*Iran. J. Environ. Health. Sci. Eng., 2007, Vol. 4, No. 1, pp. 37-42*

# PHOTOOXIDATION OF CRUDE PETROLEUM MALTENIC FRACTION IN NATURAL SIMULATED CONDITIONS AND STRUCTURAL ELUCIDATION OF PHOTOPRODUCTS

***S. Taghvaei Ganjali , B. Nahri Niknafs, M. Khosravi**

Department of Marine Chem., Islamic Azad University, North Tehran Branch, Tehran, Iran.

Received 10 August 2006; revised 30 August 2006; accepted 25 September 2006

## ABSTRACT

Photooxidation is an important process in the degradation of petroleum spilled in the marine environment. Most crude oils spilled at sea spread rapidly to form slicks with greatly increased surface area. Thus, a fundamental understanding of the effect of photooxidation on oil is a prerequisite for providing an accurate description of the recent history and potential fate of oil spilled in a marine environment. The present work describes a reliable method for evolution and studies the nature of the photoproducts and composition of the residual hydrocarbons of an oil film over the seawater. The maltenic fraction of Iranian oil was exposed to sunlight with simulated natural conditions as a film of oil over seawater. The effect of ultraviolet illumination on using a variety of techniques including GC/MS and FT-IR was examined. The saturated hydrocarbons were very resistant, but the aromatic hydrocarbons were particularly sensitive to photochemical degradation. Greater size and increasing alkyl substitution increased the sensitivity of aromatic compounds to photooxidation.

**Key words:** Photooxidation, oil spill, infrared spectrometry, gas chromatography, mass spectroscopy

## INTRODUCTION

Significant amounts of petroleum enter the marine environment from different sources such as; transportation, natural oil seeps, and oil spills each year (Etkin, 1998). It is estimated that 3.2 million tons of petroleum enters the world oceans each year (Heller, 1993). Most crude oils spilled at sea spread rapidly to form slicks with greatly increased surface area (Nicodem, 1998). Oil entering the seas can have a harmful impact, not only on the marine ecosystem, but also on commercial and recreational resources of coastal areas (Garrett, 1998). Oil is spilled immediately subject to a variety of abiotic processes and associated physical changes such as dispersion, photooxidation, evaporation, dissolution and spreading (Nicodem, 1998) with accompanying changes in density, viscosity and interfacial tension (Heller, 1993) also biotic processes including microbial degradation, biodegradation (Nicodem, 1998). Thus, photooxidation is an important transformation pathway for oil spilled in the marine environment that between 5-40 percent of the oxygen produced by photosynthesis is used by photooxidation (Laane, 1985). The photochemical degradation of hydrocarbons yields a great variety of oxidized compounds, which are highly soluble in a water column (Jacquot, 1996). One year after the Persian Gulf War the seawater contained a high level of oxygenated photoproducts originating from spilled crude oil hydrocarbons (Manfred, 2003). On the other hand, some studies have shown that photoproducts could be greatly toxic (Lacaze, 1989; Jayanti, 1979; Lacaze, 1976; Qstgaard, 1987). Therefore to determine the effects of photooxidation it could be interesting to study the nature of the photoproducts and composition of the residual hydrocarbons (Jacquot, 1996). In the marine environment, photooxidation of crude oil via natural sunlight is difficult to determine because it is included in a very complex process called weathering (Brakstad, 1988; Frances, 1994). In fact a major difficulty in understanding the fate of oil in the environment is the complexity of oils, the crude oils are mixtures of hundreds of different

---

*Corresponding author-Email: *Taghvaei@hotmail.com*
Tel.: +98 21 6643 3507, Fax: +98 21 6693 5779

hydrocarbons and other organic molecules containing heteroatoms (Nicodam, 1998). While this study can give useful information on possible reaction under simulated natural conditions. The purpose of the present work consisted of the evolution of the effects of the *in vitro* photooxidation of crude oils in environmental conditions. We used a maltenic fraction of crude oil obtained after asphaltene precipitation and which mainly contained saturated and aromatic hydrocarbons. The saturated compounds include the straight and branched chain alkanes and cycloalkanes. The aromatic consists of aromatic mono or polycyclic compounds, often with alkyl or cycloalkane substituents. The data presented here afford a greater understanding of the effect of photooxidation on crude petroleum.

