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Asphaltene concentration and compositional alterations upon solar irradiation of petroleum

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ABSTRACT

An Arabian light crude and an intermediate Brazilian crude petroleum were subjected to tropical solar irradiation. In both cases there was an immediate and progressive increase in the asphaltenic content that was perceptible after only 5 h. This asphaltene was characterized using fluorescence, FT-IR, proton NMR, and TGA analyses. In both cases the asphaltene became progressively less fluorescent but more aromatic, and also revealed some oxidation.

1. Introduction

The recent environmental disaster involving the platform Deepwater Horizon in the Gulf of Mexico, off the coast of Louisiana, highlights mankind's conflict between current energy requirements and how to obtain that energy. Petroleum is still the main energy source and the use of this non-renewable resource will continue to support our way of life, despite the efforts to develop clean technologies, during the next decades.

Leakage of crude oil into the environment does occur through natural means. However, in the last one hundred years and more so recently, the quantity of oil spilled has reached unprecedented volumes as a result of mankind's activities. In the case of the Deepwater Horizon disaster, and in accidents before, what man has not cleaned up has been left to nature. Once spilled into oceanic waters, petroleum undergoes physical, chemical, and biological weathering [1–4]. The photochemical processes involved in the degradation of petroleum have been much less studied than degradation by biological processes. However, it is now known that photochemical processes produce important oil on water transformations [1,3,5–7], and that there is a synergetic relationship between photochemical and biological processes where photochemical reactions of non-biologically degradable petroleum fractions transform these compounds into products that are amenable to biological degradation [8].

Petroleum is a highly complex material that can be fractionated into aliphatic, aromatic, resins, and asphaltenes. The analysis of this material is highly complex and until recently the compositional analysis using GC–MS and LC–MS techniques was limited to petroleum distillates. However, recent advances in mass spectroscopic techniques, electrospray ionisation (ESI) and easy ambient sonic-spray ionisation (EASI), have resulted in detailed investigations of crude petroleum [9,10]. Asphaltenes are the heaviest, most polyaromatic and least soluble portion of the petroleum [11–13]. The normal alkane soluble fraction is called maltene, this fraction shows a chemical composition similar to that found for the petroleum itself. Asphaltenes are defined by their solubility in toluene and insolubility in a normal alkane solvent (e.g. n-heptane). They are a heterogeneous mixture that is highly disperse in both molecular size and chemical composition, with a high content of heteroatoms (N, O, and S) and metal ions [14–16]. This is the most complex and intriguing fraction of petroleum due to the irregularity of its chemical structure, the presence of heteroatoms and a C/H ratio close to 1.1, where approximately 40% of the carbon atoms are present in polyaromatic structures with 4–10 rings. Additionally, these polyaromatic structures can be linked by aliphatic units with as many as 23 carbon atoms and by more polar functional groups such as –S–, –(CH_2)–, ethers and esters [17]. Different techniques have been used to evaluate the asphaltene average molecular weight. Although there are discrepancies, values ranging from 500 Da (dilute solutions) to 4800 Da (concentrated solutions)

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have been found [14,18–25]. These structural features promote the self-aggregation through polar and π-stacking interactions [26]. Further, this self-organization is dependent upon solvent, concentration, and temperature parameters, and can result in the precipitation of solids in pipes through which the oil is pumped [27–30]. By using time resolved fluorescence spectroscopy our group was able to observe asphaltene aggregation and quantitatively assigned a dimerization mechanism for the process [31].

Additionally, the asphaltene fraction is the most resistant to biological degradation in the environment [8,32], and is thought to be important in the formation of the water in oil emulsion called chocolate mousse [33–35] which makes removal of oil after a spill more difficult [32,36].

