditions were used for both T16 and T17, their demulsification results

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were quite different, probably because of slight experimental fluctuations during emulsion preparation and the resulting microwave energy irradiated to each emulsion.

4. Conclusions

In this paper, an experimental study was conducted to evaluate the effects of a set of operating variables on the demulsification performance through microwave irradiation. Microwave irradiation tests were performed using a commercial microwave reactor system, which was operated in a batch for 15 min. The results from this study support the conclusion that an increase of the microwave energy applied to a sample leads to an enhanced demulsification. Therefore, any factor that improves the absorption of this energy by the emulsion may favor the demulsification, unless this factor also contributes to the emulsion stability. For instance, at a high WC value (45%), dielectric heating was favored, allowing for demulsification with the highest efficiency among all tests, except when dealing with high pH and salt contents, which are supposed to improve the emulsion stability. Besides, the increase in the salt content leads to a reduction on the microwave energy required to heat the system during controlled-temperature experiments, yielding poor demulsification results.

The best demulsification results were achieved when dealing with emulsions involving high WC contents (45%) at pH 7.0, exempt of salts and under the highest temperature. It should be highlighted however that the microwave irradiation procedure presented here was able to provide satisfactory demulsification results for different water-in-heavy crude oil emulsions with small droplet sizes at a very short time (15 min). As a final remark, care must be taken, if we are to apply microwave irradiation to demulsify crude oil emulsions involving high pH values and salt contents simultaneously. Reasonable demulsification results can be achieved using microwave irradiation when only one or the other condition occurs.

Further studies will be made to investigate the microwave demulsification on a broader range of conditions and also to predict the demulsification efficiency and variance based on the emulsion properties and the operation conditions.

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