^{1}H low- and high-field NMR study of the effects of plasma treatment on the oil and water fractions in crude heavy oil

Hercílio D.A. Honorato [a], Renzo C. Silva [a], Cleiton K. Piumbini [b], Carlos G. Zucolotto [b], André A. de Souza [c], Alfredo G. Cunha [a,b], Francisco G. Emmerich [b], Valdemar Lacerda Jr. [a], Eustáquio V.R. de Castro [a], Tito J. Bonagamba [c], Jair C.C. Freitas [a,b,*]

[a] LabPetro – Laboratório de Pesquisa e Desenvolvimento de Metodologias para Análise de Petróleos, Departamento de Química, Universidade Federal do Espírito Santo, Av. Fernando Ferrari, 514, 29075-910 Vitória, Espírito Santo, Brazil
[b] Departamento de Física, Universidade Federal do Espírito Santo, Av. Fernando Ferrari, 514, 29075-910 Vitória, Espírito Santo, Brazil
[c] Instituto de Física de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560-970, São Carlos, SP, Brazil

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ABSTRACT

The chemical and physical properties of a Brazilian heavy oil submitted to plasma treatment were investigated by ^{1}H low- and high-field nuclear magnetic resonance (NMR) combined to the characterization of rheological properties, thermogravimetry and measurement of basic sediments and water (BSW) content. The crude oil was treated in a dielectric barrier discharge plasma reactor, using natural gas, CO_2 or H_2 as working gas. The results indicated a large drop in the water content of the plasma-treated samples as compared to the crude oil, giving rise to a reduction in the viscosity. No significant chemical change was produced in the oil portion itself, as observed by ^{1}H NMR. The water contents determined by ^{1}H low-field NMR analyses agreed well with those obtained by BSW, indicating the low-field NMR methods as a useful tool for following the effects of plasma treatments on heavy oils, allowing the separation of the effects caused on the water and oil fractions.

1. Introduction

^{1}H nuclear magnetic resonance (NMR) has been widely used for decades to provide information about the chemical and physical properties of different types of light and heavy oils, including especially the indirect evaluation of viscosity and the measurement of diffusion coefficients [1–5]. ^{1}H NMR is also routinely used for the petrophysical characterization of porous rocks, allowing the measurement of rock porosity and permeability, among other properties [6–9]. ^{1}H low-field NMR presents a number of advantages when compared to other methods of oil analysis, including its non-destructiveness, low cost, reasonable sensitivity and the possibility of in situ measurements [9–12].

Usually such investigations involve ^{1}H NMR measurements performed at magnetic fields of low magnitude, aiming the assessment of the distribution of longitudinal (T_1) and/or transverse (T_2) relaxation times associated with the protons contained in the studied fluid. Both relaxation processes are commonly multiexponential in crude oils, with the mean T_1 and T_2 values decreasing with the increase of the oil viscosity. Empirical correlations sometimes combined to statistical methods of analysis are then used to infer about the viscosity of the oil [1,2,4,9]. In the case of fluids trapped in a porous rock, the strong influence of the restricted pore size on the T_1 and T_2 values allows the achievement of information on the petrophysical properties of the rock [6]. Usually the T_1 and T_2 measurements are carried out with the use of the inversion-recovery and the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequences, respectively. The relaxation time distributions are then obtained by the inverse Laplace transform (ILT) of the time-domain signal [9,13].

NMR experiments conducted at low magnetic field strengths (typically below 100 mT) are preferred for well-logging purposes mainly due to the effects of magnetic field inhomogeneities associated with the magnetic susceptibility contrast between rock grains and pore fluid, which increase linearly with the field [10,14–16]. Magnetic field strengths in this range are nowadays easily produced by commercially available magnets used in well-logging tools, which employ the "inside-out" NMR design (i.e., the detected signal comes from the material located within the formation, thus outside the NMR tool) [10–12]. From the point of view of benchtop analysis, the main drawback of low-field NMR experiments is the lack of frequency resolution to allow the differentiation of chemical shifts. Thus, it is sometimes necessary to complement the NMR

* Corresponding author at: Departamento de Física, Universidade Federal do Espírito Santo, Av. Fernando Ferrari, 514, 29075-910 Vitória, Espírito Santo, Brazil. Tel.: +55 27 4009 2483; fax: +55 27 4009 2823.
E-mail address: jairccfreitas@yahoo.com.br (J.C.C. Freitas).

relaxometry results with high-field NMR spectroscopy methods, aiming a deeper understanding of the chemical properties of oils and derivatives [15,17].

