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## NATURAL RESOURCES

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## THE UNIQUE COMPOSITION AND STABILITY OF WATER-FUEL EMULSION

Research article

### Abstract

Analysis of methods of creation and use of water-fuel emulsions (WFE) showed their relevance in order to save fuel, but mainly for environmental purposes. The main objective of the study is to develop a method for producing a highly stable WFE from diesel fuel with a high water content. The method is based on the use of the following operations: the introduction and mixing of complex hydrophobic emulsifiers in diesel fuel (DF); the introduction and mixing of a complex of hydrophilic emulsifiers in distilled water; mixing of both compositions and their mechano-chemical treatment by pumping 5 min in a combined static mixer-activator (activator) according to the RF patent No. 2411074 in the flow rate mode of 10 cm/s. According to the results of long-term studies, more than an annual stability of WFE, which contains 65% diesel fuel, 33% water and 2% complex emulsifiers, was obtained.

The proportion of light hydrocarbons in the WFE to C<sub>15</sub>H<sub>32</sub> more than in activated and significantly more than in not activated DF. And the proportion of heavy hydrocarbons in the WFE, since C<sub>16</sub>H<sub>34</sub>, significantly less than in not activated and activated DF «Euros». Re-inspection of WFE showed the immutability of its properties. A comparison of the spectrograms of the water and WFE showed the absence of water in the WFE. Modification of diesel fuel and WFE itself is explained by mechanical chemistry in the activator. And it continued when storing fuels and WFE has no adequate explanation. It is possible, that this is caused by active radicals formed in the activator. The predominance of the lungs and lower content of heavy hydrocarbons in diesel fuel and WFE after their mechano-chemistry in the activator, its irreversibility, the extension of storage of fuels and WFE are extraordinary, demonstrates the high efficiency of the activator and uniqueness of the received WFE. Chemical and chromatographic analyses of WFE showed its compliance with technical regulations for motor fuels. It reduces diesel fuel consumption by 9%, costs 25 rubles per liter.

**Keywords:** 65 % diesel fuel, 33 % water, 2 % emulsifiers, activator, mechano-chemistry, water-fuel emulsion, chromatograph, fractional composition, irreversibility, environmental.

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# УНИКАЛЬНАЯ ПО СОСТАВУ И СТАБИЛЬНОСТИ ВОДО-ТОПЛИВНАЯ ЭМУЛЬСИЯ

Научная статья

## Аннотация

Анализ методов создания и использования водо-топливных эмульсий показал их актуальность в целях экономии топлив, но главным образом в экологических целях. Главной целью исследования является разработка способа получения высокостабильной водо-топливной эмульсии из дизельного топлива с высоким содержанием воды. Способ основан на применении следующих операций: введении и перемешивании в дизельном топливе (ДТ) сложных гидрофобных эмульгаторов; введении и перемешивании в дистиллированной воде комплекса гидрофильных эмульгаторов; смешивание обоих составов и их механо-химическая обработка путем прокачивания 5 мин в комбинированном статическом смесителе-активаторе по патенту РФ № 2411074 в режиме расхода потока 10 см/с. По итогам длительных исследований получена более годовая стабильность WFE, которая содержит 65% дизельного топлива, 33% воды и 2% сложных эмульгаторов.

Доля легких углеводородов в WFE до C15H32 больше, чем в активированном и значительно больше, чем в неактивированном DF. А доля тяжелых углеводородов в WFE, начиная с C16H34, заметно меньше, чем в неактивированном и активированном DF евро. Повторный контроль WFE показал неизменность её свойств. Сравнение спектрограмм воды и WFE показало отсутствие воды в WFE. Модификация дизельного топлива и самой WFE объясняется механо-химией в активаторе. А её дальнейшее продолжение при хранении топлив и WFE не имеет должного объяснения. Не исключено, что это вызвано активными радикалами, образующимися в активаторе. Преобладание легких и более низкое содержание тяжелых углеводородов в дизельном топливе и в ВФЭ после их механо-химии в активаторе, её необратимость, пролонгация в хранении топлив и WFE являются экстраординарными, свидетельствует о высокой эффективности активатора по патенту РФ № 2411074 и уникальности получаемой ВФЭ. Химмотологический и хроматографический анализы WFE показали её соответствие техническому регламенту на моторные топлива. Она уменьшает расход дизельного топлива на 9%, стоит 25 руб. за литр.

