# Reducing the anthropogenic load on the environment through the use of reformulated automotive fuels based on oxygenates

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**Abstract.** This paper analyzes environmental problems caused by pollutant emissions from automobile engines and substantiates the relevance of using reformulated diesel fuels containing oxygenates as additives. The possibility of obtaining stable fuel–ethanol emulsions based on commercial winter diesel fuel with an ethanol content from 1 to 10 vol.% was investigated. The effect of stabilizing additives, namely primary saturated aliphatic alcohols such as propan-1-ol, butan-1-ol, heptan-1-ol, and octan-1-ol, on the aggregative stability of emulsions was studied. It was established that, without emulsifiers, phase separation of the mixtures occurs rapidly, whereas the introduction of 1 vol.% alkanols slows down coalescence. The cloud point of emulsions stabilized with propan-1-ol was determined, and its increase with a growing volume fraction of ethanol was shown. The cetane index of the obtained compositions was calculated; for all samples, its value was found to be no lower than 52, which meets regulatory requirements. The electrokinetic potential of emulsion particles was measured using phase analysis light scattering. Propan-1-ol and butan-1-ol are proposed as economically justified stabilizers. It is concluded that the use of alkanol additives is promising for reducing harmful emissions, improving the environmental safety of diesel engines, and decreasing the negative impact of motor transport on the environment.

## 1 Introduction

Intensive motorization, the rate of which has remained high over recent decades, ensures a high level of population mobility and generally contributes to improving quality of life. At the same time, it also has negative aspects, the most important of which are the consumption of non-renewable natural resources and the pollution of environmental objects, including atmospheric air, soil, surface water, and wastewater, by harmful substances emitted with vehicle exhaust gases.

With the growing number of vehicles, the contribution of road transport to the greenhouse effect is also increasing, which leads to climate change. Globally, road transport generates approximately 25% of carbon dioxide emissions and up to 14% of total greenhouse gas emissions, including nitrogen and sulfur oxides as well as certain hydrocarbons [1, 2]. In addition, exhaust gases participate in photochemical reactions, resulting in the formation of

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secondary pollutants such as aldehydes, ketones, carboxylic acids, peroxyacyl nitrates, and nitro-polycyclic aromatic hydrocarbons, which often exceed the original substances in toxicity. These processes contribute to the formation of smog and acid rain, which leads to deterioration of air quality in residential areas and directly affects public health.

In this context, the development and improvement of methods for reducing the negative impact of motor transport on the environment are a priority task.The main areas of development include improving engine design, using catalytic converters and particulate filters, applying alternative fuels such as hydrogen and electric vehicles, and optimizing traffic flows. However, a mass transition to electric vehicles and hydrogen fuel cells is unlikely in the coming decades. According to forecasts, even by 2040, 85–90% of vehicles will still be equipped with internal combustion engines operating on conventional hydrocarbon fuels [3].

Under these conditions, a realistic and economically justified way to reduce exhaust gas toxicity is to improve the properties of petroleum motor fuels by introducing oxygenates, that is, oxygen-containing organic compounds. The presence of weakly bound oxygen in oxygenate molecules contributes to more complete combustion of hydrocarbons, which leads to a reduction in emissions of CO, total hydrocarbons, and particulate matter. Among oxygenates, C1–C5 alcohols and ethers have been studied most extensively [4–7]. Ethanol deserves special attention, since it can be produced from renewable plant-based raw materials, which corresponds to the principles of sustainable development and the circular economy [8]. Ethanol may be used as an independent fuel or as a fuel additive. The main advantage of ethanol-containing fuels is their high environmental performance, including reduced exhaust smoke opacity and lower emissions of CO and total hydrocarbons. Ethanol-containing fuels are already successfully used in gasoline engines; however, their application in diesel engines is limited by the low self-ignition capacity of alcohols and the insufficient aggregative stability of mixtures [7, 9].