Plasma treatment has been investigated in recent years as a promising conversion method for different kinds of hydrocarbons [18–20], including some studies on heavy oils [21–23]. In this work, we report a study of the changes occurring in a plasma-treated Brazilian heavy oil containing emulsified water using ^{1}H low-field NMR relaxometry as the main characterization tool. The chief motivation was to investigate and to understand the reasons for the changes in viscosity of heavy crude oil submitted to plasma treatment. ^{1}H high-field NMR was also used in order to investigate the chemical changes brought about by the plasma treatment. The crude and plasma-treated oil samples were further characterized by rheological measurements, thermogravimetry (TG) and determination of bottom sediments and water (BSW) contents. The combined results of these methods showed that the water content in the crude oil was severely reduced as a consequence of the plasma treatment, leading to a significant drop in the viscosity of the oil–water mixture. Good agreement was obtained between the NMR-derived water contents and the BSW values corresponding to the crude and plasma-treated oils. On the other hand, no significant change in the viscosity of the oil fraction itself was observed, as detected by ^{1}H low-field NMR relaxometry.

2. Experimental section

2.1. Materials

The starting material used was a Brazilian heavy crude oil with an API gravity of 10.1, containing emulsified water. This material was treated in a dielectric barrier discharge (DBD) plasma reactor [24], using different plasma gases: natural gas (NG), CO_2 and H_2, with reaction times of 1, 1.5 and 4 h, respectively. The labels of the samples together with the experimental methods of plasma treatment and characterization are summarized in Fig. 1. The plasma treatments were conducted using the apparatus depicted in Fig. 2. The reactor was a stainless steel box with dimensions $30 \times 30 \times 37$ cm^3. The top electrode was made of brass, involved in silicone rubber and placed inside a glass vessel, making the dielectric barrier. An insulating Teflon cylinder with a wire in its center connected the top electrode to the external part of the reactor. The bottom electrode consisted in a set of six spinning metallic wheels with a diameter of 17 cm. The two electrodes were set ca.
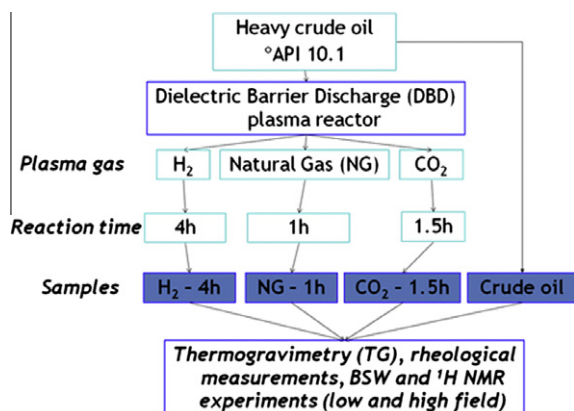

Fig. 1. Summary of the experimental methods of plasma reaction and characterization of the oil samples.

2 cm apart. First, the crude oil was placed inside the reactor, filling it up to the height of the spinning axis of the bottom electrode. The high voltage was generated by a transformer coupled to a Variac, as illustrated in Fig. 2. After closing the system and changing the atmosphere to the working gas of interest (NG, CO_2 or H_2), the wheels were put to spin at 90 rpm, dragging the oil and filling the space between the electrodes. Produced water was collected as vapor in the reactor exit and as liquid phase inside it. The plasma treatments were performed using a fixed voltage of 13 kV, at an internal temperature of (65 ± 5) °C. The times of the plasma treatments varied from 1 to 4 h, depending on the achievable working time of the reactor for each gas in the conditions used for the treatments.

2.2. Methods of characterization

2.2.1. Low-field ^{1}H NMR relaxometry

The low-field ^{1}H NMR experiments were performed at room temperature (27.5 ± 0.5) °C in a Maran-2 Ultra NMR spectrometer from Oxford Instruments, operating at 52 mT (^{1}H NMR frequency of 2.2 MHz), using a RF probe with 51 mm diameter. The CPMG pulse sequence was employed for the T_2 measurements, with $\pi/2$ and π pulse lengths of 8.0 and 14.8 μs, respectively, and an inter-pulse delay of 100 μs. 32,768 echoes (with 1 point per echo) were recorded for each transient and 16 transients were added to get the final time-domain signal, with a recycle time of 10 s between successive transients. The T_1 measurements were performed using the inversion-recovery method, with the same pulse lengths above, inter-pulse delays varying from 100 μs to 10 s and four added transients for each point. At least five independent CPMG experiments and three independent inversion-recovery experiments were carried out for each sample, in order to determine the mean T_1 and T_2 values and estimate the experimental uncertainties. The T_1 and T_2 distribution curves were computed by the ILT of the time-domain signals, using the WinDXP® software provided by Resonance Instruments [25]. The T_2 measurements were also recorded as a function of the temperature for a selected sample (CO_2 plasma-treated oil), in order to investigate the correlation between T_2 and the temperature-dependent viscosity. In such experiments, the sample was first pre-heated in a dry bath at temperatures ranging from 38 to 75 °C. Next, the sample was put in the NMR probe for 2 min to allow temperature stabilization prior to the NMR experiment. The sample temperature was measured at the beginning and the end of the experiment (which lasted ~4 min), with the aid of an optical temperature sensor (Minipa MT-350), allowing the determination of the average temperature and its uncertainty.

