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STUDY OF THE INFLUENCE OF BIODIESEL FUEL ON CONSTRUCTION MATERIALS OF TRANSPORT VEHICLES

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Abstract:
Biodiesel is considered as one of the most common biofuels used to replace conventional motor fuels. Some of the problematic issues related to the operation of vehichles using biodiesel fuels are disscussed, among which is quick deterioration of metal and polymer details of fuel system. The cause of this problem in relation to the structure and properties of biodiesel fuel was analyzed. The influence of conventional diesel fuel and biodiesel fuel and its blends on metals (copper and steel) as well as rubber materials (polyvinylchloride) during long-term storage was studied. Biodiesel with camelina oil ethyl was used at the basis for this experiment. Highly aggressive impact of biodiesel on copper was found. Steel is considered to be resistant to corrosion in the medium of biodiesel. biodiesel similarly to conventional diesel fuel led to degradation of rubber materials causing swelling. Based on the achieved results the set of measures and recommendations for providing reliability and durability of vehicles operation using biodiesel or its blends was developed and proposed.
Key words:
Diesel fuel, biodiesel, construction materials, corrosion, metal, rubber

INTRODUCTION

The reduction of world oil reserves and products of its processing, as well as the worsening of the state of the environment, raise the question of the use of alternative energy sources (Chandrasekar et al., 2022). Moreover, this issue has become even more relevant for European countries; today there is a strong need for the provision of independence from crude oil import and the development of its own energy resources. One of the solutions for the transport sector is the use of alternative motor fuels produced from renewable feedstock. One of the possibilities is biodiesel, which is typically produced from various available oil feedstock (Yakovlieva et al., 2019). The technology of biodiesel production is already well-known, comparatively cheap and not complicated, and the use of biodiesel may significantly reduce the consumption of petroleum fuel and decrease the number of aggressive emissions into the atmosphere (Yakovlieva et al., 2019; Xue et al., 2011).

However, the conversion of vehicles that are in operation today to alternative fuels may lead to several changes in their operation: power, fuel consumption, exhaust gas emissions, the durability of components, etc. It means that the conversion of vehicles to alternative fuels requires comprehensive research and analysis of the impact of new fuel on the reliability, durability and environmental parameters of transport operation (Xue et al., 2011).

Today, the issues related to the influence of biodiesel fuel on structural elements of vehicle fuel systems have not been studied enough. In addition, the issue of developing technological solutions to increase the durability of the operation of vehicles using alternative fuels needs to be considered and developed. Therefore the study of the impact of biodiesel fuels on the construction materials of vehicles‘ fuel systems is a relevant and important scientific and applied task.

The study *aims* to assess the impact of biodiesel fuels on metal and rubber construction materials during technological operations with the fuel and its use. To reach the aim of the study the following tasks should be solved:

1. To study experimentally the influence of biodiesel fuel and its blends on the degree of metal corrosion during long-term storage.
2. To study experimentally the influence of biodiesel fuel and its blends on rubber materials during long-term storage.
3. To develop and propose the set of measures for providing reliability and durability of vehicle operation using biodiesel or its blends.

1 LITERATURE OVERVIEW

Among the alternative types of motor fuels, biodiesel fuel is the most common and promising (Cvengros, 2011). The use of biodiesel has several advantages, in particular from an environmental point of view: a reduction of the toxic components in exhaust gases, the use of renewable raw materials for production and, as a result, a reduction in the consumption of petroleum feedstock (Yakovlieva et al., 2019; Xue et al., 2011).

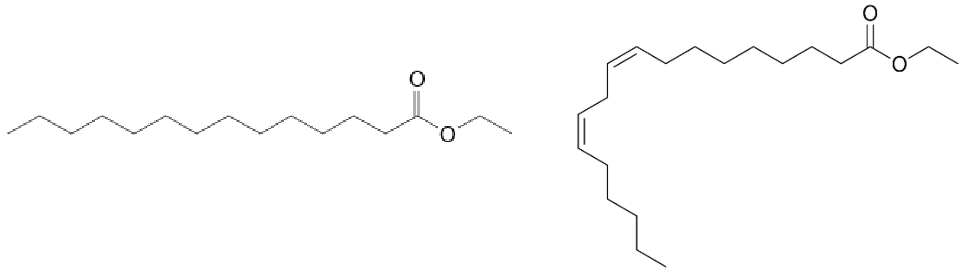
Biodiesel fuel is produced by esterification of oily feedstock by simple alcohols. According to its chemical composition, biodiesel fuel is a mixture of fatty acid esters of different structures. The technological processes of biodiesel fuel production are considered in detail in studies by (Patrylak et al., 2013; Ortega et al., 2021; Boichenko et al., 2020a). Various oils are used as feedstock (rapeseed, camelina, soybean, jatropha oil, etc.). Animal fats, used cooking oil and various oily waste can be also used (Boichenko et al., 2020a; Matvieieva et al., 2019). Among the simple alcohols used for esterification, the most famous are methanol and ethanol. In recent years, the prospects of using butanol, propanol and their isomers to improve the properties of biodiesel fuel have been actively investigated (Matvieieva et al., 2019; Boichenko et al., 2020b).

