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Chemical Aspects of Onshore Crude Oils from the Carmópolis Field, Sergipe-Alagoas Basin, Brazil: A Case Study on the Industrial Process for Water−Oil Separation

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ABSTRACT: The importance of the Carmópolis field in Brazil for the exploration of onshore crude oil dates back to 1963. Currently still in operation, this is a major field, serving as a model for enhanced oil recovery tests. In this field, the differences in the physicochemical characteristics have awakened an interest in understanding the implications of the chemical composition of crude oils. Four blends of crude oil from this field were characterized using the SARA (saturates, aromatics, resins and asphaltenes) method and advanced methods such as energy dispersive X-ray fluorescence spectroscopy (EDX), laser desorption/ionization mass spectrometry (LDI-MS), infrared (IR), ultraviolet (UV), and thermogravimetric (TG) analysis. Of the four blends investigated, CEOL3 had the greatest affinity for water. The results for the SARA analysis did not reveal significant differences between the blends. The analysis of CEOL3 asphaltenes by IR spectroscopy revealed greater O−H stretching associated with water, and the TG indicated a more advanced state of thermal evolution compared with the other samples investigated in this study. Similarly, according to the EDX analysis, this oil sample had a greater affinity with produced water. Also, based on the UV analysis, the asphaltenes present in CEOL3 were of higher molecular mass compared with the other samples. Finally, the LDI-MS analysis of the blends showed a higher content of naphthenic acids and carbazoles in the CEOL3 sample which, together with the asphaltene content, is related to the stabilization of emulsions.

■ INTRODUCTION

Petroleum is considered to be one of the main products produced in modern society. Also referred to as crude oil, it is comprised of a mixture of hydrocarbons and other compounds with varying amounts of sulfur, nitrogen, and oxygen, which can considerably modify its volatility, specific gravity (density), and viscosity.[1] The characterization of the constituents of the oil provides information which is relevant to all production operations, from estimating existing reserves to planning the transportation, refining, and distribution of the final products.[2]

One of the principal aspects that affect the primary treatment of oil is the formation of crude oil-in-water or water-in-crude-oil emulsions. The formation of emulsions of the type water-in-crude-oil occurs with water contents ranging between 5 and 15%, and these emulsions are stable due to natural surfactants present in the oil, such as asphaltenes, resins, and naphthenic acids.[3,4] The presence of water in crude oil causes the corrosion and scaling of pipes and reactors,[5] and thus it is necessary to de-stabilize the emulsions formed to obtain commercial oil.[6] Also, incrustations can form during the refining processes, especially in the presence of salt and of sodium and calcium naphthenates. Studies on water-in-crude-oil and crude-oil-in-water interactions have been reported in the literature.[3,6−9] One of the main characteristics studied is the stability of water-in-crude-oil emulsions. Through the use of spectroscopy techniques, such as IR and UV, Li et al.[10] have demonstrated that emulsion stability is dependent on a combination of factors, and the crude oil fraction, with higher molecular weight, aromaticity, aromatic condensation, and carbonyl group concentration, promotes emulsion stabilization.

The effects of the resin and asphaltene contents, along with other factors, on the stability of water-in-crude-oil emulsions have been extensively studied over the years.[9,11−14] A useful approach to this field is to understand the mechanisms related to the stability of water-in-crude-oil emulsions, and this stability is directly affected by the complex composition of crude oils and their asphaltenes.[15] Synthetic water-in-crude-oil emulsions stabilized by a polymer/surfactant in rheology studies can aid an understanding of the influence of this chemical class of compounds on the emulsion behavior.[16] Recently, significant advances have been made in relation to the development of techniques for use in the area of petroleomics. In this regard, FT-ICR MS (Fourier transform ion cyclotron resonance mass spectrometry) has been employed in the study of emulsion interfacial materials, highlighting the influence of acidic and basic asphaltenes and oxygenated naphthenic species on emulsion stabilization.[17]

Due to the complexity of crude oil samples, separation techniques have been developed and used to characterize certain fractions. The SARA (saturates, aromatics, resins, and asphaltenes) method of crude oil fractionation has been described in the literature.[18−23] A portion of crude oil which is soluble in pentane or heptane, often referred to as maltene, can be separated by

decantation of the asphaltene fraction (insoluble portion), and it has macromolecular characteristics. Maltene is present in the heaviest fraction of crude oil.[24] It contains the remaining three fractions, saturates, aromatics, and resins, which are generally separated using liquid chromatography columns by percolation with organic solvents.[21]

The Sergipe-Alagoas Basin is located in northeastern Brazil and covers the states of Sergipe and Alagoas. Its onshore portion has an area of 13,000 km^2. One of the main fields belonging to the basin is Carmópolis, and its development can be divided into two stages: the first, known as CP-1-1-SE, occurred in 1963 and featured the confirmation of crude oil accumulation in the sediment area of the basin, while the second, known as CP-7-20-SE, occurred in 1965 and relates to the well drilling, which was marked by the verification of oil present in the fractured basement of the region, corresponding to an area of 100 km^2. According to the ANP (National Agency of Petroleum, Natural Gas and Biofuels),[25,26] the Carmópolis field has contributed to the largest onshore crude oil volumes produced in Brazil over the past 40 years. Currently, the Sergipe-Alagoas Basin has high prospects for offshore oil production in ultradeep waters with the Barra field.

The station belonging to the Carmópolis Field in the Sergipe-Alagoas sedimentary basin has four input lines of blends of crude oils from onshore wells. Of these, line 3 presents distinct physicochemical characteristics (higher concentration of water and gas from the upstream process and viscosity) in relation to the others, and the injection of greater amounts of demulsifiers is required to treat this blend (according to the technical field, line 3 (CEOL3) requires approximately 30% more of the same demulsifier used in other lines).