An understanding of the changes in petroleum composition and especially in the asphaltenic fraction caused by solar irradiation is important for an understanding of petroleum weathering; however this has been little studied. It has been observed that the asphaltene fraction increases upon irradiation of oil under un-natural conditions using a UV-lamp [37]. Maki et al. [8] noted that when biodegraded oil was suspended in seawater and exposed to sunlight irradiation for several weeks, the most significant change, caused by the irradiation, was an increase in the asphaltene fraction. Asphaltenes were also precipitated after Blend Arabian light crude oil was irradiated by UV and visible light [38]. The analysis showed significant changes in the gravimetric distribution of asphaltene constituents, accompanied by changes in functionality linked to oxidation processes. It was found that the signal due to free radicals found in the asphaltene fraction of crude oil diminished and became narrower upon solar irradiation and that this was accompanied by a reduction in the long wavelength fluorescence associated with asphaltene fluorophores [39]. There have also been studies of the irradiation of solid asphaltene films [12,38,40], and asphaltenic components in waste waters [41].

Although it has been reported that the irradiation of petroleum generates asphaltenes little is known about the rate of their formation and the exposure time dependence. Further nothing is known about how this asphaltene changes with irradiation and how it differs from the original material present in petroleum. This paper presents the results of a study of the alteration of films of both a crude Brazilian petroleum and an Arabian light crude, using natural sunlight under tropical conditions, in order to obtain more information on the photochemistry of the formation and transformation of asphaltene using petroleum which have been well characterized and studied photochemically [8,38], using methods developed to analyze asphaltenes [13,42,43].

2. Experimental

The solvents used in all experiments were purchased from TEDIA Company, pentane and toluene. The petroleum samples were obtained from CENPES (Petrobras Research Center) he fractions used were separated using standard procedures (ASTM D2007). The asphaltene was extracted using 20 volumes of pentane.

Samples of petroleum films were irradiated by exposure to sunlight (5 h, 10 h, 20 h, 30 h, 50 h and 70 h), as 0.8 mm films in Petri dishes. The covers used transmit the entire UV and visible solar spectrum [6]. Following irradiation, the samples were separated into asphaltene and maltene fractions and stored for analyses. For every irradiated sample there was a non-irradiated blank treated in the same way except that a black cover plate was used to eliminate irradiation.

Fluorescence spectra were recorded in toluene at a dilution of 1.2 mg/l using a HITACHI fluorimeter model F4500. Analyses were synchronous with a 20 nm offset between excitation and emission monochromators and a bandpass of 1.0 nm. Infrared spectra of asphaltenes as KBr pellets were obtained using a Nicolet 740-FT-IR. Due to the difficulty in reproducing KBr pellet IR spectra, the individual spectra were corrected for differences in baseline then normalized to 10% transmission using the 2920 cm^{-1} C–H stretch using software furnished by Nicolet with the spectrometer. Proton NMR spectra were obtained at 300 MHz in deutero-chloroform using a Varian Gemini-300. Thermogravimetric analyses utilized a Shimadzu TGA 51. The temperature was programmed from room temperature to 800 °C at 20°/min under a nitrogen atmosphere.

3. Results and discussion

Solar irradiation of films of an intermediate Brazilian Petroleum led to the progressive increase in the quantity of asphaltene present. After 70 h, the amount had increased from 4 to 7%. The same treatment of the Arabian crude led to an increase from 6 to 8%. Control samples, which were treated in the same way but without solar irradiation, showed no change in the concentration of asphaltene. These results are shown in Fig. 1.

There appears to be a linear relationship between the irradiation time and the amount of asphaltene for the Arabian crude, while the Brazilian crude initially shows a faster increase followed by a slower growth. Even though these two petroleum samples vary in density and composition they show similar rates of asphaltene increase.

The asphaltene generated in these experiments was analyzed using synchronous fluorescence spectroscopy, FT-IR, ^{1}H NMR, and TGA.

3.1. Fluorescence spectra

The synchronous fluorescence spectra of the asphaltene from the petroleum samples which were irradiated show a progressive decrease in the spectral intensity with irradiation time. Fig. 2 shows the representative spectra for the Brazilian and Arabian crudes.