From the first point of view, properties of biodiesel fuel are considered to be quit similar to petroleum diesel fuel (Boichenko et al., 2020b). This is mainly explained by that fact, that distribution of carbon atoms number in molecules in both types of fuels is close and co-inside to some extent. Carbon number in petroleum diesel fuels varies between C10 and

C16. Average carbon number in fatty acids esters is about C13 – C19 (Yakovlieva et al., 2019). Thanks to this, biodiesel can be mixed with diesel fuel without restrictions and in any ratio (up to complete replacement). Its use does not require fundamental changes to the design of the diesel engine and fuel system of the vehicles. According to the existing studies and practical experience mixtures of diesel fuel with biodiesel in small proportions (up to 5%) do not affect the characteristics of the engine performance at all (Boichenko et al., 2020b; Singh et al., 2022). However, despite the similarity in carbon number distribution of molecules of diesel fuel and biodiesel one, they have completely different chemical structure. Petroleum diesel fuel is composed by saturated n-, iso-, cyclo-paraffins, and aromatics, while biodiesel is composed by saturated and non-saturated fatty acids, which contain two oxygen atoms. Respectively, this cause a difference in some of its properties compared to petroleum diesel (Iliev and Mitev, 2019). In particular, this is manifested in slightly lower heat of combustion, oxidation stability, higher viscosity, etc. In this regard, there is a need to carry out minor adjustments to the operation of the engine and fuel system to stabilize their functioning. Today, quite a lot of studies are known, in which the mentioned issue was successfully solved and put into practice (Ortega et al., 2021; Iliev and Mitev, 2019; Alves et al., 2017).

However, some problematic issues are still connected to the use of biodiesel and its blends. Mainly, these issues are related to the aggressive effect of biodiesel on construction materials (steel, aluminium, copper or its alloys, polymers, rubbers, etc) of vehicles and its quick deterioration (Fazal et al., 2018; El Hawary et al., 2022). Typically, different types of metals and alloys are used as details of vehicles and which may be subjected to the influence of fuel. Steel is usually used for producing fuel tanks and reservoirs (tanks in vehicles, reservoirs at filling stations, trucks, etc). This type of metal is chosen due to its resistance to corrosion (Thangavelu et al., 2015). A number of fuel system components are made of copper (i.e. parts of fuel filters, nozzles, etc.) (Baena and Calderon, 2020). Cast iron, leaded bronze, and aluminium are also used for different purposes in transport construction. Polymers and various rubber materials are also widely used in vehicles. Different rubber hoses are used to supply fuel from the fuel tank to the engine. Various polymeric sealing is used in connections of mechanical parts to prevent fuel of other liquid leakages. Both metal and polymeric materials as parts of the fuel system and engine are usually in permanent contact with fuel (Fazal et al., 2018). The aggressive action of biodiesel is caused by its chemical composition and structure. As was mentioned, it is composed of fatty acids esters (Fig. 1). From the chemical point of view, it is a derivative of saturated or unsaturated fatty acid, in which hydroxyl –OH is replaced with alcohol radical with oxygen atom (Yakovlieva et al., 2019).

Due to the presence of oxygen atoms and double bonds in the structure, biodiesel has low chemical stability (Yakovlieva et al., 2019; Singh et al., 2022). Under unfavourable conditions, oxygen initiates a chain reaction of oxidation and formation of a large number of products, such as aldehydes, ketones, water, alcohols, and carboxylic acids (Fazal et al., 2018; Baena and Calderon, 2020). Due to the double bonds molecules become subjected to easier chemical transformation. Except that biodiesel may contain some trace amounts of free fatty acids, which result from the incomplete process of esterification. All the mentioned compounds increase biodiesel acidity, which causes corrosion of metal parts and destruction of polymers (Kugelmeier et al., 2021).



a *b*

Fig. 1. *Chemical structure of fatty acids ethyl esters: a – saturated, b – unsaturated*
Source: Yakovlieva et al., 2019

Biodiesel is also characterized by higher hygroscopicity compared to conventional diesel. Due to this, it easily absorbs water from the external environment and dissolves it. On one side water in fuel promotes its degradation and reacts with metal parts of the vehicle causing corrosion. On another side, during changes in external conditions (i.e. temperature rise), water evaporates and promotes corrosion of details (Thangavelu et al., 2015; Pusparizkita et al., 2018).

Another factor that contributes to the degradation of biodiesel fuel is microbial pollution. The main products of microorganisms development are sludge and water, which are metal corrosion stimulators (Hoang et al., 2020).