This study focuses on the chemical characterization of crude oils, with a view to understanding the relation between the oil composition and aspects observed in primary treatment which is based on the breaking of water-in-crude-oil emulsions to produced water separation. Specifically, the aim of this research was to carry out an advanced chemical characterization of the blends originating from the Carmópolis Field, Sergipe-Alagoas sedimentary basin, in order to elucidate problems associated with the emulsification of oils through their interaction with the produced water.

■ EXPERIMENTAL SECTION

Field of Study. The Carmópolis Field of the Sergipe-Alagoas Basin produces 500 m^3 of crude oil daily, accounting for 53.5% of the total oil production in the State of Sergipe in 2012 (7872.62 barrels of oil). The State of Sergipe holds the fifth position in the national ranking of oil exploration, and its activities can be divided into 78.3% onshore and 21.7% offshore exploration.[26−28]

The four crude oil blends investigated were collected through the combination of oils from many wells arriving at the primary treatment station through four pipelines. The blends, with an average BSW (basic sediment and water) content of 90% and an average API gravity of 21, were initially collected in a glass bottle with a capacity of 20 L. After a few minutes the natural separation of the aqueous phase occurred, and this was removed from the bottom of the bottle. The supernatant oil was then transferred to a plastic drum with a capacity of 5 L, and the samples were sent to the laboratory. In the laboratory, aliquots of ∼40 mL were immediately centrifuged at 2500 rpm in order to remove free residual associated water and placed in hermetically sealed glass vials with poly(tetrafluoroethylene) (PTFE)/silicone septa. The blends were identified as CEOL1, CEOL2, CEOL3, and CEOL4, respectively, for lines 1, 2, 3, and 4 of the station.

Density. The density of the crude oil blends was determined by the pycnometry method at 18 °C according to the standard method ASTM D70.[29]

Development and Application of the SARA Method. The methodology applied for the fractionation of the crude oil blends (SARA) was adapted from the method proposed by Vazquez and Mansoori.[21] An aliquot of 250 mg of the blend sample was submitted to the precipitation of asphaltenes in 10 mL of *n*-heptane according to the method described by Azevedo et al.[2] A predetermined mass of the soluble fraction (maltene) was transferred to a 50 mL round-bottom flask and then concentrated under reduced pressure and dried to constant weight to determine the fraction of light hydrocarbons (LH). The maltene of each blend was solubilized in 5 mL of *n*-heptane and transferred to an open chromatography glass column with 1.5 cm diameter and 20 cm length, previously filled with approximately 6.3 g of silica gel (Silica Flash G60; 70−230 mesh) packed with the aid of *n*-heptane. Elution was carried out with 40 mL of *n*-heptane (saturates fraction), 40 mL of toluene (aromatics fraction), and 40 mL of 90:10 toluene:MeOH (resins fraction), in succession, respecting the elution solvent limits, and the fractions were collected separately in glass vials with PTFE/silicone septa. To verify the presence of other polar fractions, the column was last eluted with 40 mL of MeOH. Each fraction was concentrated under reduced pressure in a rotary evaporator with the temperature varying between 40 and 100 °C, and the mass was then determined on an analytical balance.

Thermogravimetric Analysis. Thermogravimetric (TG) analysis was performed on the blends and their respective asphaltenes employing a Shimadzu TGA-50 analyzer and using N$_2$ as the purge gas at a flow of 40 mL min^{-1}. Approximately 8 mg of sample was heated from room temperature to 900 °C at a rate of 10 °C min^{-1}.

Infrared Spectroscopy. Infrared spectroscopy (IR) analysis was performed on the blends and their asphaltenes, in the range of 400−4000 cm^{-1}, using a PerkinElmer Spectrum BXFTIR system. The samples were prepared in the form of films, and KBr tablets were used. For the asphaltene samples the solid was macerated with KBr using an agate pestle and then submitted to hydraulic pressing. The blank analysis was performed using a tablet without the inclusion of the sample.

Ultraviolet Spectroscopy. For the ultraviolet (UV) analysis the solutions were prepared from blends of crude oils in tetrahydrofuran (THF; 0.1 mg mL^{-1}). A Genesys 10 UV scanning spectrometer (ThermoScientific) was used operating in scanning mode at a range of 190−400 nm. The blank was obtained employing only THF.

Energy Dispersive X-ray Fluorescence Spectrometry. The crude oil blends were characterized by energy dispersive X-ray fluorescence spectroscopy (EDX) on a Shimadzu EDX-720/800HS instrument equipped with a rhodium X-ray tube generator, a silicon detector, and a collimator (10 mm) with system cooling by liquid nitrogen. The working range varied between atoms Na−Sc (15 kV) and Ti−U (50 kV), comprising a period of atoms with atomic numbers of 11−92, and the total analysis time was 100 s, representing qualitative−quantitative analysis. The equipment was calibrated using a reference metal alloy standard material containing the following: Cr, 18.395%; Mn, 1.709%; Fe, 70.718%; Ni, 8.655%; Cu, 0.278%; Mo, 0.245%. During the analysis of the sample, a film is formed between the sheets of Mylar film (thickness, 0.05 mm).

Laser Desorption/Ionization Mass Spectrometry. The technique of laser desorption/ionization mass spectrometry (LDI-MS) was performed on an Autoflex III MALDI-TOF mass spectrometer (Bruker Daltonics, Billerica, MA, USA) with a Nd:YAG laser at 355 nm, applying a frequency of 100 Hz. Samples of the blends were prepared by solubilization in THF (100 mL mg^{-1}) and applied directly onto the MALDI plate (Bruker MTP 384 ground steel) by the method of dried droplets. The data were acquired in reflected negative mode, with an accelerating voltage of 19 kV in a detection range of 60−1000 Da. The data processing software Flex Analysis Version 3.0 (Bruker Daltonics) was used. The matrices 3-indoleacrylic acid (3-IAA) and 9-cyanoanthracene (9-CA) were tested in the analysis in MALDI-MS mode.

■ RESULTS AND DISCUSSION

Density. The results for the density of the blends determined by pycnometry at a temperature of 18 °C are showed in Table 1.

