

Photodegradation of Crude Oil: Liquid Injection and Headspace Solid-Phase Microextraction for Crude Oil Analysis by Gas Chromatography with Mass Spectrometer Detector

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Abstract

The fate of crude oil under irradiation is studied. After UV irradiation, the fraction present in the highest percentage shifts from the C8–C9 fractions to C13, using gas chromatography–mass spectrometry (GC–MS) analysis in solution. An increase of the relative amount of the C13–C25 fraction is observed, while a decrease in the relative amount of the C7–C12 fractions is present. In headspace solid-phase microextraction (HS–SPME) analysis, the C8–C10 fractions represent 53% of all the compounds detected. A decrease in the relative amount of the C8–C10 fractions is observed, while C11–C15 fractions increase. The irradiation of crude oil with a solar simulator gives a mixture the analysis of which using GC–MS in solution furnishes the same type of results: the relative amounts of linear alkanes and aromatic compounds increase, while a sharp decrease in the relative amounts of branched and cyclic alkanes is observed. In the SPME analysis, a decreased relative amount of branched alkanes and alkenes, and an increase in the relative amounts of cyclic alkanes and aromatic compounds are observed. Analysis of the distribution of the compounds in all the types of compound shows that a dynamic equilibrium between different compounds and different types of compounds is present. To confirm the presence of a dynamic equilibrium, the irradiation of methylcyclohexane in the presence of 2-methylnaphthalene shows the presence in the reaction mixture of a small amount of tetradecane.

Introduction

Crude oil can escape into the environment. Spilling techniques (using gas mixtures or water) and transportation of crude oil can cause pollution due to the dispersion of these compounds into the environment. Thus, terrestrial spills may

soak into the ground, while spills at sea or on lakes and rivers often disperse into the water column (1).

Recently, we reported that liquid injection and headspace solid-phase microextraction (HS–SPME) analysis of crude oil with a gas chromatography–mass spectrometry (GC–MS) apparatus gave complementary results (2). Liquid injection allowed us to obtain an accurate description of the high molecular weight fraction that cannot be identified using SPME. On the contrary, SPME gave an accurate description of the low molecular weight fraction that cannot be studied using liquid injection.

Crude oil is subject to certain degradation processes. Biodegradation can be one of the most important processes in the environment. Photochemical degradation mediated by sunlight is an important pathway for the transformation of crude oil in tropical seawater, especially when the oil is rich in aromatics. Because chromophores are abundant in crude oils, many of these transformations are the result of direct photochemical processes.

In recent works, GC–MS analysis of crude oil after irradiation showed that the alkanes are unaffected, but the majority of the aromatic hydrocarbons have been converted to resins or polar molecules (3–6). These results are not in agreement with the observed photo-oxidation of *n*-pentadecane (7) or the mineralization of *n*-alkanes in photocatalytic conditions (8,9).

A GC–MS analysis of water-soluble fractions of crude oil showed that only the peaks with retention times between 8.46 and 12.36 min disappeared after 24 h under photolysis (10).

The constant rate for hydrogen abstraction in alkyl aromatics has been previously determined (11). This result was in agreement with the observed preferential photo-oxidation of alkyl-substituted polycyclic aromatic hydrocarbons and heterocyclic aromatics, in comparison with their unsubstituted parent compounds (12,13).

In this work, we conducted photodegradation experiments on crude oil from Basilicata (Southern Italy) using a high-pressure mercury lamp and a solar simulator. The crude oil and

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the photodegradation mixture were analyzed using liquid injection GC–MS and HS–SPME–GC–MS.

Materials and methods

Oil extraction represents one of the most important extractive industries in the world. Basilicata is a region in Southern Italy where extraction activity has recently been started by ENi SpA. The extraction of crude oil present in Basilicata can cover 10% of Italian needs in the energy production. The oil extraction was performed mainly in Val d'Agri, a valley in Basilicata where extensive agricultural activity and some environmental constraints with the presence of the National Park of Val d'Agri are present.

In this study, we used a sample of crude oil deriving from Centro Oli in Val D'Agri (Basilicata, Southern Italy). The sample showed the following composition in the elemental analysis: C, 85.13%; H, 12.31%; N, 0.00%; S, 2.74%.