2.2.2. High-field ^{1}H NMR spectroscopy

The high-field ^{1}H NMR experiments were conducted using a Varian INOVA 400 spectrometer operating at 9.4 T (^{1}H NMR frequency of 399.84 MHz). Single pulse experiments were run with static samples, using a 7-mm Doty probe, with $\pi/2$ pulse length of 5.5 μs, recycle delay of 6.0 s and acquisition time of 600 ms. Each free induction decay (FID) was averaged with 16 scans. ^{1}H NMR spectra were obtained by Fourier transform (FT) of the FIDs, being externally referenced to tetramethylsilane (TMS). The samples were heated to 40 °C and then transferred and sealed in 6-mm diameter glass tubes. The NMR experiments were conducted at room temperature, after allowing the samples to cool down before starting acquisition.

2.2.3. Thermogravimetry (TG)

The TG curves were recorded on a Shimadzu instrument (TGA-50H), from room temperature up to 900 °C, with a heating-rate of 10 °C/min, under N_2 flow (60 mL/min). The samples
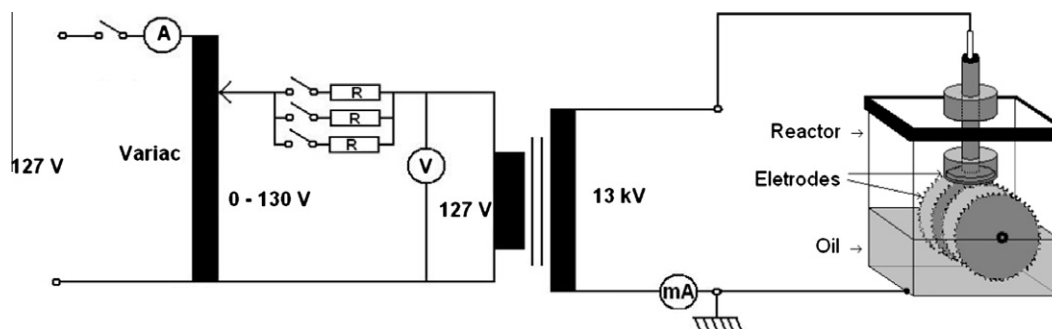
Fig. 2. Apparatus used for plasma treatments of the oil samples.

with 10–15 mg initial weight were placed in open platinum crucibles for these experiments.

2.2.4. Rheological properties

The rheological properties of the oils were measured in a rheometer from Anton Paar (RheolabQC) at 70 °C, with shear rate (γ) ranging from 2 to 200 s^{-1}. Dynamic viscosity measurements as a function of the temperature were also conducted for a selected sample (CO$_2$ plasma-treated oil), in the range 40–80 °C, with a fixed shear rate $\gamma = 50$ s^{-1}.

2.2.5. Bottom sediments and water (BSW)

The BSW contents were determined according to the ASTM D4007-02 standard [26], adapted for the analysis of heavy oils. The samples were dissolved in saturated toluene and then centrifuged at 2000 rpm for 15 min, after a period of 30 min in a bath at 80 °C.

2.2.6. Elemental analysis

The carbon, hydrogen and nitrogen contents of the crude and plasma-treated oils were measured using a Leco CHNS932 instrument.