When considering polymeric materials, biodiesel may also negatively affect its quality and properties. Due to the high oxygen content biodiesel easily oxidizes polymeric molecules (Komariah et al., 2019; IEA, 2008). Intermediate products of oxidation chain reaction – hydroperoxides also contribute to this process. Biodiesel can also cause changes in the volume or mass of polymers due to penetration and swelling. It results in changes in mechanical properties such as elongation, hardness, and tensile stress in polymers (El Hawary et al., 2022; Kugelmeier et al., 2021). Acids, which are present in biodiesel also affect rubbers and may contribute to their gradual deterioration.

Taking into account the mentioned above it is necessary to consider the influence of biodiesel on vehicle construction materials and develop measures to provide reliability and durability of details while using biodiesel fuel.

In previous studies a number of researches were carried out, which were devoted to the analysis of the feedstock potential for the production of biofuels (Boichenko et al., 2020b), the development of technological processes for biodiesel production using various types of oils and alcohols (Matvieieva et al., 2019), and the determination of the physical-chemical and operation properties of the obtained fuel samples, as well as its mixtures with traditional diesel fuel (Yakovlieva et al., 2019; Boichenko et al., 2020b). Among the studied samples, ethyl esters of camelina oil (COEE) possess characteristics that are the closest to the characteristics of petroleum diesel fuel. Comparative analysis of the quality parameters of COEE and their mixtures with diesel fuel are presented in Table 1 (Boichenko et al., 2020b).

From the data presented in Table 1, it is seen that the main physical-chemical properties of samples of biodiesel, diesel fuel, and fuel blends with different content of COEE (10%, 30 and 50%) completely satisfy the requirements of the European standard for conventional diesel fuel EN 590 (2013) "Automotive fuels – Diesel – Requirements and test methods" (BSI, 2017), Europen standard for biodiesel EN 14214 Automotive fuels – Fatty acid methyl esters (FAME) for diesel engines – Requirements and test methods(UNE, 2019), and Ukrainian standard for biodiesel DSTU 7178:2010 "Alternative fuel. Ethyl esters of fatty acids" (DP UkrNDNC, 2010).

Tab. 1. *Comparative characteristics of quality parameters of blended biodiesel fuels with different content of COEE*

Property	Diesel fuel	Diesel fuel +10% COEE	Diesel fuel +30% COEE	Diesel fuel +50% COEE	COEE
Density at 20 °C, kg/m³	832.0	834.0	844.0	856.0	882.0
Viscosity at 40°C, mm²/s	2.17	2.33	2,78	3.28	4.45
Flash point, °C	58	57	70	73	>170
Pour point, °C	-49	-46	-41	-33	-23
Cetane number	47.7	49,4	44	52	45,6
Mechanical admixtures, mg/kg	n/a*	n/a	n/a	n/a	n/a
Corrosion of the copper strip	1a	1a	1a	1a	1b

Source: Boichenko et al., 2020b
**not analyzed*

Therefore, blended fuel containing COEE was chosen for further studies of its influence on construction materials of the transport vehicle.

2 MATERIALS AND METHODS OF STUDY

Within the framework of the work samples of blended biodiesel fuels were investigated. Conventional diesel fuel of grade "Euro" was produced at the oil processing plant JSC "Ukrtatnafta" in Kremenchuk city, Ukraine. Biodiesel fuel based on camelina oil ethyl esters (COEE) was produced at the Institute of bioorganic chemistry and petrochemistry of the National academy of sciences of Ukraine (Boichenko et al., 2020b).

A sampling of components was done using an automatic bottle dispenser. Fuel samples were prepared by simple mechanical blending and stored in closed borosilicate glass bottles. The description of the studied fuel samples is given in Table 2.

Tab. 2. *Description of studied fuel samples*

Designation	Description of the fuel sample
DF	Conventional diesel fuel
BD	Biodiesel based on COEE
BD10	Blended fuel that contains 10 % (vol.) of COEE
BD20	Blended fuel that contains 20 % (vol.) of COEE
BD30	Blended fuel that contains 30 % (vol.) of COEE
BD40	Blended fuel that contains 40 % (vol.) of COEE
BD50	Blended fuel that contains 50 % (vol.) of COEE

Source: Own development

The following elements were used to study the effect of fuels on construction materials:

- steel strips of the grade 08KP, size 50x15 mm and thickness 2 mm;
- copper strips 50x15 mm in size and thickness 3 mm;

- parts of a PVC rubber hose used as a fuel pipe in the fuel system of vehicles equipped with a diesel engine. The internal diameter d_{int}=7.66 mm and external diameter d_{ext}=10.5 mm and thickness l=1.38 mm.

Samples of construction materials were immersed in glass laboratory bottles with a volume of 100 ml and stored under the following conditions:

- the temperature in the range of 10–20 °C;
- term – 2 months;
- lighting – natural, without access to direct sunlight.