## MATERIALS AND METHODS

The crude oils used in this study were from Iranian oil fields in the region of MARON and AHWAZ. The specific gravities (SP.GR.@ 60°F/60°F ) were 0.8595, 0.8560 and API (American petroleum institute ) gravities were 33.1, 33.8 and kinematic viscosity were 19.6, 19.5 centistockes at 20 °C (10, 9.9 cSt at 40 °C ) and sulfur contents of 1.69 %, 1.5%.The seawater (salinity, 40psu and pH=7.8~8) was collected from Persian Gulf.

### *Photooxidation experiments*

The majority of the experiments used an artificially weathered MARON crude oil that had been heated under a partial vacuum in rotary evaporator so as to have lost light compounds of crude oil (yield on crude oil was 3% V/V). This approximates the extent of weathering this oil is likely to undergo while floating as an oil slick (Payne, 1991). The photooxidation experiments were made on the maltenic fractions obtained after the removal of the asphaltenes (a 2 hour reflux in n-heptane and purification by open column liquid/ solid chromatography on 14 g of Florisil, elution with 100 mL of toluene) Seawater was poured into a clean pentan- rinsed glass container and filtered through pre-cleaned Millipore filter paper, pore size 0.45 micrometer (Jacquot, 1996). Artificial oil slicks were created by floating 5 mL of a maltenic fraction of crude oil on 25 mL of seawater containing 0.2% sodium azide contained in a glass pyrex dishes with pyrex lids. This pyrex transmits 75% at 295 nm and 85% at 300 nm and does not appreciably attenuate sunlight. Samples were exposed to sunlight on the chemistry building roof on cloudless days from 11 AM until 3 PM for 1 month (from june 22th, to july 22th, 2003) until the total number of hours (60h) was accumulated. Control sample was kept in the dark during the same period. Following irradiation, the two phases were separated by centrifugation and the oil samples were stored in the dark in a freezer until required. This precaution was taken to insure that there was no biological degradation while a waiting analysis.

### *Gas chromatography/MS spectrometry (GC/MS) analysis*

Analysis of the oil by GC/MS essentially followed by the procedure of F. Jacquot etal, 1996 (Jacquot, 1996). The analyses of photoproducts and residual hydrocarbons were performed on a Thermo finnigane GC 2000 equipted to trace MS. The following chromatographic conditions were used: 60m x 0.25 mm HP-5 fused silica capillary column. Helium was used as the carrier gas at a flow rate of 1mL/min. The column temperature was set to 70°C for the first 4min, increased 5 °C/min to a temperature of 295°C and maintained at 295°C for 30min. Mass spectral data were obtained with a quadrupolar analyzer mass selective detector at an electron energy of 70 ev over a mass range of 35-500 atomic mass units in the total ion mode. Polycyclic aliphatic biomarker such as hopane were analysed by GC/MS using selected ion recording mode of mass to charge ratio (m/z) of 191 for hopanes. Biomarker identifications were based on a previous study on the crude oil (Jacquot, 1999). Polycyclic aromatic hydrocarbons were identified by ion profiles of m/z 128, 142, 156 for naphthalenes, m/z 178, 192, 206 for phenanthrenes, m/z 184, 198, 212 for dibenzothiophenes and m/z 114, 228, 242 for chrysenes (Peters, 1993; Letellier, 1993).