Methanol, $CH_3OH$, which has an almost unlimited raw material base, has also attracted the attention of a number of researchers as an additive to petroleum motor fuels [10]. However, despite its obvious advantages, including low cost, since methanol is the cheapest oxygenate, the possibility of synthesis from various types of raw materials, and improved environmental indicators when used as a fuel additive, methanol is highly toxic, which represents a real obstacle to its broad practical application. In addition, methanol has low energy and performance characteristics.

Several studies [11] present results on the effect of oxygenate additives in diesel fuels on harmful emissions from exhaust gases. It has been shown that the use of oxygenates as additives increases the completeness and efficiency of diesel fuel combustion and, consequently, reduces the formation of incomplete combustion products: carbon monoxide, total hydrocarbons, and particulate matter or soot. CO emissions decrease with increasing compression ratio and alcohol concentration in the mixture. The lowest CO emissions were observed for diesel fuel containing 20% n-butanol. Exhaust smoke opacity decreased compared with mineral diesel fuel at all compression ratios, since alcohols decompose more easily and evaporate more efficiently than diesel fuel.

For diesel engines, reducing exhaust smoke opacity is extremely important, which is associated with the characteristics of the working process in compression-ignition engines. Incomplete combustion of diesel fuel, especially fuel with a heavy fractional composition, results in the formation of particulate matter consisting mainly of soot. These particles have a porous structure and therefore act as adsorbents of carcinogenic polycyclic aromatic hydrocarbons [12].

The mechanism of action of oxygenates involves the oxidation of fuel hydrocarbons by HO· radicals during dissociation of the fuel molecule. The release of weakly bound oxygen during combustion reduces the fuel-to-air ratio, while oxygen accelerates the oxidation of carbon-containing components and prevents soot formation. In general, the volumes of harmful emissions depend on engine operating conditions and on the quantitative composition of fuel–ethanol mixtures. All the above-mentioned studies note a decrease in pollutant emissions with exhaust gases when oxygen-containing organic additives are used. Some authors also report a certain decrease in the indicated effective efficiency of the engine when it operates on mixtures of diesel fuel with oxygenates [11].

It should be noted that the issues of phase stability of emulsions based on diesel fuel and alkanols, as well as the selection of effective stabilizers, remain insufficiently studied.

The purpose of this study is to obtain stable mixtures of automotive diesel fuel with ethanol, to investigate their aggregative stability in the presence of various stabilizers, namely alkanols, and to determine important physicochemical characteristics such as cloud point, cetane index, and electrokinetic potential depending on the composition and nature of the oxygenate.

## 2 Materials and methods

Ethanol was used in this study as the main oxygenate additive to automotive diesel fuel.

### 2.1 Preparation of fuel–ethanol compositions

Ethanol-containing fuel emulsions were prepared on the basis of commercial diesel fuel with a cold filter plugging point of –20°C. Emulsions containing from 1 to 10 vol.% ethanol were prepared by dispersion using a laboratory rotor-type mixing device at a temperature of 20 ± 2°C. Primary saturated aliphatic alcohols, namely propan-1-ol, butan-1-ol, heptan-1-ol, and octan-1-ol, were used as emulsion stabilizers. The alkanols were preliminarily distilled at atmospheric pressure under laboratory conditions to eliminate the presence of impurities. During laboratory distillation, the boiling point was recorded; after completion, the refractive index of the alkanols was determined. Paper thin-layer chromatography was used to determine the degree of purity. Absolute dehydration of alcohols, that is, removal of traces of water, was not carried out, since under operating conditions it is impossible to exclude alcohol watering due to their hygroscopicity.

### 2.2 Measurement of the cloud point of fuel–ethanol emulsions

The cloud point was defined as the maximum temperature at which visible signs of turbidity appeared in the emulsion. To determine the cloud point, a fuel–ethanol emulsion was placed in a special heat-resistant double-walled glass vessel equipped with a low-temperature thermometer and then slowly cooled in a Haier HYCD laboratory refrigerator.

Every 1–2 degrees, the transparency of the liquid and the appearance of turbidity were visually assessed. The cloud point was recorded when a dispersed phase appeared, indicating the onset of demulsification, that is, the destruction of the dispersed system. For each sample, at least two parallel determinations were performed, provided that satisfactory reproducibility of the results was achieved.