For the corresponding samples that were treated in exactly the same manner but without solar irradiation, no significant alteration in the fluorescence intensity or spectra were noted. The two crudes show the same spectra and essentially the same decrease

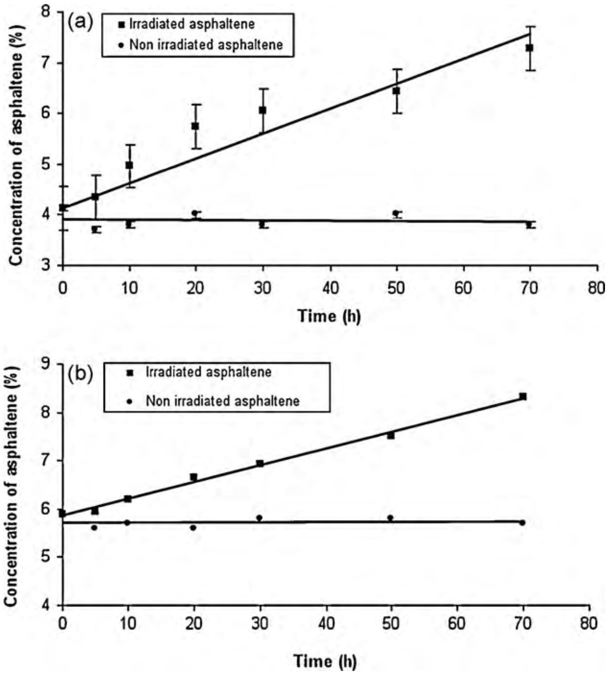


Fig. 1. Concentration of asphaltene present in: (a) the Brazilian petroleum and (b) Arabian petroleum as a function of the solar irradiation time.

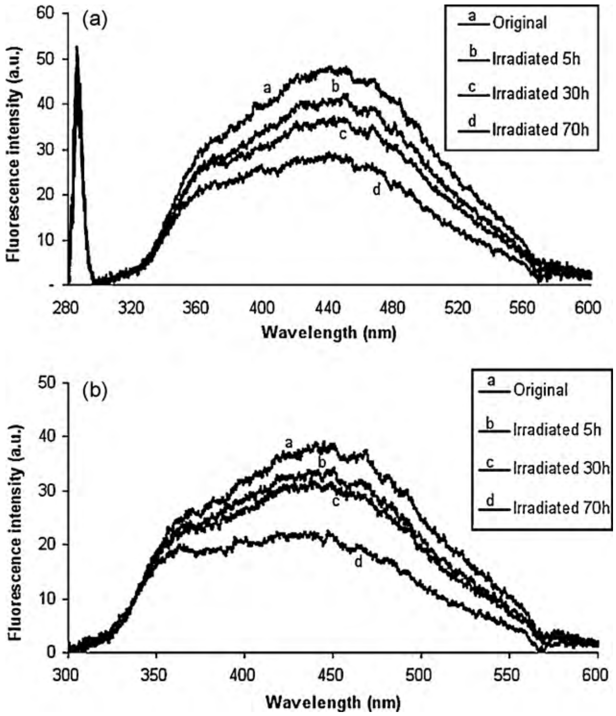


Fig. 2. Synchronous fluorescence spectra of: (a) Brazilian asphaltene and (b) Arabian asphaltene as a function of the solar irradiation time.