**Ключевые слова:** 65 % дизельного топлива, 33 % воды, 2 % эмульгаторов, активатор, механо-химия, водо-топливная эмульсия, хроматограф, фракционный состав, необратимость активации, экология

## 1. Introduction

The tasks of energy saving and environmental safety are constant. To solve them, it is advisable to use water-fuel emulsions (WFE), for example, fuel oil + water, motor fuel + water [1-3].

WFE from fuel oil, diesel fuel (DF), heating oil, gas gives their savings, a noticeable increase in the resource of heat and power units, their efficiency by 2-3%, a significant reduction in the release of harmful gases. Radical purification of exhaust gases (EG) from NO<sub>x</sub> (by 90%) by catalytic regenerators requires costs of 40-70 \$/kW of diesel power [2]. Are they in the feed to the diesel steam while reducing NO<sub>x</sub> emission only up to 70%.

For the testing of the Navy, other branches of the water in the fuel of internal combustion engines (ICE) provides the following [1, 2]:

- reduces the temperature and prevents the explosive combustion of fuel,
- smoothes the dynamics of gas pressure in the cylinder,
- increases the average pressure in the cylinders,
- increases the completeness of fuel combustion,
- increases efficiency, no reduces power, but several reduces dynamism engines,
- accelerates the conversion of CO to CO<sub>2</sub>,
- reduces exhaust soot, NO<sub>x</sub> and to a much carcinogenic benzopyrene C<sub>20</sub>H<sub>12</sub> (Fig. 1 [1]),
- cleans the combustion chamber from carbon deposits, ensures the operation of the engine in the current mode, reduces wear, vibration, noise.

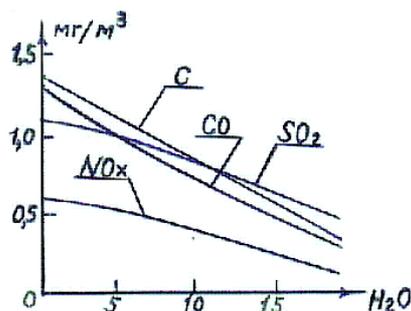


Figure 1 – Dependence of the concentration (mg/m<sup>3</sup>) of harmful substances in the exhaust gas on the moisture content of WTE [1]

Water, as a component of motor fuel, has been tested in the world practice by various methods [1-6], including:

- direct injection into the cylinders of the engine, which from the pre-war until recently was used in aircraft engines;

- supply of dispersed water to the intake manifold of the ICE by a separate device or a separate carburetor;
- humidification of the fuel-air mixture, the formation of water-air or steam-air mixture before its supply to the intake duct of the ICE;
- formation of WFE outside the ICE and putting it into the fuel tank [7-9].

The first method is known, for example, the method of patent RU No. 2069274. Its disadvantage is the complexity of regulating the water supply and the lack of formation of a highly homogeneous water-fuel mixture.

According to the second method, amateur methods of supplying water from micro-channels behind the throttle of the carburetor are known, as well as the, for example, «Fordzon-Putilovets» tractor in Russia with an additional water carburetor.

According to the third method, there are several ways to moisten the air or fuel-air, or to prepare an air-water mixture. So you know spraying water in the intake tract of the ICE before the carburetor (patent RU № 2092709).

Another is the saturation of the fuel-air mixture by water vapor produced by the heat of EG of (patent RU No. 2136942). Here the disadvantage is the need for an efficient steam generator and relatively low energy performance of water vapor. Analogues of this method are protected by patents of the RF No. 2094642, 2352805.

The disadvantage of all methods of humidification of fuel-air or creation of water-air mixture is that they do not give an adjustable composition of highly dispersed fuel-air mixture, as well as underestimated, in comparison with clean fuel, energy indicators of fuel-water-air mixture.

On the fourth reception there are many ways of cooking WFE outside of the ICE, which consists in the preparation of 15-20% of water, of 75 % of fuel, of the complex substances from emulsifiers, stabilizers, catalysts of combustion, and further their joint stirring. Here are a variety of patents SU No. 699005, 816524, 1230470, 1243342, 1246593, patent RU No. 2213768, patent RF No. 2294448, US patents No. 1498340, 1533158, 1701621, 1701691, 3807973, 3876391, 4199316, 4244702, 4696638. The disadvantages of entering the water in the ICE in the above patents is the complexity of techniques and tools to create a WFE and its lack of stability.

