

Article

Oxygenated Diesel Fuels and Their Effect on PM Emissions

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Abstract: Particulate matter (PM) emitted by diesel engines is one of the most harmful components of exhaust gases, including its carcinogenic effect. Due to the widespread use of diesel engines, the health effects of PM emissions affect millions of people around the world. At the same time, diesel particulate matter is characterized by a very complicated structure and mechanisms of formation compared to other exhaust gas components. It is obvious that PM emissions should be limited by all means. This article focuses on the reduction of PM emissions with the use of oxygenated fuels. The mechanisms of oxygenated fuels influence on the soot formation process in the working process of diesel engines have been discussed. The importance of the chemical structure of oxygenated compounds for the effectiveness of PM emissions reduction was considered. The results of empirical research on the influence on PM emissions of oxygenated fuels containing 12 oxygenates from chemical groups such as glycol ethers, maleates, carbonates and butanol were analyzed. The emissions tests were undertaken on a diesel passenger car over the NEDC and FTP-75 cycles. The results showed a high potential of oxygenated fuels in PM emissions reduction, even at a low oxygenates concentration of 5% v/v; namely, PM emissions were reduced by up to 32%. According to tests results, 1% of oxygen in the fuel resulted in an average reduction of PM emissions by 7% to 10%. In the view of already limited possibilities of modifying conventional parameters of diesel fuels, the use of oxygenated compounds is a promising way to trade on the potential of fuels in PM emissions reduction.

Keywords: particulate matter; emissions; diesel engine; diesel fuel; oxygenated compounds



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1. Introduction

Particulate matter (PM) is one of the most toxic and, at the same time, most complicated components of diesel exhaust gas. Particulate matter is composed of a center core of elemental carbon (soot) and adsorbed organic compounds including polycyclic aromatic hydrocarbons (PAHs) and small amounts of sulfate, nitrate, metals and other trace components. PM components can be divided into nonvolatile or insoluble and volatile or soluble fractions [1]. The first group of components includes soot; the second group consists of organic substances deposited on it which are mainly compounds derived from unburned or partially burnt fuel and lubricating oil. The composition of the emitted PM depends on many factors, e.g., engine load, type of combustion chamber and fuel properties. However, for particulate matter formed in the combustion chamber of a diesel engine, soot is typically the primary component. The main component of PM from automotive diesel engines is carbon [2].

The combustion process in a diesel engine is very short, as is the process of soot formation. The fuel molecules contain essentially 12 to 22 carbon atoms and approximately twice as many hydrogen atoms. Within milliseconds, soot particles containing thousands of carbon atoms and about 10 times fewer hydrogen atoms are produced. A more detailed analysis of this process shows that it runs in several stages. The pyrolytic reactions lead to the decomposition of the fuel molecules and the production of soot precursors that are involved in the nucleation process of the first visible particles (nuclei). The process of the surface growth of the nuclei then takes place, associated with the attachment of

carbon atoms and removal of hydrogen atoms. As a result, spherules with a diameter of 20–50 nm are created. Simultaneously with the increase in surface area, agglomeration of the spherules takes place, leading to the formation of particle clusters. Another process, i.e., oxidation, has the opposite effect to those mentioned above; namely, it removes soot at each stage of its development [3,4].

Due to the widespread use of diesel engines, a large population of people is exposed to diesel exhaust and particulate matter. The high harmfulness to humans of particulate matter from diesel engines results not only from their chemical composition, but also from the ineffectiveness of the defense mechanisms of the human respiratory system against them [5]. Particles are not efficiently filtered from the air we breathe, so they penetrate deep into the respiratory tract, settle or penetrate the lung epithelium. By carrying highly toxic condensed compounds on its surface, soot allows semi-volatile and non-volatile chemicals to access organs, fluids and cells that they could not reach without soot as a carrier.

The spectrum of harmful effects of particulate matter on human health is very wide. Acute or short-term exposure to PM may cause acute irritation (of eyes, throat and bronchi), neurophysiological symptoms (dizziness, nausea) and respiratory symptoms, as well as intensification of allergic reactions [6]. Long-term exposure to particulate matter increases the morbidity and mortality and inter alia increases the incidence of chronic bronchitis and chronic obstructive pulmonary disease. Long-term exposure to diesel particulate matter increases the risk of lung cancer [7]. There are many studies confirming the more frequent occurrence of this disease for people who frequently come into contact with exhaust gases from diesel engines [8,9]. In 2012, the International Agency for Research on Cancer (IARC) officially recognized diesel exhaust as a carcinogen [10]. Recent studies show that a large number of ultrafine particles can pass through the brain–blood barrier, exerting direct detrimental effects on the central nervous system [11].

There is no doubt that the reduction of PM emissions should be achieved by all means. The particulate emissions from diesel engines can be influenced in a number of ways. It is very important to properly prepare the air–fuel mixture, which can be influenced by appropriate selection of injection timing, injection pressure, and multiple and auxiliary injections. For example, higher injection pressure leads to better atomization and better air–fuel mixture homogeneity, which results in finer combustion characteristics leading to PM reduction [12]. A significant reduction in PM emissions is achieved through the use of particulate filters, which, however, must be regenerated. Lowering the soot burning temperature is achieved by using appropriate catalytic layers in filters or catalytic fuel additives. For about 30 years, the limits of PM emissions from vehicles have been regularly reduced [13–15]. Vehicles of higher emission classes are assumed to emit less PM, with studies showing that they are also less harmful [16].

The type and properties of the fuel used have a very important role in reducing emissions [17–21]. The type of fuel used also affects the toxicity of PM emitted [22]. In the case of conventional diesel fuel, parameters such as density, viscosity, cetane number, PAH content, distillation and sulfur content are important for PM emissions [17,23]. However, the possibilities of modifying these parameters have already been used to a large extent and their further modification is very limited. For example, it is difficult to further reduce the sulfur content once it is close to zero. Therefore, in order to use the potential of fuels to reduce the toxicity of diesel exhaust gases to an even greater extent, unconventional modifications of their properties are necessary. One of the promising directions of this type of activity is the use of oxygenated fuels, i.e., the introduction of oxygen carrier components (oxygenated compounds) into the composition of diesel fuels. Due to the specificity of combustion in a diesel engine, i.e., non-homogeneity of the air–fuel mixture and local oxygen deficiencies favoring the formation of PM, the emission benefits associated with the use of oxygenated fuels in diesel engines should be significant. This paper is devoted to the issue of the influence of oxygenated fuels on PM emissions from diesel engines.