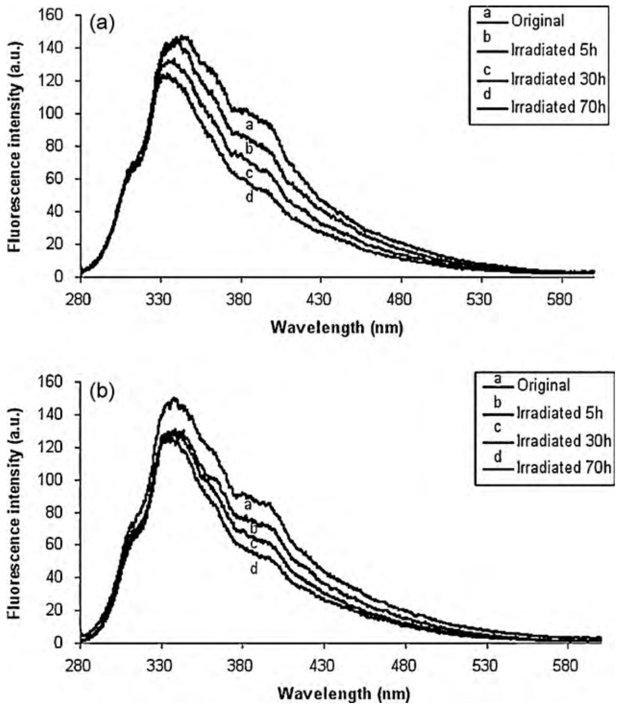


Fig. 3. Synchronous fluorescence spectra of: (a) Brazilian maltene and (b) Arabian maltene as a function of the solar irradiation time.

in intensity with time. Both show a wide emission spectra ranging from 300 to 600 nm. This region is dominated by the polyaromatic compounds containing more than 2 condensed rings [44]. The maximum fluorescence signal for the asphaltene from the Brazilian crude decreases 40% after 70 h of irradiation while the Arabian crude decreases 37%. Since the quantity of asphaltene is increasing, this may indicate that the new asphaltene generated is much less fluorescent or that irradiation is consuming fluorescent components of this fraction. Analysis of the corresponding maltene samples shows a much smaller decrease in the maximum fluorescence intensity of about 15% after 70 h for both types of petroleum (Fig. 3).

When the fluorescence spectra of the asphaltenes after 5 h, 30 h, and 70 h of irradiation are divided by the corresponding non-irradiated sample spectrum, the value at each wavelength should range from one to zero if the fluorescence intensity is decreasing. This value indicates the relative fluorescence intensity at each wavelength. The result will be a straight horizontal line if the relative composition of the fluorescing components is not changing. Fig. 4 shows that at shorter wavelengths corresponding to two and three ring poly-condensed aromatic compounds, the composition is not changing, but at longer wavelengths corresponding to larger poly-condensed aromatics [45], there is a gradual loss of fluorescence and this effect becomes larger with longer irradiation times. The same effect is observed for both types of petroleum. In fact, analysis of infrared and NMR spectra (*vide infra*) show that the new asphaltene being formed is much more polar than the original. As oxygen atoms are added to the asphaltene molecules, the formation of oxygenated polar groups, such as carbonyl groups, will result in decreasing fluorescence emission as found for the irradiated samples, as ketones are poorly fluorescent compounds. Further, the decreasing fluorescence emission could be due in part to the destruction of the polyaromatic structures in the original asphaltene by photochemical reactions such as the Diels-Alder reactions, photogeneration of radical species and singlet oxygen addition to the asphaltene compounds (Scheme 1). All of these processes will reduce the polyaromatic components resulting in a loss of emission from the red region of the spectra and a growth in the emission from the blue region of the spectra [6,46–48].

The same analysis for the maltene fluorescence is shown in Fig. 5 for the Brazilian petroleum and for the Arabian crude.

These spectra show a more complex behavior than is observed for the asphaltene samples. The maltene spectra show a strong