Russian patents No. 2306447, 2365618, 2367683 [8, 9] two groups of substances are used for WFE. In the 1-st - low molecular weight anionic surfactant and non-ionic surfactant in a ratio of 3:1 to 6:1. In the 2-nd - stabilizing hydrophobizator and high molecular weight surfactant. In the 3-rd - polar organic solvents from betaine, propanol-2, sorbitol, oil distillate. In the 4-th - oil-compensating agents.

Examples of emulsifying system under patent No. 2365618 [8] for 76% of diesel fuel and for 23% of process water, emulsifying system (1% by weight.% to water) includes:

- component 1 - anionic surfactants (sulfates of the general formula), 6,5%; nonionic surfactant (sorbifolia), 2%;
- component 2 - polyolefins (poly-alpha-olefins), 8,7%;
- component 3 – betaine, 3%;
- component 4 - nitrated oil, 6%.

Macrocomposition agent apply engine oil or their promoters, providing or facilitating the lubrication of, for example, tributylphosphite, tridecanol, tricarbonyl, industrial diethylene triamine, poly-4-methylphenen-1, phosphate esters, thioether dialkyldithiophosphoric acid.

There is a similar version of the emulsifying system for benzo-aqueous emulsion.

These complexes of substances provide stability of WFE for up to 72 hours. However, the empirical selection of emulsifying and auxiliary substances (up to 33 substances), as shown by the testing of their cars in publications and patents, still does not provide long-term (up to 3 months) stability of WFE.

It should be noted the positive features of the combustion of WFE. So for example, described this mechanism of combustion of water-fuel emulsions [2]: The fuel oil from the injectors has a droplet size of 0,1 to 1 mm. If they included a drop of water 1...7 microns, when heated, they give couples. It breaks a drop of fuel, increasing its dispersion, the surface of contact with air. In the high-temperature combustion zone, a drop of WFE explodes, a drop of fuel is dispersed secondarily, the combustion torch increases and reduces the local maxima of temperatures in the chamber. It is clear, that in comparison with the dispersed droplet of a large particle, the radiation area and the heat flux are smaller, burn lengthwise and not fully. At WFE with a uniform distribution of dispersed water, the size of fuel particles is reduced by 1.5...2.5 times, the combustion conditions and efficiency are also improved, the underburning of fuel is reduced, the volume of blast is reduced to an indicator of 1,0 and heat loss with it. The temperature of the dew point of the outgoing gases decreases to 100 °C. Significantly reduces sulfuric acid corrosion and increases the efficiency of energy and heat units, although it increases the emission of SOx into the atmosphere.

But WFE after storage is less effective than prepared directly before combustion and without emulsifiers, giving carbon deposits in the ICE. In addition, ensuring long-term stability of WFE is possible only with its careful and time-consuming preparation. Therefore, with the 80-ies in Russia and abroad, successfully work installations of direct supply of WFE in a variety of marine diesel engines, boilers, steam generators. The units have been tested on Russian and foreign tractors, MAZ, KamAZ vehicles, confirmed fuel economy up to 10-15%, and on stationary power units up to 40%. The installations are simple, has no moving parts except pumps, the energy flow of which is provided by the cyclic impact on the WFE.

The All-Russian Institute of agricultural electrification (VIESH) also conducted research of water-fuel mixtures for many years. Here [3] it is believed, that the activation of a mixture of water and hydrocarbons, creates new phases of substances, stabilized by electrostatic forces from induced charges. Because of them, free radicals appear in the mixtures, which allows to realize low-temperature combustion, significantly reduce the formation of incomplete combustion products, increase the service life and efficiency of the ICE. The authors [3] conducted, for example, such studies:

**A. Testing of diesel YamZ-238L on fuel with 20% water** (St. Petersburg, Institute of Technology, 19.04.2007, fig. 2, 3)