Table 1. Density and °API of Blends of Onshore Crude Oils Collected from the Carmópolis Field

blend	density (g ml⁻¹)	°API[a]
CEOL1	0.9369	19.53
CEOL2	0.9363	19.53
CEOL3	0.9737	13.82
CEOL4	0.9276	21.04

[a] $°API = (141.5/(\text{density of blends/density of H}_2\text{O})_{18°C}) - 131.5$.

The blend CEOL3 showed the highest density and consequently the lowest °API of the four blend samples under study, indicating that this sample is comprised of heavier oils in relation to the other blends. The extraction techniques enhanced the formation of emulsions in the case of this blend, and thus the injection of a greater amount of demulsifier was required. This enhanced formation of emulsion can be attributed to the possible presence of a high content of natural surfactants (e.g., asphaltenes, resins, and naphthenic acids) or the different chemical characteristics of the surfactants, these being directly associated with the formation of emulsions.[3,4] In this context, the fractionation and separation of crude oil into classes can be applied to determine the contents of these natural surfactants.

SARA Method. During the experiment an adaptation of the methodology proposed by Azevedo et al.[2] was applied, focusing on reducing the time and reagents required to determine the content of asphaltenes. The modification consisted of weighing out 250 mg of the blend sample in a test tube and adding 10 mL of n-heptane. The mixture was centrifuged at 2500 rpm for 5 min, and the asphaltenes were separated out by decantation. The procedure was repeated four times to yield the percentage of asphaltenes after oven drying at 60 °C for 6 h. Table 2 shows the contents of asphaltenes, LH, saturates, aromatics, resins, and polar compounds (CP) obtained through the SARA method for the blends.

The final recovery of the method was high with values above 90% for the SARA fractionation for all blends except CEOL1 (86.53 ± 0.58%). For the asphaltenes and LH fractions some values had a high confidence interval ($U = 95\%$, 2SD (standard deviation)) due to the complexity of the experimental procedure, particularly the transfer of maltene solubilized in n-heptane which can involve an asphaltene mass loss. The highest contents of asphaltenes were found in the blend CEOL3, with 10.42 ± 2.56% of asphaltenes in its composition; however, all blends

studied showed equivalent contents based on the uncertainty of the classical methods for asphaltene precipitation, such as IP143 and ASTM D3279. This indicates that considering only the content of asphaltenes does not explain the hypothesis that these compounds promote oil−water emulsion stabilization.[30,31]

For the saturates fraction, the highest percentage was obtained for the blend CEOL2 (55.39 ± 1.95%). For the aromatics fraction the blends CEOL1, CEOL2, and CEOL3 showed equivalent results (17−18%); however, CEOL4 presented a higher value, aromatics representing 20.44 ± 3.04% of its total composition.

According to Thompson[32] and Escobar et al.,[33] a plot of the aromatic fraction (toluene) versus saturates (n-heptane) provides an indication of the geochemical aspects of crude oils. Figure 1
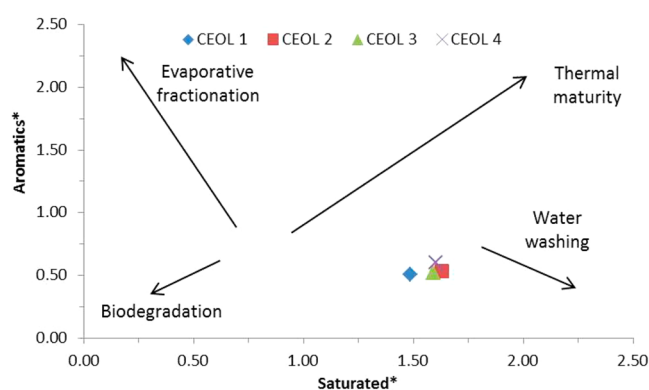
*Fraction Saturated and Aromatics divided by 35% for padronization

Figure 1. Graph of saturates versus aromatics fractions of the crude oil blends.

shows the saturates versus aromatics content divided by a factor of 35, to adjust the values to the graphical scale of the geochemical aspects. The saturates × aromatics correlation can be used to obtain information on geochemical aspects such as biodegradation, evaporative fractionation, thermal maturity, and water washing. Based on these parameters, the four blends studied presented the characteristics of oils not submitted to the biodegradation process and indicated that the oils had undergone a water washing process. This explains the affinity of these oils for the produced water, considering the BSW content of 90% found in the upstream process.

The third fraction in this study relates to the resins, accounting for approximately 5% of the composition of the four oil blends studied, considering the means and confidence intervals, with the highest value being obtained for the blend CEOL2 (5.72 ± 0.96%).

Table 2. Fractions of Saturates, Aromatics, Resins, Asphaltenes, Light Hydrocarbons (LH), and Polar Compounds (PC) for the Blend Samples

fraction[a]	for given blend			
	CEOL1	CEOL2	CEOL3	CEOL4
asphaltenes (%)	5.80 ± 1.79	9.40 ± 0.47	10.42 ± 2.56	8.11 ± 2.47
LH (%)	9.24 ± 1.75	9.10 ± 2.80	8.81 ± 2.22	4.37 ± 1.32
saturates (%)	50.47 ± 2.95	55.39 ± 1.95	54.14 ± 0.26	54.50 ± 2.03
aromatics (%)	17.25 ± 0.40	18.24 ± 1.02	17.63 ± 0.19	20.44 ± 3.04
resins (%)	3.45 ± 0.83	5.72 ± 0.96	5.46 ± 1.34	5.25 ± 1.55
PC (%)	0.32 ± 0.24	1.00 ± 0.23	1.17 ± 1.16	0.48 ± 0.40
recovery (%)	86.53 ± 0.58	98.85 ± 3.62	97.63 ± 1.15	93.15 ± 1.34

[a]Results expressed as mean ±2 standard deviations (SDs).