### 2.3 Measurement of the electrokinetic potential of fuel–ethanol emulsion particles

The electrokinetic potential of particles was determined by phase analysis light scattering (PALS) using a LA-960 NanoBrook Omni particle size analyzer. The essence of the method

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consists in measuring the electrophoretic mobility of charged particles of the dispersed phase of the emulsion under the action of an electric field and calculating the electrokinetic, or zeta, potential.

Glass or quartz cuvettes resistant to organic substances were used for the measurements; 5 cm³ of the analyzed emulsion was placed in each cuvette. Measurements were carried out at a temperature of 25°C and a scattering angle of 15 degrees. To ensure reliability of the results, at least two measurements of one sample were performed, provided that high reproducibility was achieved.

## 3 Results and discussions

Fuel–ethanol compositions were obtained on the basis of commercial winter diesel fuel whose physicochemical characteristics met the requirements of the standard.

A significant disadvantage of mixtures of diesel fuels with ethanol is their low aggregative stability, which leads to coalescence of dispersed particles, phase separation of the mixture, destruction of the emulsion, and separation of the dispersed phase from the dispersion medium. To improve phase stability and increase the separation time of fuel–ethanol mixtures, stabilizing additives, or emulsifiers, were used in this study. Without an emulsifier, it was not possible to obtain stable fuel–ethanol compositions with a prolonged separation time; under experimental conditions, emulsion coalescence occurred rapidly. The dependence of the separation time of fuel–ethanol emulsions on ethanol content in the absence of a stabilizer is presented in Fig. 1.

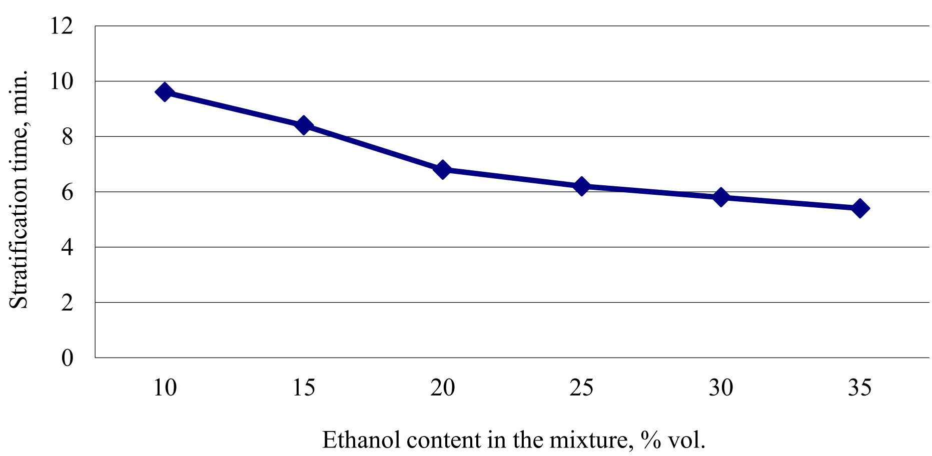


**Fig. 1.** Dependence of emulsion separation time on ethanol content.

Further studies were carried out with compositions containing ethanol in the amount of 1–10 vol.%. The obtained fuel–ethanol mixtures are inverse emulsions in which the dispersion medium is a mixture of nonpolar hydrocarbons, namely diesel fuel, while the dispersed phase is ethanol, whose polarity, determined by its dielectric constant, is significantly higher. Dispersed systems consisting of two liquids with limited mutual solubility are aggregatively, or thermodynamically, unstable and tend toward coalescence, that is, the merging and enlargement of ethanol droplets, which represent the dispersed phase. As a result, phase stability is disturbed and the emulsion separates. To stabilize fuel–ethanol mixtures, small amounts of saturated monohydric alcohols, or alkanols, were used. Thus, multicomponent

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compositions containing commercial diesel fuel, ethanol, and an emulsion stabilizer were obtained.