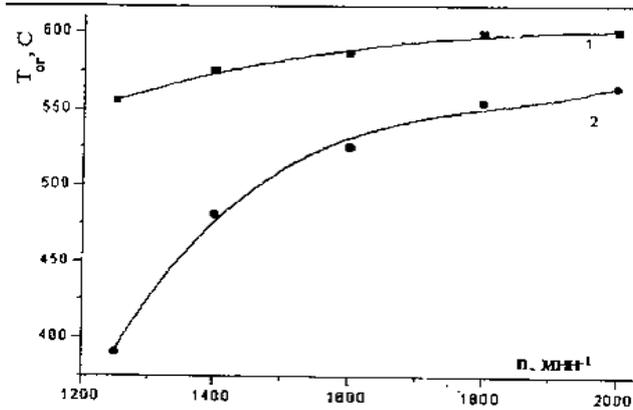


Figure 2 – The dependence of the temperature ( $T$  °C) of the EG on the speed of the crankshaft of the diesel: 1 – for diesel fuel, 2 – for WFE

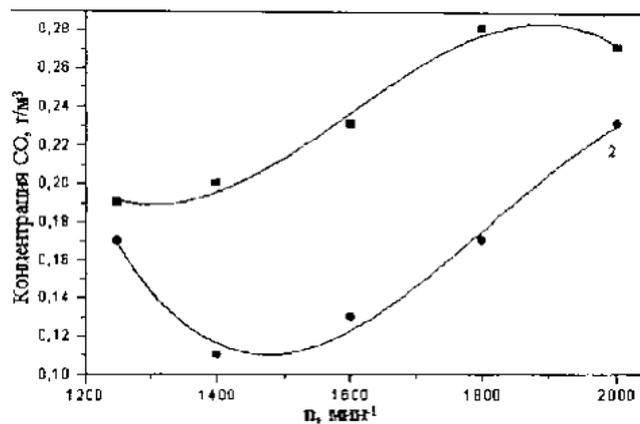


Figure 3 – The dependence of the concentration of CO ( $g/m^3$ ) on the speed of the crankshaft of the diesel: 1 – with DF, 2 – with WFE

Indicators EG of the ICE with WFE in figures 2, 3 review is not required.

**B. Studies of the emulsion of diesel fuel and water (table 1).**

Table 1 – Emulsion parameters with water content up to 40% [3]

Content water, %	Heat of combustion, kCal/kg	Mass fraction of sulfur, %	Cetane number	Density, kg/dm <sup>3</sup>	Pour point, °C
40	10970	0,1	53 (π)/s	0,85	- 40
50	11160		54 (π)/s	0,832	- 39,4
DF	10300	0,2	35(π)/s, 45(з)/w	0,83	-35

As can be seen from table 1, even with a water content of 40 and 50%, WFE in all respects exceed the standard diesel fuel

**B. Investigation of the molecular spectrum of WFE from 60% DF, 40% water**

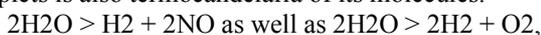
Water and WFE spectrograms (Bruker AVANCE-300 spectrometer) showed:

- WFE spectrum consists of groups of signals, corresponding to CH<sub>3</sub>, CH<sub>2</sub> and another CH - groups and groups of signals, corresponding to aromatics,
- signals, corresponding to water molecules, are not detected,
- comparison of the spectrograms of WFE and tap water [3] showed new properties of fuel from WFE, where water was not detected.

So, in WFE a mixture of organic matter was detected, and the water was chemically bonded. Similar results were obtained by other researchers [1, 2, 7].

Special originality combustion WFE described Zavgorodny B.V. [2]:

- in addition to the improved atomization and mixing of fuel with air due to the vaporization and explosion of water droplets is also termocandelaria of its molecules:



- therefore, the beginning of the oxidation of fuel molecules is more real products of water decomposition, than air oxygen; fuel needs an instant rate of oxidizer, it gives an instant thermal decomposition of water molecules at 1500 °C; thus; 60% of the oxygen from the WFE is used to ignite the fuel in areas, inaccessible to air oxygen,

- hydrogen from dissociated water diffuses into a zone with excess oxygen and compensates for the costs of the heat of combustion for the dissociation of water,

- water vapor increases the volume of combustion products per H/4 kMol of water, which increases the work of gases in the cylinders of the engine (H - content of hydrogen atoms).