The influence of fuel samples on parts of a rubber hose was estimated by the following indicators:

– d_{int} – internal diameter, mm;
– d_{ext} – external diameter, mm,
– l – thickness, mm.

The influence of fuel samples on metal strips was estimated by the degree of corrosion.

Parameters were measured using the following equipment:

– analytical scales with an accuracy of up to 0.001 g,
– a calliper with an accuracy of 0.1 mm.

Measurements of the parameters were done at the start of the experiment and every two weeks till the end of the experiment. Measurements of the parameters were done two times for each sample. The research was carried out at the Education & Research Laboratory of Alternative Motor Fuels of the National Aviation University.

3 RESULTS AND DISCUSSION

At the first stage of the research, the influence of biodiesel and its blends on metals (cooper and steel) was studied. Before the start of the experiment the standard copper strips were cleaned up and de-greased. The external view of fuel samples and copper is shown at Fig. 2. Copper plates were immersed into the bottles with fuels and stored for two months, fixation of the changes was done every two weeks.

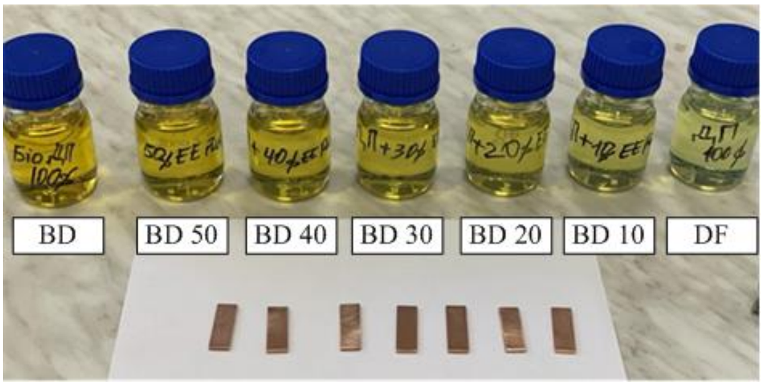


Fig. 2. *External view of the fuel samples and copper strips before the start of the experiment*
Source: own development

Fig. 3 presents the result of the corrosive influence of fuels on copper strips during a two-months period. From Fig. 3 it is seen that copper strips stored in biodiesel and all biodiesel blends were subjected to gradual oxidation and corrosion. The level of metal destruction increased with time. Naturally copper is a metal, which is oxidized easily in the open air and the surface of the metal becomes covered with a thin film of copper oxide.

Biodiesel molecules pose an aggressive effect on copper strips. As a result of this effect, the surface of the metal is dissolved and a black soft coat is formed, which may be easily removed from the metal surface. This happens as a result of the reduction of the oxide film of copper with carbon. It can be observed that with time the thickness of the film created by the products of the reaction increases.

We can observe from Fig. 3 that copper strips placed in samples of biodiesel fuel and its blends and stored for 2 months were oxidized and corroded. 14 days of exposure of the copper strips to the fuel sample resulted in a moderate degree of corrosion with typical pale grey spots. During longer storage up to two months, the copper strips became covered with a black coating. The copper strip stored in conventional diesel fuel was not subjected to oxidation and corrosion. This is explained by two factors. First is the chemical composition of diesel fuel. It is composed of *n*-, *iso*- and *cyclo*-alkanes and aromatics, which are non-polar molecules, and, therefore inert and resistant to oxidation. Second is the presence of antioxidant additives in diesel fuel, which prevent its oxidation and further corrosion.