The main objective of this study is the experimental verification of the influence of oxygenated compounds addition to diesel fuel on PM emissions under dynamic driving

tests. These tests correspond well to the conditions of actual car operation and provide an indication of the most favorable oxygenates' variants. The results of our research are discussed against the background of the works of other researchers. An additional objective of this study is to collect and analyze views on the mechanism of the influence of oxygenated compounds on PM (soot) formation in diesel engines. What distinguishes this study is, on the one hand, the fact that as many as 12 oxygenated compounds from 4 chemical groups were tested. On the other hand, emissions tests were performed under dynamic cycles on a chassis dynamometer, i.e., conditions close to the actual operation, which allows for a reliable inference about the possible environmental benefits resulting from oxygenated fuels application in practice.

2. The Mechanism of the Influence of Fuel Oxygenates on the Process of Soot Formation in Diesel Engines

An increased interest in oxygenated fuels since the mid-1990s and the significant reduction in black smoke and PM emissions via the use of oxygenated compounds [24–29], found in research undertaken at that time, prompted researchers to seek a deeper understanding of the mechanism of the influence of these compounds on the soot formation process in diesel engines. This mechanism is related to the oxygen contained in the molecules of oxygenated compounds, but there were many unknowns—for example, at which stage of the formation of particulate matter and how the interaction of oxygenates takes place, whether oxygen introduced with any oxygenated compound is equally effective, etc. Similar issues are related to the research using air with a higher than atmospheric oxygen content (e.g., [30–33]), which led to a locally leaner air–fuel mixture. However, the significant difference is that in oxygenated compounds, oxygen is present in a bonded form, most often with a very strong oxygen–carbon bond.

One of the first studies explaining the mechanism of the influence of oxygenated compounds on PM emission was presented by Rubino and Thomson [34]. Their research included the analysis of oxygenates' influence on the process of soot precursors formation in a diffusion flame. A stationary diffusion flame generated in a counter-flow burner was used in this experiment. The fuel stream consisted of propane and nitrogen, with the oxidant stream composed of a mixture of oxygen and atmospheric air. The overall composition of the mixture was rich ($\lambda \approx 0.55$). Before being introduced into the flame, the oxygenated component was vaporized by heating in a bath. Two oxygenated compounds were used in the research: dimethyl carbonate and ethanol. In preliminary tests, it was found that within the flame, the concentration of fuel, i.e., propane, drops sharply, while intermediate products such as ethylene, methane, ethane, acetylene and propylene appear. The presence of n-butane, n-hexane, propyne and benzene was also found. The addition of 10% *v/v* of dimethyl carbonate to the fuel stream resulted in a significant reduction of intermediate products content in the flame, including soot precursors: acetylene by 15% and benzene by 27%. Increasing the content of dimethyl carbonate to 15% resulted in an even greater reduction in the content of acetylene and benzene, by 28% and 50%, respectively. By introducing ethanol into the fuel, a reduction in the concentration of acetylene and benzene was also achieved, but it was clearly lower than with the addition of dimethyl carbonate.

In further work [34], Rubino and Thomson analyzed the potential mechanisms of reducing acetylene concentration in a flame in the presence of oxygenated compounds. Flame temperature change was indicated as a possible mechanism of this phenomenon. The adiabatic propane flame temperature is actually lower in the presence of oxygen compounds. However, the lowest flame temperature was found for ethanol, and nonetheless a clearly higher concentration of acetylene than for dimethyl carbonate was observed. This indicates that the flame temperature is not critical to the acetylene concentration. The reduction of the carbon content in fuel, which only occurs with the addition of ethanol, is also not of significant importance; the dimethyl carbonate molecule contains three carbon atoms, as does the propane molecule.

An important factor in reducing the concentration of acetylene is the oxygen content in the fuel. The concentration of acetylene in the flame decreases approximately linearly with increasing oxygen content in the fuel. According to Rubino and Thomson [34], the reduction of acetylene concentration takes place due to the presence of additional oxygen atoms in the areas of the rich mixture within the flame. The pyrolysis of oxygenated compounds in this area leads to the emission of O atoms and OH radicals. They then react with acetylene and other propane pyrolysis products, promoting their oxidation. The O atoms and OH radicals compete with the H atoms, which play a major role in the fuel pyrolysis process, thus changing the propane pyrolysis process towards lower acetylene production. The amount of acetylene produced presumably also depends on the number of C–C bonds of the fuel components. It is worth noting that dimethyl carbonate does not contain such bonds at all, while there is one such bond in the ethanol molecule and two in propane.

Similar to those presented above, the results of research on the reduction of soot precursor concentrations were obtained by Renard et al. [35] by examining ethylene flame (rich mixture, $\lambda \approx 0.4$). The oxygenated component used was dimethoxymethane. A decrease in the concentrations of C2–C4 intermediates and a very significant decrease in C5–C10 products were observed.

Confirmation of the reduction of soot precursors by oxygenates was also obtained by modeling the kinetics of chemical reactions occurring during the combustion of oxygenated fuels [36,37]. Particular attention should be paid to the extensive work by Westbrook et al. [38]. They based their modeling of kinetics on the combustion model in a diesel engine developed by Dec [39]. According to this model, the self-ignited fuel is not fully oxidized due to insufficient oxygen availability, resulting in the presence of partial oxidation products such as CO, H₂ and simple hydrocarbon products, including acetylene, ethylene, propylene and others, that in effect lead to soot formation. Due to the very complex composition of conventional diesel fuel, Westbrook adopted n-heptane as a diesel surrogate in his modeling work. The modeling covered self-ignition and combustion of a pre-mixed, rich mixture, with the initial simulation conditions: T = 770 K, p = 10 MPa and $\lambda \approx 0.33$. After a short period of auto-ignition delay, the temperature rapidly increased to about 1600 K and the products of this combustion phase were released. The described research showed that about 44% of the carbon contained in the fuel and participating in this combustion phase is converted into unsaturated soot precursors, mainly ethylene, acetylene, propylene and propyne. These products form simple aromatic compounds and then soot.