GC–MS analysis in solution

Crude oil solution in THF (0.1 g/L) (Aldrich, Milan, Italy) was injected into an HP6890 (Agilent Technologies, Milan, Italy) plus GC equipped with a Phenomenex Zebron ZB-5 MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) (Supelco, Bellefonte, PA). As a detector, we used an HP5973 mass selective detector (mass range: 15–800 amu; scan rate: 1.9 scans/s; EM voltage: 1435); helium at 0.8 mL/min was used as carrier gas. The injection port was split at 250°C. The injection volume was 1 μL. The detector was maintained at 230°C. The oven was maintained at 60°C for 2 min, then the temperature was increased to 250°C (10°C/min); this temperature was maintained for 20 min. All the analyses were performed in triplicate (relative standard deviation [RSD] 0.02%). The chromatograms obtained from the total ion current (TIC) were integrated without any correction for coelutions, and the results were expressed in arbitrary surface units (asu). All the peaks were identified from their mass spectra by comparison with spectra in Wiley6N and NIST98 libraries.

SPME–GC–MS analysis

An SPME fiber coated with 100 μm of nongrafted poly(dimethylsiloxane) (PDMS) phase (Supelco 57300-U, mounted on a Supelco 57330 support) was conditioned for 1 h at 250°C in a stream of helium. A single fiber was used for the complete study. A blank run was performed after the analysis to confirm that no residual compound was polluting the fiber or the column. The headspace was generated from 10 mL samples placed in a 20-mL flask. The flask was sealed and heated for 20 min in an aluminium block maintained at 45°C (40°C in the flask). During this time, the fiber was maintained over the sample. The fiber was then introduced into the injection port of a HP6890 plus GC equipped with a Phenomenex Zebron ZB-5 MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness). As the detector, we used an HP5973 mass selective detector (mass range: 15–800 amu; scan rate: 1.9 scans/s; EM voltage: 1435); helium at 0.8 mL/min was used as carrier gas.

The injection port, equipped with a glass insert (internal diameter 0.75 mm) was splitless at 250°C. A desorption time of 1.0 min was used. The detector was maintained at 230°C. Oven was maintained at 40°C for 2 min, then the temperature was increased to 250°C (8°C/min); this temperature was maintained for 10 min. All the analyses were performed in triplicate (RSD 0.03%). The chromatograms obtained from the TIC were integrated without any correction for coelutions and the results were expressed in asu. All the peaks were identified from their mass spectra by comparison with spectra in Wiley6N and NIST98 libraries.

Irradiation of crude oil

Crude oil (10 mL) was irradiated in a sealed vial for SPME analysis with a 125 W high-pressure mercury arc (Helios Italquartz, Milan, Italy) and a solar simulator (Suntest CPS+, Heraeus Industrietechnik GmbH, Hanau, Germany) equipped with a xenon lamp (1.1 kW) that was protected with a quartz plate. The irradiation chamber was maintained at 25°C by a conditioned airflow. In all the experiments, the samples were irradiated for a week.

Photochemical behavior of methylcyclohexane in the presence of 2-methylnaphthalene

2-Methylnaphthalene (1 g, 0.007 mol) and methylcyclohexane (0.7 g, 0.007 mol) were dissolved in acetonitrile (80 mL). The mixture was degassed with nitrogen for 1 h and then irradiated with an immersion apparatus with a 125 W high-pressure mercury arc (Helios-Italquartz, Milan, Italy), surrounded with a Pyrex water jacket. The mixture was irradiated for 3 days and then analyzed using the SPME–GC–MS methodology previously described.

Results and Discussion

We performed our experiments irradiating the crude oil in an SPME vial with a 125 W high pressure mercury arc for seven days and repeating the same experiment, irradiating the crude oil for a week using a solar simulator equipped with a xenon lamp. The results are reported in Figures 1 (GC–MS analysis) and 2 (SPME–GC–MS analysis).

In Figures 1A and 2A, we collected the distribution in a function of the number of carbon atoms. We observed that, in the UV irradiation, the fraction present in the highest percentage shifted from the C8–C9 fractions to the C13 in GC–MS analysis in solution. In this condition, we observed an increase in the relative amount of the C13–C25 fractions, and a decrease in the relative amount of the C7–C12 fractions. In the SPME analysis, the C8–C10 fractions represented 53% of all the compounds detected. However, we observed a decrease in the relative amount of the C8–C10 fractions, while C11–C15 fractions increased. After solar irradiation, the observed trend is very similar. In the GC–MS analysis in solution, the fraction present in the highest percentage shifted at the C13 fraction, we observed increased amounts of the C13–C22 fractions and decreased relative amounts of the C7–C12 fractions. In the

SPME analysis, the maximum was observed at the C8 fraction with an increase in the C6–C9 fractions.

