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THERMOCHEMICAL LUMINESCENCE AND CHEMICAL TRANSFORMATION MECHANISMS IN HEAVY CRUDE OIL RESIDUES

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ABSTRACT

This study investigates the thermochemical luminescence (TCL) behavior of heavy residues derived from Karabakh, Absheron, and Naftalan crude oils to examine their chemical transformations and implications for quality. Crude oil is a complex mixture of hydrocarbons, dissolved gases, water, salts, and impurities, with its composition varying significantly. Advanced spectroscopic techniques, including UV, NMR, IR, and luminescence analysis, were utilized to explore the structural-group composition and physicochemical properties of these oils. TCL analysis revealed consistent characteristics among the heavy oil residues, marked by hybrid molecular structures and weakly bonded C–H linkages. The residues, after undergoing de-resinification and deasphalting, exhibited a notable uniformity, making them promising candidates for use as biologically active substances. Photoirradiation experiments demonstrated that the TCL maxima for heavy residues appear in lower-temperature spectral regions compared to many distillate fractions. The visible light emission was attributed to the decomposition of endoperoxides during the recombination of peroxide radicals. This observation opens the possibility of utilizing hydrocarbons as alternative light sources, including applications involving solar energy. These results have implications for improving refining processes, optimizing the transportation and storage of crude oil, and broadening the industrial applications of petroleum and its by-products.

1. Introduction

Since crude oil is a natural source for obtaining valuable hydrocarbons, its study has attracted the attention of scientists for many years. The study of crude oil and its products, composed of various hydrocarbons, their physical-chemical properties, structural-group composition, changes in its characteristics after photo- and thermal effects, including chemical transformations, is a pressing issue that requires resolution. This is of significant scientific and practical interest. In the investigation of the composition of crude oil, the examination of the structures of initial biological compounds and their transformation products plays an essential role. The study of the hydrocarbon composition of crude oils greatly aids in classifying them into different types.

The saturated hydrocarbons in crude oil determine the initial biomolecules during geochemical processes, as well as the chemical transformations occurring within them [8, 9]. On the other hand, studying the chemical group composition of these substances is crucial in selecting a more efficient method during the crude oil refining process, as well as in solving the issues related to the transportation and storage of crude oil. Moreover, it is essential for the utilization of crude oil and its products in various industries (such as petrochemicals, heavy machinery manufacturing, etc.), medicine, and other fields [1-3]. This is because the properties of crude oils and natural gases affect their application. By studying the thermal properties of crude oil and the oils derived from it, the impact of temperature changes on their physical-chemical properties over time can be determined. After removing asphaltene from well oil, the separation of its fraction composition and the analysis of hydrocarbons with a low boiling point are among the critical aspects [10].

It should be noted that the composition of crude oil includes not only various hydrocarbons but also dissolved gases, water, mineral salts, and mechanical impurities. Due to the presence of numerous different organic substances in crude oil, it is characterized not by a single boiling point but by a boiling range (which, depending on density, varies between 28-360°C) and by its fraction composition. The density of crude oil ranges from 750 to 1050 kg/m^3, and its freezing point is from minus 60°C to plus 30°C (this temperature increases with a higher content of paraffins in the oil and decreases with an increase in lighter fractions). The flash point, in a closed cup, varies between minus 40°C and plus 30°C, depending on the fraction composition [6, 7]. Crude oil dissolves in organic substances, does not dissolve in water, and forms a stable emulsion with it.

In earlier studies on Azerbaijani crude oils, the primary focus was directed towards obtaining narrow fractions of the oil (such as gasoline, ligroin, diesel, etc.) and examining their physical-chemical properties and composition. This approach did not allow for a comprehensive study of the characteristics specific to crude oils, accurate determination of relevant parameters, and identification of structural changes resulting from various external influences (such as radioactive rays, temperature, ultrasound, etc.). However, modern methods and methodologies applied to the study of the composition of crude oil and oil products allow for a complete investigation both individually and in a complex manner. The analysis of crude oil samples can be divided into three parts:

1) Investigation of the structural-group composition of crude oils using UV, NMR, EPR, IR, and chromato-mass spectroscopies, as well as luminescence methods; 2) Determination of the physical-chemical indicators of crude oil using standard methods; 3) General evaluation of crude oils based on their composition and properties.

One of the main methods in studying the hydrocarbon composition of crude oil and oil products is the highly sensitive luminescence method. This is because mono-, bi-, tri-, etc. cyclic aromatic hydrocarbons present in crude oil have the ability to luminesce. These types of compounds also affect the physical-chemical and optical properties of crude oil. In [14-16], the luminescence spectra of crude oil were obtained by excitation with xenon lamps of 400 W power.

