PHOTOOXIDATION AND PHOTOCHEMICAL IMPACT ON CRUDE PETROLEUM AND STRUCTURAL ESTIMATION OF PHOTOPRODUCTS

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Abstract

Photolysis is one of the most important processes affecting to the oil chemical composition. In this study we used the Russian Export Blend. The oxidizing agent used for the photochemical oxidation test was potassium permanganate. As shown in IR spectra of the initial sample, the irradiated sample and irradiated in the presence of KMnO4 sample after 60 hours, although the spectra are very similar in irradiated 60-hour samples appeared increased absorption at 1168 cm^{-1} (alkylsulfonated derivatives) from 27-th hour in the first set and early in the second series of experiments, and at 3729 cm^{-1} (alcoholic derivatives) from 48-th hour in the first set and early in the irradiation of the second set of tests. The results of the experiments also show that alkane hydrocarbons are stable to photooxidation while much of arene derivatives become resins and other polar compounds.

Keywords: Photooxidation; Crude petroleum; Photoproducts; Infrared spectrometry; Gas chromatography and mass spectrometry.

1. Introduction

Photolysis is one of the most important processes affecting to the oil chemical composition once it is released into the environment, in a time span between few weeks to several months. Photolysis involves a large number of chemical oxidation reactions leading to the carbon oxidation. It can occur directly when molecules can absorb the solar irradiation or indirectly when a photosensitizer is needed because the target molecule does not contain any chromophore. The intermediate products of photooxidation can be more toxic than the parent compounds and, therefore, be of higher ecotoxicological concern [1].

The removal of sulfur compounds from liquid fuels has become an important task in recent years, not only due to stringent environmental regulations, but also for fuel cell applications. Sulfur content needs to be cut to below 0.1 ppm [2, 3] or 0.05 ppm [4] to avoid poisoning reforming catalysts and the catalysts in fuel cell electrodes. At present, catalytic hydrodesulfurization (HDS) [5-10] is commonly used for sulfur removal from fuels. This process involves high temperatures exceeding 300°C, elevated pressures of over 2 MPa [11, 12], precious metal catalysts, high hydrogen consumption, and large reactors. Dibenzothiophenes (DBTs), especially 4 and/or 6 alkyl-substituted DBTs, are difficult to remove using the HDS process unless an energy-intensive process is applied. To reduce the energy needed for desulfurization, a large number of non-HDS processes, such as alkylation, extraction, precipitation, oxidation and adsorption, have been investigated [13-16]. Of these, oxidative desulfurization (ODS) and adsorptive desulfurization appear promising, since they can be applied at ambient temperature and pressure. The ODS processes, including microbial oxidation, chemical oxidation and photooxidation, generally lead to the formation of sulfoxides or sulfones that can be subsequently removed by conventional separation methods such as extraction, adsorption or distillation. We are particularly interested in photooxidation because of the possibility of using atmospheric oxygen as an oxidizing agent [17].

2. Experimental

In this study we used the Russian Export Blend which properties are shown in Table. 1. The oxidizing agent used for the photochemical oxidation test was potassium permanganate (Fluka Analytical, super special grade).

The sample 1 (pure Russian Export Blend) and sample 2 (Russian Export Blend + 10%

of potassium permanganate) were exposed to light at room temperature. Samples were irradiated for 60 hours at a distance of 40 cm with two 250 W quartz lamps (Philips, IR250S) covering the UV and visible ranges.

Table 1 Properties of Russian Export Blend.

Properties	Method	Result
Distillation characteristics:	ASTM D 86	
- up 200 °C, % v/v		22.5
- up 300 °C, % v/v		42.0
- up 350 °C, % v/v		55.0
Water content, %	ASTM D 95	0.12
Sediments, %	ASTM D 473	0.0064
Density, g/cm^3	ASTM D 1298	
- 20 °C		0.8637
- 15 °C		0.8671
Salts, %	ASTM D 3230	0.0028

2.1 FT-IR spectrometry

The FT-IR spectra were recorded using KBr pellets. The samples were prepared as follows: 2 mg of the studied samples were grounded together with 200 mg KBr (Merck) into the fine powder with the particles size below 5 μm and compressed to form of clear disk. The FT-IR spectra were recorded using Brücker Tensor-27 spectrometer at ambient temperature in the wave number 4000-400cm^{-1}.