3. Results and discussion

3.1. Physical and chemical properties of the plasma-treated samples

The rheological measurements (Fig. 3a) showed a marked reduction in the viscosity of the plasma-treated oil samples, when compared to the crude oil. For low shear rates ($\gamma < 50$ s^{-1}), the lowest viscosity was found for the sample prepared with the CO$_2$ plasma. Whereas this indicates a positive effect of the plasma treatments, the TG results (Fig. 3b) evidenced that the viscosity drop was accompanied by a substantial reduction in the water contents for all plasma-treated samples, following roughly the same trend observed for the viscosity reduction. These facts suggested that the water loss occurring during the plasma treatments was a key factor determining the reduction in the viscosity of the oil samples. The treatment in the DBD plasma reactor caused the destabilization of the water–oil emulsion and the consequent water release, resulting in a reduced water content of the plasma-treated oils. This was confirmed by the BSW contents measured for the crude and the plasma-treated oils. These values are given in Table 1, together with the viscosity values at a fixed shear rate, the water contents calculated from the low-field ^{1}H NMR relaxometry analysis and the atomic H/C ratio calculated for the oil fraction (see below).
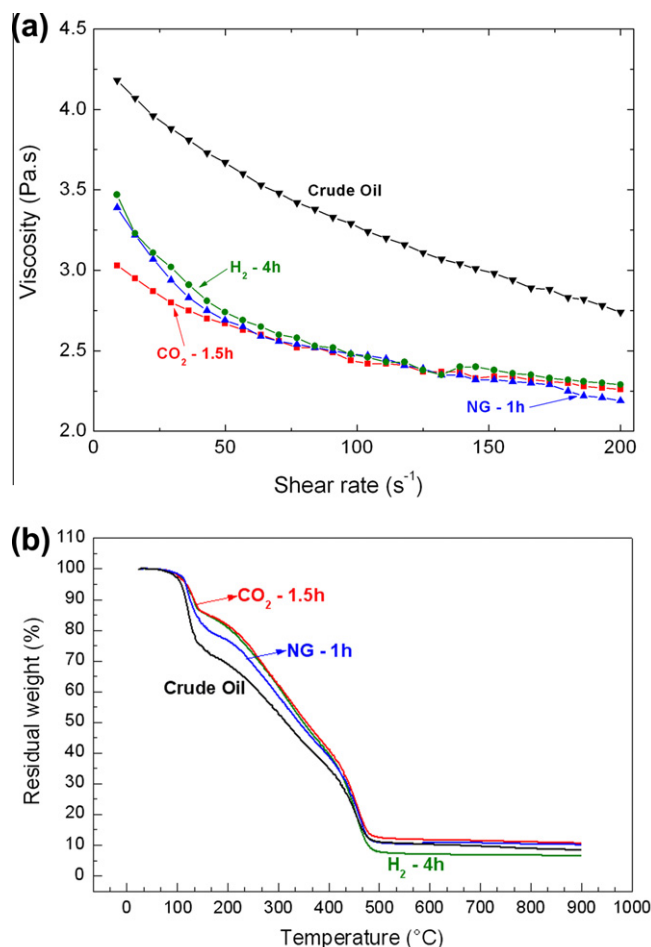

Fig. 3. Rheological analysis (a) and TG curves (b) for the heavy crude and the plasma-treated oil samples.

3.2. NMR analysis

Whereas the TG and rheological measurements give information on the overall behavior of the oil–water mixtures, the use of ^{1}H low-field NMR relaxometry and ^{1}H high-field NMR spectroscopy allows a separate analysis of the effects of the plasma treatments on the water and oil fractions present in each sample.

3.2.1. ^{1}H low-field relaxometry

Fig. 4 shows the T_1 and T_2 distribution curves obtained for the set of analyzed samples. The two peaks corresponding to oil (first peak, at lower T_1 and T_2) and water (second peak, at higher T_1 and T_2) were easily visible in both distributions [9,16]. These two

Table 1
Viscosity values, water contents (obtained by BSW measurements and ^{1}H low-field NMR) and atomic hydrogen to carbon ratio calculated for the oil fraction in crude and plasma-treated oil samples.

Sample	Viscosity[a] (Pa s)	BSW (%)	NMR[b] (%)	H/C[c] (oil)
Crude oil	3.96	21.6 (5)	25.3 (1)	1.45 (4)
NG – 1 h	3.11	12.6 (5)	15.7 (2)	1.46 (4)
CO_2 – 1.5 h	2.87	12.0 (5)	12.2 (1)	1.49 (5)
H_2 – 4 h	3.07	10.5 (5)	10.2 (1)	1.53 (4)