Finally, the column was eluted with methanol to give the PC fraction, this having the lowest contribution in the blends studied, the highest percentage being found for the blend CEOL3 (1.17 ± 1.16%), followed by CEOL2 > CEOL4 > CEOL1. The chemical composition of the blends by chemical classes (SARA) revealed no significant differences between the samples, notably in relation to their asphaltenes content. Thus, a relation between the chemical composition and the affinity of the blends for water could not be verified. Therefore, the affinity for produced water may be associated with differences in the chemical structures of the asphaltenes, which can be assessed by TG, IR, and UV.

Thermogravimetric Analysis. The results obtained for the thermal analysis of the four blends are shown in Figure 2.
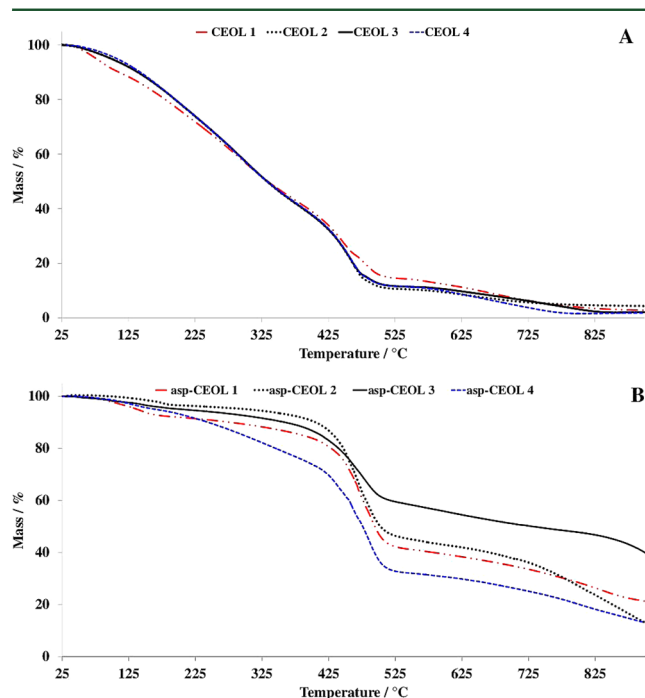

Figure 2. Thermogravimetric curves of the crude oil blends (A) and respective asphaltenes (B).

Figure 2A shows the results for the crude oil blends. The initial region up to 400 °C, representing the distillation of hydrocarbons (HCs), shows approximately 60% mass loss for all blends. A second region at 400−600 °C represents the thermal cracking process and the production of HC, and approximately 92% weight loss was observed in this region. At 500 °C, approximately 85% of the crude oil present in the blend CEOL1 and 90% in the other blends is converted into products yielding, respectively, 15% and 10% of coke.

In the analysis of the asphaltenes by TG (Figure 2B) it was possible to observe three ranges of mass loss: (i) ambient temperature up to 400 °C, where asphaltene mass losses of 16%, 10%, 13%, and 25% were observed for blends CEOL1, CEOL2, CEOL3, and CEOL4, respectively; (ii) 400−450 °C, related to the first stage of mass loss associated with HCs (volatile); and (iii) above 450 °C, related to the second stage of mass loss associated with HCs, with a notably higher weight loss compared with the previous stage. Total asphaltene mass losses of 79%, 87%, 60%, and 87% for the blends CEOL1, CEOL2, CEOL3, and CEOL4, respectively, were observed at the final temperature. It should be noted that the asphaltenes of the blend CEOL3 showed a lower total mass loss in the TG (around 60%),

indicating that the production of HCs is lower than in the case of the other samples, which is possibly related to the molecular structure of the asphaltenes, suggesting that they may be thermally more evolved than the asphaltenes of the other samples.[34]

Infrared Spectroscopy. The results for the infrared spectroscopy in Figure 3 show that all four blends of crude oil had similar spectra. The greatest intensities were observed for the aliphatic C−H stretching at 2853 and 2923 cm^{-1}, rotational vibrations of CH_2 and CH_3 groups at 1456 and 1376 cm^{-1} and out of plane =CH stretching at 730−675 cm^{-1}. This indicates that these samples consist mostly of hydrocarbon structures, corroborating the results obtained from the SARA fractionation (Table 2).

The IR spectra for the asphaltenes of the blends (Figure 4) show similar results for all samples. Recent research using attenuated total reflectance (ATR) infrared spectroscopy identified isosbectic points for liquid water, both ordinary and heavy, with respect to temperature. For H_2O these are at around 600, 1600, 1680, and 3550 cm^{-1}.[35] The absorption in the region of 3100−3600 cm^{-1} shows asymmetric and symmetric O−H stretching of water associated with the asphaltenes, stretching at 2853 and 2923 cm^{-1} is related to aliphatic C−H, and at around 1600 cm^{-1} water bending vibrations are present. It was also possible to identify regions of absorption at 1456 and 1376 cm^{-1} related to the rotational vibration of CH_2 and CH_3 groups, respectively, and also a signal related to the stretching vibration of phenol C−O at 1215 cm^{-1}.[36]

In terms of regions with different absorption characteristics, the CEOL3 blend shows absorption at around 600, 1600, and 3500 cm^{-1} related to the water associated with asphaltenes, all of these signals being of greater intensity than those for the other samples. This profile can also be noted in the region of the absorption band at around 2000 cm^{-1}, which may be attributed to the greater water content associated with the asphaltenic structure.[35]

The water molecule has a very small moment of inertia on rotation which gives rise to a rich combined vibrational−rotational spectra for the vapor, containing tens of thousands of absorption lines between 3600 and 4000 cm^{-1}.

Ultraviolet Spectroscopy. The spectra in Figure 5 show the differences in the intensities of the ultraviolet absorption bands for the blends. It can be observed that the highest intensities were obtained for the blend CEOL1 and the lowest for CEOL3. In the cases of CEOL2 and CEOL4 the intensities were intermediate and similar, as evidenced by the overlapping of the spectra.