2.2 Gas chromatography/MS spectrometry (GC/MS) analysis

Analysis of the oil by GC/MS essentially followed by the procedure [18]. The analyses of photoproducts and residual hydrocarbons were performed on a Varian 450-GC equipped to trace MS. The following chromatographic conditions were used: 60mx 0.25 mm HP-5 fused silica capillary column. Helium was used as the carrier gas at a flow rate of 1 mL/min. The column temperature was set to 70°C for the first 4 min, increased 5°C/min to a tempe-rature of 295°C and maintained at 295°C for 30 min. 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 [18]. 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. The identification data of pure Russian Export Blend (REB) and irradiated samples based on GC/MS is shown in Table 2.

Table 2 Identification data of pure REB and irradiated samples based on GC/MS.

No	Compound	Formula	MW	CAS No	Rt min	DB
1.	Nonane	C9H20	128	000111-84-2	5.47	Nist
2.	Decane	C10H22	142	000124-15-5	8.21	Mist
3.	Undecane	C11H24	156	001120-21-4	11.43	Nist
4.	Dodecane	C12H26	170	000112-40-3	14.80	Nist
5.	Tridecane	C13H28	184	000629-50-5	17.84	Nist
6.	Tetradecane	C14H30	198	000629-59-4	20.66	Nist
7.	2,6-Dimelhylnaphthalene	C12H12	156	000581-42-0	21.3	Nist
8.	Pentadecane	C15H32	212	000629-62-9	23.24	Nist
9.	Hexadecane	C16H34	226	000544-76-3	25.58	Nist
10.	Hepladecane	C17H36	240	000629-78-7	27.79	Nist
11.	Octadecane	C18 H38	254	0005&3-45-3	29.79	Nist
12.	2,6,10,14- Tetramethylhexadecane	C20H42	282	000638-36-8	29.92	Nist
13.	Nonadecane	C19H40	268	000629-92-5	31.81	Nist
14.	Eicosane	C20H42	282	000112-95-8	33.83	Nist
15.	Heneicosane	C21H44	296	000629-94-7	35.82	Nist
16.	Docosane	C22H46	310	000629-97-0	37-78	Nist
17.	Tricosane	C23H48	324	000638-67-5	39.68	Nist
18.	Ttetracosane	C24H50	338	000646-31-1	41.55	Nist
19.	Pentacosane	C25H52	352	000629-99-2	43.34	Nist
20.	Hexacosane	C26H54	366	000630-01-3	45.04	Nist
21.	Heptacosane	C27H56	380	000593-49-7	46.64	Nist
22.	Octacosane	C28H58	394	000630-02-4	48.14	Nist
23.	Nonacosane	C29H60	408	000630-03-5	49.57	Nist
24.	Triacontane	C30H62	422	000638-68-6	51.09	Nist