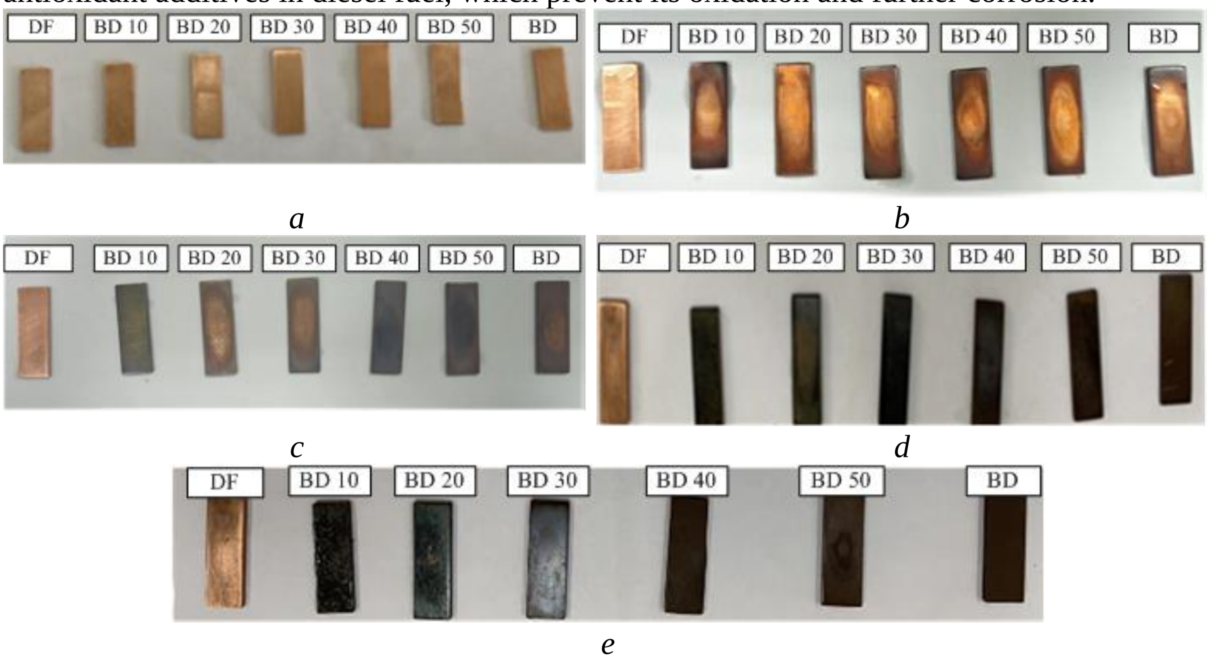


Fig. 3. *Corrosive influence of fuel samples on copper strips during the two-months period: a – clean strips before the experiment, b – after 14 days, c – after 28 days, d – after 42 days, e – after 56 days*

Source: own development

At the late stages of the experiment (Fig. 3 *e* and 3 *d*), the highest degree of corrosion and destruction was observed for copper strips, which were stored in blended biodiesel fuels. Here we can assume that blending conventional diesel fuel and biodiesel may lead to the formation of new compounds, which are more aggressive and lead to more intensive destruction of metals.

Next, the influence of biodiesel and its blends on steel was studied. The conditions of the experiment were the same as for copper. The external view of fuel samples and steel strips is shown in Fig. 4. Fig. 5 presents the result of the corrosive influence of fuels on copper strips during a two-months period.

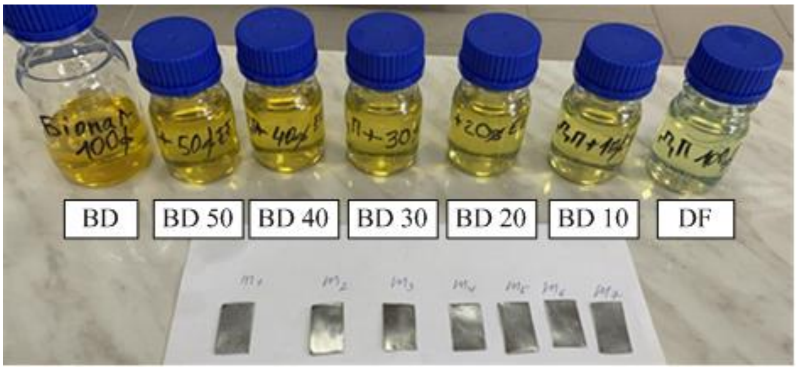
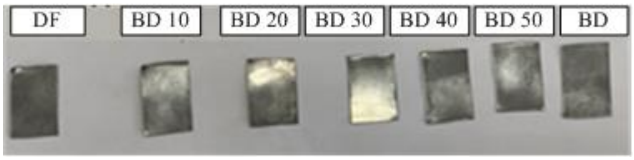
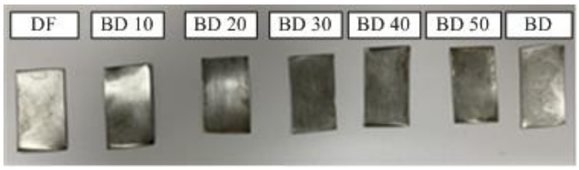


Fig. 4. *External view of the fuel samples and steel strips before the start of the experiment*
Source: own development

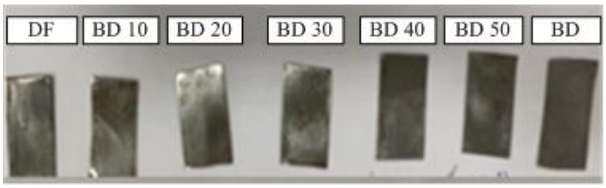
Analyzing the results presented at Fig. 5, we observe that the level of corrosion of steel strips is quit low. It is seen that 14 days exposure of the steel strips to fuel samples didn't change their external view. Longer storage up to two months results in the appearance of a slight corrosion coating. Steel strip that was stored in conventional diesel fuels has almost no corrosion even after two months of storage. The steel strip immersed in pure biodiesel has been slightly oxidized with signs of corrosion. Steel strips stored in biodiesel blends also have almost no signs of corrosion. From the received results it may be concluded that steel is characterized by a high level of resistance to biodiesel. Biodiesel blends don't make some significant corrosive action due to the chemical structure of hydrocarbons of conventional diesel fuel.