In the analysis of the mechanism of the influence of oxygenated compounds, the identification of products formed after the ignition of a rich mixture which increase and reduce the emission of soot plays an important role. The soot formation kinetics, which are described in the works of Frenklach et al. (e.g., [40,41]), are that simple aromatic and polycyclic hydrocarbons, such as benzene, toluene, naphthalene, pyrene and styrene, are formed from simple unsaturated hydrocarbons, such as: acetylene, ethylene, propylene, allene, propyne and cyclopentadiene, and also from hydrocarbon radicals such as propargyl, allyl, methyl allyl and cyclopentadienyl. The authors of [42,43] described changes in the concentrations of acetylene, ethylene and propargyl inside the diffusion flame caused by adding oxygenated compounds to the fuel.

Calculations made by Westbrook's team [38] for mixtures containing oxygenates showed a reduction in the content of soot precursors in the combustion products of a rich mixture, proportional to the amount of oxygen in the fuel. At the same time, an increase in the amount of CO and CO₂ was noted, whereas oxygen in this phase arose mainly in the form of CO and H₂O. The combustion temperature also increased due to the composition of the mixture closer to the stoichiometric one. The concentration of the soot precursors dropped to a very low level for 30–40% oxygen content in fuel.

The calculation of PAH concentration in rich mixture combustion products using the model developed by Appel et al. [44] showed that the concentration of PAHs also decreased to a very low level with a fuel oxygen content of about 30%. Siebers and Higgins showed

that soot formation ceases when the local excess-air coefficient λ at ignition exceeds the value of 0.5 [45].

Detailed analysis of the ignition kinetics of oxygenated compounds shows that most of the oxygen atoms initially contained in the molecules of these compounds react directly to produce CO. The strong bond of CO is not broken during ignition; hence, the bonded C atom is not involved in the formation of soot. For example, for the simplest oxygenated compound, methanol, the reaction has the following course [46]:



For more complex oxygenates, the reactions are more complicated. Figure 1 shows one of the variants of decomposition of the tripropylene glycol monomethyl ether molecule. The products of this process are: two formaldehyde molecules, two propylene molecules, one acetaldehyde molecule and one OH radical [38]. Three of the four oxygen atoms are attached to carbon atoms, which hence do not participate in the formation of soot. The OH radical participates in the oxidation of soot precursors.

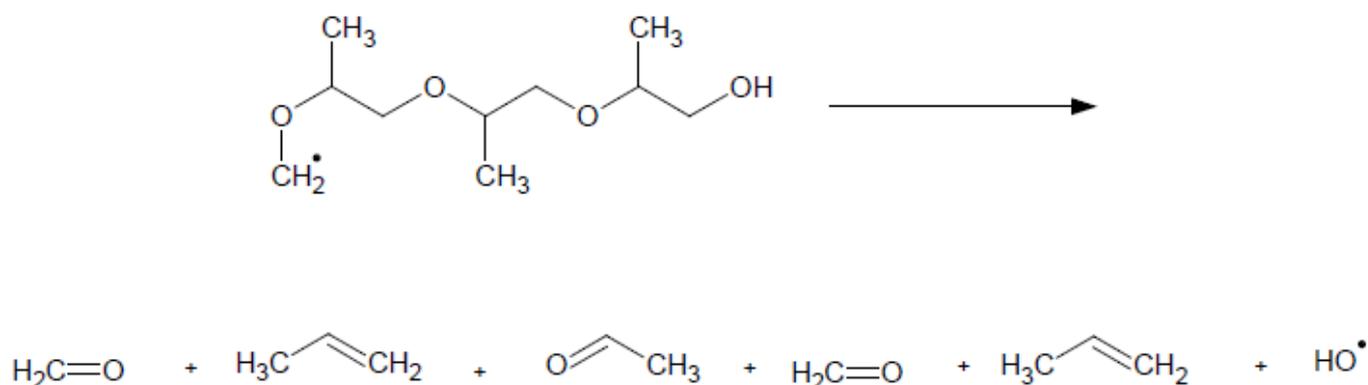


Figure 1. One of the variants of the tripropylene glycol monomethyl ether molecule decomposition in the process of its ignition.

The structure of the oxygenated compound, for example, single or double bonds between carbon and oxygen atoms, or the distribution of oxygen atoms in the molecule, may influence its effectiveness in reducing PM emissions. As a result of the research of Mueller et al. [47,48], it was found that ester-type oxygenates are less effective in soot inhibition than ether-type compounds. The modeling of the kinetics of chemical reactions described in [49] showed that dibutyl maleate is less effective in the reduction of soot formation because of the direct formation of CO₂ by some of the oxygen atoms in its molecule. The preventive effect of oxygen could extend to two carbon atoms if the same amount of oxygen were used to form two CO molecules. Additionally, it is unfavorable for the dibutyl maleate that the two carbon atoms in its molecule, connected by a double bond, directly form the soot precursor acetylene.

In Buchholtz et al. [50], the above-mentioned observations have been verified by accelerated mass spectroscopy. This method allows for the labeling of individual carbon atoms in the molecule, and then experimental tracking of their fate in the combustion process. For the purposes of this experiment, three batches of dibutyl maleate were synthesized, and in each of them, carbon atoms in the positions indicated in Figure 2 were substituted with isotope ¹⁴C. Due to the very low content of the isotope ¹⁴C in petroleum products (¹⁴C/C < 10⁻¹⁵), most of this isotope in the analyzed combustion products (PM, CO₂) came from labeled atoms.