3. Results and discussion

FT-IR spectra of Russian Export Blend (Fig. 1) showed the characteristic bands of aliphatic (CH_2 and CH_3 stretching at 2854 cm^{-1} и 2957 cm^{-1}, CH_2 and CH_3 bending at 1461 and 1378 cm^{-1}), aromatic hydrocarbons (ring stretching at 1605 cm^{-1}, CH out-of-plane bending at 725 and 742 cm^{-1}), and aliphatic nitrocompounds (stretching at 1378 cm^{-1}). The infrared spectrum of pure Russian Export Blend sample and irradiated samples are shown in Fig. 1-3.
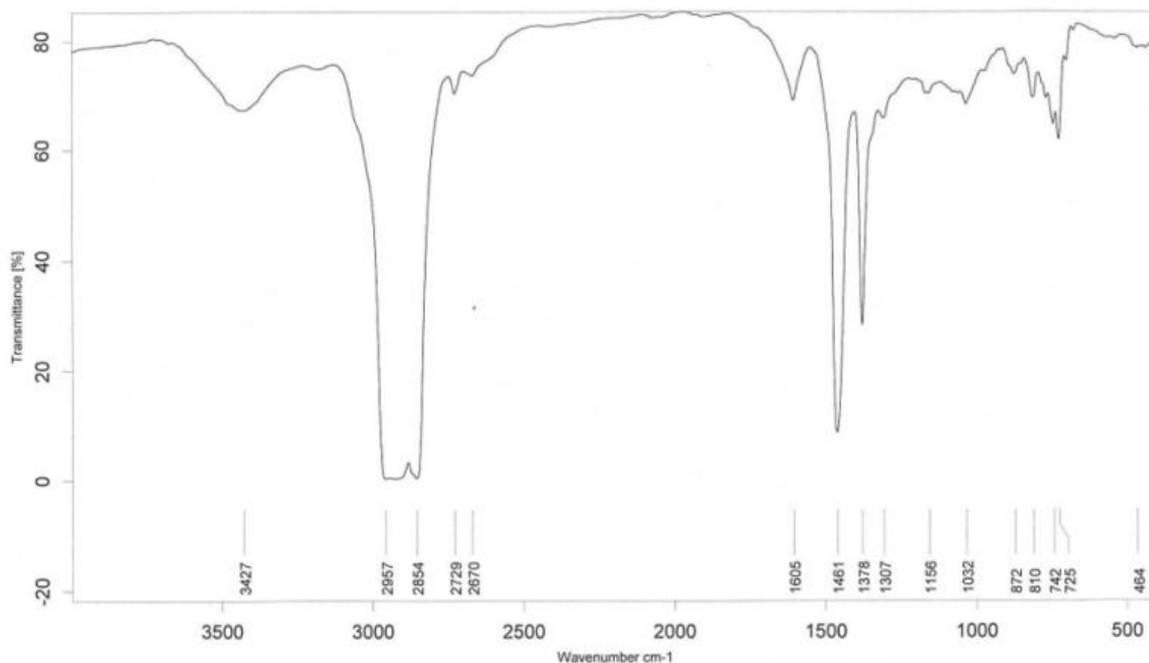
Fig. 1. The infrared spectrum of pure Russian Export Blend
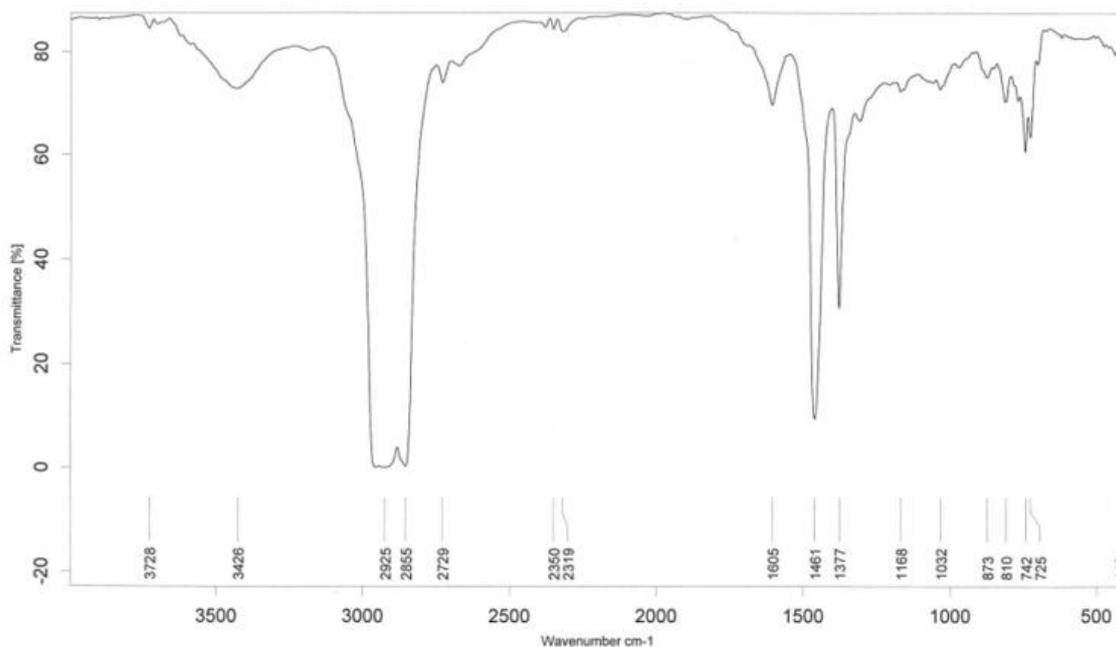
Fig. 2. The infrared spectrum of irradiated after 60 h sample
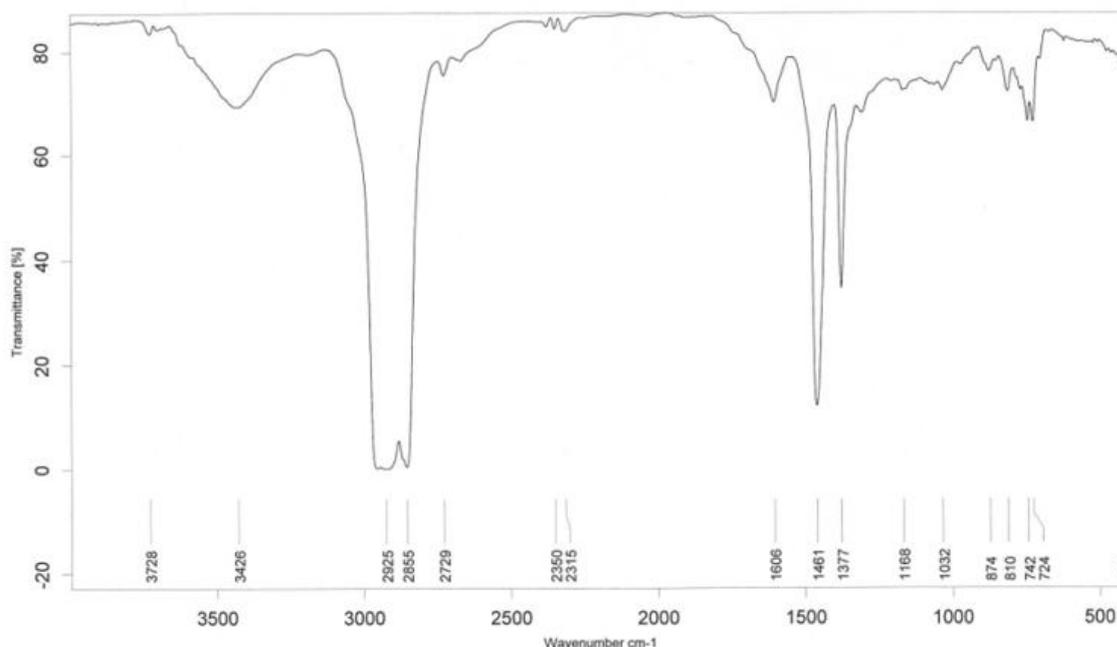
Fig. 3. The infrared spectrum of irradiated after 60 h sample with potassium permanganate.