Based on reports in the literature,[10] aromatics with lower molecular mass lead to higher absorption at 235 nm. Thus, we can deduce that in the oil blend CEOL3 the aromatic structures are of higher molecular mass. According to Honse et al.,[24] the observed differences in terms of the stability of water-in-oil emulsions originate from the type of asphaltene molecules added to the system. This is consistent with the results of this case study, where the CEOL3 blend had a higher affinity for water (compared with the other three blends) and also showed the presence of aromatic structures with higher molecular mass.

To present more clearly the spectral data in Figure 5, the analysis was performed as a function of the aromatic compounds present in the oil blends using the absorbance data obtained in the UV analysis relating to the monoaromatic (benzene as a reference at 255 nm), diaromatic (naphthalene as a reference at 286 nm), and triaromatic (anthracene as a reference at 375 nm) contents. To calculate the concentration of aromatic groups shown in Table 4 the Beer−Lambert Law was used, employing
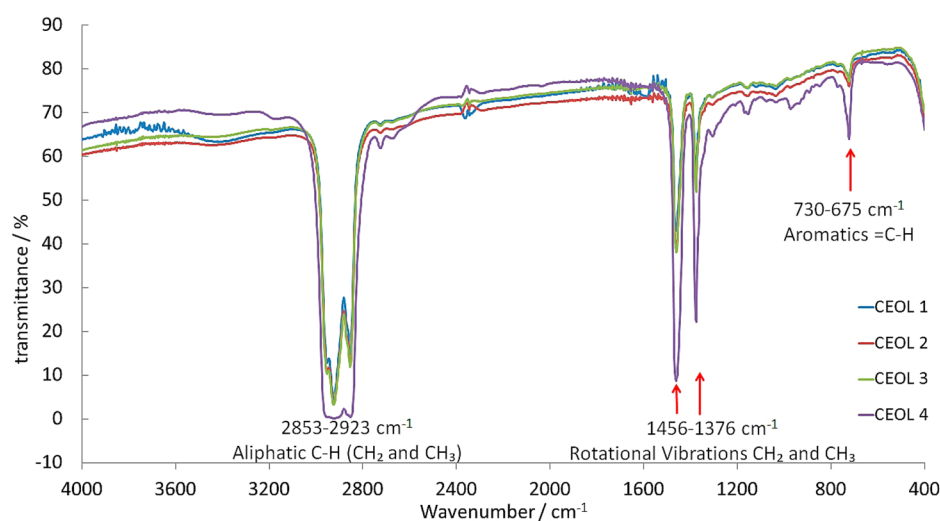
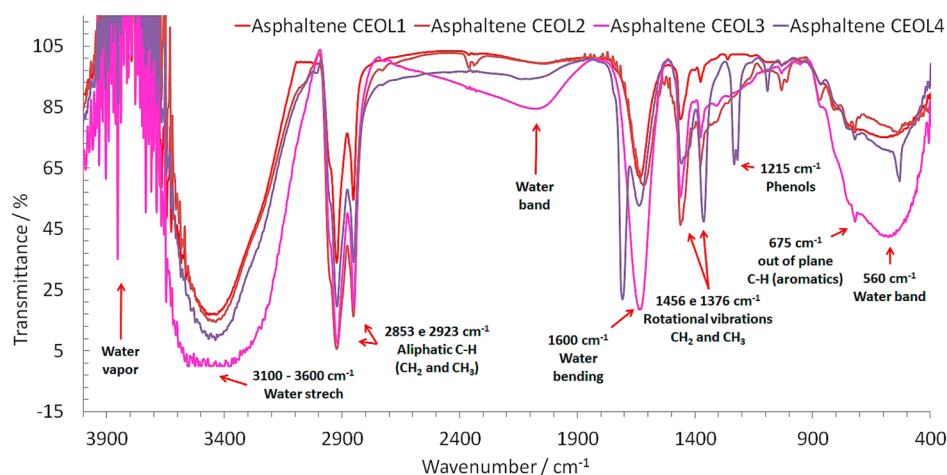**Figure 3.** Infrared (IR) spectra for the crude oil blends.

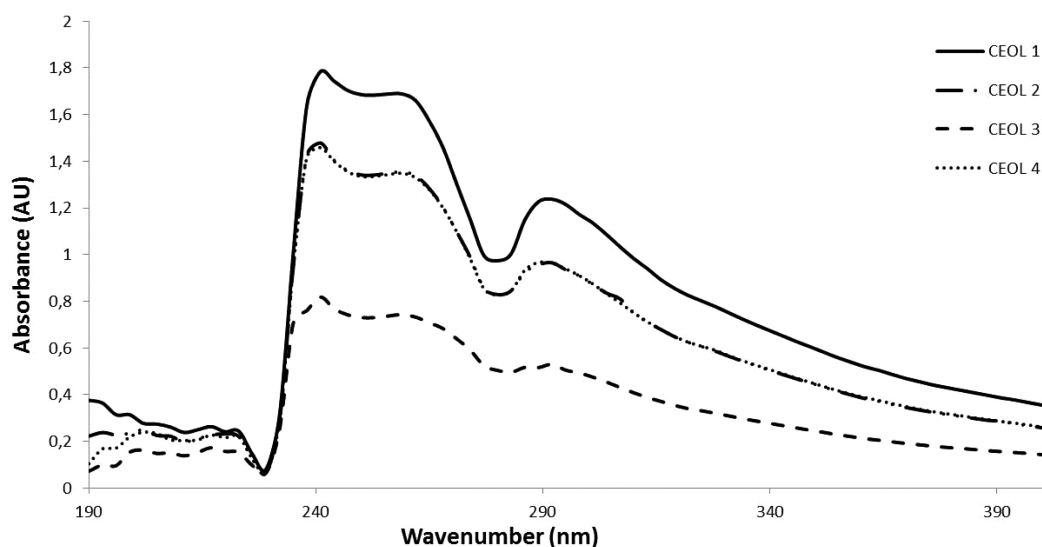**Figure 4.** Infrared spectra for asphaltenes in the crude oil blends.