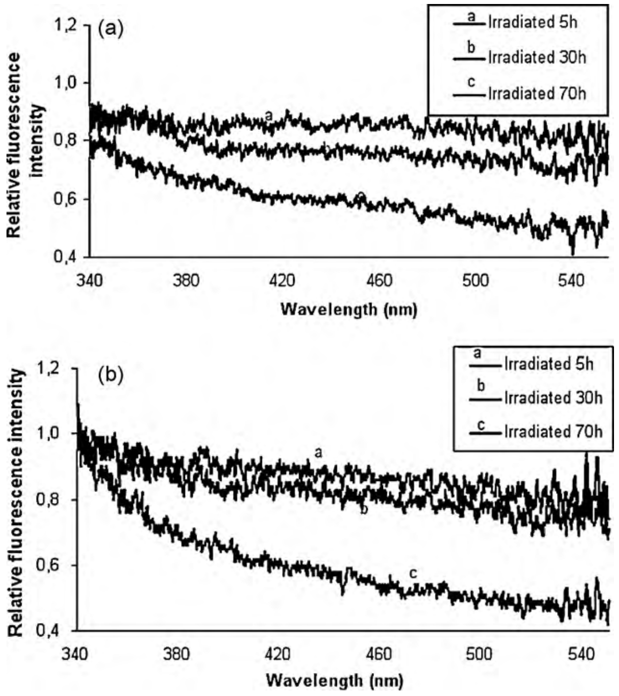
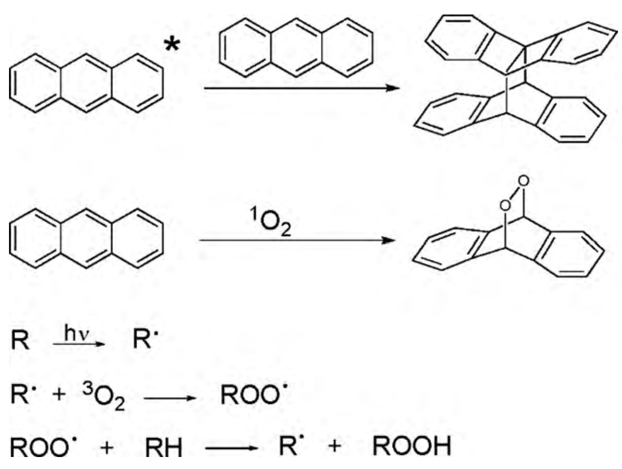


Fig. 4. Relative fluorescence intensity of: (a) Brazilian asphaltene and (b) Arabian asphaltene from irradiated petroleum (Air) relative to the asphaltene originally present in the petroleum (Ao) as Air/Ao.



Scheme 1.

dependence on wavelength. The Brazilian maltene (Fig. 5a) shows little change in fluorescence intensity at the maximum fluorescence wavelength (330 nm) but much greater change at 400 and 500 nm which further decreases with longer irradiation times. The Arabian maltene (Fig. 5b) also shows little change at 320 nm and also shows a minimum at 400 nm. It differs from the Brazilian maltene in that at longer wavelengths a minimum in the relative fluorescence intensity is observed at 600 nm where the spectrum ends. At the longest wavelengths analyzed the Brazilian maltene shows relatively little change in fluorescence intensity with irradiation while the Arabian maltene shows the greatest change and this occurs in the first 5 h. Once again, the differences in the spectra are more intense for the red region, where polyaromatic compounds emit, suggesting, as expected, that these are the more reactive components when subjected to solar irradiation. These effects would not be readily observable if only the synchronous spectra were compared. The different responses to solar irradiation may be due to differences in the composition of the larger polycyclic aromatics which appear at longer wavelengths.

