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CORRECTION OF PROPERTIES OF MODERN DIESEL FUELS USING ADDITIVES

Research article

Abstract

Creation of high quality diesel fuels for internal combustion engines that meet stringent operational and environmental requirements is currently an urgent task. The most rational way to improve the performance characteristics of diesel fuel, its environmental properties, as well as to reduce losses during its storage, is to use polyfunctional additives. Requirements for the structure of polyfunctional additives are formulated. It is shown that their stabilizing and protective effects are the higher, the greater the value of the dipole moment and total electron density on heteroatoms. Amides and esters of higher aliphatic acids, synthesized from renewable diesel raw materials, as well as molecules of azo compounds including aromatic fragments and electron-donating functional groups, are promising multifunctional additives to diesel fuel.

Keywords: diesel fuel, polyfunctional additives, dipole moment, electron density

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КОРРЕКЦИЯ СВОЙСТВ СОВРЕМЕННЫХ ДИЗЕЛЬНЫХ ТОПЛИВ С ПОМОЩЬЮ ПРИСАДОК

Научная статья

Аннотация

Создание дизельных топлив высокого качества для двигателей внутреннего сгорания, отвечающих строгим эксплуатационным и экологическим требованиям, является актуальной задачей в настоящее время. Наиболее рациональным способом улучшения эксплуатационных характеристик дизельного топлива, его экологических свойств, а также снижения потерь в процессе его хранения является использование полифункциональных присадок. Сформулированы требования к структуре полифункциональных присадок. Показано, что их стабилизирующий и защитный эффекты тем выше, чем больше величина дипольного момента и суммарной электронной плотности на гетероатомах. Амиды и эфиры высших алифатических кислот, синтезируемые из возобновляемого дизельного сырья, а также молекулы азосоединений, включающие ароматические фрагменты и электронодонорные функциональные группы, являются перспективными полифункциональными добавками к дизельному топливу.

Ключевые слова: дизельное топливо, полифункциональные присадки, дипольный момент, электронная плотность.

1. Introduction

In recent decades, all areas of industry and transport are forced to restructure their work in such a way as to reduce the negative impact on the environment. To this end, the design of internal combustion engines is being continuously improved, and the requirements for the fuel they use to operate are becoming more stringent. Modern agricultural machines must run on fuels that meet the most stringent environmental regulations to reduce the possibility of contamination of agricultural products by exhaust components. In addition, fuel quality should not deteriorate significantly during off-season storage. The course of oxidative and corrosive processes during storage entails a whole range of negative consequences. This is an increase in the toxicity of exhaust gases, equipment failure, leakage of oil products, followed by pollution of agricultural land, and the accumulation of sludge in tanks that require disposal.

The main type of fuel used in the agricultural sector is diesel fuel. The requirements of GOSTs and specifications for it are slightly different in different countries, but recently there has been a general trend towards an increase in the cetane number and a decrease in the concentration of aromatic and polycyclic hydrocarbons, as well as compounds containing nitrogen and sulfur atoms.

To obtain fuel that meets high environmental requirements, it is necessary to make more and more serious adjustments to the oil refining processes. Oil undergoes deeper processing, additional stages of hydrotreating, dearomatization, hydrodesulfurization, etc. As a result, the fuel loses natural heteroatomic organic compounds, which leads to a decrease in its cetane number and lubricity, and an increase in corrosiveness. At the same time, the content of unsaturated compounds in the fuel increases, which leads to an increase in the rate of oxidation processes.

Currently, the most realistic way to improve the characteristics of fuels and reduce storage losses is the use of additives. At the same time, many cetane-enhancing additives have an increased oxidizing ability, and oxidation products worsen the lubricating and antiwear properties of the fuel [1, P.10-16].

Thus, additives are an essential component of modern fuels, and their range is constantly expanding. The most expedient is the use of polyfunctional additives that simultaneously perform two or more functions and improve the operational and environmental properties of the fuel. Additives can be added during production or added directly to the storage tank.

The search for additives should not be carried out by random selection of various classes of organic compounds; it is necessary to determine the structural features of the additives molecules and find criteria that allow one to assess the proposed structure of the compound and select substances for experimental verification.

The purpose of this study is the search for compounds that can improve the operational properties of modern diesel fuel and extend its storage life in oil depots.

2. Methods

Methods of fine organic synthesis were used for the synthesis of additives. The resulting additives were added to hydrotreated summer diesel fuel. The lubricating properties of the fuel were determined in accordance with GOST ISO 12156-1-2006 [2]. To assess the chemical stability of fuels during storage, a special qualification method was used, based on the principle of modeling the storage of liquid fuels in laboratory conditions at elevated temperatures in the presence of a copper plate [3].