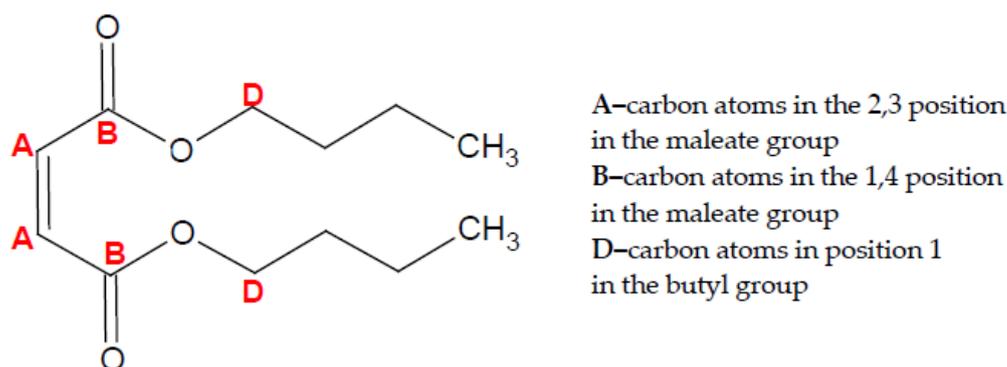


Figure 2. Nomenclature of the positions of carbon atoms in the dibutyl maleate molecule.

If all oxygen atoms in the fuel molecule react according to the same scheme during combustion, the proportion of individually labeled atoms in the combustion products should be the same as in the fuel. The results presented in [50] indicate that this is not the case with dibutyl maleate.

Carbon atoms in the dibutyl maleate molecule in the 1,4-positions of the maleate group (B) are not present at all in the composition of particulate matter but are entirely present in the form of CO_2 in exhaust gas. This confirms the results presented in [48,49] in which the carbon-oxygen double bond in the ester molecule is not broken during combustion.

Carbon atoms in the dibutyl maleate molecule in the 2,3 positions in the maleate group (A), despite the presence of a double bond, show the same tendency to soot formation as the average carbon atom contained in the tested fuel. This indicates that unsaturated hydrocarbon bonds do not necessarily favor more soot formation if sufficient oxygen is available. In the analyzed case, the tendency of the carbon double bond to produce soot is inhibited by the adjacent oxygen atoms bound to the carbon atoms in position B. The connection of carbon atoms with oxygen atoms means for the adjacent carbon atoms, not linked to oxygen atoms, a better availability of gaseous oxygen present in the air–fuel mixture.

Carbon atoms in the dibutyl maleate molecule in the 1 positions of the butyl group (D), assuming the best use of the oxygen contained in the molecule of this compound during combustion, should remain connected with the neighboring oxygen atoms, first forming CO , which is later, already under lean conditions, oxidized to CO_2 . It transpires that the carbon atoms in the D positions form PM only to a slightly lesser extent than the average carbon atom contained in the fuel. That is, in about 90% of the cases, an oxygen atom with a single bond to adjacent carbon atoms, i.e., at positions B and D, eventually fuses to the carbon at position B, directly forming CO_2 .

Other studies using the labeled atoms method are described in [51]. In these tests, the research engine was fueled by mixtures of diesel fuel and ethanol containing from 9% to 37% of this alcohol. Analysis of the obtained particulate matter showed that the carbon contained in the ethanol also participates in the formation of PM. However, the probability of soot formation is 50% lower for ethanol carbon atoms than for diesel fuel carbon atoms.

Cheng et al. [52] presents the results of modeling soot formation during the combustion of n-heptane with the addition of oxygenated compounds such as dimethoxymethane and ethanol. As shown in this study, the addition of oxygenates causes significant drops in peak concentrations of soot precursors in the rich mixture kinetic combustion zone, which in turn inhibits the formation of aromatic compounds and, as a result, reduces the intensity of soot formation. The concentration of acetylene and benzene decreases approximately linearly with increasing oxygen content in the fuel, while the concentration of propargyl begins to decrease significantly after exceeding 20% of oxygen in the fuel.

According to model studies in [52], ethanol is slightly more effective than dimethoxymethane in reducing acetylene and benzene concentrations. For the same amount of oxygen in the fuel, but introduced with the addition of ethanol, greater decreases in the concentration

of soot in the diffusion flame were noted. At lower oxygen concentrations, the soot concentration decreased linearly with increasing oxygen content; after exceeding about 15% of oxygen, its influence became weaker. The combustion was soot-free when the fuel contained approximately 35% of oxygen.

Oxygenated compounds are less likely to form soot precursors than conventional hydrocarbons, which results, *inter alia*, from the fact that the C–O bond is stronger than the C–C bond. However, an additional and probably more important factor is the increase in the concentrations of radicals such as O, OH and HCO in the combustion chamber resulting from the introduction of oxygenates. The increased supply of these radicals influences the soot formation process in two ways. First, high concentrations of O and OH promote the oxidation of carbon atoms in the flame, which reduces the amount of carbon that can form soot precursors. The formation of large amounts of HCO works similarly as it is quickly converted to CO or CO₂ in a single reaction. Second, an increased concentration of radicals, in particular OH, in the soot formation region downstream of the rich mixture combustion zone inhibits soot nucleation by oxidizing aromatics and limiting the development of PAHs.

The aforementioned slightly better effectiveness of ethanol than that of dimethoxymethane in reducing the concentration of soot is probably due to the fact that significantly more OH radicals are formed with the addition of ethanol. For dimethoxymethane, more HCO radicals are formed, which also reduces the concentration of soot precursors, but they are not as effective in the subsequent suppression of the expansion of aromatic compounds [52].

As already mentioned, the formation of PM depends on the specific local temperature and the local air–fuel ratio (λ coefficient). The soot formation does not occur at too low a temperature and requires the production of precursors. Soot precursors oxidize at higher temperatures, and therefore the soot formation process is limited by a temperature range of about 1500–2500 K. Due to its high heat of vaporization, N-decanol was used as a fuel by Janssen et al. [53] and lowered the local temperatures in the reaction zone, reducing the amount of soot released. The second proposed mechanism of PM emission reduction by this oxygenated compound is based on an earlier start of soot oxidation than in the case of conventional fuel, which begins at the initial stage of its formation, *i.e.*, under rich mixture conditions, due to the presence of OH radicals from the alcohol molecule. According to Marinov [54], for ethanol in the conditions of a rich mixture, the release of the OH radical occurs at temperatures above 1670 K.