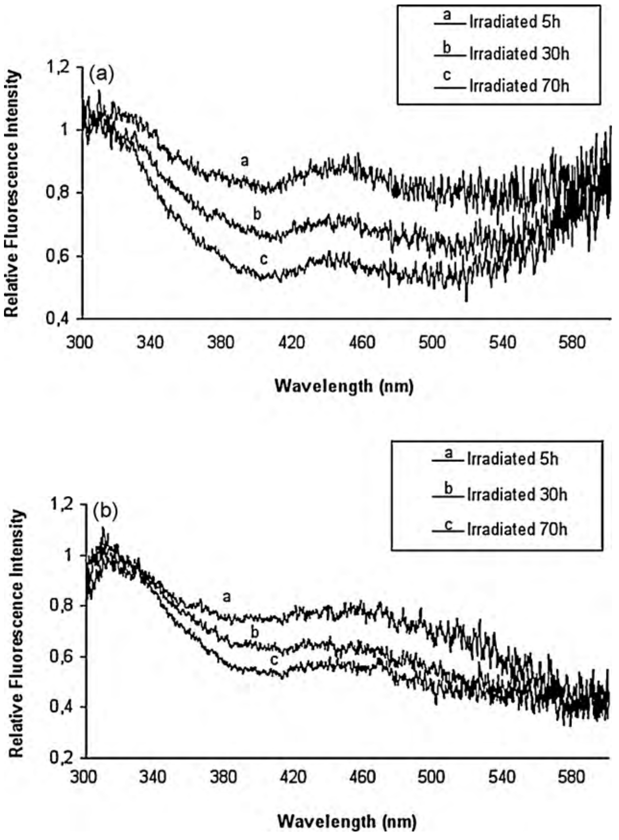


Fig. 5. Relative fluorescence intensity of: (a) Brazilian maltene and (b) Arabian maltene from irradiated petroleum (Air) relative to the maltene originally present in the petroleum (Ao) as Air/Ao.

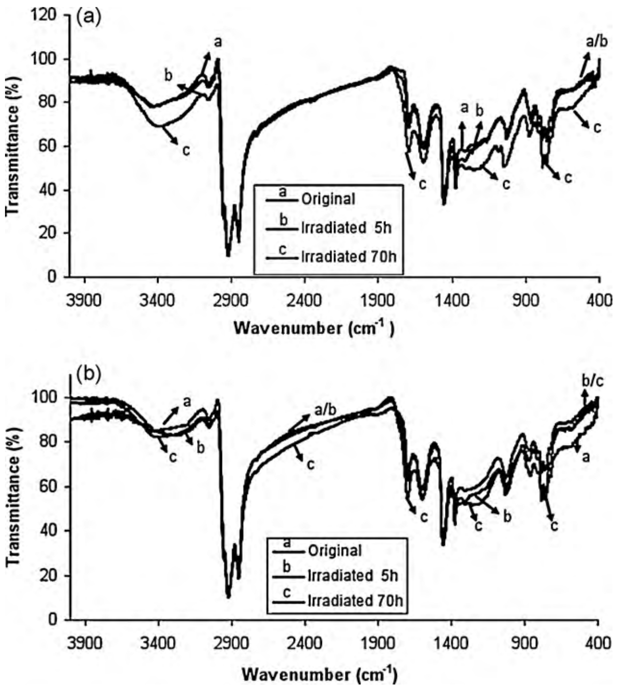


Fig. 6. Infrared spectra (4000–400 cm^{-1}) of the: (a) Brazilian asphaltene and (b) Arabian asphaltene from irradiated and non-irradiated petroleum.

3.2. Infrared spectra

The FT-IR spectra of the initial asphaltene and the asphaltene obtained after 5 h and 70 h of irradiation for the asphaltene from both types of petroleum are shown in Fig. 6. The spectra from the asphaltene from both types petroleum are very similar and show the same alterations on irradiation. The spectra of the non-irradiated sample and the 5 h sample are quite similar. The 70 h sample, on the other hand, shows increased absorption at 3400, 1700, and 1100 cm^{-1}. These positions correspond to absorptions originating from OH, carbonyl, and C–O, functions respectively. After 70 h of solar irradiation, the resulting asphaltene has incorporated functional groups characteristic of oxidation processes. These results agree with those found using synchronous fluorescence, where a reduction of the emission was proposed to be due to oxidation of the asphaltene compounds by singlet oxygen.