To carry out quantum-chemical calculations, the semiempirical method MNDO was used, which makes it possible to calculate the equilibrium geometry, energy and distribution of electron density in complex organic molecules.

3. Results

For the effective search for fuel additives it is necessary to determine the structural features of the molecules of additives of one action or another on the basis of the analysis of already available literature data, and to find criteria that allow one to assess the proposed structure of the compound and select substances for experimental verification.

The features of the structure of organic compounds exhibiting antioxidant and anticorrosive properties have been studied. Polyfunctional additives with such properties contribute to an increase in the chemical and physical stability of diesel fuels during storage by slowing down oxidation reactions and related processes of polymerization and precipitation; and also a decrease in the rate of corrosion processes in the zone of produced water. Slowing down all of these processes will prevent deteriorating the reservoir due to corrosion, as well as fuel spillage, and maintain fuel performance, which will extend engine life. Based on the analysis of the literature data [4], [5, P.31-35], [6], [7], [8, P.28-31], the requirements for the structure of such polyfunctional additives are formulated:

1. The additive molecule must contain proton-donor functional groups. The presence in the structure of the molecule of an additive of functional groups with a positive inductive and (or) mesomeric effect increases its activity.
2. The presence of a system of conjugated π-bonds in an organic compound molecule also gives it the ability to slow down the processes of oxidation and corrosion.
3. The molecule of the additive must be able to bind metal cations. The ability to form intracomplex chelated salts is very effective.
4. Since the additives must show their activity both in the environment of fuel hydrocarbons and in the environment of produced water, they must be diphilic molecules. This will allow them to have an affinity for non-polar hydrocarbons of petroleum fuels, on the one hand, and the ability to spontaneously pass from the fuel volume to the most corrosive phase - produced water, on the other hand. Only in this case the effective prevention of both oxidative and corrosive processes is possible.

In accordance with the formulated requirements, we have synthesized azo compounds formed by azo coupling of substituted and unsubstituted o-benzoquinone diazides with resorcinol and 1-phenyl-3-methyl-5-pyrazolone [9, P.26-30].

The structure of the additives is shown in Fig. 1:

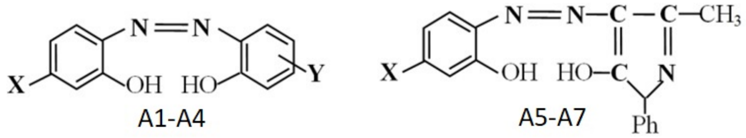

Figure 1 – Structure of additives. Ph is a phenyl radical, and X, Y are substituents (Table 1)

Table 1 – The structure of 2,2'-dihydroxyazo compounds investigated as polyfunctional additives

Additive	X	Y	Additive	X	Y
A1	H	5'-NHCOOH	A5	H	—
A2	H	4'-OH	A6	NO2	—
A3	Cl	5'-NHCOOH	A7	Cl	—
A4	Cl	4'-OH			

These substances can be classified as amphiphilic compounds, because the molecules contain both non-polar hydrocarbon fragments and polar electron-donating groups, for example, hydroxyl groups. These compounds have a developed conjugated π-system that includes aromatic fragments. They have two hydroxyl groups in ortho-position to the azo group. Due to this fact they are able to form chelate complexes with transition metal cations, primarily copper and iron (Fig. 2). A metal cation firmly bound by four bonds cannot catalyze the oxidation processes in fuel.

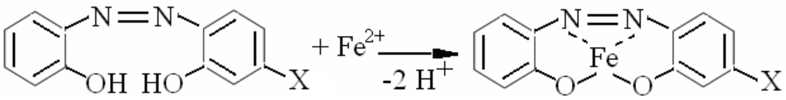

Figure 2 – Scheme of the formation of a chelate complex of azo compound with iron cation
(the ionic bond of iron cation is shown by a solid line, the coordination bond – by a dotted line)

As our experimental studies have shown, the introduction of these additives contributes to an increase in the chemical and physical stability of not only petroleum, but also biodiesel fuels during storage (in the presence of additives, a decrease is observed: in the concentration of actual resins – up to 60%, acidity – up to 25%, the amount of sediment formed during storage - up to 70% compared to diesel fuel without additive). In the zone of produced water, the rate of corrosion processes decreases (the protective effect reaches 60%).

The best effect is exhibited by compounds containing a resorcinol fragment in the molecule. The most effective additive, which has not only stabilizing and protective, but also dispersing properties, is compound A4. This is due to the presence of two aromatic fragments, the third hydroxyl group and a chlorine atom, which have a positive mesomeric effect.