The authors of [55] showed that the main factors limiting the formation of soot precursors are high oxygen content in the fuel and a small number of C–C bonds in the fuel molecules. Subsequently, auto-ignition delay and lift-off length will have an impact on soot formation. The tests confirmed the low intensity of soot precursors (C₂H₂) formation when tripropylene glycol methyl ether was used as a fuel.

3. Materials and Methods

The research on the influence of oxygenated fuels on PM emissions was performed with the use of 12 different oxygenated compounds belonging to four chemical groups: glycols, ethers, maleates, carbonates and alcohols (Table 1). The key parameters for the selection of the oxygenated compounds analyzed in this study were: high oxygen content, good miscibility with diesel fuel, high cetane number, similar physical properties as diesel fuel and, of course, availability. Butanol was also included in the research, although it meets the above-mentioned criteria to a lesser extent, but is considered as a prospective renewable fuel component since it can be produced in the process of biomass fermentation. All oxygenates were tested at a concentration of 5% *v/v*, and some also at 10%. Oxygenated compounds from the group of glycol ethers were supplied by Clariant (with a purity of at least 95%). Maleates and carbonates were purchased from Sigma Aldrich and were characterized by a purity of no less than 96%. N-butanol (assay—minimum 99%) came from Avantor Performance Materials Poland. Diesel fuel with no oxygen content (Table 2) was used to blend test fuels. The same diesel fuel was used as the reference fuel to

determine the changes in emissions caused by the use of oxygenated fuels containing individual oxygenates.

Table 1. Several properties of the oxygenates used in the tests.

| Number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---------------------------------------|--------------------------------|----------------------------------|-----------------------------------|-------------------------------------|---------------------------------|-----------------------------------|----------------------------------|-----------------|-----------------|--------------------|-------------------|-----------|
| Chemical Group | Glycol Ethers | | | | | | Maleates | | Carbonates | | Alcohols | |
| Chemical Name | Ethylene Glycol Dimethyl Ether | Diethylene Glycol Dimethyl Ether | Triethylene Glycol Dimethyl Ether | Tetraethylene Glycol Dimethyl Ether | Diethylene Glycol Dibutyl Ether | Dipropylene Glycol Dimethyl Ether | Tripropylene Glycol Methyl Ether | Diethyl Maleate | Dibutyl Maleate | Dimethyl Carbonate | Diethyl Carbonate | N-Butanol |
| Molecular weight, amu | 90.12 | 134.17 | 178.23 | 222.28 | 218.33 | 162.23 | 206.28 | 172.18 | 228.28 | 90.08 | 118.13 | 74.12 |
| Oxygen content, % (m/m) | 35.6 | 35.8 | 36.0 | 36.0 | 22.0 | 29.6 | 31.1 | 37.3 | 28.1 | 53.3 | 40.7 | 21.6 |
| Boiling point, °C | 85 | 162 | 220 | 275 | 256 | 175 | 243 | 225 | 281 | 90 | 127 | 117 |
| Density @ 20 °C, kg/m ³ | 867 | 944 | 987 | 1010 | 884 | 903 | 963 | 1064 | 988 | 1069 | 975 | 810 |
| Viscosity @ 20 °C, mm ² /s | 0.5 | 1.2 | 2.5 | 4.1 | 2.3 | 1.12 | 5.5 | n.a. | n.a. | 0.56 | 0.78 | 3.64 |
| Flash point, °C | −6 | 51 | 113 | 141 | 120 | 65 | >110 | 93 | >110 | 18 | 25 | 34 |
| Cetane number (calculated) | 86 | 112 | 144 | 144 | 144 | 86 | 58 | 57 | 44 | 10 | 14 | 10 |

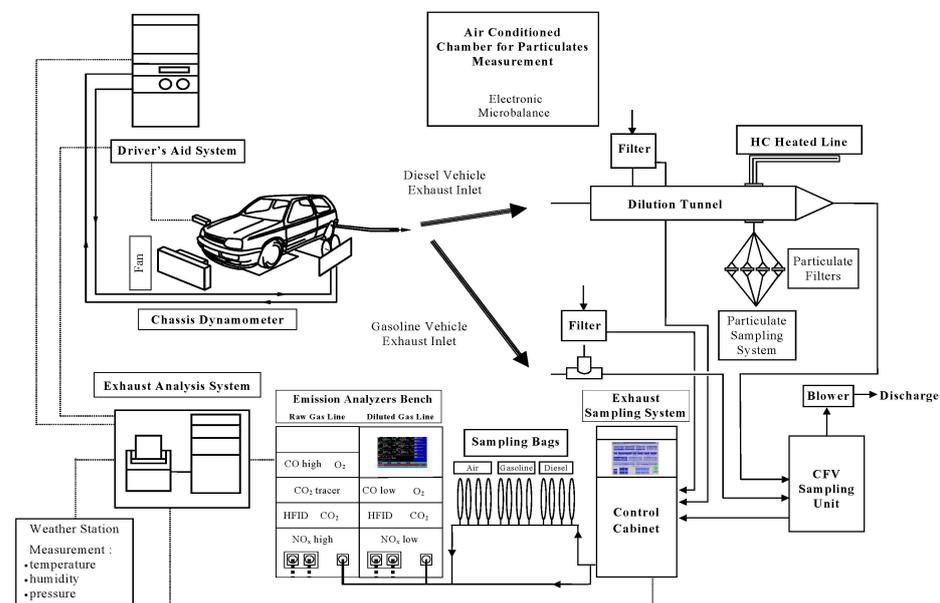
Table 2. Characteristics of conventional diesel fuel used in tests.