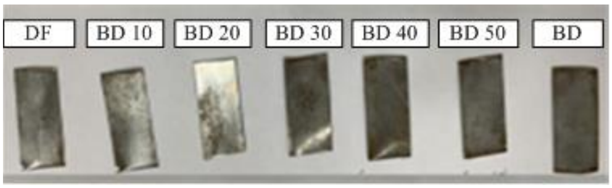
a



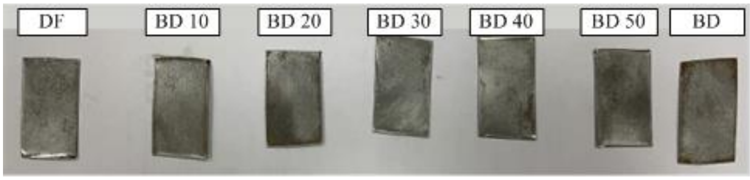
b



c



d



e

Fig. 5. *Corrosive influence of fuel samples on steel strips during the two-months period:*
a – clean strips before the experiment, b – after 14 days, c – after 28 days, d – after 42 days, e – after 56 days
Source: own development

At the next stage of the research, the influence of biodiesel and its blends on rubber materials was studied. Before the start of the experiment, the parts of the rubber hose (about 3 cm long) were cleaned and de-greased and then immersed into the bottles with fuels and stored during two months. The external view of fuel samples with the parts of the rubber hose are shown at Fig. 6.

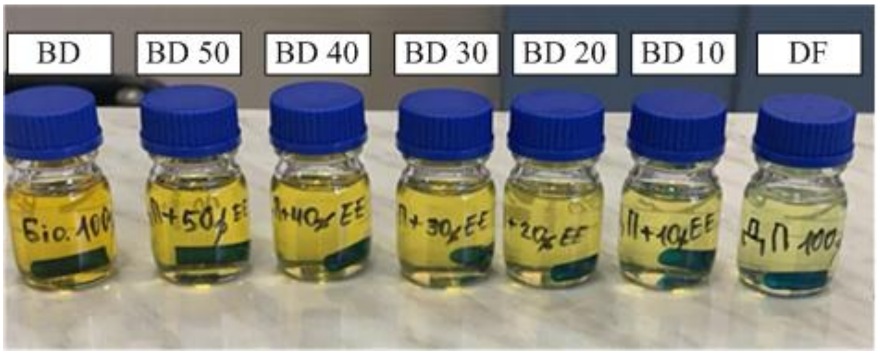


Fig. 6. *External view of the fuel samples with parts of the rubber hose before the start of the experiment*
Source: own development

Measurements and fixation of the changes were done before the start of the experiment and every two weeks. Changes in the state of the rubber hose were estimated by the values of its internal diameter, external diameter and thickness. Data in the figures below represent the result of the measurements of external diameter $d_{ext.}$ (Fig. 7), internal diameter $d_{int.}$ (Fig. 8) and thickness l (Fig. 9) of the parts of the rubber hose stored in fuel samples during two months.