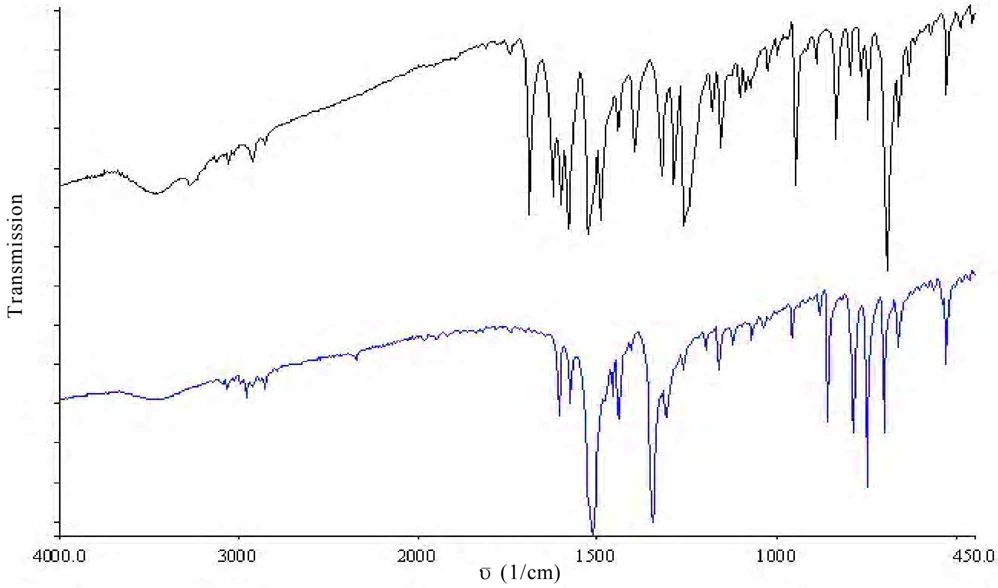
### *FT-IR analysis*

Infrared spectra were obtained using a Perkin-Elmer spectrum on FT-IR spectrometer. The samples were deposited as thin films between NaCl plates. The petroleum samples were applied without dilution.

## RESULTS

### *Infrared spectrometry*

FT-IR spectra of crude oil (control) showed the characteristic bands of aliphatic ($CH_2$ and $CH-_3$ stretching at 2962, 2934 and 2872 1/cm, $CH_2$ and $CH_3$ bending at 1443 and 1342 1/cm) and aromatic hydrocarbons (ring stretching at 1606 1/cm, CH out-of-plane bending at 558, 782 and 749 1/cm). The infrared spectrum of irradiated sample in comparison with control sample is shown in Fig. 1.



FT-IR spectra of irradiated sample (up) in comparison with control sample (down)

Fig. 1: The infrared spectrum of irradiated sample in comparison with control sample

### *GC/MS*

Gas chromatography/mass spectroscopy was used to examine the initial maltenic oil, and irradiated sample. The mass spectrometer was operated in both total ion mode to characterize as much of the oil as possible and in selected ion mode to examine the degree of photooxidation of selected polynuclear aromatic hydrocarbons including phenanthrene, dibenzothiophene, naphthalene, chrysene, and their alkylated homologous. The total ion chromatograms of the four samples are dominated by the straight chain saturates and appear quite similar with the exception of the lightest compounds loss in the experimental samples, suggesting that the linear alkanes are resistant to photooxidation under these conditions. We detected the triterpanes including the hopanes (m/z=191), it is important to note that the hopane distribution was unaffected by solar irradiation under these conditions. Hopane is quite resistant to many biological and chemical processes. The linear alkanes such as phytane and pristine are resistant to photooxidation, since in this study biological process has not been observed, results indicates that photooxidation of pristine and phytane are not important for the exposure times used here. Unlike the saturated compounds, the alkyl substituted aromatic molecules are exhibited remarkable sensitivity to solar radiation. Increasing the alkyl substitution of the aromatic molecules was resulted in a dramatic increase in the sensitivity to solar irradiation, with the $C_3$ compounds being approximately 50% degraded. The three aromatic compounds, naphthalene, phenanthrene, dibenzothiophene presented here all exhibit increasing sensitivity to photooxidation with increasing alkyl substitution. Our data in this study indicate that photochemical oxidation and biodegradation have opposite effects on aromatic hydrocarbons in crude oils. Table 1 shows the constituents of control and irradiated samples based on GC/MS data.

