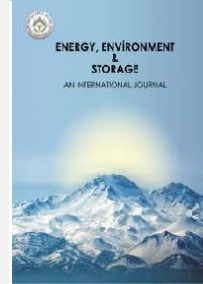


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1,4-Dioxane and the Phenolic Compound Against UV Irradiation of Diesel

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ABSTRACT. During storage and transportation, some classes of hydrocarbons in diesel fuel can undergo chemical transformations over time due to ambient temperature, sunlight, and oxygen in the air. As a result of these reactions, there are changes in the composition of the fuel, such as sediment, color change, turbidity, which have a negative effect on the physico-chemical indicators of the fuel. Such a change can cause engine wear and adversely affect engine efficiency, performance, emissions and durability. The main objective of this study is to investigate antioxidant additives to delay the aging process in diesel fuels. The compounds 1,4-dioxane and 3-hydroxy-1-(2-hydroxyphenyl)-3-(4-nitrophenyl)-propan-1-one were selected for this study. UV rays have been used to stimulate the aging process. As a result of research, the use of 1,4-dioxane has significantly improved the chemical stability, density and kinematic viscosity of fuel and its use in diesel fuel has shown greater stabilization potential.

Keywords: diesel, 1,4-dioxane, UV irradiation, chemical stability

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1. INTRODUCTION

As we know, diesel fuel is a complex mixture obtained from the fractional separation of crude petroleum and consists of a mixture of aliphatic, aromatic, naphthenic hydrocarbons and a small amount of heteroatomic compounds [1]. It is generally recognized that aromatic, heteroatomic and unsaturated compounds from the petroleum refinery processes present in fuels strongly influence fuel stability [2]. During storage and transportation, these types of hydrocarbons in diesel fuel can undergo chemical transformations over time due to ambient temperature, sunlight, and oxygen in the air [3-5]. In particular, the presence of polyaromatic hydrocarbons (PAHs) in petroleum diesel can accelerate fuel aging, depending on storage and transportation conditions. PAHs can be oxidized by environmental exposure. For example, some PAHs, such as perylene and benzo[a]pyrene, undergo photodegradation after solar or UV irradiation. The chemical reactions may occur inside the sample and in contact with the surroundings, notably tank walls and the atmosphere, at specific conditions. These chemical changes significantly influence the properties and exploitation indicators of the fuel, causing some problems with the stable regime and operation of diesel motors. As metal tanks are now replaced by polymer tanks with visible transparency, the photostability of the fuel becomes important [1, 6].

Adding additives such as oxidation inhibitors to diesel fuel increases its chemical stability [7]. Taking account of the above, the goal of this work is to

investigate the changes in the chemical content of diesel fuel due to the influence of sunlight during storage and transportation, their effect on operational characteristics, and to find additives to prevent fuel aging. For this purpose, 1,4-dioxane and 3-hydroxy-1-(2-hydroxyphenyl)-3-(4-nitrophenyl)-propan-1-one were used as antioxidants. A lamp with a wavelength of 300–450 nm was used to stimulate natural solar irradiation. Testing of chemical changes under UV irradiation was studied using NMR spectroscopy.

2. EXPERIMENTAL

2.1 Materials and methods

Diesel fuel samples were taken from a petrol station in Baku, Azerbaijan.

To stimulate natural solar irradiation, a visible and UV-emitting PRK2-IV-59 model using a lamp with a wavelength of 300–450 nm was used.

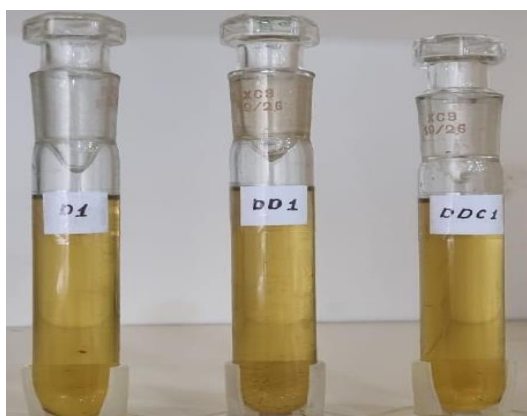
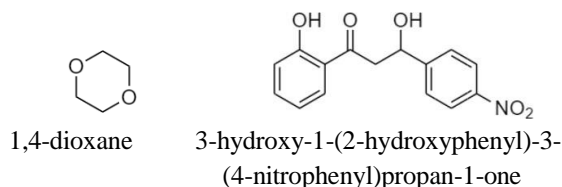
NMR spectra were obtained on a Bruker FT NMR (UltraShield™ Magnet) AVANCE 300 (300.130 MHz for ¹H and 75.468 MHz for ¹³C) with a 5 mm sample tube using Bruker Standard software (TopSpin 3.1). The ¹H and ¹³C chemical shifts were referenced to internal tetramethyl silane (TMS). NMR-grade CDCl₃ was taken for the analysis of fuel samples.