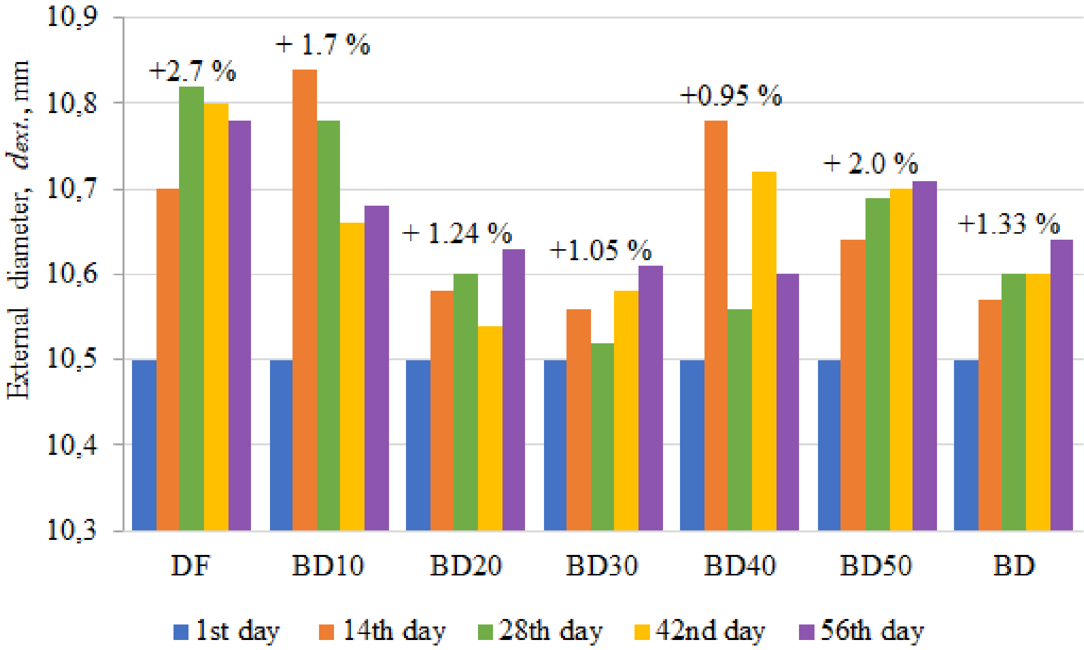


Fig. 7. *Change of the external diameter of the rubber hose*
Source: own development

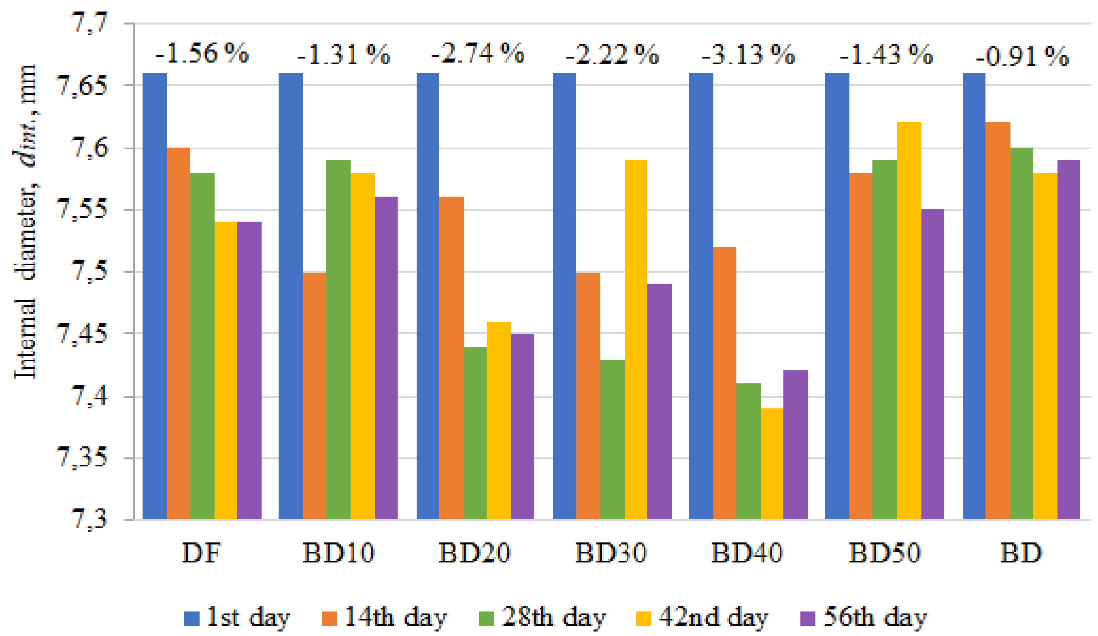


Fig. 8. *Change of the internal diameter of the rubber hose*
Source: own development