Table 1: Constituents of control and irradiated samples based on GC/MS

| Compound | formula | MW[a] | CAS No[b] | m/z[c] | $R_t$(control) | $R_t$(irradiated) | DB[d] |
|---|---|---|---|---|---|---|---|
| n-Heptane | $C_7H_{16}$ | 100 | 142-82-5 | 43 | 7.56 | 7.55 | wiley |
| Benzene | $C_6H_6$ | 78 | 71-43-2 | 78 | 11.2 | 11.2 | mainlib |
| Ethyl benzene | $C_8H_{10}$ | 106 | 100-41-4 | 91 | 11.9 | 12 | wiley |
| Naphtalene | $C_{10}H_8$ | 128 | 91-20-3 | 128 | 13.10 | 13.30 | mainlib |
| Methyl naphthalene | $C_{11}H_{10}$ | 142 | 91-57-6 | 142 | 13.85 | 13.70 | nistdemo |
| Isopropyl naphthalene | $C_{13}H_{14}$ | 170 | 6158-45-8 | 155 | 15.90 | 15.60 | wiley |
| Phenanthren | $C_{14}H_{10}$ | 178 | 85-01-8 | 178 | 18.1 | 18 | wiley |
| Anthracen | $C_{14}H_{10}$ | 178 | 120-12-7 | 178 | 18.2 | 18.2 | wiley |
| Dibenzothiophene | $C_{12}H_{10}S$ | 184 | 132-65-0 | 184 | 21 | 21.11 | wiley |
| Methyl dibenzothiophene | $C_{13}H_{10}S$ | 198 | 16587-52-3 | 198 | 21.9 | 21.56 | mainlib |
| Dimethyldibenzothiophen | $C_{14}H_{12}S$ | 212 | 1207-15-04 | 212 | 24.60 | 24.70 | mainlib |
| Pristane | $C_{19}H_40$ | 268 | 1921-70-6 | 57 | 28.6 | 28.6 | wiley |
| Phytane | $C_{20}H_{42}$ | 282 | 638-36-8 | 57 | 31.2 | 31.1 | mainlib |
| Chrysene | $C_{18}H_{12}$ | 228 | 218-01-9 | 228 | 39.52 | 41.63 | wiley |
| Methyl chrysene | $C_{19}H_{14}$ | 242 | 3351-28-8 | 242 | 44.1 | 44 | wiley |
| Hopane | $C_{30}H_{52}$ | 412 | 471-62-5 | 191 | 48.30 | 47.21 | wiley |

a: Mulecular Weight, b: Chemical Abstract Registration Number, c: Base Peak, d: DataBase

*Photoproduct identifications*

The samples were obtained from Iranian crude oil and photooxidation products of the aromatic compounds were detected. A very large number classes of compounds were identified as photoproducts. Nevertheless, identifiable photoproducts of the photochemical oxidation process amounted to only about 12% of the total products. There are other photoproducts and undetected intermediates. Possible explanations can be put forward for the undetected products. Oxygenated compounds are formed but migrate into the aqueous phase, or the oxidation process products low molecular weigh oxidized components which are volatile and therefore lost. We identified eleven photoproducts after 60h irradiation (Table 2).