The stabilizing and protective efficiency of A5-A7 additives containing a pyrazolone fragment is 10-30% lower. This may be a consequence of tautomeric rearrangement (Fig. 3), which leads to a decrease in the complexing ability in form (II) due to the absence of the second hydroxyl group.

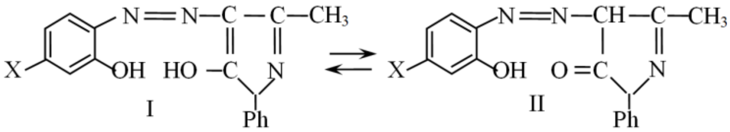

Figure 3 – Scheme of tautomeric rearrangement of 2,2'-dihydroxyazo compounds containing a pyrazolone ring

The antioxidant and protective effect of the studied compounds correlates with the electron density excess calculated by the semiempirical method MNDO for all heteroatoms (nitrogen, oxygen, and halogen) present in the additive molecule, and with an increase in the molecular size, and, consequently, the shielded metal surface area. The effect is the higher, the higher the total negative charge on heteroatoms, which is provided by groups and atoms with a positive mesomeric effect.

As our studies have shown, similar requirements (with the exception of the ability to form chelate complexes with metal cations) are imposed to the structure of additives with antiwear properties.

Antiwear additive molecules must contain polar functional groups to interact with metal surfaces and create layers of strictly oriented molecules on rubbing engine parts. This creates a film that prevents the metal surfaces of the rubbing pairs from contacting, which reduces the wear of engine parts. It is possible to increase the adhesion energy between molecules due to van der Waals forces; therefore, hydrocarbon radicals in the additive molecule must be unbranched. Thus, the antiwear additive molecule must have an amphiphilic structure, i.e. contain a polar group, and a long unbranched hydrophobic radical.

All these requirements are met by esters and amides of higher aliphatic acids. Non-food crops oils could be a raw material for their synthesis [10, P.54-62]. Amides were obtained by reacting vegetable oils with monoethanolamine. Esters include vegetable oil methyl esters, which are the main component of biodiesel. The same class also includes diesters of higher aliphatic acids formed by the transesterification reaction of triacylglycerols of vegetable oils and triethanolamine. The latter, unlike methyl esters of vegetable oils, contain not only oxygen atoms in the ester group, but also a nitrogen atom in the imino group (–NH–).

The resulting additives were added to hydrotreated diesel fuel (1% by volume). The lubricating properties of the fuel with additives were determined by comparing the lubricity of the obtained additives and biodiesel fuel, the antiwear properties of which are known.

As our studies have shown, the products of interaction of vegetable oil with triethanolamine have the most pronounced effect of improving lubricity (by 25-45% depending on temperature). The smallest effect was observed in the case of methyl esters of vegetable oils.

To explain these differences, a quantum-chemical calculation of the compounds under study was carried out. The geometry was optimized, and the values of dipole moments of molecules and charges on nitrogen atoms were determined (Tab. 1). The most polar molecules are diesters of higher aliphatic acids and triethanolamine. A satisfactory correlation between the values of dipole moment and charge on the nitrogen atoms of the tested compounds and their lubricity is observed. The antiwear properties are higher for additives with higher charge and dipole moment. Under real operating conditions, adsorption occurs on an inhomogeneous metal surface with oxide films. Additives with higher polarity are naturally more active in this interaction. Probably, the presence of two unbranched hydrocarbon radicals in diester molecules also plays a role.

Table 2 – Values of dipole moments and charges on electronegative atoms of some additives

№	Additive	Dipole moment, D	q, $\overline{e}$
1	Amide of higher aliphatic acid	3,121	N: -0.433 O_1: -0.356 O_2: -0.329
2	Diester of triethanolmine and higher aliphatic acid	6,881	N: -0.450 O_1: -0.328 O_2: -0.309 O_3: -0.336 O_4: -0.303 O_5: -0.344
3	Vegetable oil methyl ester	1,818	O_1: -0.356 O_2: -0.329

4. Conclusions

For the cultivation of ecologically clean agricultural products, it is advisable to use diesel fuel that meets the requirements of Euro standards. To improve the antiwear properties of such fuels, amides and diesters of higher aliphatic acids, synthesized from renewable raw materials (vegetable oil), can be used. It is advisable to add azo compounds, the molecules of which contain aromatic fragments and electron-donor functional groups, as fuel additives to reduce oxidative and corrosive processes. The criterion for choosing compounds with antioxidant, anticorrosive and antiwear properties can be the value of the dipole moment of the molecule and the distribution of the electron density in the molecule, primarily on heteroatoms. The stabilizing, protective, and antiwear effects are the higher, the greater the value of the dipole moment and the total electron density on heteroatoms.

Conflict of Interest

None declared.

Конфликт интересов

Не указан.

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