For fuel–ethanol mixtures stabilized with propan-1-ol at a concentration of 1%, the cloud point characterizing the initial stage of the coalescence process was determined (Fig. 2). With an increase in the volume fraction of ethanol, the cloud point rises; at the same time, phase separation does not occur, and the fuel remains operational.

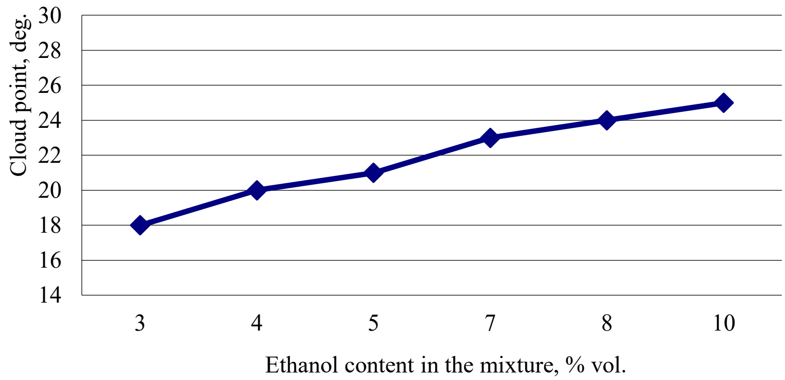


**Fig. 2.** Dependence of emulsion cloud point on ethanol content.

In a diesel engine, the self-ignition capacity of fuel has a noticeable effect on the completeness of fuel combustion and, consequently, on mass emissions of pollutants with exhaust gases. The quantitative characteristic of this property is the cetane index. A decrease in self-ignition performance leads to harsh engine operation, reduced combustion completeness, and, as a result, increased emissions of total hydrocarbons, carbon monoxide, and particulate matter. The cetane index of the obtained compositions was determined by calculation according to the procedure specified in ASTM D4737. The cetane index of diesel fuel emulsions containing ethanol additives decreases as the volume fraction of the oxygenate increases, since ethanol has low self-ignition characteristics (Fig. 3).

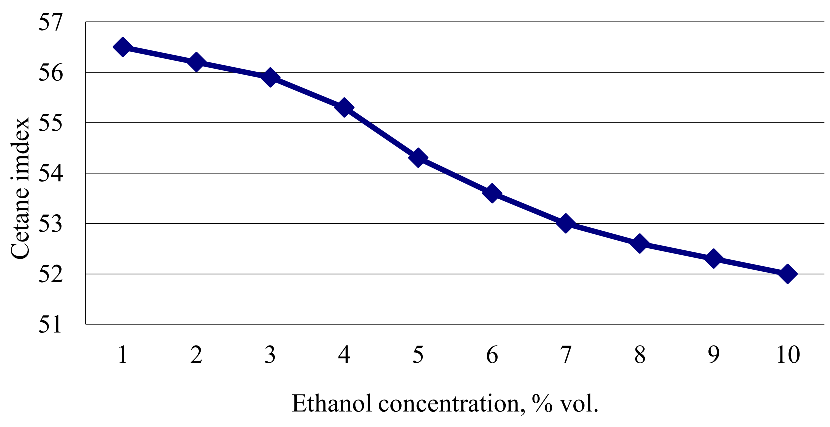


**Fig. 3.** Dependence of the cetane index of diesel fuel emulsions with ethanol on ethanol content, expressed as volume fraction.

For all studied samples of ethanol-containing diesel fuels, the cetane index was no lower than 52, which meets the self-ignition requirements for commercial diesel fuels and ensures smooth engine operation. In addition to propan-1-ol, butan-1-ol, heptan-1-ol, and octan-1-ol were also investigated as emulsion stabilizers. The mixtures were obtained under identical conditions. To study the influence of the nature of the stabilizer on the stability of fuel–ethanol mixtures, the electrokinetic potential of dispersed particles in the obtained emulsions was measured. The electrokinetic, or zeta, potential is the electrical potential of a particle at the slipping plane, along which mutual displacement of the dispersed phase and the dispersion medium occurs when the particle moves in a constant electric field. The electrokinetic potential is one of the factors determining the aggregative stability of dispersed systems: the greater the zeta potential, the higher the aggregative stability of the system. The zeta potential was measured for fuel compositions containing 3 vol.% ethanol and 1% stabilizer (Table 1).