[a] Value obtained for $\gamma = 22.5\ s^{-1}$.
[b] Calculated from the relative area of the water peak, after calibration with deionized water.
[c] Atomic hydrogen to carbon ratio corresponding solely to the oil fraction; calculated from the elemental analysis data, after correcting for the different water contents of each sample determined from low-field NMR.
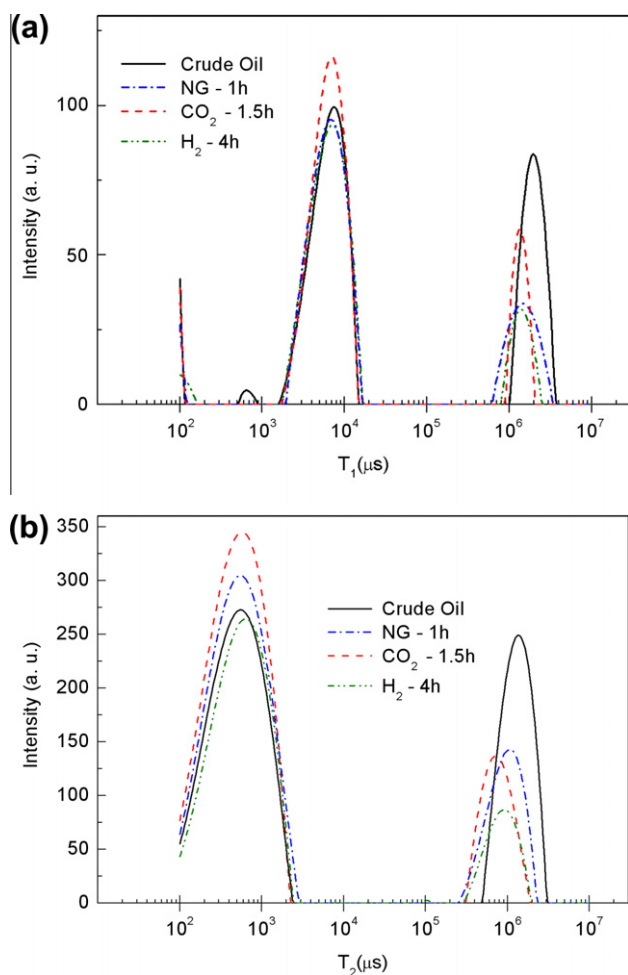

Fig. 4. T_1 (a) and T_2 (b) distributions for the heavy crude and the plasma-treated oil samples.

peaks appeared at very different time scales due to the high viscosity of the heavy oil. Thus, the T_2 peak values of the oil fraction were

~1 ms, whereas the values corresponding to water were ~1 s. The T_1 values showed a similar trend, being ~7 ms and ~1–2 s for the oil and water peaks, respectively. The precise T_1 and T_2 peak values for each sample are given in Table 2. It is interesting to observe that the T_1 values were well above the corresponding T_2 values for the oil peaks, showing that the viscosity is indeed the determinant factor for transverse relaxation in this case. As for the water peak, the T_2 and T_1 values were quite close (although still $T_1 > T_2$). However, both values were considerably lower than the values corresponding to pure bulk water determined in the same instrument ($T_1 \cong T_2 \cong 3$ s), which is clearly a consequence of the facts that water is not in the pure form in the crude and also because surface effects affect the transverse and longitudinal ^{1}H relaxation for the water droplets [9].

The reduction in water content of the plasma-treated samples was clearly observed as a decrease of the corresponding water peaks in the T_1 and T_2 distributions. On the other hand, the oil peak values were little changed by the plasma treatment; the water peak values changed more, probably as a consequence of the change in the size of the water droplets. The changes in peak values and in peak areas among the different samples followed the same general trends for T_1 and T_2 distributions. As the T_1 distributions were obtained from time-domain data with lower signal-to-noise ratio (due to the lower number of transients and of points recorded in the longer inversion-recovery experiments as compared to CPMG ones), the detailed quantitative analysis of the distributions was performed only for the T_2 measurements.

From the areas corresponding to each peak in the T_2 distributions shown in Fig. 4b, the water contents of each sample can be computed. The values of the relative areas corresponding to the water peak are given in Table 2. Although the areas under each T_2 peak are in the same ratio as the number of ^{1}H nuclei associated with the respective component, this information cannot be used alone to determine the relative weight proportion of water and oil, since the number of hydrogen atoms per mass unit is not the same in both phases (i.e., the oil fraction has a relative hydrogen index different from unity) [9,16]. A previous calibration procedure is then required for the calculation of the water contents, which was made using the T_2 peak area obtained in a separate CPMG experiment carried out with a known mass of pure water. The water contents determined in this way are given in Table 1 for each analyzed sample, in comparison with the corresponding BSW values. As it can be seen, a quite good agreement was achieved between the BSW and the NMR-derived values, especially for the CO_2 and H_2 plasma-treated samples. The discrepancy in these values was higher (although still modest) for the samples with larger water content, which can be related to a limitation of centrifuge methods when applied to heavy oils containing emulsified water. In this regard, low-field ^{1}H NMR methods appear as a good alternative for the analysis of oil–water mixtures present in heavy crude, without the necessity of laborious separation methods, allowing a direct and fast quantitative analysis based on the T_2 distribution profiles.

