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Investigation on the Possibility of Increasing the Environmental Safety and Fuel Efficiency of Vehicles by Means of Gasoline Nano-Additive

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Abstract: Environmental safety problem originated from vehicles requires development and exploration of integrated and effective solutions, which considers the development level of technologies, the cost of their widespread use, the legislation requirements and other relevant aspects. One improvement method of the petroleum-derived fuels characteristics is the use of additives that complement the refining methods and provide ample opportunities to influence the individual characteristics. The aim of this work is to study the influence of the developed multifunctional surface-active nano-additive on the gasoline characteristics and engine performance. The measurement results confirmed the effective reduction of the surface tension of gasoline at the boundary with air, improving the mixture formation in the engine. On the other hand, the saturated vapor pressure was significantly decreased, which dramatically reduces evaporation losses and air pollution by light hydrocarbons. The use of the additive, due to a combination of its surface-active and catalytic action, significantly increases the fuel efficiency of engines and reduces octane requirements, greenhouse gases emissions, as well as noise level during operation of vehicles, and the environmental safety of vehicle operation increases.

Keywords: multifunctional surface-active nano-additive; surface tension; saturated vapor pressure; specific fuel consumption; noise level

1. Introduction

The continuous growth of the global vehicle fleet is accompanied by an increase in the consumption of motor fuels and environmental pollution. According to BP Global Energy Outlook [1], global demand for both freight and passenger transport may double by 2040. The data obtained on the average daily and average annual air pollutants emission in urban area cause a special concern for the harmful effects on the population [2]. The necessity to increase the octane number of the gasoline in some fuel-production scenarios leads to an increased density of the motor fuels, associated with the high aromatic content, which has a negative impact on the environmental characteristics and performance of cars [3]. For the urban environment, the vehicles are the major source of benzene, which is known to

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induce cancer risk to humans [4]. Acoustic pollution is another harmful impact associated with road transport, which remains the main source of noise for the environment [5]. One of the opportunities to reduce vehicles' pollution is associated with the development of alternative fuels and energy sources. Meanwhile, the hybrid electric vehicles, existing at present, have proved to be not as environmentally efficient as expected [6]. The solutions are suggested to improve the efficiency of application of the ethanol fuel in the spark ignition engines [7,8]. Despite a slight increase in the share of alternative fuels and energy sources, due to the efficiency of using traditional fuels in internal combustion engines and the adaptability of the existing vehicle fleet to their application, the petroleum-based fuels will remain the dominant energy sources in the nearest future. The study on the impact of emerging next-generation vehicles with smart vehicle technologies on the vehicle market [9] revealed that the cars using conventional motor fuels would keep their current position. The problem of the ecological danger of fuels and their combustion products requires one to look for integrated solutions, including new approaches in car and engine constructions [10]; improving the technological parameters of transport, with emphasis on multi-material construction for weight reduction [11]; increasing the adaptability of vehicles to operating conditions [12], in particular under weather changes [13], with application of such instruments as the dynamic vehicle scheduling [14]; tightening international and national requirements for fuel quality [15–17], use of tax instruments [3,18–21]. Limited possibilities for improving the quality of motor fuels by refining methods [22–24] necessitate the use of fuel additives of various purposes, the combination of which in small amounts ensures the environmental and operational characteristics achieve the desired level [25–30]. Often the use of additives is the only way to ensure an optimum engine mode that allows one the commodity fuel to be quickly and flexibly adapted to the operating conditions without increasing the fuel assortment.

A significant part of the additives used are surfactants. In addition, many additives have catalytic properties. Taking into account unique catalytic properties of nanoparticles and advantages of nano-technologies, the use of nano-additives is one of the promising modern trends in the development of a culture of the additives' application for improving the quality of fuels [31–33]. It has been previously shown that, in order to comprehensively improve the environmental and operational characteristics of automobiles, the additive must combine the properties of a surfactant and a catalyst for gasification reactions [27]. Since the vanguard of fuel additive development is represented mainly by large companies (such as Exxon Mobil, Chevron, Lubrisol Corp, Shell, Basf AG, The Dow Chemical Com, BP PLC, etc.), the results are patented, and the publication of scientific articles is very limited. In this paper, the results of experimental investigations on the effect of the multi-functional surface-active nano-additive developed on some properties of gasoline and engine characteristics, which are significant for the environmental safety and fuel economy of vehicles, are presented.