In Figures 1B and 2B, we collected the distribution of the compounds in a function of chemical type of the compounds as reported previously. The GC–MS in solution analysis of the

mixture deriving from UV irradiation showed an increase of the relative amounts of both linear alkanes and aromatic compounds, while we observed a sharp decrease in the relative amounts of branched and cyclic alkanes. After irradiation, we did not find alkenes. The SPME analysis of the same sample

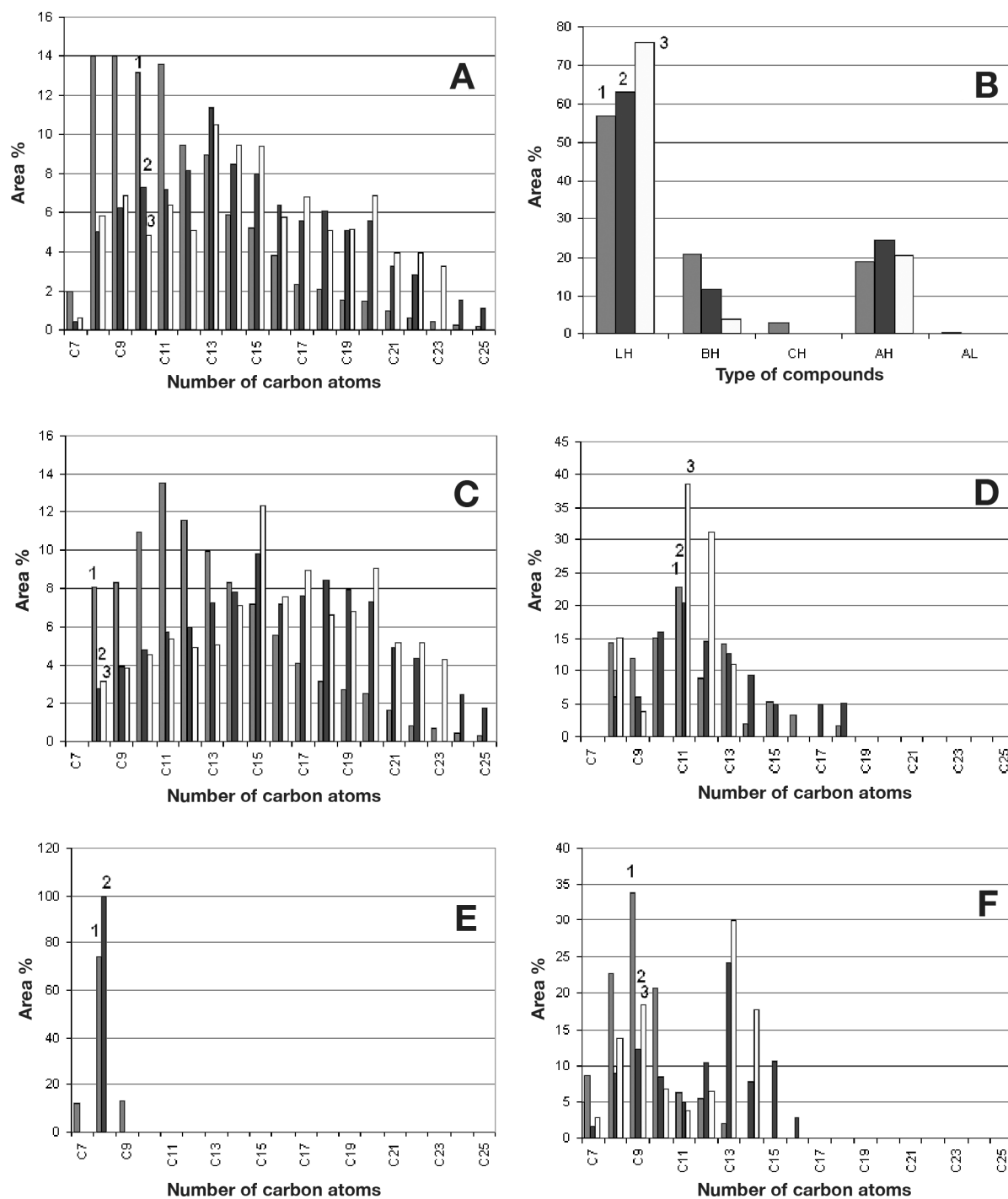


Figure 1. GC–MS analysis of crude oil in solution: composition of crude oil (column 1), UV irradiated crude oil (column 2), and solar simulator irradiated crude oil (column 3), as a function of the number of carbon atoms (A); composition of crude oil as a function of the type of compounds, LH: linear aliphatic hydrocarbons; BH: branched aliphatic hydrocarbons; CH: cyclic aliphatic hydrocarbons; AH: aromatic hydrocarbons; AL: alkenes (B); composition of the linear aliphatic hydrocarbons fraction as a function of the number of carbon atoms (C); composition of the branched aliphatic hydrocarbons fraction as a function of the number of carbon atoms (D); composition of the cyclic hydrocarbons fraction as a function of the number of carbon atoms (E); composition of the aromatic hydrocarbons fraction as a function of the number of carbon atoms (F).