| | Unit | Value |
|---|--------------------|-------|
| Cetane number | - | 52.0 |
| Cetane index | - | 53.1 |
| Density @ 20 °C | kg/m ³ | 830.8 |
| Viscosity @ 40 °C | mm ² /s | 4.188 |
| Evaporation @ 250 °C (E250) | % (v/v) | 36.9 |
| Evaporation @ 350 °C (E350) | % (v/v) | 97.8 |
| Temp. at which 90% of the fuel evaporates (T95) | °C | 340.0 |
| Final Boiling Point (FBP) | °C | 350.2 |
| Total aromatic hydrocarbons | % (m/m) | 23.9 |
| Polyaromatic hydrocarbons | % (m/m) | 2.5 |
| Sulfur content | ppm | 8.9 |
| Oxygen content | % (m/m) | 0.0 |

The test vehicle on which the influence of oxygenated fuels on exhaust emissions was measured was a passenger car of the A-segment with a turbocharged diesel engine, manual gearbox and front-wheel drive. The specifications of this vehicle and its engine are shown in Table 3. The emissions tests were performed on the Schenck 500/GS60 chassis dynamometer (Figure 3). The CVS AVL CEC system with full-flow dilution tunnel AVL CET-LD/20 type and particulate sampling system AVL CEP-LD/100 PTS 60 l/min, controlling system CESAR and Sartorius microbalance were used to measure exhaust emissions.

Table 3. Characteristics of the test vehicle.

| Vehicle Type | Passenger Car |
|------------------|--|
| Weight | 950 kg |
| Engine type | Diesel, 4-cylinder in-line |
| Engine capacity | 1.3 dm ³ |
| Maximum power | 51 kW @ 4000 rpm |
| Maximum torque | 145 Nm @ 1500 rpm |
| Combustion type | Direct injection Common Rail, turbocharged (intercooled) |
| Emission control | Oxidation catalyst, Exhaust gas recirculation |
| Emissions level | Euro 4 |

**Figure 3.** Chassis dynamometer and schematic of exhaust emissions measurement system.

The emission tests were performed over the conditions of the New European Driving Cycle (NEDC). NEDC (Figure A1) is the European approval cycle for passenger car emissions tests, including Euro 4 emission class vehicles. Some fuels were additionally tested over the US FTP-75 cycle (Figure A2) to check how the test cycle conditions affect the changes in emissions caused by oxygenates. Testing in cycles on a chassis dynamometer allows results to be obtained close to the actual operation, and thus a reliable conclusion to be drawn about the possible benefits in the practical application of oxygenated fuels.

4. Tests Results and Discussion

The authors' research on the influence of oxygenated compounds in fuel on PM emission from a diesel passenger car was implemented in several stages. Initial tests were performed at the content of 5% *v/v* of each of the oxygenated compounds [56]. The test results regarding changes in PM emissions are shown in Figure 4. The results regarding changes in gaseous exhaust components (i.e., CO, HC and NO_x) are presented in Appendix A (Figures A3–A5). The symbol OC stands for oxygenated compound, then its number (according to Table 1) and its percentage in the fuel are shown. The presented results show that all tested oxygenated compounds, used as components of diesel fuel in the concentration of 5% *v/v*, lead to reductions in PM emissions. Omitting component number 12, i.e., n-butanol, it should be noted that the 5% addition of oxygenated compounds caused a significant change in PM emissions. It is easy to notice that for the same component

content, the greatest reduction of PM emission was achieved for carbonates (about 30%). For glycol ethers, it was on average 15%, and for maleates about 20%.

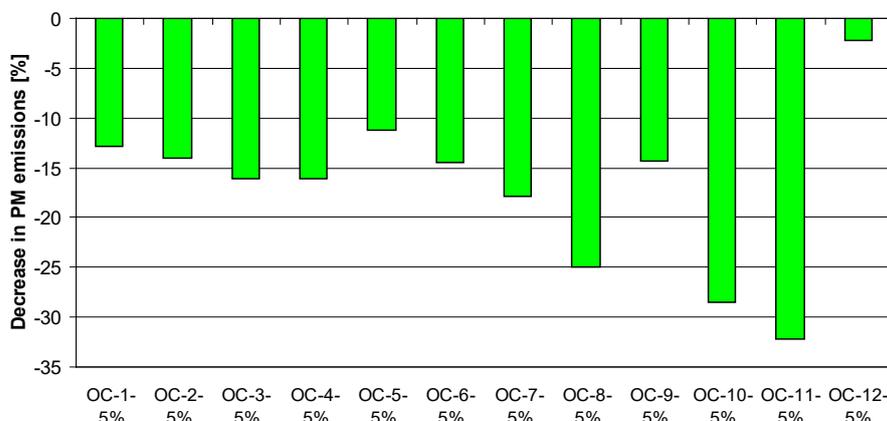


Figure 4. Percentage changes of PM emissions over the NEDC from a test car with fuels containing individual oxygenates at a concentration of 5% v/v compared to running on conventional diesel fuel.

In the literature on the influence of oxygenated compounds on PM emissions from diesel engines, there are divergent opinions as to whether the reduction of PM emissions depends only on the amount of oxygen introduced into the fuel [24,26,57,58], or also on the type of oxygenated compound which is used for this [28,47,59,60]. This divergence of opinions is also due to the fact that only a few studies present the results of testing a wide range of oxygen compounds under identical measurement conditions. The comparison of the changes in PM emissions over the NEDC cycle presented in Figure 4 to the oxygen content in individual oxygenated fuels indicates that 1% of oxygen contained in the fuel most often reduces PM emissions (over NEDC) by 7–10% (Figure 5). It can therefore be concluded that the oxygen content in the fuel is a very important parameter, though not the only one, in determining the level of PM emission reduction.