2. Materials and Methods

The effect of the surface-active additive with the composition of $(C_{12}H_{25}COO)_2Me$ (where Me is the metal, which is a highly effective catalyst for gasification reactions), modified in relation to the additive previously developed by the authors [27,28], on the individual characteristics of the gasoline and engine was investigated. The synthesis was carried out according to the author's technology, which allows combining the positive effects of the surface-active action of the additive with the application of a protective catalytic nanolayer on the working surfaces of the engine, ensuring carbon-free engine operation [34,35].

The effect of the additive on surface tension was studied for the individual hydrocarbons (n-hexane, n-hexene-1, cyclohexane, benzene, with a purity level of no less than 99%) and for two samples of the gasoline, both with research octane number (RON) 95, differing in the saturated vapor pressure values (71 and 62 kPa). The effect of the additive on vapor pressure was investigated also for these two samples of the gasoline.

The gasoline with RON 95 (Reid vapor pressure 62 kPa) was used for testing the effect of the additive on the gasoline specific consumption in bench and road tests.

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Surface tension was determined by the drop volume method (Tensiometer DVT50, KRUSS). Two parallel experiments were conducted for the basic organic liquids under study (gasoline and its individual components) and for each concentration of the additive introduced into the basic organic liquid. The deviation of the results from the average value did not exceed 2%.

Reid vapor pressure (RVP) was determined by the test method ASTM-D-323 using an apparatus for determining the saturated vapor pressure K11500 (Koehler). Two parallel experiments were conducted for the gasoline without additives, and for each concentration of the additive introduced into the gasoline. The deviation of the results from the average value did not exceed 2%.

Testing the effect of the additive on the gasoline specific consumption was carried out in idling test on the four-stroke four-cylinder engine ZMZ-4062.10, with a fuel injection system, the working volume of 2.3 liters and the compression ratio of 9.3. The engine was installed on a brake stand consisting of a balancer machine, AKB 92–4 (motor-generator of direct current), a weight device VKM -32 of a RP-10 type SH13 and a liquid rheostat. The gasoline consumption was measured by the volumetric method using the graduated measuring vessel. At the beginning of the experiment, the engine was warmed up close to the working temperature using the standard gasoline (RON 95). Then the engine worked using 200 mL of the gasoline sample to ensure that the fuel lines were filled with the gasoline to be studied. After this volume of the gasoline was exhausted, the engine worked with this fuel sample for an hour. The experiment was performed three times for each fuel sample. The deviation of the results, obtained in parallel experiments, from the average value did not exceed 5%. The tests were carried out at the engine speed of 1100 rpm.

The road tests on the influence of the additive on the specific gasoline consumption were carried out for a given run distance of 420 km, driving on the highway Ekaterinburg-Tyumen (Ural Federal District, Russia) with a given constant speed (60 km/h) on the same road section, under similar weather conditions ($T = 12 \pm 2$ °C, wind speed 1–1.5 m/sec), with the introduction of an additive in a concentration of 18 ppm. The tests were carried out using cars type Lada Priora (fully loaded mass is 1578 kg, the engine peak break power is 78 kW/5800 rpm), Toyota Corolla Axio (fully loaded mass is 1735 kg, the engine peak break power is 73 kW/6000 rpm), Ford Focus 1.6 MT Ultra Comfort (fully loaded mass is 1825 kg, the engine peak break power is 92 kW/6300 rpm). The mileage of all the cars used in the road tests was approximately 20,000 km. The road tests were performed twice for each car type using the standard gasoline (RON 95), and twice using the gasoline with the additive. The gasoline, fueled into the tanks, was accurately measured using the graduated measuring vessel before the test. At the end of each road test, to determine the gasoline consumption, the gasoline that remained was outpoured from the tank and accurately measured using the graduated measuring vessel. The deviation of the results, obtained in the parallel road tests, from the average value, did not exceed 3%.