3.2.2. [1]H high-field spectroscopy

The ^{1}H low-field NMR results described above showed that the plasma treatments produced little change in the mean T_2 values
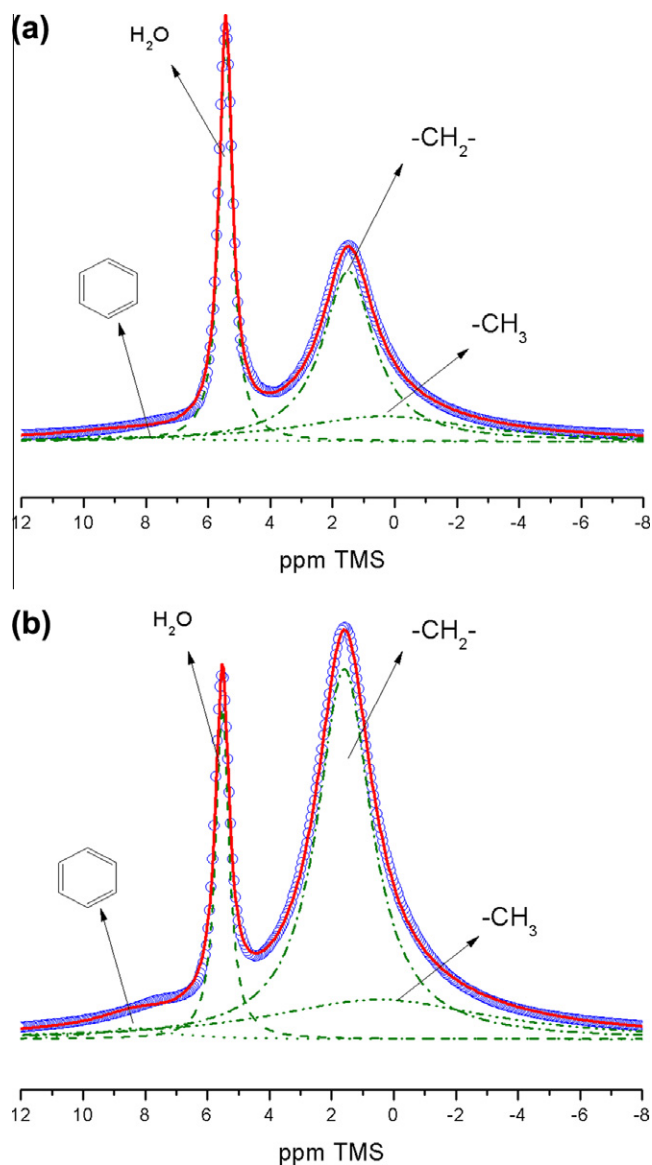
Table 2
T_1 and T_2 values corresponding to the peaks in the distribution curves, along with the relative area of the water peak in the T_2 distributions.

Sample	T_2 – 1st peak (ms)	T_2 – 2nd peak (s)	Relative area – 2nd peak (%)	T_1 – 1st peak (ms)	T_1 – 2nd peak (s)
Crude Oil	0.56 (3)	1.32 (7)	32.2 (5)	7.3 (3)	1.9 (1)
NG – 1 h	0.57 (2)	1.05 (9)	21.0 (4)	7.2 (3)	1.4 (1)
CO_2 – 1.5 h	0.58 (2)	0.76 (4)	16.8 (2)	6.9 (2)	1.3 (1)
H_2 – 4 h	0.60 (5)	0.82 (5)	14.9 (5)	6.8 (2)	1.4 (3)

(a)

(b)

Fig. 5. ^{1}H high-field NMR spectra of the heavy crude (a) and the CO_2 plasma-treated oil (b). The points represent the experimental data, the solid red line is the overall fit and the dash/dotted lines are the spectral components for the fitting.

Fig. 6. T_2 distributions for the CO_2 plasma-treated sample obtained at different temperatures.