Table 2:Identification Data for identified photoproducts

| Compound | Formula | MW[a] | CAS No[b] | m/z[c] | DB[d] |
|---|---|---|---|---|---|
| 1,2-Benzenediol | $C_6H_6O_2$ | 110 | 120-80-9 | 110 | Mainlib |
| 2,4-Hexadienedioic acid | $C_6H_6O_4$ | 142 | 505-70-4 | 97 | Mainlib |
| 1-Naphthalenol | $C_{10}H_8O$ | 144 | 90-15-3 | 144 | Wiley |
| 9H-Fluoren-9-one | $C_{13}H_8O$ | 180 | 486-25-9 | 180 | Wiley |
| 2,3:4,5-Dibenzoxepin | $C_{14}H_{10}O$ | 194 | 220-06-4 | 165 | Wiley |
| 3,4-Benzocoumarin | $C_{13}H_8O_2$ | 196 | 2005-10-9 | 196 | Wiley |
| 9,10-Anthracenedione | $C_{14}H_8O_2$ | 208 | 84-65-1 | 180, 208 | Wiley |
| 9,10-Phenanthrenedione | $C_{14}H_8O_2$ | 208 | 84-11-7 | 180, 152 | Wiley |
| 2,2`-Diformylbiphenyl | $C_{14}H_{10}O_2$ | 210 | 1210-05-5 | 181 | Wiley |
| Benzene,1,1`-[thiobis(methylene)]bis | $C_{14}H_{14}S$ | 214 | 538-74-9 | 91 | Wiley |
| Dibenzanthracene-5,6-quinone | $C_{22}H_{12}O_2$ | 308 | 52755-66-5 | 280 | Mainlib |

a: Mulecular Weight, b: Chemical Abstract Registration Number, c: Base Peak, d: DataBase

## DISCUSSION

As shown in Fig. 1, from the figure, although two spectra are very similar but the irradiated sample does show decreased absorption in the 700-900 cm region and some increased absorption in the 3463, 1746,1089 1/cm regions. FT-IR spectra of photooxidized fraction of irradiated sample shows carbonyl stretching of carboxylic acids at 1705 1/cm, carbonyl stretching of ketones at 1716 1/cm. The shoulder at 1746 and 1766 1/cm maybe attributed to *gamma*-lactones as previously observed (El-Anba-Lurot, 1995). Region of control sample of 950 to 1200 1/cm (the initial weak absorption at 960, 1030, 1080, and 1170 1/cm of n-alkane and substituted benzene) are gradually submerged by a broad absorption of C–O bond in alcohols, ethers, esters, and acids in irradiated sample. The simplest explanation for this change involves the formation of carbon-oxygen bonds due to photochemical oxidation. The results of FT-IR spectra were confirmed by the GC/MS data, which mainly indicated the structure of the photoproducts. Photoproducts were identified by comparison of the relative retention times and mass spectra to those of authentic compounds and literature data. These compounds, formed after opening of one or two aromatic rings or epoxide formed, predominate but also quinines, aldehydes, alcohols, and acetyl derivatives are detected. The photooxidation of PAHs via a singlet oxygen mechanism was previously shown for phenanthrene and anthracene (Dowty, 1974). The studies pointed out that singlet oxygen is a highly selective oxidant reacting rapidly only with electron-rich compounds such as PAHs. Also, singlet oxygen is a more powerful oxidant than dioxygen and can be formed even if oxygen is present in only trace amounts (Zepp, 1985). Although spilled oil is subject to range of natural processes,only combustion,photooxidation and biodegradation destroy hydrocarbons and remove them from the biosphere.Photooxidation is an important transformation pathway for petroleum spilled in the marine environment.The maltenic fraction of Iranian crude oil was irradiated under sunlight and the alterations in its composition produced by solar irradiation were investigated using gas chromatography/mass spectroscopy (GC/MS), infrared spectrometry (FT-IR). Our desire wasto generate an easily measurable effect on the oil, thus, conditions were designed to yield a high degree of photooxidation. The crude oils maltenic fraction was floated on the surface of artificial seawater to simulate a marine oil slick. After 60h of irradiation the oil was extracted and concentrated for analyses. The methods and experiments in this study individually and collectively gives information about the types and distribution of petroleum components and structural elucidation of photoproducts.

## ACKNOWLEDGEMENTS

The authors would like to thank the Iranian Pesticide Industrial Research Center (PIRC) for their support services; Drs. A. Shahrezaie and J. Ghotbesharif are highly acknowledged for their advicings on experiments.

## REFERENCES

Brakstad, F., Nielsen, G., (1988). Identification of weathered oils J. Marine. Pollut.Bulletin., **19**: 319-326.