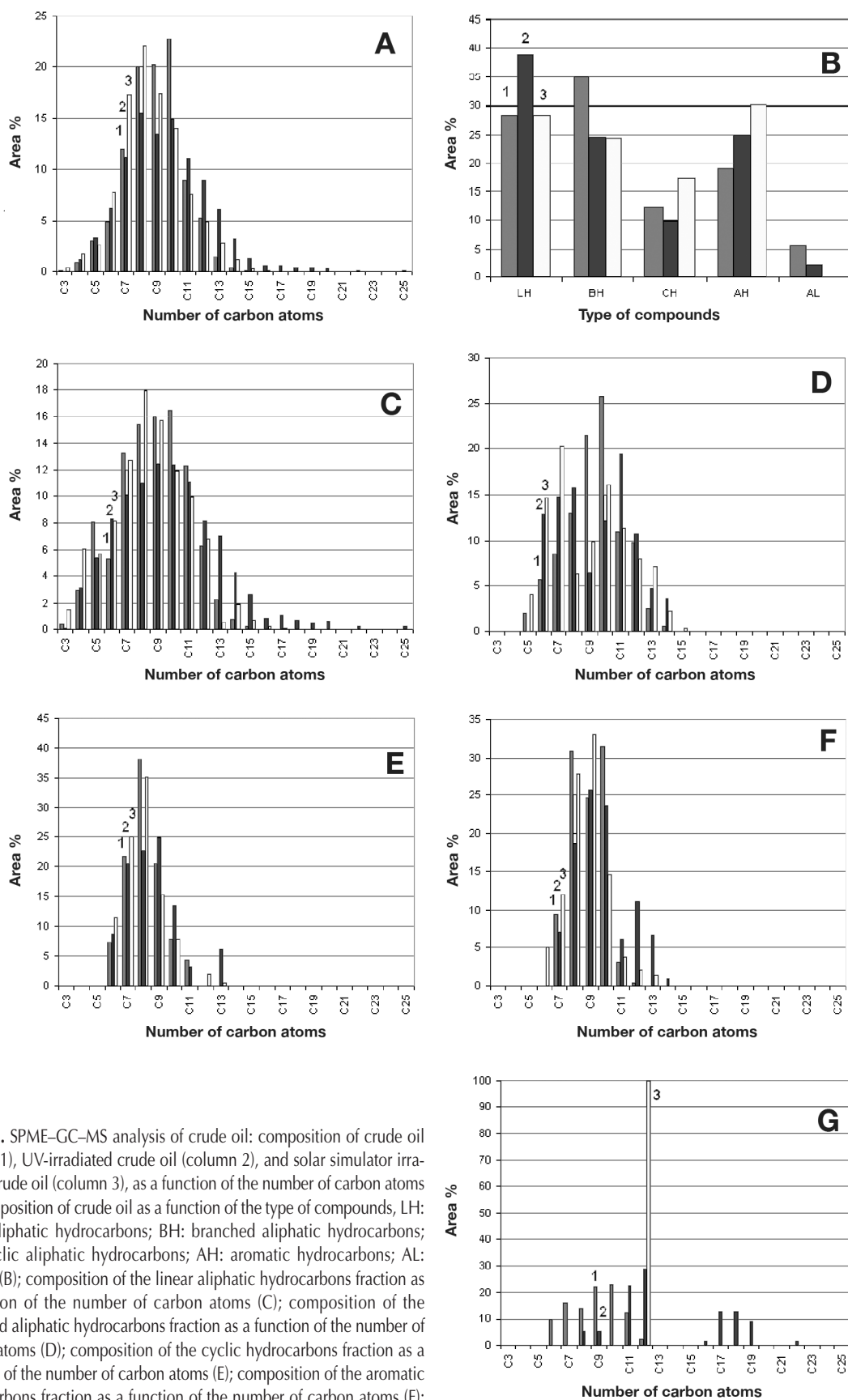


Figure 2. SPME-GC-MS analysis of crude oil: composition of crude oil (column 1), UV-irradiated crude oil (column 2), and solar simulator irradiated crude oil (column 3), as a function of the number of carbon atoms (A); composition of crude oil as a function of the type of compounds, LH: linear aliphatic hydrocarbons; BH: branched aliphatic hydrocarbons; CH: cyclic aliphatic hydrocarbons; AH: aromatic hydrocarbons; AL: alkenes (B); composition of the linear aliphatic hydrocarbons fraction as a function of the number of carbon atoms (C); composition of the branched aliphatic hydrocarbons fraction as a function of carbon atoms (D); composition of the cyclic hydrocarbons fraction as a function of the number of carbon atoms (E); composition of the aromatic hydrocarbons fraction as a function of the number of carbon atoms (F); composition of the alkenes fraction as a function of the number of carbon atoms (G).

showed the same trend: linear alkanes and aromatic compounds increased, while we observed a decrease in the relative amounts of both branched and cyclic alkanes. In this case, we determined the presence of alkenes, but we observed a sharp reduction in the relative amount. The irradiation with a solar simulator gave the same type of results in the GC–MS analysis in solution: the relative amounts of linear alkanes and aromatic compounds increased, while we observed a sharp decrease in the relative amounts of branched and cyclic alkanes. We did not find alkenes. In the SPME analysis, we observed a decreased relative amount of branched alkanes and alkenes and an increase in the relative amounts of cyclic alkanes and aromatic compounds.

On the basis of the previously reported results, we can suppose that linear alkanes did not participate in the photochemical reaction. In fact, the observed increase of the relative amounts could be due to the decrease of the other components (i.e., branched and cyclic alkanes) in the mixture. Our results do not confirm this hypothesis. In fact, the analysis of the composition of linear alkanes