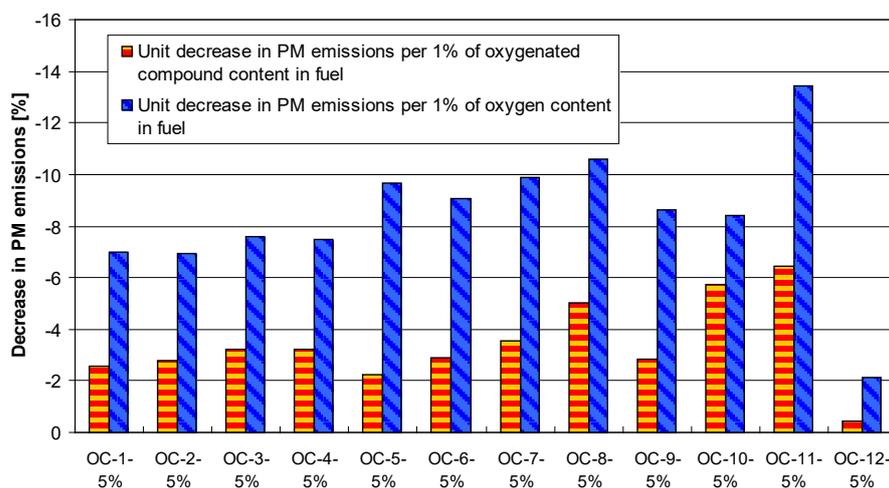


Figure 5. Unit effect of oxygenate and oxygen content in fuel on PM emissions over the NEDC from a test car with fuels containing individual oxygenates at a concentration of 5% v/v compared to running on conventional diesel fuel.

Further research concerned the influence of the oxygenated compound content on the change in PM emissions. For these studies, components from the group of ether glycols, maleates and carbonates were selected. The tests were performed under the conditions of the NEDC and with the same vehicle as before, but the concentrations of oxygenated compounds in fuel were increased to 10% v/v. The results presented in Figure 6 show that

increasing oxygenates' content brings beneficial results, albeit to a different extent. For glycol ethers, doubling the fuel content also doubled the decrease in PM emissions. For maleate and carbonate, the benefit of increasing content was significantly smaller. It can be seen that at the 10% content, there are no significant differences in reducing PM emissions for glycol ethers and carbonates that were so characteristic at the lower content (5%). Thus, with a content of 10%, the effectiveness of the best components from all tested chemical groups was similar, i.e., PM reduction by 30–40%.

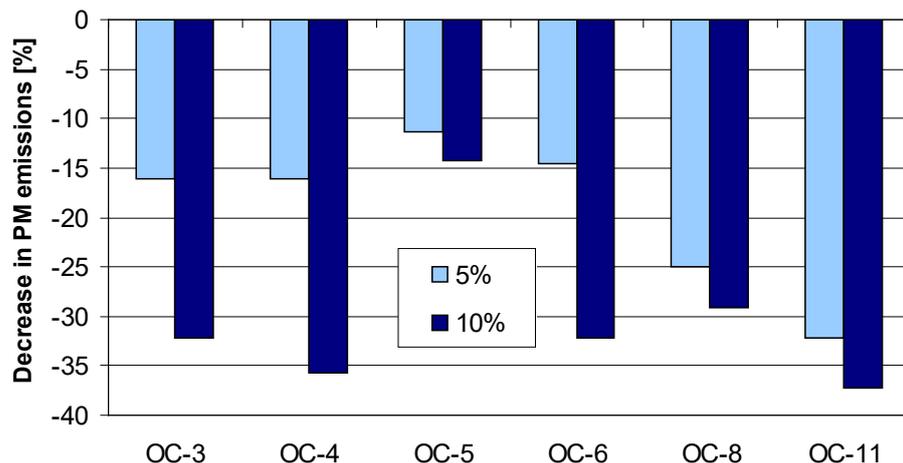


Figure 6. Reduction of PM emissions as a function of type and content of oxygenated compound in relation to fueling with conventional diesel fuel.

The last part of the authors' research concerned the influence of the test cycle conditions on the obtained effects in PM emission reduction. Figure 7 shows a comparison of the impact on PM emissions of fuels containing 10% of individual oxygenated compounds obtained under the conditions of the NEDC and FTP-75 (US Environmental Protection Agency Federal Test Procedure) test cycles. The American cycle (FTP-75) is a more dynamic, non-stationary cycle, while in the European cycle there is a higher maximum speed. Ultimately, based on the measurement results, it can be concluded that, for the same fuels, a greater reduction of PM emissions occurs under the NEDC cycle conditions.

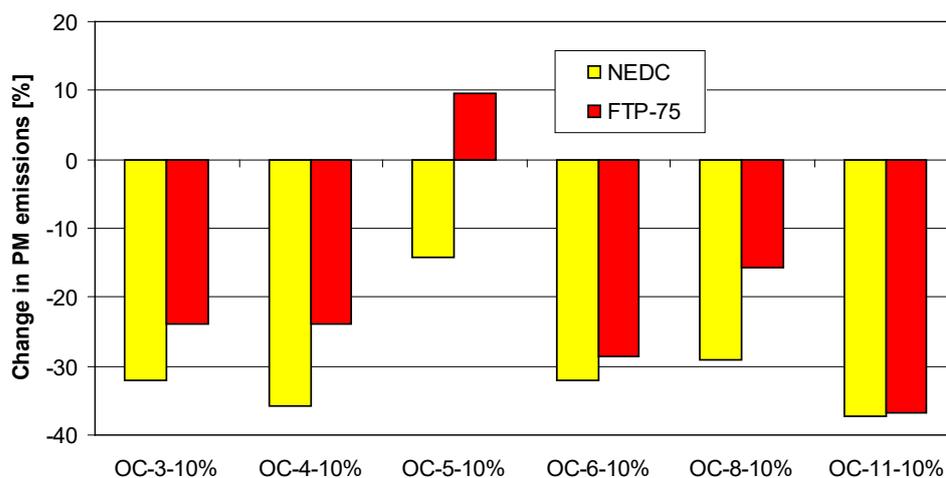


Figure 7. Percentage changes in PM emissions over the NEDC and FTP-75 cycles when the test car's fuels contained 10% of various oxygenated compounds compared to running on conventional diesel fuel.