**Table 1.** Electrokinetic potential of particles in diesel fuel emulsions with ethanol.

| Stabilizer | Stabilizer formula | Electrokinetic potential, mV |
|---|---|---|
| Propan-1-ol | $CH_3–(CH_2)_2OH$ | –0.51 |
| Butan-1-ol | $CH_3–(CH_2)_3OH$ | –0.38 |
| Heptan-1-ol | $CH_3–(CH_2)_6OH$ | +0.52 |
| Octan-1-ol | $CH_3–(CH_2)_7OH$ | +0.63 |

The mechanism of the stabilizing action of alkanols is apparently associated with the specific molecular structure of these compounds. Molecules of saturated monohydric alcohols have an amphiphilic structure that includes a polar hydrophilic hydroxyl group, –OH, and a nonpolar hydrophobic hydrocarbon radical. This allows stabilizer molecules to adsorb at the interface between the polar and nonpolar liquids forming the emulsion. As a result, a structural and mechanical barrier is formed, preventing particle coalescence.

The electrokinetic potential of the obtained mixtures is low, less than 1 mV, which explains the insufficient phase stability of the mixtures during long-term storage and their tendency toward aggregation. In this regard, it is advisable to search for stabilizers among surfactants whose adsorption at the liquid–liquid interface would increase the electrokinetic potential and, accordingly, the stability of the mixtures. Since the cost of alkanols increases with their molecular weight, the use of propanol and butanol as emulsion stabilizers is economically justified.

From an environmental point of view, the use of ethanol as an additive to diesel fuel has several significant advantages:

- reduction of emissions of carbon monoxide, total hydrocarbons, and particulate matter, or soot, due to more complete fuel oxidation;
- possibility of partial replacement of non-renewable fossil fuel with renewable raw material, namely bioethanol, which contributes to the rational use of natural resources and reduction of the carbon footprint;
- reduction of the anthropogenic load on atmospheric air, especially in urban agglomerations where the concentration of motor transport is highest.

The use of ethanol additives in diesel fuels will contribute to rational nature management through the transition to renewable energy sources, as well as to reducing anthropogenic impact on the environment by decreasing pollutant emissions from vehicle exhaust gases.

## 4 Conclusions

As a result of the study, stable emulsions of diesel fuel with ethanol containing up to 10 vol.% alcohol were obtained. It was shown that, without stabilizers, such mixtures rapidly separate due to coalescence of ethanol droplets as the dispersed phase. The introduction of 1 vol.%

primary aliphatic alcohols, namely propan-1-ol, butan-1-ol, heptan-1-ol, and octan-1-ol, increases the aggregative stability of emulsions due to the formation of a structural and mechanical barrier at the interface between polar and nonpolar liquids.

The values of the electrokinetic potential of emulsion particles were measured by phase analysis light scattering (PALS). It was established that, for all studied compositions, the absolute value of the zeta potential does not exceed 1 mV. This explains the limited long-term stability of the mixtures and indicates the need for further search for more effective surfactants. At the same time, from an economic point of view, the use of propan-1-ol and butan-1-ol is the most justified, since the cost of higher alkanols is significantly higher.

The calculated cetane index of the obtained fuel compositions in all cases was no lower than 52, which meets regulatory requirements for commercial diesel fuels and guarantees smooth engine operation without harsh combustion processes.

Thus, the developed ethanol-containing fuel compositions may be considered one of the accessible and economically feasible ways to improve the environmental safety of diesel engines in the near and medium term. Further research should focus on selecting stabilizers that provide a higher electrokinetic potential, above 1 mV, which would increase the storage life of emulsions without phase separation, as well as on conducting engine tests to quantitatively assess the reduction of pollutant emissions.

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