The effect of the application of the additive on acoustic vibrations was also investigated. A Brűel & Kjær noise audiometer (Denmark) 2226 was fixed on the engine of VAZ-2106 automobile and noise was measured at steady-state (constant) modes of the car driving on the gasoline without additive and containing 18 ppm of the additive.

Table 1 summarizes the equipment applied for experimental measurements.

Table 1. Equipment for experimental measurements.

Variable to be Measured	Equipment
Surface tension	Tensiometer DVT50, KRUSS
Reid vapor pressure (RVP)	Koehler K11500
Fuel consumption: bench tests	four-stroke four-cylinder engine ZMZ-4062.10
Fuel consumption: road tests	cars Lada Priora, Toyota Corolla Axio, Ford Focus 1.6 MT Ultra Comfort
Acoustic vibrations	Brűel & Kjær noise audiometer (Denmark) 2226

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3. Results and Discussion

3.1. Effect of the Additive on the Surface Tension and Saturated Vapor Pressure

Figure 1 presents the results of the study of the additive influence on the surface tension of the gasolines and their individual components. The additive decreased the surface tension of the individual components by 16.8–20.1 %. For two gasolines with the octane number 95 by the research method, differing in the saturated vapor pressure values, the surface tension decreased by 17.7–18.8%. The results obtained are in good agreement with the type of dependences obtained as a result of previous studies of the effect of microconcentrations of surfactants of the composition of $((C_nH_{2n+1}COO)_2Me, (n = 9-15))$ on the surface tension of organic liquids [28,36]. The optimal surface-active effect of the additive $(C_{12}H_{25}COO)_2Me$ was observed when it was introduced into the basic organic liquid at a concentration of 18 ppm. Obviously, in this case, the distribution of the additive molecules in the surface layer occurs, ensuring the maximum reduction of the free surface energy of the liquid. When the additive concentration increases, the additive molecules are likely to associate with the formation of supramolecular structures, the surface-active effect decreases and the free surface energy increases.

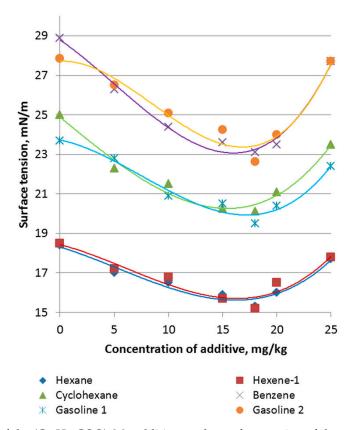


Figure 1. Effect of the $(C_{12}H_{25}COO)_2$ Me additive on the surface tension of the gasolines (gasoline 1—RVP of 71 kPa; gasoline 2—RVP of 62 kPa) and individual hydrocarbons at the interface with air at 20 °C.

Figure 2 demonstrates the obtained results on the additive influence on the gasoline saturated vapor pressure. The additive decreases the saturated vapor pressure significantly. The maximum decrease was observed at the introduction of the additive in a concentration of 18 ppm, and for two gasoline samples, differing in the saturated vapor pressure values, was 38.2 and 41.2%, respectively.

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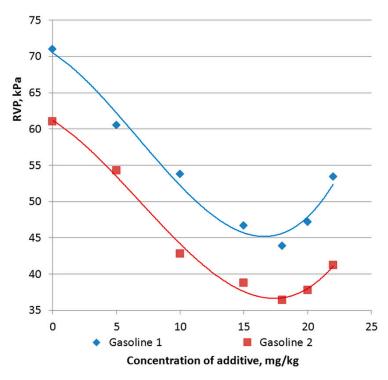


Figure 2. Effect of the $(C_{12}H_{25}COO)_2$ Me additive on the gasoline Reid vapor pressure (gasoline 1—RVP of 71 kPa; gasoline 2—RVP of 62 kPa).