3.3. Proton NMR spectra

The proton NMR spectra of the asphaltene samples from the irradiated and non-irradiated petroleum from both crudes were analyzed and the relative areas of the aliphatic, polar, and aromatic hydrogens are presented in the bar graph (Fig. 7). For both crudes, the samples from the non-irradiated petroleum show no change. The asphaltene obtained from the Brazilian irradiated petroleum shows a general trend towards reduction in the percentage of aliphatic hydrogen while the percentage of polar and aromatic hydrogen increases slightly. After 70 h of irradiation, the percentage of polar hydrogen has increased significantly. The Arabian asphal-

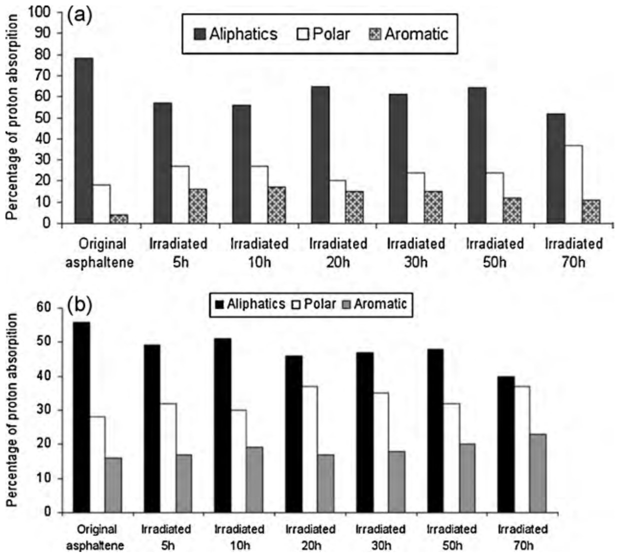


Fig. 7. ^{1}H NMR analysis of asphaltenes present in the irradiated: (a) Brazilian and (b) Arabian petroleum as the percentage of aliphatic, polar and aromatic protons (0 and 2 ppm—aliphatics); (2 and 4 ppm—polar) and (6 and 9 ppm—aromatic).

tene is initially less aliphatic and more aromatic than the Brazilian asphaltene as shown in Fig. 7b, and the aliphatic hydrogen content of this asphaltene further decreases, while the polar and aromatic hydrogen components increase with irradiation. Although the NMR analysis reveals that the asphaltenes from the Brazilian and Arabian crudes are initially somewhat different both show the same general transformation with irradiation time. The results corroborate with the observations made using IR and fluorescence synchronous emission techniques and are in agreement with literature results that indicate a more emulsifiable asphaltene after irradiation. This is attributed to oxidation of hydrocarbon compounds, which increases the water/oil or oil/water solubility [32,47,49].

3.4. Thermogravimetric analysis

A thermogravimetric analysis (TGA) of a sample of asphaltene from the Brazilian petroleum irradiated 30 h was compared with that of the non-irradiated blank. The analyses show that both irradiated asphaltene lose mass at a slightly lower temperature (320–530 °C) when compared with the original asphaltene (375–530 °C), and lost slightly greater mass due to evaporation and or pyrolysis. This may indicate that irradiation generates a slightly more volatile asphaltene due to transformation of the asphaltene. The result is similar to the literature value an asphaltene which lost 54% of mass in the temperature range of 400–647 °C [50], but differs from the results for a Daqing crude asphaltene which lost 91.6% of mass in a temperature range of 390–500 °C [51].

In conclusion, it has been found that after irradiation, petroleum shows a greater tendency to form stable water in oil emulsions (mousse) [33]. The results reported here help explain why this happens. It is known that the asphaltene fraction is tenso-active and stabilizes emulsions [4,34,35], the increase in the quantity of asphaltene as a result of solar irradiation would therefore increase this action. The formation of polar oxygen containing groups in this asphaltene would further serve to increase the tenso-active character of this asphaltene.

This study shows that irradiation increases the asphaltene concentration, alters the characteristics of this asphaltene, and that the time necessary for this to happen is short enough to be environmentally important. Further, it is shown that different initial crudes with somewhat different initial asphaltene content respond to solar irradiation in a quite similar manner. This may indicate that the transformations observed here are of general occurrence.

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