fraction after the irradiation showed several changes in the composition of this fraction. The results are reported in Figures 1C and 2C. In the GC–MS analysis, both in UV and in solar simulator irradiation, in crude oil the hydrocarbon present in the highest percentage was undecane, while in the irradiated crude oil pentadecane was the alkane present with highest percent area. We observed a decrease in the C8–C14 fractions and an increase in C15–C25 fractions. In the SPME analysis of the crude oil, the most abundant component was decane, in the UV irradiated sample it was nonane, and in the solar simulator irradiated sample it was octane. We observed a decrease in the amount of pentane, heptane, octane, nonane, and decane in UV irradiation, and a decrease in the amount of pentane, decane, and undecane in the solar simulator experiment. We observed an increase in C12–C25 fractions. For the origin of this increase, where we cannot suppose evaporation of the sample (we observed an increase of propane and butane in the solar simulator experiment), see later.

All our analytical determinations are in agreement with a decrease in the amount of branched alkanes in crude oil after irradiation. The modifications of the composition of this fraction are shown in Figures 1D and 2D. The GC–MS analysis showed that the most abundant fraction did not change after irradiation. However, in UV irradiation, we observed an increase in C14, C17, and C18 fractions; in the irradiation with the solar simulator, branched alkanes underwent a sharp reduction and only C8, C9, C11, C12, and C13 fractions were present. In the SPME analysis, we obtained different results. In UV irradiation, we observed an increase in C5–C8 fractions, a sharp decrease in C9–C10 fractions, and an increase in C11–C14 fractions. In the experiment with the solar simulator, we observed the same trend: an increase in C5–C7 fractions, a sharp decrease in C8–C10 fractions, and an increase in C13–C14 fractions. All branched alkanes were destroyed during irradiation, but C8–C10 fractions suffered a more extensive degradation.