Up to the optimum concentration of the additive, its introduction reduces the proportion of molecules of the basic organic liquid in the surface layer from which evaporation occurs, which, according to Raul's law, will reduce the saturated vapor pressure. The formation of associates of molecules with an increase in the additive concentration above the optimum will lead to an increase in the proportion of molecules of the base liquid in the surface layer and, correspondingly to this increase, the saturated vapor pressure increases. As a result of reducing the saturated vapor pressure with the introduction of the additive in the optimum concentration, the loss of gasoline from evaporation will be reduced to the same extent. According to [37], gasoline losses from evaporation at the petroleum station could attain 2.3 kg/t and even with application of the control technologies, the economic loss associated with the gasoline loss at the petroleum station is substantial [38]. Thus, the application of the developed additive will give a significant environmental and economic effect.

Earlier, the data were obtained on the effect of the $(RCOO)_2Me$, $(R=C_9H_{19} \div C_{15}H_{31})$ additive on the saturated vapor pressure of various gasolines [28,36]. The dependence was also extremal, but the maximum decrease in the saturated vapor pressure was 26.5%. It can be assumed that significantly stronger effect of the additive with the modified formula on the saturated vapor pressure is related to the fact that it is a single substance, $(C_{12}H_{25}\ COO)_2Me$, whereas the $(RCOO)_2Me$ additive, previously developed, was a mixture of homologues $(R=C_9H_{19} \div C_{15}H_{31})$. Identical molecules are more compactly located on the surface, occupying its larger proportion and causing displacement of a larger number of gasoline molecules and, accordingly, a greater decrease in the saturated vapor pressure.

It could be noted that the decrease in the saturated vapor pressure is not accompanied by the problems with the cold engine start, since simultaneous decreasing the surface tension will lead to an increase in the total surface area of the droplets of the gasoline injected, which improves the mixture formation in the engine. It has been shown previously that the rate of evaporation of gasoline droplets in an engine increases with a decrease in surface tension in inverse proportion to the square of the surface tension value [28].

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3.2. Influence of the Additive on the Gasoline Specific Consumption

Results of bench tests of the effect of the additive on the gasoline specific consumption are shown in Table 2.

Table 2. Effect of the $(C_{12}H_{25}COO)_2$ Me additive of the gasoline specific consumption by the ZMZ-4062.10 engine (at the engine crankshaft speed of 1100 rpm).

Fuel	Gasoline Specific Consumption, l/h	Change, %
Gasoline without the additive	3.43	-
Gasoline with the additive (10 ppm)	3.35	2.3
Gasoline with the additive (18 ppm)	3.28	4.4

Taking into account the data set on the additive effect on the surface tension and saturated vapor pressure and the bench test results, it is advisable to carry out road tests on the cars of various brands, comparing the specific consumption of the standard gasoline and the gasoline with an additive in a concentration of 18 ppm.

Figure 3 presents the results of the additive effect on the gasoline specific consumption in road tests.

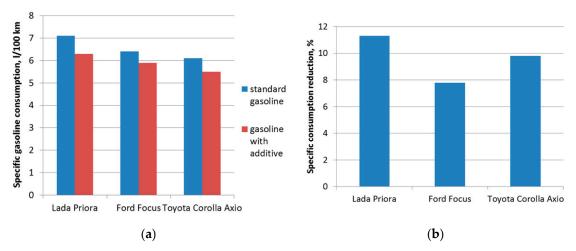


Figure 3. Effect of the $(C_{12}H_{25}COO)_2$ Me additive (18 ppm) on the gasoline specific consumption by the cars of various brands: (a) gasoline specific consumption; (b) specific consumption reduction.

Gasoline consumption after the run on the gasoline with the additive reduced for different cars by 7.8–11.3%. The pronounced effect of the additive introduction on the fuel efficiency of engines in the road tests can be explained by combining the surface-active action of the additive, which improves the mixture formation, with its catalytic influence on the gasification of carbon in the engine [34]. Elimination of carbon formation leads to a reduction in energy consumption for friction in the cylinder-piston group and mitigation of the temperature conditions in the engine, which leads to a reduction in the gasoline specific consumption [35]. The developed additive provides significant increase in fuel economy at the concentration significantly lower than the commonly applied surface-active additives [29,30]. In the bench tests, the volume of the spent fuel and the amount of the additive introduced were significantly less, and the main effect of the additive on the fuel consumption was associated with the improvement of the mixture formation due to the surface-active action of the additive.