In [17, 18], to investigate the effect of the side chain length on the fluorescence properties of solid substances, anthracenes with n-alkyl chains of different lengths were used. Based on the obtained results, it was found that as the length of the side chain increases, the luminescence of solid substances increases, and conversely, it decreases when the chain length decreases. Depending on the chain length, the luminescence shifts towards the red or blue side.

The aim of this study is to investigate the thermochemical luminescence (TCL) of the heavy residues of crude Karabakh, Absheron, and Naftalan oils as the research object, to study the chemical transformation processes occurring within them, to explore their mechanisms, and to determine the impact of these transformations on their quality.

2. Methodology Section

During the photo- and thermal-oxidation of crude oil and oil products, their properties deteriorate, resulting in a decline in quality and making them unsuitable for use. Therefore, as with other substances, one of their main characteristics is thermo-oxidative stability. In all standards, especially for oils and fuels, this value is taken into account. As a rule, this value is determined according to GOST 23175, GOST 305-82, and GOST 10227-86. These methods are labor-intensive, multi-stage, less efficient, not sufficiently accurate, and only applicable in the initial stages of oxidation. They are time-consuming and, consequently, inconvenient for conducting series analyses. However, unlike these methods, the TCL method is more precise and rapid [19].

The photoelectric apparatus used in the study of Karabakh oil and its components for TCL includes: a diffuse reflection base with an elliptical mirror, where the sample is placed at one focal point and the cathode of the photoelectron collector (FET-39A or FET-100) is positioned at the other focal point; a direct current amplifier; a heated cryostat; and an electronic potentiometer KSP-4. In the research process, the samples are placed at the center of a special spherical cuvette with a thickness of 0.1–1 mm and a diameter of 20 mm, and they are positioned parallel to the base of the photoelectron collector on a non-vacuum cryostat. This cryostat allows measurements in the temperature range of 196–300°C.

3. Results and Discussion

The TCL (Thermo-Chemiluminescence) of 50°C fractions of Karabakh crude oil with a boiling temperature range of 100–700°C was investigated. As shown in Figure 1, no TCL maximum was observed in the temperature range of 20–200°C for the 400–450°C fraction, similar to the lower boiling fractions of this oil, without any specific irradiation (only under laboratory light conditions). However, in the hydrocarbon residue (>500°C) of the mentioned oil, intense maxima at 75°C and 110°C were recorded due to the effect of irradiation (Figure 1, curves 2-4).

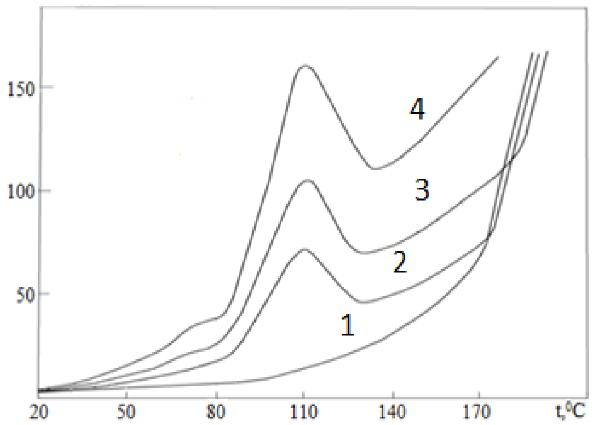

Fig 1. TCL curves of Karabakh crude oil: (400–450°C) irradiated with laboratory light (curve 1), and residuals (>500°C): 2 - irradiated with laboratory light (3 minutes), 3 - irradiated with daylight (3 minutes), 4 - irradiated with a mercury lamp (10 seconds).

It is known that, in the presence of weak hydrogen bonds and molecular oxygen in the oil's composition, radicals such as $H^{\bullet}$, $R^{\bullet}$, $HO_2^{\bullet}$ and $RO_2^{\bullet}$, are formed as a result of weak energetic effects according to the following scheme.

$$RH \longrightarrow R^{\bullet} + H^{\bullet}$$

$$RH + {}^3O_2 \longrightarrow R^{\bullet} + HO_2^{\bullet} \quad (1)$$

$$R^{\bullet} + {}^3O_2 \longrightarrow RO_2^{\bullet}$$

When the concentration of oxygen is high, the concentration of peroxide radicals slightly exceeds that of alkyl radicals $R^{\bullet}$, and a recombination process occurs, forming tetraoxides [20-24]. These tetraoxides decompose continuously when heated, resulting in luminescence, which is recorded as a thermochemical luminescence curve: (2)

$$RO_2^{\bullet} + RO_2^{\bullet} \longrightarrow ROOOOR \longrightarrow \, >C = O^{*} + ROH + {}^1O_2 \longrightarrow \, >C = O + ROH + {}^3O_2 + h\nu_1$$