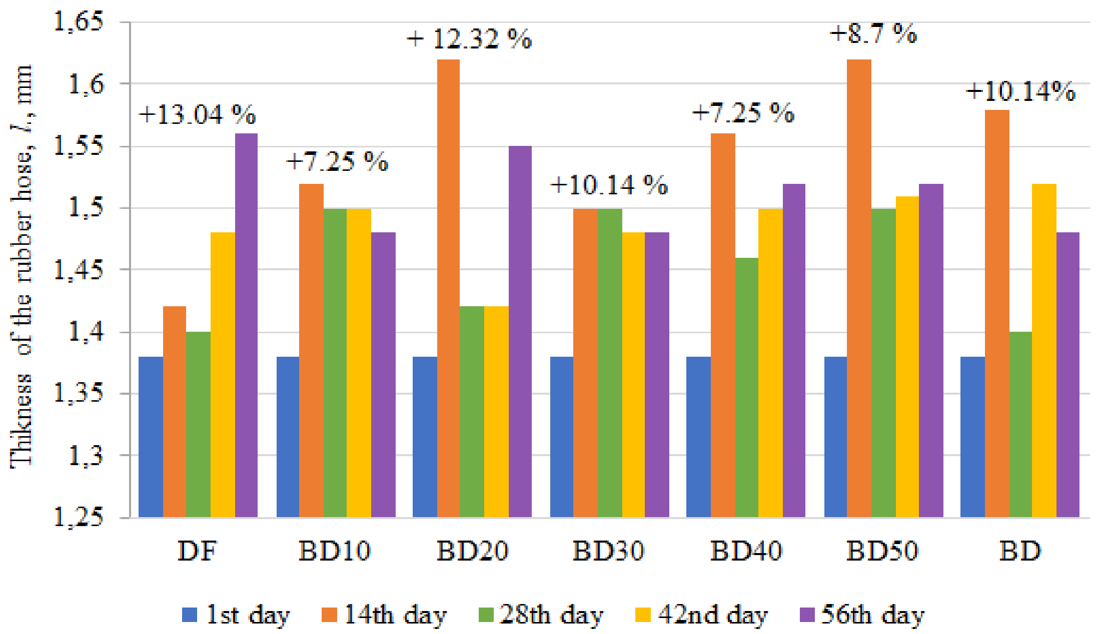


Fig. 9. *Change of the thickness of the rubber hose*
Source: own development

Based on the data in figure 7 we can conclude that all of the parts of the rubber hose stored in fuel samples have increased in external diameter. The values of the $d_{ext.}$ during two months rised by 0.95–2.7 %. At the same time, the data in figure 8 show that they decreased in internal diameter. The values of the $d_{int.}$ during two months decreased by 0.91–3.13 %. This indicates the influence of conventional diesel fuel, biodiesel and its blends on the state of rubber material. Molecules of fuel samples penetrate the structure of the rubber hose and lead to its swelling. The most intensive increment in values of the $d_{ext.}$ and, therefore, the swelling was observed after the first two weeks of the experiment. Then the swelling process slowed down. Similarly, the most intensive reduction in values of the $d_{int.}$ was observed after the first two weeks of the experiment. The highest overall increase of the $d_{ext.}$ was observed for a sample of conventional diesel fuel (2.7 %). This may be explained by the smaller size of hydrocarbon molecules, due to that they can penetrate rubber material easier. Data in figure 9 show the increase of the values of *l* of the parts of the rubber hose that correlates to the previous results and conclusion about the swelling of rubber materials in the medium of studied fuel samples. At the same time, after analyzing all the array of data it can be concluded that conventional diesel fuel makes the highest effect on the swelling of rubber materials.

The obtained results allow making conclusions about the long-term effect of biodiesel and its blends on construction materials used in transport vehicles. Biodiesel and its blends aggressively affect copper and details made of copper, diesel fuel doesn't promote corrosion of this metal. Stainless steel is quite resistant to biodiesel fuel and its blend. Rubber materials, such as PVC are subjected to the impact of both conventional diesel and biodiesel fuel during long-term storage. All the fuels cause the gradual swelling of rubber materials. However, PVC is more subjected to swelling under the action of conventional diesel fuel.

The aggressive action of biodiesel fuel and its blends is explained by its chemical structure, therefore lower chemical stability, and ability to absorb oxygen and water from the atmosphere, which intensifies the degradation of biofuel.

Basing on the results of the study the following set of measures and recomendations for providing reliability and durability of vehicles operation using biodiesel or its blends may be proposed:

- Providing proper conditions for biodiesel fuel storage and transportation, which eliminate access of negative factors (oxygen, water, sunlight), which can promote its degradation;
- Keep the term of use, recommended by the producer (typically about 3 months);
- Control the quality and composition of biodiesel fuel, which shouldn't contain free fatty acids, alcohol, or intermediate products of the manufacturing process;
- Using specialized anti-oxidation additives for preventing oxidation and degradation of biodiesel fuels and which are developed especially for use in biofuels;
- Using of biodestructing additives to prevent microbial pollution of biofuel, which is one of the reasons promoting corrosive action of fuel;
- Using stainless metals or alloys for constructing parts and details of the vehicle's fuel system;
- Using resistant anti-corrosion coating for metal details of the vehicle's fuel system;
- Selection of rubber materials (hose, sealing *etc*.) with improved resistance and durability during content with biodiesel fuel;
- Using specialized washing and cleaning additives for removing results of fuel degradation and products of corrosion from the vehicle fuel system.

4 CONCLUSIONS

Within the research, the long-term impact of biodiesel fuels based on camelina oil ethyl esters on metal and rubber construction materials of transport vehicles was studied.

An aggressive influence of biodiesel fuel and its blends on copper and copper details was found. Studied biofuels caused strong corrosion and degradation of copper during two months of storage. Such effect is explained by the chemical structure of biodiesel fuel, its low chemical stability and addiction to absorbing moisture from the external environment. At the same time, no significant impact of biodiesel fuel and its blends of steel was found. Steel kept its resistance to corrosion for two months.

Negative influence of biodiesel fuel and its blends on rubber materials during long-term storage was found. At the same time, a similar or greater effect was found for conventional diesel fuel. All studied fuels led to swelling of rubber materials.

Based on the obtained results and taking into account the processes, which take place during long-term storage of fuels the set of measures and recommendations for providing reliability and durability of vehicles operation using biodiesel or its blends was developed.

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