Figure 5. Ultraviolet spectra for the blends of crude oils originating from the Carmópolis Field.

the molar absorption coefficients for benzene (ε = 180 L mol^{-1} cm^{-1}), naphthalene (ε = 360 L mol^{-1} cm^{-1}), and anthracene (ε = 7100 L mol^{-1} cm^{-1}), as described by Shimadzu.[37]

Table 3 shows that the blend CEOL1 had higher concentrations of mono-, di-, and triaromatics in relation to the other samples, while CEOL3 showed the lowest concentrations.

Table 3. Concentration of Mono-, Di-, and Triaromatics in the Crude Oil Blends Determined by UV Spectroscopy Analysis

	concn per given class (mol L^{-1})^a		
blend	monoaromatics	diaromatics	triaromatics
CEOL1	9.4	3.2	6.0
CEOL2	7.5	2.6	5.0
CEOL3	4.1	1.4	3.0
CEOL4	7.5	2.6	5.0

^{a}(mol L^{-1}) × 10^{-3}.

The same behavior was observed for the UV spectra of the asphaltene solution. The SARA, UV, IR, and TG results provided information on the blend characteristics, which can be used to predict the relations between the oil and the produced water and to support the exploration process, and EDX was employed to confirm the presence of elements related to the produced water associated with the crude oil blends.

Energy Dispersive X-ray Fluorescence Spectrometry. Table 4 shows the results for the EDX analysis, revealing the predominance of Cl, S, Ca, Ni, Fe, Cu, and C in all of the crude oil blends. Metallic atoms of Sr, Co, and Ag, which rarely appear in this type of matrix, were observed in only some of the samples.

Chloride, which is associated with the high degree of salinity of the produced water emulsified in the crude oil during the upstream process, was identified in all blends, with the highest concentration being observed for CEOL3 (2.32 ± 0.03%). In crude oils, chlorides are directly related to the presence of residual produced water in the oil, which can be in a dissolved, occluded, or chemically bonded form and can be associated with the capacity of the crude oil for formation and stabilization of emulsions between the produced water and crude oil. This verifies the need for treatment with the injection of a greater amount of demulsifier agents, as previously reported. Chloride appears to be mainly associated with the atoms of Na, which was not included in the EDX analysis, and Ca and K present in the form of salts in crude oils and thus the blend CEOL3 showed higher concentrations of chlorides and of Ca and K. According to Escobar et al.,[33] Ca in crude oils is associated with the occurrence of carbonate mineral phases being present together with naphthenic acids.

The lowest sulfur content was observed for the blend CEOL3 (0.28 ± 0.01%). The other samples analyzed showed S values close to 0.60%. According to Speight,[38] sulfur compounds can be present in crude oils in the form of sulfides, thiophenes, benzothiophenes, and dibenzothiophenes, and these are among the most undesirable oil components in the petroleum industry, since they can lead to corrosion in industrial plants and are associated with atmospheric pollution.

The values for nickel ranged from 6.38 ± 0.56 to 10.23 ± 1.36 μg g^{-1}, with the highest value being obtained for the blend CEOL1. The highest concentrations of the elements Fe, Cu, and Br were observed for the blend CEOL3 (16.69 ± 1.96, 4.82 ± 0.80, and 6.72 ± 0.24 μg g^{-1}, respectively). Strontium was detected only in the blend CEOL3 (2.18 ± 0.42 μg g^{-1}), and Co and Ag were determined only in the blend CEOL4 (5.05 ± 1.82 and 4.98 ± 2.00 μg g^{-1}, respectively). The carbon balances close the composition with percentages ranging from 97 to 99%. The most notable difference was the lowest value found for the blend CEOL3 (97.28 ± 0.04%).

These data suggest that CEOL4 does not have a direct relationship with the other blends because it was the only sample with Co and Ag in its composition. The blend CEOL3 also has no direct relationship with any of the other blends, since it had Sr in its composition. The blends CEOL1 and CEOL2 show similar compositions, which may indicate a direct oil−oil relationship, indicating that these two blends may have been generated under the same environmental conditions and with similar organic matter inputs and thermal evolutions.

Laser Desorption/Ionization Mass Spectrometry. LDI-MS was applied with the purpose of verifying the distribution of polar compounds in the blends, especially natural surfactants, which are responsible for the formation and stabilization of emulsions in oil. Initially, analysis was carried out in tests with two matrices, that is, 3-IAA and 9-CA, by MALDI-MS. The results showed that these matrices did not provide ionization conditions suitable for the analysis of crude oils, since the spectrogram showed that the major signals from the ionization of the matrices overlap with those of the crude oil blends. The best results were obtained using the dried droplets method with a solution of the sample blend in THF (100 mg mL^{-1}) applied directly on the plate of the equipment. According to Morgan et al.,[39] colored samples absorb the laser directly and function as a self-matrix which can be analyzed directly. Robins and Limbach[40] concluded that some matrices produce fragments which can interfere in the analysis of fractions of crude oils of low molecular weight. Figure 6 shows the spectrogram for the LDI-MS in a reflected mode for the blends, covering the range of 60−1000 Da.

Table 4. EDX Results for the Blends of Crude Oils from the Carmópolis Field

	for given blend			
element	CEOL1	CEOL2	CEOL3	CEOL4
Cl (%)	1.36 ± 0.01	0.77 ± 0.01	2.32 ± 0.03	1.88 ± 0.01
S (%)	0.58 ± 0.01	0.60 ± 0.01	0.28 ± 0.01	0.68 ± 0.02
Ca (μg g^{-1})	382.65 ± 0.58	275.57 ± 5.92	1091.19 ± 10.92	71.92 ± 12.60
K (μg g^{-1})	110.76 ± 0.44	60.86 ± 4.50	174.33 ± 7.66	
Ni (μg g^{-1})	10.23 ± 1.36	8.89 ± 0.86	6.38 ± 0.56	7.43 ± 0.84
Fe (μg g^{-1})	6.62 ± 0.66	3.48 ± 0.32	16.69 ± 1.96	5.92 ± 4.92
Cu (μg g^{-1})	4.32 ± 2.00	3.28 ± 0.08	4.82 ± 0.80	4.47 ± 2.00
Br (μg g^{-1})	1.80 ± 0.16	1.01 ± 0.04	6.72 ± 0.24	
Sr (μg g^{-1})			2.18 ± 0.42	
Co (μg g^{-1})				5.05 ± 1.82
Ag (μg g^{-1})				4.98 ± 2.00
C (%)	98.01 ± 0.08	98.59 ± 0.02	97.28 ± 0.04	99.13 ± 0.02