2.2 Preparation of samples and UV irradiation

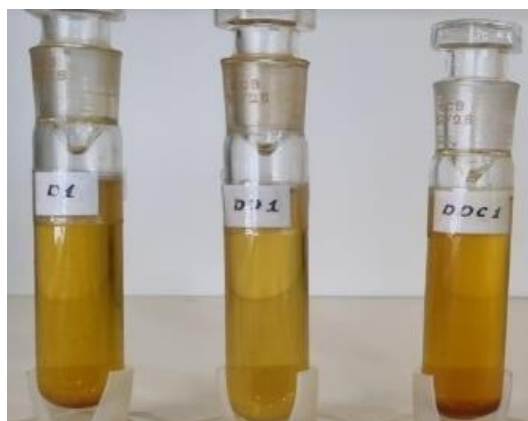
Three heat-resistant closed glass ampoules are taken for sample preparation. 20 ml of crude diesel (D1) for the first sample, 20 ml of diesel and 2 ml of dioxane (DD1) for the second sample and 20 ml of diesel, 2 ml of dioxane and

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0.01 g of 3-hydroxy-1-(2-hydroxy-phenyl)-3-(4-nitrophenyl) propan-1-one (DDC1) for the last sample were added into appropriate glass ampoules and stirred at room temperature. The samples were irradiated for 24 hours at room temperature (20°C) using a PRK2-IV-59 model lamp emitting visible and UV (300–450 nm) light rays. Within 24 hours, visible changes occurred in each of the samples (Figure 1).



(a)



(b)

Figure 1. Diesel (D1), DD1, DDC1 blends before (a) and after (b) the UV irradiation

3. RESULTS AND DISCUSSION

In our previous works, information was given about the occurrence of photodegradation processes under the influence of ultraviolet irradiation, which affect the physico-chemical and exploitation properties of fuel [3]. This work is devoted to testing different performance characteristics of diesel fuel with (or without) antioxidant additives before and after exposure to ultraviolet and visible rays from the sun. D1, DD1, DDC1 fuel samples were irradiated with UV rays for 24 hours in order to study the effect of sunlight on the chemical stability of diesel fuel produced at the Heydar Aliyev Oil Refinery and to find anti-aging additives. Changes in the chemical composition of the fuel samples after the end of the

storage period were studied with the help of NMR spectroscopy. The obtained results are given in Table 1.

Table 1. Hydrocarbon content of fuel blends from the ^1H NMR spectra before and after UV irradiation

Before UV	Par. h/c	Ole. h/c	Ar. h/c	After UV	Par. h/c	Ole. h/c	Ar. h/c
D1	95.14	0.05	4.72	D1	96.40	0.02	3.60
DD1	96.49	0.06	3.39	DD1	96.44	0.02	3.54
DDC1	96.57	0.07	3.34	DDC1	96.34	0.06	3.6

As can be seen from Table 1, the change in paraffinic/aromatic hydrocarbon ratio after 24 hours of UV irradiation in fuel samples D1, DD1, DDC1 was 26.8, 27.2 and 26.7%, respectively (the same results before UV irradiation were 20.2, 28.5 and 28.9). Simple diesel fuel without additives had the greatest change in chemical composition, while the diesel sample with dioxane and 3-hydroxy-1-(2-hydroxy-phenyl)-3-(4-nitrophenyl)propan-1-one additions had the least change.

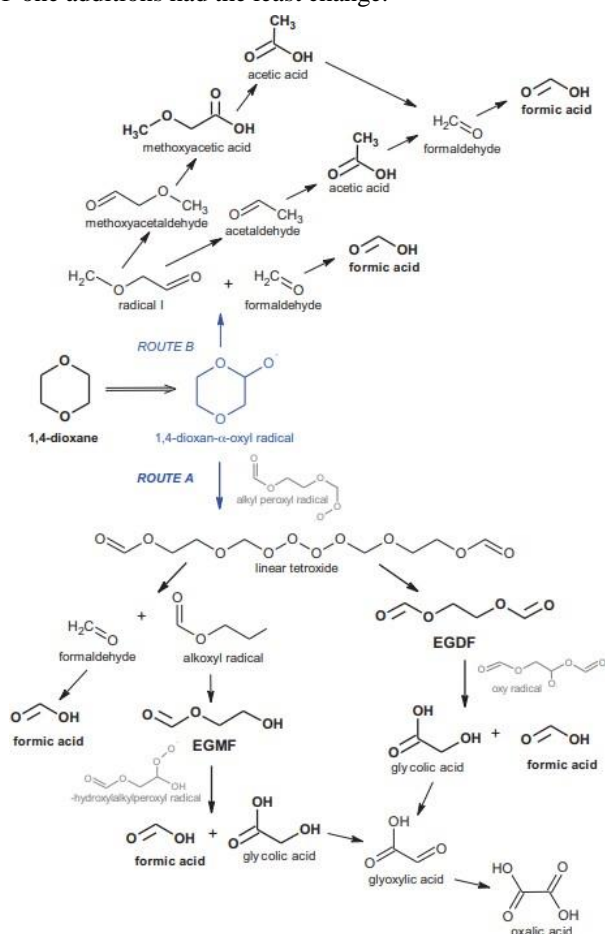


Figure 2. Simplified schematic of the major reaction pathways proposed for 1,4-dioxane degradation