The changing dynamics of combustion of WFE are shown on indicator diagrams of internal combustion engines [2]. Here, the expansion line is spaced from the compression line at a greater distance, the average pressure increases, combustion is completed earlier by 30° of rotation of the crankshaft, the EG temperature decreases by 6..8 ° C, the heat density of the cylinders decreases, the oil in them is less saturated with combustion products, which increases reliability, reduces engine wear. The acceleration of combustion, thanks to the products of water dissociation, ensures its completeness and ecological compatibility. The annual economic effect of only reducing fuel consumption, for example, on ships is \$ 15 per 1 kW of power of the main diesel [2].

The above allows us to consider WFE as a special type of fuel.

However, the creation of a stable WFE is a difficult problem. WFE should be resistant to coalescence and sedimentation for at least 72 hours in the operation of the engine, at least a month in its parking lot, at least 3 months in addition, it should provide a lower cost of fuel. But water and hydrocarbons are not soluble in each other. Conventional emulsifiers make them only limitedly soluble. Thus in long-term storage there are unclear chemical reactions even with change of colouring of WFE.

Physical impact on water structures its state only for a short time due to the high mobility of molecules. Hydrogen bonds between them are changeable, molecules with high frequency change their neighbors. In addition, the properties of water are changeable and the presence of salts, gases, organic matter. The so-degassed water is saturated with them again for a long time. And under the action of cosmic and other radiations free radicals and many other formations are formed in it [2, 3], so WFE can change its properties.

Hence, it is clear that the preparation of homogeneous, highly stable WFE as a motor fuel is a difficult task, confirmed by a lot of unsuccessful attempts to create it. So, only in Russia it is tested 19 firms.

**The purpose of research:** to develop a method of preparation of a stable WFE, that meets the requirements for motor fuels, containing a large volume of water, to check its fractional composition, stability and dynamics of the composition in annual storage.

## 2. Materials and methods

Two batches of unique WFE were prepared from 65% diesel fuel, 33% water and 2% emulsifiers, namely from previously studied 10 organic substances [6, 8, 9], which are included in two different functional groups. In the 1-st – hydrophobic substances soluble in diesel fuel, introduced into it and mixed in it. In the 2-nd – substances with hydrophilic properties, soluble in water, introduced into it and mixed in it.

Fuel with its mixed emulsifiers, water with other mixed emulsifiers were drained together and pumped for at least 5 minutes at a flow rate of 10 cm/s through a combined static mixer-activator under RF patent No. 2411074. Further, the obtained WFE was controlled chemically, especially for compliance with the regulations for motor fuels and on the crystallux-4000M chromatograph with the PID-PFD detector in the certified Tambov laboratory of forensic medical examination. After long exposure of WFE its composition on the chromatograph was checked again. Conducted comprehensive operational testing of WFE in diesel by the car «Mitsubishi Pajero» 1995 issue. And with triple repetition bench tests of diesel YAMZ-226 with VTE are carried out.

## 3. Results and discussion

**Implementation of the goal and discussion of the results.** The formation of WFE was facilitated by the introduction of stabilizers consisting of oils, acid esters with a high viscosity index, auxiliary substances from hydroxides, alcohols, esters [6, 8, 9]. Chemotology and chromatography of the obtained WFE showed: density 897 kg/m<sup>3</sup>, flash point not lower than 67°C, filterability temperature not higher than -5°C, corrosion on the copper plate in class I no, sulfur content corresponds to RF GOST 305.

Compared to the composition of WFE and DF according to their chromatography are shown in table 2. It follows from:

Table 2 – Comparison of WFE and DF

№	Component	The concentration of components in the WFE and diesel fuel, % vol.								
		WFE 2018 г.		Diesel fuel not activated			Diesel fuel activated			
		1-я	2-я	Fuel from Tambov	Rosneft fuel	Fuel Euro	Fuel Euro	Fuel Tambov	After 57 days	
1	Komplex	2,06	8,9733	-	-	-	-	18,735	-	31,2393
2		23		-	-	-	-	-	12,4643	0,1744
3	C8H18	2,41	1,4548	0,7914	0,6165	0,4710	0,7914	0,7627	0,5728	0,4770
4	C9H20	5,38	3,969	1,0773	2,0122	1,94	1,0773	0,8636	1,9178	1,4916
5	C10H22	10,6	8,2844	1,6927	4,8365	4,17	1,6927	1,2876	4,3327	1,6204
6	C11H24	14,7	11,56	3,7948	9,5619	7,87	3,7948	2,8221	7,0027	7,5722
7	C12H26	13,6	11,10	7,9954	8,2222	8,859	7,9954	5,2168	7,4221	5,6975
8	C13H28	14,8	11,725	10,1914	9,8051	13,05	10,1914	8,5468	8,8126	6,7065