(and thus in the viscosity) of the oil fraction in the plasma-treated oil samples. In order to verify if any noticeable chemical change had or not been caused by the plasma treatments, ^{1}H high-field NMR spectra were recorded for the crude oil and for the CO_2 plasma-treated oil. Fig. 5 shows the spectra corresponding to these two samples. Both spectra were analyzed considering four partially superimposed components, associated with water (peak at chemical shift close to 5.5 ppm), aliphatic groups (methyl and methylene moieties, with chemical shifts in the range 0–2 ppm) and aromatic groups (chemical shift in the range 8–9 ppm) [27]. The latter component was minor in both spectra, contributing only with 2–3% of relative intensity. The water peak again showed a marked reduction in its relative area in the spectrum corresponding to the plasma-treated oil as compared to the crude one, in agreement with the low-field results. On the other hand, no change in the chemical shifts was detected for any of the chemical moieties identified in the spectra when comparing the crude and the plasma-treated oil. This is a strong indication, again in agreement with the low-field NMR relaxometry data, that the plasma treatments under the conditions used in this work did not produce important chem-
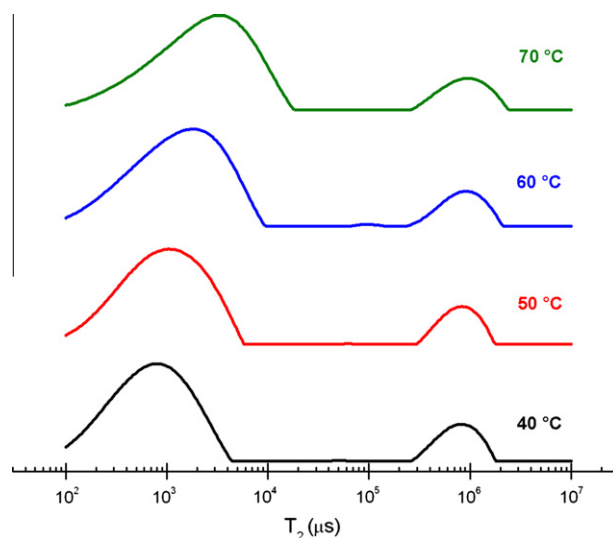
ical alterations in the oil fraction of the products. Accordingly, the H/C atomic ratio computed for the oil fraction (given in Table 1; values derived from elemental analysis after correcting for the water contents determined by ^{1}H low-field NMR) remained constant within experimental uncertainty for the crude oil and the plasma-treated oil samples.

3.2.3. Viscosity vs. T_2 correlation

In order to evaluate the viscosity dependence of the T_2 values, the CO_2 plasma-treated sample was taken again as representative of the set of heavy oils and a variable temperature study was carried out. Both ^{1}H low-field NMR relaxometry and rheological analysis experiments were conducted for temperatures in the range 38–75 °C. The temperature-dependent oil viscosity imparted then a strong temperature dependence to the ^{1}H NMR relaxation times [9,28,29], as it can be observed in the sequence of T_2 distributions shown in Fig. 6.

The oil peak in the T_2 distributions showed a systematic shift to higher T_2 values with the increase in the temperature (moving from 0.80 to 3.70 ms between 38 and 75 °C), clearly indicating the effect of oil viscosity reduction at higher temperatures [2,9,16,28,29]. On the other hand, the water peak moved only very slightly to higher T_2 values (changing from 0.83 to 0.98 s between 38 and 75 °C). In order to verify the T_2 vs. viscosity relationship, first the log-mean T_2 (T_{2LM}), defined as the value that bisects the area under the T_2 distribution curve [9,16], was computed using the whole distribution. It is well known from empirical models (established from the analysis of sets of oils with different viscosities) that T_{2LM} is related to the viscosity in many cases by a simple power law of the form:

$$T_{2LM} = \frac{A}{\eta^\alpha}, \qquad (1)$$

where η is the oil viscosity and A and α are constants. The exponent α is usually close to 1, depending on the oil type. A value $\alpha = 0.9$ was reported in Ref. [16], for example, whereas other authors assume $\alpha = 1$ (exactly) and include other parameters in the model (such as the hydrogen index) [28].