In the TCL process, aromatic hydrocarbons (AHs) in oil act as both activators and photosensitizers, participating in a two-photon mechanism that leads to the decomposition of hydrocarbons and the formation of radicals:

$AH(S) + h\nu_2 \rightarrow AH(S^*) \rightarrow AH\ (T)$ (3)

$AH(T) + h\nu_3 \rightarrow AH(T^*)$

$AH(T^*) + RH(S) \rightarrow AH(S) + RH(S^*) \rightarrow AH(S) + RH(T) \rightarrow AH(S) + R_f^{\bullet} + H_f^{\bullet}$

Here, S, S*, T, and T*- represent the ground singlet, triplet, and excited singlet and triplet states of AHs, respectively. $R_f^{\bullet}$ və $H_f^{\bullet}$. represents radicals formed during the photoluminescence process.

When the sample is exposed to photoirradiation in an oxygen atmosphere, new peaks appear in the TL (Thermoluminescence) curve [25, 26]. The photodecomposition of photooxidized compounds formed under irradiation leads to the release of light quanta. This process is termed photothermochemical luminescence (FTCL). However, it should be noted that AHs, in an oxygen environment, oxidize through a single-quantum mechanism to form cyclic peroxides. Linear AHs (such as acenes) oxidize through a molecular mechanism, resulting in the formation of endoperoxides:

(4)

$AH(S) + {}^1O_2$

$AH(S^*) + {}^3O_2$ endoperoxide AH + $AH(S) + {}^3O_2 + h\nu_4 \longrightarrow$

$AH^{+\cdot} + O_2^{-\cdot}$

This reaction is reversible, where light energy is stored as chemical energy. When the system is heated, the stored energy is released as light. Phenols, on the other hand, form cyclic peroxides that do not emit light upon decomposition, and this process is irreversible.

The dependence of the intensity of the TCL maxima of the Karabakh oil residue on laboratory light led to the idea that under the influence of this light, $R_f^{\bullet}$ radicals and AH endoperoxides are formed. To clarify the role of irradiation, additional FTCL studies were conducted on samples of Karabakh oil irradiated with a mercury lamp and sunlight (Figure 1, curves 1-4). It was found that the intensity of the 75°C and 110°C TCL maxima generally increases compared to the case with only laboratory light irradiation.

Considering that the light from the indicated source mainly excites only the AHs of the studied oil samples, it can be assumed that the increase in the intensity of the TCL maxima occurs solely due to the photoxidation process and the reactions associated with the accumulation of light energy.

To compare with Karabakh oil, similar studies were conducted on Naftalan oil. It was previously shown that the distillate fractions of Naftalan oil (NN) exhibit lower temperature TCL related to free radicals and their recombination, unlike the analogous fractions of other well oils. The hydrocarbon residue (>500°C) of Karabakh oil shows intense TCL maxima at 65°C and 105°C, with an additional TCL peak observed at 175°C (Figure 2, curves 1-3).

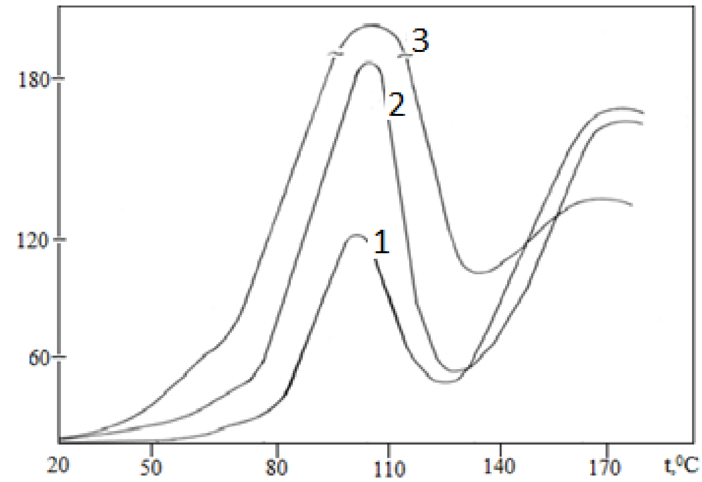

Fig 2. TCL curves of the hydrocarbon residue (>500°C) of Naftalan oil: 1 – after exposure to laboratory light (3 min.); 2 – after exposure to daylight (3 min.); 3 – after exposure to a mercury lamp (10 sec.).