(−)Values below the detection limit of the equipment. *Results expressed as mean ±2 SD for $n = 2$.
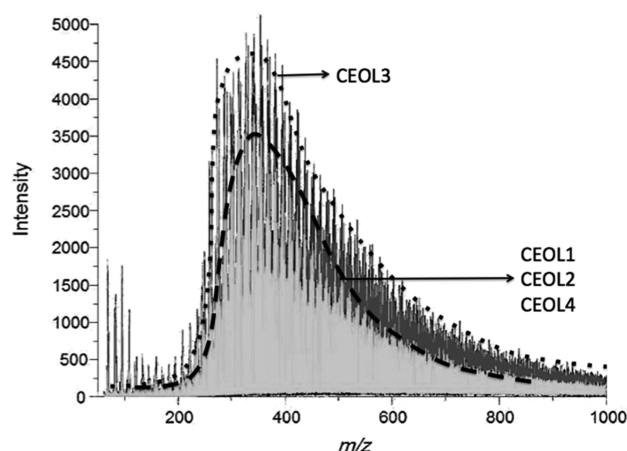
Figure 6. LDI-MS spectra for the crude oil blends originating from the Carmópolis Field.

The profiles of the spectrogram shown in Figure 6 are similar for the four blends, showing a bimodal distribution of compounds. The strongest signal strength for the blend CEOL2 is located in the initial region between 60 and 200 Da, the presence of compounds with greater intensity between 200 and 400 Da being observed in all samples. For the blend CEOL3, the spectrum shows the greatest signal intensities for compounds at around 400−1000 Da, showing the predominance of polar compounds of higher molecular weight in this oil blend.

In the analysis of crude oils originating from the offshore fields assigned to the State of Espírito Santo, Freitas et al.[41] highlighted that the region at around m/z 400 Da is related to compounds of the naphthenic acids and carbazole derivatives classes, allowing their identification from the signal strength.

The greatest signal intensities in the region relating to naphthenic acids and carbazole derivatives were obtained for the blend CEOL3 (Figure 7). According to Fortuny et al.,[3] naphthenic acids
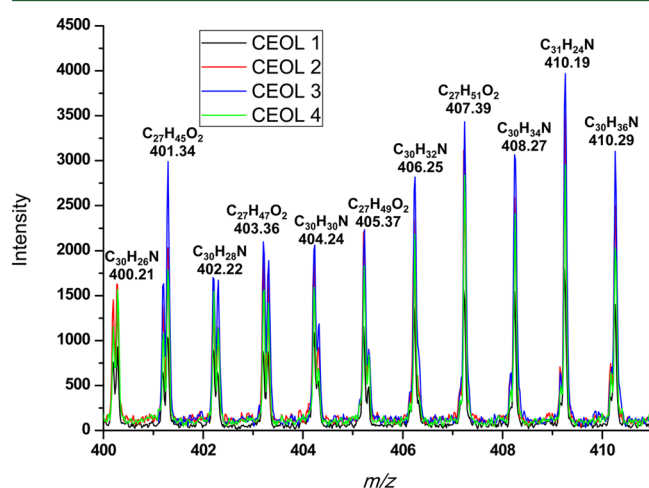

Figure 7. Expansion of the LDI-MS spectra in the region of 400 Da for the crude oil blends originating from the Carmópolis Field.

present in petroleum act as natural surfactants contributing to emulsion formation and this may be directly associated with a higher proportion of these acids in the crude oils that comprised the blend CEOL3. This result is consistent with those reported in the literature[31] which describe the important role of resin compounds in the solvency of asphaltenes, aiding the stabilization of the emulsion.

CONCLUSION

Based on the advanced characterization of the four crude oil blends using several techniques, we observed that the blend CEOL3 had distinct chemical characteristics compared with the other three samples studied, which was directly related to interactions with the produced water. The SARA composition showed no significant differences between the oils; however, the analysis of asphaltenes by IR differentiated the CEOL3 sample by way of the presence of greater O−H stretching associated with water. Furthermore, EDX showed the presence of Ca and K in higher concentrations, which may be related to the presence of a greater amount of produced water due to a more stable interaction between the produced water and the crude oil. Based on the UV spectra, it was possible to verify that the asphaltenes of the blend CEOL3 had higher molecular mass compared with the other blends studied, which is related to a greater ability to stabilize emulsions. In addition, the TG of the asphaltenes showed that CEOL3 produces a lower amount of hydrocarbons than the other blends, indicating that the oil asphaltenes are thermally more evolved. Finally, the LDI-MS analysis showed that CEOL3 had higher contents of naphthenic acids and carbazole derivatives, which can act as natural surfactants, making the interaction of emulsions stronger in this blend.

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Notes
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REFERENCES

(1) Speight, J. G. *The Chemistry and Technology of Petroleum*, 4th ed.; CRC Press: New York, 2006.

(2) Azevedo, D. A.; Silva, T. F.; Silva, D. B. *Quim. Nova* **2009**, *32*, 1770−1776.

(3) Fortuny, M.; Ramos, A. L. D.; Dariva, C.; Egues, S. M. S.; Santos, A. F.; Nele, M.; Coutinho, R. C. C. *Quim. Nova* **2008**, *31*, 1553−1561.