Budzinski, H., Letellier, M. and Garrigues, P., (1993). Les composes aromatiques Alkyles dans les echantillons petroliers: aspects physicochimiques et. Thermodynamiques. Thesis ,University of Bordeaux, France., 26: 301.

Dowty, B. J., Brightwell, N. E., Laseter, J. L., Griffin, G. W., (1974). Dye-Sensitized photooxidation of phenantherrne. J. Biochem. Biophys. Res. Commun., **57**: 452-455.

Ehrhardt, M. G., Burns, K. A., (1993). Hydrocarbons and related photooxidation In saudi arabian gulf coastal waters and hydrocarbons in underlying Sediments and bioindicator bivalves .Marine. Pollut. Bulletin., **27**:187-193.

El-Anba-Lurot, F., Guiliano, M., Doumenq, P., Bertrandj, C., Mille, G., (1995). Photooxidation of biphenyls in natural sea water. Intern. J. Environ. Annl. chem., **27**: 61-69.

Etkin, D. S., Wells, P., Nauke, M., Campbell, J., Grey, C., Koefoed, J., Meyer, T. And Reddy, S., (1998). Estimates of oil entering the marine environment In the past decade, Proceedings of the twenty-first Arctic and marine Oil spill program technical seminar;Environment Canada: Edmonton, Alberta, 903.

Garrett, R. M. and Pickering, I. J., (1998). Photooxidation of crude oil. J. Environ. Sci. Technol., **32**: 3719-3723.

Heller, A. and Brock, J. R., (1999). Materials and methods for photocatalyzing oxidation of organic compounds on water, United States Patent 5: 256616.

Hostetller, F. D., Kvenvolden, K. A., (1994). Geochemical changes in crude oil Spilled from the Exxon Valdez supertanker in to prince William Sound, Alaska.Org. J. Geochem., **21**: 927-933.

Jacquot, F., Guiliano, M., Doumenq, P., Mundz, D., Mili, G., (1999). In vitro Photooxidation of crude oil maltenic fractions:Evalution of fossil Biomarkers and polycyclic aromatic hydrocarbons. J. Chemosphere., **33** (4): 671-681.

Laane, R. W, Gieskes, W. W., Kraay, G. W., (1985). Oxygen consumption from Natural water by photo-oxidizing processes. Neth. J. Sea. Res., **19**: 125-132.

Lacaze, J. C., Villedon De Naide, O., (1976). Influence of illumination on phytotoxicity of crude oil. J. Marine. Pollut. Bulletin., **7**: 73-77.

Lacaze, J. C, Paquet, F., (1990). Pollution des sediments marins sur la production, J. R. O., **15** (3-4): 72-77.

Nicodem, D. E., Guedes, C. B., Correa, R. J., ( 1998). Photochemistry of Petroleum. J. Marine. Chemistry., **63**:93-104.

Ostgaard, K., Auborga, A., Klungsoyr, J., Jensen., (1987). A Comparative Studies of phytotoxicity and chemical composition of aqueous Oil solutions affected by evaporation , illumination and extraction. J. Water. Res., **21**:155-162.

Patel, J. R., Overton, E. B., Laseter, J. L., (1979). Environmental photooxidation Of dibenzothiophenes following the Amoco Cadiz oil spill. J. Chemosphere., **8**:557-560.

Payne, J. R., Clayton, J. R., Mcnabb, G. D. and Kirstein, B. E., (1997). Exxon valdez oil weath fate and behavior. *Proceedings* of the 1991 International oil spill conference; American Petroleum Institute: Washington American Petroleum Institute: Washington, D. C., 641-645.

Peters, K. E., Moldowan, J. M., (1993). The biomarker guide. Interpreting Molecular fossils in petroleum and ancient sediments,Prentice Hall,Englewood cliffs, Nj.: 72-776.

Zep, R. G., Schlotzhauer, P. F., Sink, R. M., (1985). Photosensitized Transformations involving elctronic energy transfer in natural Water. J. Environ. Sci. Technol., **19**: 74-81.