Our previous work confirmed the high antioxidation property of 1,4 dioxane in fuel mixtures under high temperature conditions [8]. As a continuation of the work, the protective effects of this antioxidant additive against ultraviolet irradiation were investigated. For this purpose, a model fuel was prepared from 1,4-dioxane and hexadecane (HD) and subjected to UV irradiation for 24 hours and chemical composition changes were investigated with the help of NMR spectroscopy. However, while 1,4-dioxane itself was converted to 44% in sample DD1 and 42% in sample DDC1, no

photodegradation was observed in the reference sample HD. Due to its special chemical structure, 1,4-dioxane is not directly affected by photolysis. It is believed that the pH conditions of diesel fuel affect the photodegradation of dioxane. Thus, the photochemical decomposition of 1,4-dioxane increases in acidic fuel conditions to defend fuel from oxidation. At this time, several intermediate products, namely aldehydes, organic acids, mono- and diformate esters of 1,2-ethanediol, are formed. Depending on the formation and re-degradation of intermediate products, pH values, irradiation time, dose, etc. have an effect (Figure 2) [9, 10]. When 1,4-dioxane added to fuel is exposed to ultraviolet rays, acid intermediates are formed from the pH change. Thus, the diesel we studied was a weakly acidic environment with a pH value of 5.8–6 [11–14]. This allows the decomposition of 1,4 dioxane into acids and aldehydes, which can be clearly seen during NMR analysis. As can be seen from Table 1, a slight decrease in paraffinic hydrocarbons and an increase in aromatic hydrocarbons region are observed in the DD1 fuel sample during photodegradation. This can be explained by the formation of acids and aldehydes from the 44% conversion of dioxane, as a result of which the peaks in the NMR ^1H spectrum shift to the range of aromatic hydrocarbons, which may present aldehyde, phenolic and acid hydroxyl fragments.

As we know, compounds with a long-conjugated structure consisting of aromatic rings and side chains with double bonds and carbonyl groups have UV-absorbing properties [4, 5, 15]. For this purpose, we tested the property of the phenolic compound [3-hydroxy-1-(2-hydroxyphenyl)-3-(4-nitrophenyl) propan-1-one] added to diesel fuel as a UV absorber. As can be seen from the NMR results, the addition of the compound has a positive effect on the chemical stability of the fuel. However, visually, after 24 hours of irradiation, turbidity, precipitate and discoloration were observed in the fuel sample. This can be explained by the possibility that 3-hydroxy-1-(2-hydroxyphenyl)-3-(4-nitrophenyl) propane-1-one itself decomposes into another phenolic compounds, which needs more deep investigation.

Table 2. Properties of D1, DD1, DDC1 samples before and after

Properties	ASTM Methods	ASTM Diesel
Relative density at 20°C, g/cm ³	D1298	0.82-0.86
Sulfur, ppm, max.	D 975-14	15
Viscosity at 40°C, mm ² /s	D445	1.3 - 4.1
Cetane number, min.	D613	40.00
Flash point, °C, min	D93	52

Before UV irradiation			After UV irradiation		
D1	DD1	DDC1	D1	DD1	DDC1
0,845	0,864	0,863	0,848	0,854	0,856
47	39	38	-	-	-
3,128	2,11	2,15	3,017	2,49	2,57
43,35	40,29	43,76	43,45	40,13	43,63
77	54	56	87	58	61

In the continuation of the research, the operating characteristics of petroleum diesel (D1), DD1 and DDC1 fuel mixtures were studied (Table 2). Despite the slight

decrease in viscosity, ignition temperature, density, cetane number, etc. after UV irradiation, the studied fuel mixtures DD1 and DDC1 have properties that correspond to the diesel fuel standard, and the proposed mixtures can be used in diesel engines without any changes [16].

4. CONCLUSIONS

This article reports on testing the chemical stability of diesel fuel against UV radiation for 24 hours and searching for additives to ensure chemical stability. As can be seen from the obtained data, photodegradation with UV has a negative effect on the chemical stability of the fuel (change in paraffinic/aromatic hydrocarbon ratio by 32.7%) and operational properties.

One of the most important contributions of this work was to obtain a more physiochemically stable fuel mixture under the studied conditions. For this purpose, the DD1 fuel sample made on the basis of 1,4 dioxane and diesel was studied as the least sensitive to structural changes under the influence of UV rays. DD1 causes only a 4.6% change in its chemical composition after UV irradiation and retains its properties more than D1, DDC1. The DDC1 also has chemical stability under the specified conditions (structural changes: 7.6%). However, although the 3-hydroxy-1-(2-hydroxyphenyl)-3-(4-nitrophenyl) propan-1-one compound used as an additive maintained the chemical stability of the fuel sample against UV rays, it itself photodegraded after irradiation and formed a gum-like deposit on the walls of the container. At the same time, it was checked that the operating properties of the investigated fuel mixtures before and after UV irradiation were in accordance with ASTM standards.

The reported work may be interesting when studying the application of diesel fuel under different storage and transportation conditions.

Conflicts of interest

The authors declare that there are no conflicts of interest

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