(4) Sjöblom, J.; Aske, N.; Auflem, I. H.; Brandal, Ø.; Havre, T. E.; Sæther, Ø.; Westvik, A.; Johnsen, E. E.; Kallevik, H. *Adv. Colloid Interface Sci.* **2003**, *100*, 399−473.

(5) Mouraille, O.; Skodvin, T.; Sjöblom, J.; Peytavy, J. L. *J. Dispersion Sci. Technol.* **1998**, *19*, 339−367.

(6) Nadarajah, N.; Singh, A.; Ward, O. P. *Process Biochem.* **2002**, *37*, 1135−1141.

(7) Fingas, M.; Fieldhouse, B. *Colloids Surf., A* **2009**, *333*, 67−81.

(8) Tchoukov, P.; Czarnecki, J.; Dabros, T. *Colloids Surf., A* **2010**, *372*, 15−21.

(9) Spiecker, P. M.; Gawrys, K. L.; Trail, C. B.; Kilpatrick, P. K. *Colloids Surf., A* **2003**, *220*, 9−27.

(10) Li, M.; Xu, M.; Ma, Y.; Wu, Z.; Christy, A. A. *Colloids Surf., A* **2002**, *197*, 193−201.

(11) Schorling, P.-C.; Kessel, D. G.; Rahimian, I. *Colloids Surf., A* **1999**, *152*, 95−102.

(12) Kallevik, H.; Kvalheim, O. M.; Sjöblom, J. *J. Colloid Interface Sci.* **2000**, *225*, 494−504.

(13) Ortiz, D. P.; Baydak, E. N.; Yarranton, H. W. *J. Colloid Interface Sci.* **2010**, *351*, 542−555.

(14) Czarnecki, J.; Tchoukov, P.; Dabros, T. *Energy Fuels* **2012**, *26*, 5782−5786.

(15) Czarnecki, J.; Moran, K. *Energy Fuels* **2005**, *19*, 2074−2079.

(16) Kang, W.; Xu, B.; Wang, Y.; Li, Y.; Shan, X.; An, F.; Liu, J. *Colloids Surf., A* **2011**, *384*, 555−560.

(17) Standford, L. A.; Rodgers, R. P.; Marshall, A. G. *Energy Fuels* **2007**, *21*, 963−972.

(18) Kharrat, A. M.; Zacharia, J.; Cherian, V. J.; Anyatonwu, A. *Energy Fuels* **2007**, *21*, 3618−3621.

(19) Molina, V. D.; Uribe, U. V.; Murgich, J. *Fuel* **2010**, *89*, 185−192.

(20) Petersen, H. I.; Nytoft, H. P.; Nielsen, L. H. *Org. Geochem.* **2004**, *35*, 493−515.

(21) Vazquez, D.; Mansoori, G. A. *J. Pet. Sci. Eng.* **2000**, *26*, 49−55.

(22) Fan, T.; Buckley, J. S. *Energy Fuels* **2002**, *16*, 1571−1575.

(23) Cendejas, G.; Arreguín, F.; Castro, L. V.; Flores, E. A.; Vazquez, F. *Fuel* **2013**, *103*, 356−363.

(24) Honse, S. O.; Mansur, C. R. E.; Lucas, E. F. *J. Braz. Chem. Soc.* **2012**, *12*, 2204−2210.

(25) National Agency of Petroleum. *Natural Gas and Biofuels—ANP*, http://www.anp.gov.br (accessed Dec. 6, 2012).

(26) National Agency of Petroleum. *Natural Gas and Biofuels—ANP. Exploration and Production Database—BDEP*, http://www.bdep.gov.br (accessed Dec. 6, 2012).

(27) National Agency of Petroleum. *Natural Gas and Biofuels—ANP. Annual statistics yearbook*, http://www.anp.gov.br/?pg=56346 (accessed Dec. 22, 2010).

(28) National Agency of Petroleum. *Natural Gas and Biofuels—ANP*, http://www.anp.gov.br/?id=600 (accessed Feb. 25, 2013).

(29) *Standard Test Method for Density of Semi-Solid Bituminous Materials (Pycnometer Method)*, ASTM D70-09e1; Annual Book of ASTM Standards; ASTM International: West Conshohocken, PA, USA, 2009.

(30) Fingas, M. F. *J. Pet. Sci. Res.* **2014**, *3*, 38−49.

(31) Ekott, E. J.; Akipabio, E. J. *J. Eng. Appl. Sci.* **2011**, *6*, 200−204.

(32) Thompson, K. F. M. *Org. Geochem.* **1987**, *11*, 573−590.

(33) Escobar, M.; Márquez, G.; Azuaje, V.; Silva, A.; Tocco, R. *Fuel* **2012**, *97*, 186−196.

(34) Gonçalvez, M. L. A.; Teixeira, M. A. G.; Pereira, R. C. L.; Mercury, R. L. P.; Matos, J. R. *J. Therm. Anal. Calorim.* **2001**, *64*, 697−706.

(35) Maréchal, Y. *J. Mol. Struct.* **2011**, *1004*, 146−155.

(36) Adebiyi, F. M.; Thoss, V. *Fuel* **2014**, *118*, 426−431.

(37) Shimadzu Corp. *UV Talk Letter*, Vol. 2; http://www.shimadzu.com/an/literature/uv/jpa112002.html (accessed Dec. 6, 2009).

(38) Speight, J. G. *Handbook of petroleum: Product analysis*, 4th ed.; Wiley-Interscience: Hoboken, NJ, USA, 2002.

(39) Morgan, T. J.; George, A.; Alvarez-Rodriguez, P.; Millan, M.; Herod, A. A.; Kandiyoti, R. *J. Chromatogr. A* **2010**, *1217*, 3804−3818.

(40) Robins, C.; Limbach, P. A. *Rapid Commun. Mass Spectrom.* **2003**, *17*, 2839−2845.

(41) Freitas, S.; Malacarne, M. M.; Romão, W.; Dalmaschio, G. P.; Castro, E. V. R.; Celante, V. G.; Freitas, M. B. J. G. *Fuel* **2013**, *104*, 656−663.