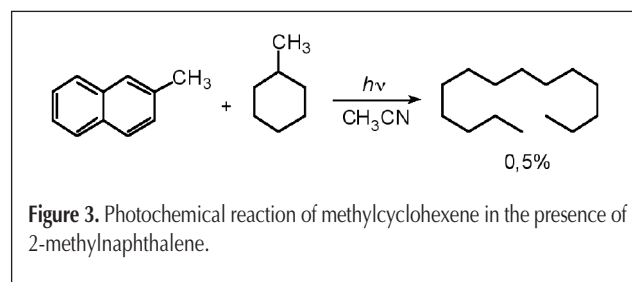
Cyclic alkanes decreased when crude oil was irradiated with the high-pressure mercury arc and increased when the irradi-

ation was performed with the solar simulator. GC–MS analysis identified very few cyclic alkanes in crude oil, all in the range C7–C9 (Figure 1E). Only C8 components were found after UV irradiation, while cyclic alkanes were not found after the solar simulator experiment. SPME showed that the main fraction in crude oil was C8 and that after UV irradiation it shifted to the C9 fraction. After UV irradiation, the C8 fraction decreased while C9, C10, and C13 increased. After irradiation with the solar simulator, C6–C7 fractions increased with C12 and C13, while C9 decreased.

The percentage area of the aromatic compounds in the GC–MS analysis increased (UV irradiation) or was almost constant (solar irradiation) (Figure 1B). However, in both cases, we observed a sharp decrease of benzene-like structures and an increase in naphthalenic structures (Figure 1F). In the SPME analysis, we observed the aromatic compounds increased in the mixture (Figure 2B). In this case, we observed a different behavior (Figure 2F): in both the analyses, the maximum peak was observed at C9, while in crude oil, the range C8–C10 covered the most of the compounds we found. However, in this case, we observed an increase in naphthalenic compounds.

Finally, SPME analysis of both crude oil and irradiated samples showed the presence of alkenes. Their presence after irradiation diminished, and the compounds we found showed a higher molecular weight (Figure 2G): in the crude oil we observed alkenes in the range C6–C12. After UV irradiation, the maximum shifted at C12, while under solar irradiation only 1-dodecene was found in the reaction mixture.

All these data are in agreement with the following conclusions: (i) the alkenes almost disappear after irradiation; (ii) branched and cyclic alkanes (with the exception of one case, see previous) are decomposed during irradiation; (iii) aromatic compounds are not destroyed during irradiation in large quantities (we observed an increase in the content of arenes in the irradiated crude oil); (iv) probably, aromatic compounds act as photosensitizers in photo-oxidation processes; (v) in all the cases, we observed a dynamic equilibrium between the components and the different types of compounds. With the term “dynamic equilibrium”, we cannot identify the presence of a chemical equilibrium between different species. We want to identify the presence of interconversion between different classes of compounds. In fact, we observed that a hydrocarbon can be converted into another one (i.e., low molecular weight linear hydrocarbons into high molecular weight linear hydrocarbons) and that a class of hydrocarbons can be converted into another one (i.e., cyclic hydrocarbons or branched hydrocarbons into aromatic hydrocarbons or linear hydrocarbons and vice versa).



To have an indication about this behavior, we irradiated in acetonitrile methylcyclohexane in the presence of naphthalenic compounds with a 125 W high pressure mercury arc (Figure 3).

The irradiation of methylcyclohexane did not give reaction products, and the irradiation of naphthalenic compounds without the cyclic alkane did not show any reaction product. The irradiation in the presence of naphthalene and 1-methylnaphthalene showed that no reaction occurred. However, the irradiation of methylcyclohexane in the presence of 2-methylnaphthalene showed the presence of tetradecane in the reaction mixture. Clearly, this compound was obtained through a sensitized reaction in the presence of 2-methylnaphthalene via an unknown mechanism. Our efforts in the future will be devoted to explaining this reaction.

Conclusion

In previous works on photodegradation of crude oil, most of the attention was given to photo-oxidation processes. In our work, using both GC-MS and SPME-GC-MS techniques, we did not find oxidation products (alcohols, aldehydes, ketones), but photodegradation occurred. The results of this study confirm that there are a lot of photochemical processes present in crude oil that could play a role inducing modifications in crude oil composition and not only photo-oxidation processes.

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