As shown in IR spectra of the initial sample (Fig. 1), the irradiated sample (Fig. 2) and irradiated in the presence of KMnO4 sample after 60 hours (Fig. 3), although the spectra are very similar in irradiated 60-hour samples appeared increased absorption at 1168 cm^{-1} (alkylsulfonated derivatives) from 27th hour in the first set and early in the second series of experiments, and at 3729 cm^{-1} (alcoholic derivatives) from 48th hour in the first set and early in the irradiation of the second set of tests.

Likely explanation of this change is the formation of carbon-oxygen links at photooxidation and photochemical oxidation processes. The results of IR spectra for the starting and irradiated 60-hour samples were confirmed by data from GC/MS study showing the structure of compounds in samples. The composition of the samples was identified by comparing the relative retention times and mass spectra of known compounds and the other from literature (Fig 4-6). These compounds, formed by rupture of one or two rings or resulting arene epoxides were identified as alcohol (1-Hexacosanol) and alkylsulfonated derivatives.
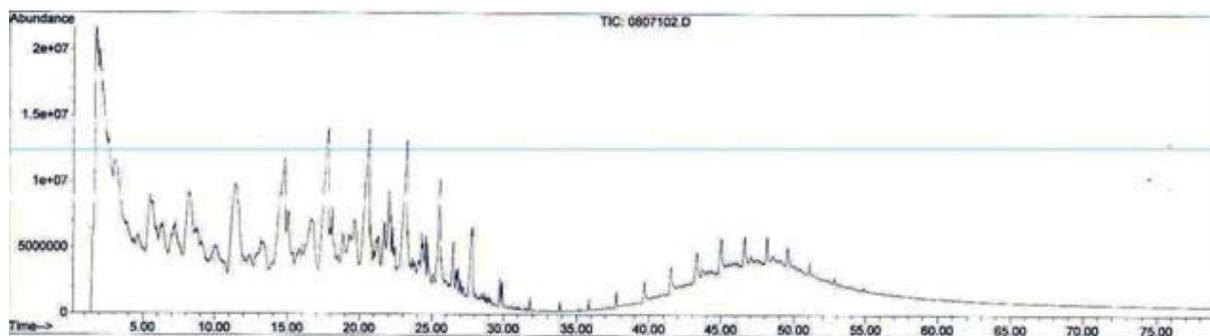
Fig. 4. The GC/MS chromatogram of pure Russian Export Blend
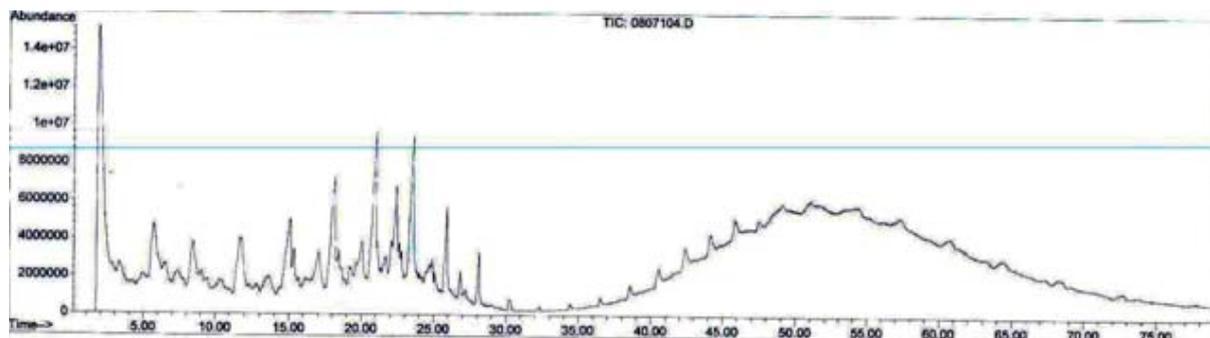
Fig. 5. The GC/MS chromatogram of irradiated after 60 h sample
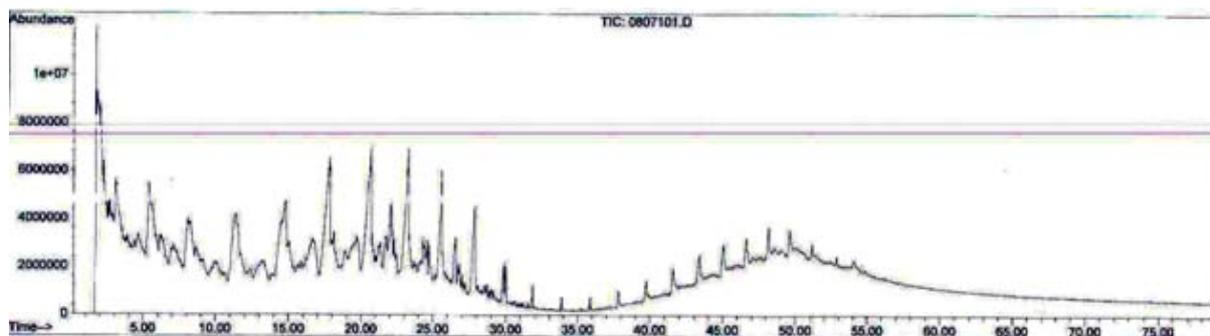
Fig. 6. The GC/MS chromatogram of irradiated after 60 h sample with potassium permanganate.

The results of the experiments also show that alkane hydrocarbons are stable to photo-oxidation while much of arene derivatives become resins and other polar compounds.

4. Conclusion

Photolysis is one of the most important processes affecting to the oil chemical composition. In this study we used the Russian Export Blend. The oxidizing agent used for the photo-chemical oxidation test was potassium permanganate. As shown in IR spectra although the spectra are very similar in irradiated 60-hour samples appeared increased absorption at 1168 cm^{-1} (alkylsulfonated derivatives) from 27th hour in the first set and early in the second series of experiments, and at 3729 cm^{-1} (alcoholic derivatives) from 48th hour in the first set and early in the irradiation of the second set of tests. The results of the experiments also show that alkane hydrocarbons are stable to photooxidation while much of arene derivatives become resins and other polar compounds.

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