The log–log T_{2LM} vs. viscosity plot obtained from the temperature-dependent measurements on CO_2 plasma-treated oil is shown in Fig. 7a. The linear fitting was not a proper choice, indicating that no simple power law relationship (as given by Eq. (1)) prevailed in
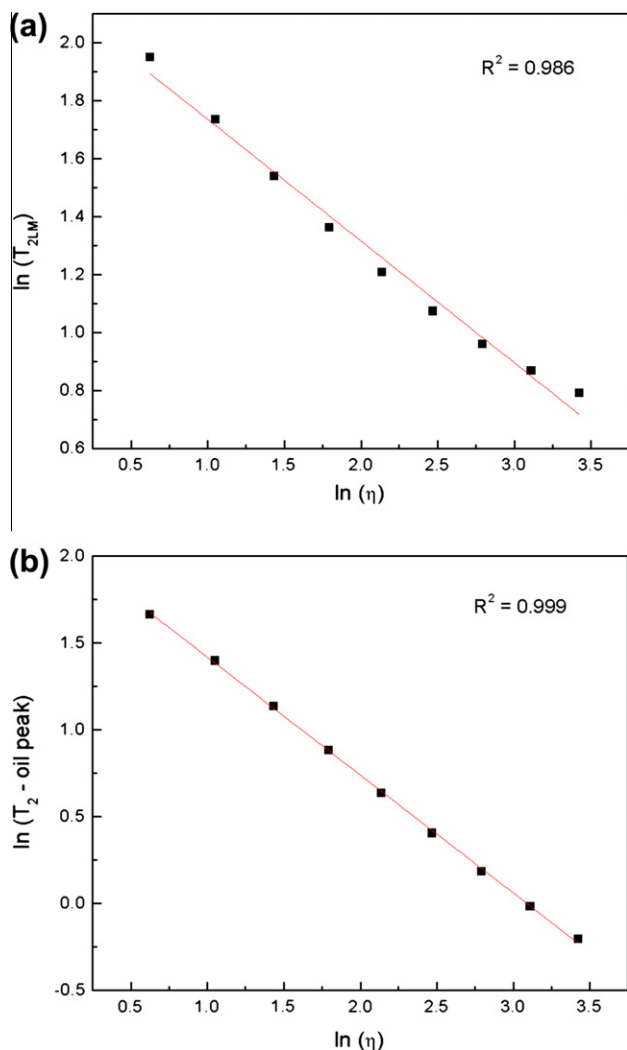
Fig. 7. T_2 vs. viscosity correlation plots constructed using the log-mean T_2 computed over the whole distribution (a) and the oil peak T_2 value (b). The solid lines are linear fittings, with the corresponding coefficients of determination (R^2).

changes caused by this type of plasma treatment. Whereas this does not allow a direct comparison between the different plasma-treated oils, the results presented here are illustrative of the effects produced in heavy oils by plasma treatments and of the usefulness of NMR methods (especially low-field NMR) for the analysis of the properties of these products. Methodical investigations will be conducted in the future about the effects of each plasma gas on the properties of the treated oils, using different reaction conditions – such as reaction time, filling factor of the reactor, and distance between the electrodes.

Although the viscosities of the samples were reduced after the plasma-treatments, ^{1}H low-field relaxometry results indicated that no significant change occurred in the viscosity of the oil fraction itself. The transverse and longitudinal ^{1}H relaxation times associated with the oil fraction remained essentially unaltered after the plasma treatments. The major effect caused by the plasma treatments was the extraction of water (naturally present as emulsified water in the heavy crude oil), with the consequent drop in the viscosity of the water–oil emulsion. ^{1}H high-field NMR spectroscopy corroborated this finding, revealing no change in the chemical shifts associated with any of the components identified in the spectra of crude and plasma-treated oils. Work is in progress to improve the plasma reactor design and the operational parameters aiming a more effective action on the heavy crude oil that can possibly lead to a significant viscosity reduction.

^{1}H low-field NMR relaxometry was also used to investigate the T_2 vs. viscosity correlation, by means of variable temperature experiments conducted in one of the plasma-treated oils. A good correlation was obtained, in agreement with previously reported empirical models, when the T_2 value corresponding solely to the oil fraction was used. Furthermore, the water contents in each of the crude and plasma-treated oils were directly computed from the relative areas of the oil and water peaks found in the T_2 distributions (after proper calibration of the NMR intensity using pure water). These values showed a satisfactory agreement with the BSW values. These results show then that ^{1}H NMR measurements (at low and high magnetic fields) are indeed useful for the study of the effects of plasma and possibly other treatments on heavy crude oils, allowing a detailed understanding about what happens separately to the oil and the water fractions without the need of laborious water separation procedures.

this case. This was indeed expected, since the sample was not composed of a single oil phase, but had substantial water content. A similar plot was then constructed, now using the T_2 value corresponding to the oil peak observed in the T_2 distributions. The plot shown in Fig. 7b exhibited a much improved linear relationship between ln (T_2) and ln (η), indicating a power law of the type given in Eq. (1) with an exponent $\alpha = 0.68$. It is important to observe that this correlation was obtained using the viscosity measured for the oil–water mixture, which is a reason for not expecting the α value found here to agree with the empirical models developed for oils. Even so the correlation was quite good, which is likely a consequence of the temperature dependence of the viscosity of the water–oil emulsion being dominated by the highly viscous oil fraction, as evidenced by the T_2 distribution curves shown in Fig. 6.

4. Conclusion

The combination of ^{1}H low- and high-field NMR methods allowed a detailed study of the effects of plasma treatment on the chemical and physical properties of a Brazilian heavy crude oil containing emulsified water. Different plasma gases and reactions times were used, in a first step towards the understanding of the

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