The last peak was also observed in photoirradiated distillate fractions of Naftalan oil with a boiling point range of 200–500°C. This fact suggests a possible link with the biological activity (BA) of the given oil.

An increase in the intensity of the lower-temperature maxima after 3 minutes of solar irradiation in the hydrocarbon residue of Karabakh oil is also observed in the hydrocarbon residue of Naftalan oil (Figure 1, curve 3). After 10 seconds of irradiation with a mercury lamp, the intensity of the TCL maxima of the hydrocarbon residue of Naftalan oil significantly increases. The intensity of the TCL maximum at 175°C decreases, suggesting that the BA of the photoirradiated Naftalan oil is associated with lower-temperature TCL maxima at 65 and 105°C.

Another heavy oil taken for comparison with Karabakh oil is the heavy Absheron oil. During the study of TCL in the hydrocarbon residue (>500°C) of this oil under laboratory light conditions, three weak maxima were observed at 55, 90, and 103°C (Figure 3, curves 1-3).

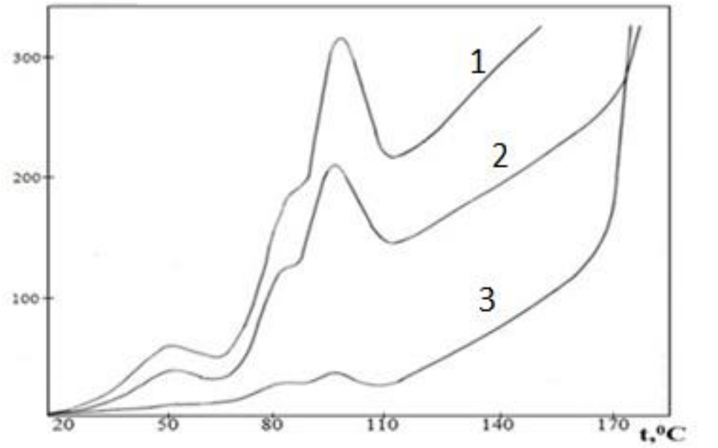

Fig 3. TCL curves of the hydrocarbon residue (>500°C fraction) of Absheron oil: 1 – after exposure to laboratory light (3 min.); 2 – after exposure to daylight (3 min.); 3 – after exposure to a mercury lamp (10 sec.).

The shift of the maxima towards the lower-temperature spectral region in the heavy hydrocarbon residue of Absheron oil, unlike Karabakh and Naftalan oils, can likely be attributed to the higher molecular weight of the hydrocarbons in this oil, which leads to the decomposition of the maxima at 105 and 110°C. The intensity of the indicated maxima increases after irradiation with a mercury lamp and daylight, with the most significant increase observed at 103°C. The TCL maxima observed under laboratory lighting conditions for the residue of Absheron oil were also recorded in the residue of Karabakh oil. This indicates that during the preparation of the studied oil residues for the experiment, they absorbed light energy under laboratory lighting conditions, which is sufficient for the appearance of TCL maxima.

To confirm the aforementioned findings, specific experiments were conducted in isolation from laboratory lighting. For this, the TCL of the Absheron oil residue was recorded twice in succession, before and after irradiation: after heating, the sample was cooled without removing it from the cuvette and kept in an oxygen atmosphere. In the first case, three TCL maxima were observed, while in the second case, two TCL maxima were recorded. These experiments confirm the idea that peroxide radicals generated during thermal exposure with oxygen play a key role in forming the relatively lower-temperature TCL maximum (55°C).

4.Conclusion

The experiments conducted on the TCL (thermochemical luminescence) of heavy residues of Karabakh, Absheron, and Naftalan oils (before and after irradiation) show many similarities in their TCL based on temperature maxima and intensity ratios. These hydrocarbon residues have a hybrid structure, with their main component consisting of compounds with weakly bonded C–H connections that are close in composition and structure. Considering that after the processes of de-resinification and deasphalting, the composition and structure of the oil hydrocarbons become more similar, they can also be used as biologically active substances. The conducted experiments demonstrate that all hydrocarbon residues of the studied oils have the same mechanism of thermochemical luminescence.

The study of the effect of photoirradiation on the petroleum hydrocarbons in the heavy residues of the oils indicates that, unlike many distillate fractions of the studied oils, their TCL maxima are in a relatively lower-temperature spectral region. During excitation in the spectral region related to electron absorption, a quantum of light corresponding to the visible spectral region is emitted as a result of the decomposition of AK endoperoxides formed during the recombination of peroxide radicals. Thus, by utilizing many oil hydrocarbons, this provides the potential to create alternative light sources based on accumulated light, including solar energy.

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