Continuation of Table 2

9	C14H30	13,4	10,2075	10,9121	10,6315	13,5569	10,9121	9,1103	9,4767	7,6143
1	C15H32	9,68	9,318	9,2575	8,9045	10,981	9,2575	7,9060	7,7791	6,4032
1	C16H34	5,96	6,696	9,8080	9,1511	10,15	9,8080	7,3523	8,2725	6,3928
1	C17H36	2,59	3,76	7,8725	6,6586	6,627	7,8725	6,7942	5,5632	3,2984
1	Fitan	0,91	1,68	7,3010	3,5902	2,764	7,3010	6,2364	3,1828	1,3887
1	C18H38	1,41	2,629	6,0368	5,5628	5,1	6,0368	5,1263	4,9620	3,3817
1	Pristan	0,65	1,463	4,0559	3,8064	3,0861	4,0559	3,2697	3,4556	2,5273
1	C19H40	0,78	2,139	5,1226	4,6599	4,169	5,1226	4,4222	4,2337	3,4803
1	C20H42	0,41	1,659	4,3236	3,8863	2,965	4,3236	3,6375	3,2585	3,0611
1	C21H44	0,19	1,201	3,1886	2,9188	2,000	3,1886	2,8035	2,6214	2,3501
1	C22H46	0,10	0,95	2,3509	2,2426	1,248	2,2509	2,1519	2,0158	2,0816
2	C23H48	0,04	0,617	1,6067	1,4190	0,61	1,6067	1,4078	1,3158	1,4797
2	C24H50	0,02	0,400	1,1408	0,9670	0,273	1,1408	0,9633	0,8627	0,9402
2	C25H52	0,01	0,214	0,7005	0,5470	0,11	0,7005	0,5833	0,4753	0,6216
Amount		100,0000		99,2203	100,0000					

1. The proportion of light hydrocarbons in WFE (without taking them into account in the complex of the activated DF «Euro» and the DF from the Institute WNIITiN) until C15H32 more than in activated DF «Euro» and considerably more than in what is not activated DF. And the share of heavy hydrocarbons in WFE, starting with C16H34, is significantly less than in unactivated and activated fuel «Euro».

2. Modification of fuels and WFE is explained by the processes of mechano-chemistry, going in the activator under patent RF No. 2411074. And the continuation of the modification outside the activator (the last column of table 2), revealed in the 2000s in the Tomsk scientific center, has no proper explanation. It is assumed that it is caused by long-lived active radicals formed in the activator. A physicist Y.P. Rassadkin and environmentalist Drunvalo Malihidisek is explained by the influence of highly energetic substances at low energetic.

The prevalence of light and lower content of heavy components in the WFE, and in the activated DF after 57 days, is of an extraordinary nature, indicates the effectiveness of the activator (RF patent No. 2411074), which is confirmed by its tests 4 times on KamAZ-740, YaMZ-236 and ZMZ-406 engines.

Received 14.12.2017 WFE survived until april 2018, again subjected to chromatography, which, like activated DF (last column of table. 2), showed the immutability of the properties of WFE. A comparison of DF and WFE spectrograms showed the superiority of WFE over DF in fractional composition and without signs of water presence, as in the complex fuel of the Institute of VIESH [3].

It should be noted that the undetected water content in WFE can be explained by the fact, that water molecules, as the most universal ligands, form complex compounds with fuel molecules, similar to gas hydrates, having specific spectral characteristics.

WFE has remained stable, without separation and 25.01.2019. And the car «Mitsubishi Pajero» is used only on this WFE. In this morning for the start of the internal combustion engine was carried out from 3-rd attempt, and after trips – 1. The engine works softer, fuel consumption and noise of work decreased, acceleration of the car is usual. There are no negative phenomena in the work of the ICE.

#### 4. Conclusion

Studies conducted in RF and in other country, as well as successful testing on automotive diesel engines have convincingly shown that WFE can be an environmental fuel for different types of transport. For this purpose, a unique composition and stability of WFE, obtained by the technology of Tambov STU can be used.

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#### Conflict of Interest

None declared.

#### Конфликт интересов

Не указан.

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