While eliminating carbon, besides the gasoline specific consumption reduction, the requirements for the gasoline octane number also reduce. It is known from the vehicle operation practice that the carbon elimination reduces the engine's requirements for the gasoline octane number by 7–10 points [39–41].

Test runs (100 km) were carried out on a mixture of 50% gasoline with RON 95 and 50% of gasoline with RON 80; the research octane number of the mixture, calculated by additivity, was 87.5. The operation of the cars tested was stable; detonation was not observed. Reducing the gasoline specific

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consumption was accompanied by a corresponding significant reduction in carbon dioxide emissions. Previously obtained results on the effect of the $(RCOO)_2Me$, $(R=C_9H_{19} \div C_{15}H_{31})$ additive on emissions of toxic substances suggest that with the introduction of the modified $(C_{12}H_{25}COO)_2Me$ additive into gasoline a significant reduction in emissions of carbon oxide, nitrogen oxide and hydrocarbons will also be observed.

3.3. Effect of the Additive on Acoustic Oscillations in the Engine

The change in acoustic oscillations in the engine allows the smoothness of the combustion of fuel to be evaluated. Figure 4 shows the results of studies of the effect of the additive introduction on the noise level.

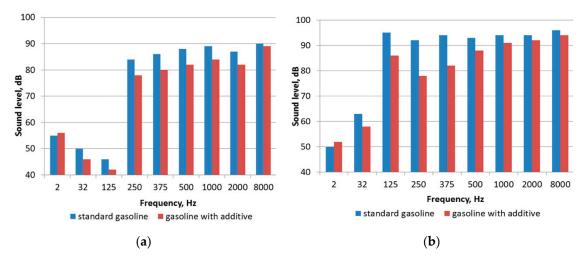


Figure 4. Effect of the $(C_{12}H_{25}COO)_2$ Me additive (18 ppm) on the noise level: (a) at a speed of 50 km/h (3rd gear); (b) at a speed of 90 km/h (4th gear).

With the introduction of the additive into gasoline, the average car noise reduction at a speed of 50 km/h in a frequency range of 32–8000 Hz was 6.23%. At a speed of 90 km/h, the average noise reduction was 6.3%. The results obtained confirm the positive effect of the additive introduction on the fuel combustion process in the engine. Reducing the noise level during car operation is important from the point of view of reducing acoustic pollution affecting both the driver and pedestrians [42,43].

4. Conclusions

Study of the influence of the $(C_{12}H_{25}COO)_2Me$ additive on the properties of gasoline and operation of vehicles showed a significant positive effect of its use. The additive, due to its considerable surface-active action, reduces the surface tension of gasoline and its individual components at the interface with air, which improves the process of mixing in the engine. The effect of the additive on the gasoline saturated vapor pressure, which under the additive action decreases by 38.2–41.2% in the tests carried out for different gasoline samples, seems to be outstanding. Losses from evaporation, proportional to the gasoline saturated vapor pressure, are very significant in countries with hot climate and cause serious environmental problems and economic damage. The use of the nano-additive developed, as a quick-impact and low-cost method, could be the best solution to this problem of air pollution by light hydrocarbons. In the future, it is advisable to investigate the possibility of using this method for gasoline-alcohol mixtures.

Combining the surface-active and catalytic influence of the developed nano-additive makes the process of gasoline combustion smoother, which reduces the requirements for the gasoline octane number, significantly reduces the gasoline specific consumption and the noise level during operation of vehicles. We can also assume a decrease in vibration effects, which requires additional research.

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Accordingly, with a decrease in the specific consumption of gasoline, a significant reduction in greenhouse gas emissions occurs. Taking into account the previously studied effects of the prototype of the modified additive, the effect on the emissions of toxic substances should also be significant.

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