The use of glycol ethers as fuel components for diesel engines also in studies presented by other authors led to a reduction in the emission of particulate matter (soot). In Zannis

et al. [61], soot emissions from a single-cylinder direct-injection diesel engine using city diesel fuel and two blends of this fuel and glycol ethers were tested. Each blend contained diethylene glycol dimethyl ether (so-called diglyme) and diethylene glycol dibutyl ether (so-called butyl diglyme) in approximately equal proportions. The first blend (named GLY10) contained about 10% glymes and the second (named GLY30) about 30%. This corresponded to 3% and 9% *m/m* oxygen content in the fuel mixture, respectively. The soot emissions were measured under conditions of constant speed (2500 rpm) and variable load. The emission of soot for the fuel containing 3% oxygen was higher than for neat diesel fuel; however, for the fuel containing 9% oxygen, it decreased on average by about 20%. It is worth noting that GLY 30 fuel had a very high cetane number (73).

The study by Delfort et al. [62] on diesel passenger car emissions over the NEDC showed a moderate effectiveness of glycol ethers in reducing PM emissions compared to other oxygenates. Yeh et al. [63] also showed the PM reducing effect of glycol ethers under the conditions of dynamic tests on a chassis dynamometer. The beneficial effect of glycol ethers on PM emissions is also described in [64].

Hallgren and Heywood [60] also showed that glycol ethers reduce PM emissions. In addition, it has been found that oxygenates mainly reduce the insoluble fraction (soot) while the soluble organic fraction (SOF) decreases slightly. The high efficiency of diethylene glycol dimethyl ether in reducing PM emissions was demonstrated in [65]. At the brake mean effective pressure (BMEP) of 0.65 MPa, the 5% addition reduced PM emission by nearly a half. With the addition of 25%, the reduction in PM emissions was nearly four times. Moreover, it was noticed that with an increase in the content of the oxygenated compound, the SOF fraction in the emitted PM increased and the soot fraction decreased.

The effective reduction of PM emissions from heavy-duty diesel engines using diethylene glycol dimethyl ether is described in [66]. The efficiency increased with the increase of the oxygen content in the fuel and was slightly higher in hot start-up conditions than in a cold start-up. It was shown in [67] that in addition to a significant reduction in PM emissions, the addition of glycol ethers to diesel fuel is beneficial for diesel particulate filter (DPF) regeneration processes (soot activation energy is reduced), as well as for extending DPF life (lower soot ash content) without affecting the efficiency of exhaust gas filtration.

The test results presented by other researchers confirm the usefulness of maleates as components of diesel fuel reducing PM emissions. We can mention Stoner and Lizinger [28], who achieved a reduction of PM emissions by using diethyl maleate and dibutyl maleate. They also tested some glycol ethers, but found that they caused less favorable changes in PM emissions than maleates.

Natarajan et al. [68] analyzed 71 potential oxygenated compounds and, based on their physicochemical properties, selected the 8 most suitable oxygenates for use in diesel fuel, including dibutyl maleate. They then performed preliminary emission tests with the use of selected components at a concentration providing 7% of oxygen in fuel [69], in which the fuel containing dibutyl maleate caused a significant decrease in PM emissions and was selected for further, wider research. These more extensive studies [70] performed in several modes of engine operation confirmed the high efficiency of the above-mentioned oxygenate in reducing particulate emissions.

In the literature, one can find the results of research on carbonates as components of diesel fuel presented by other researchers. In this context, it should be initially noted that Delfort et al. [62] used five oxygenates from the chemical family of carbonates in their extensive research on the influence of oxygenated compounds on PM emissions. Their research was conducted in a similar way to the authors of this article, i.e., in the NEDC cycle with the use of a diesel passenger car. Similar again to our case, it was found that for the same content of different oxygenates in fuel, the greatest reduction in PM emissions was achieved for carbonates. Then, among all the tested carbonates, the most effective ones proved to be diethyl carbonate and diethoxy-2-ethyl carbonate, which, added to the fuel in the amount of 5%, resulted in a reduction of PM emissions by 17–18%.

Murayama et al. [27] conducted extensive research on the effects of dimethyl carbonate on the combustion characteristics and emissions of a diesel engine. They found that for the 10% content of this compound in the fuel, the smoke emission was reduced by a value between 35% and 50%. It was also observed that the degree of smoke emission reduction is proportional to the content of oxygenates. Akasaka and Sakurai [24] presented the reduction of smoke emissions obtained with the use of a component from the carbonate group. Kocis et al. [71] showed a significant reduction in soot emissions in the exhaust gas for diesel fuel containing dimethyl carbonate.

The authors of [72] showed a strong relationship between the oxygen content in the fuel and the diesel engine exhaust opacity. With small additions of oxygen, the effectiveness in reducing smoke emissions increases rapidly. Above 10% *m/m* of oxygen in the fuel, further increase brings only a slight reduction in smoke emissions. A greater efficiency in reducing PM emissions using diethyl carbonate than diethylene glycol dimethyl ether with both components concentrations at the level ensuring the same oxygen content in fuel was observed. In turn, in this study, dimethyl carbonate showed similar effectiveness to diglyme.

In the authors' research presented in this article, a small reduction in PM emissions by adding n-butanol (5%) to diesel fuel was observed. This can be partly explained by the significantly lower oxygen content in butanol (21.6% *m/m*) compared to the other oxygenated compounds used, where it reached over 50%. Small additions of oxygenates were used in order not to significantly change the physical properties of the obtained fuel blends.

Butanol has the advantage that it can be produced from biomass in a fermentation process [73–76] as a renewable fuel (biobutanol). Fermentation occurs under anaerobic conditions by bacteria of the genus *Clostridium*. Hence, it is currently enjoying a lot of interest, also as a fuel for spark ignition engines. In the literature, there are studies conducted with high contents of butanol, which indicate that under such conditions a significant reduction in PM emissions occurs compared to the fueling with conventional diesel fuel.

In an extensive review [77] on the use of butanol as a fuel component for diesel engines, it was found that most of the tests with butanol described in the literature were performed under stationary conditions, and only a few in dynamic driving cycles. In most cases, however, significant reductions in PM emissions are recorded.

In [78], the authors showed that blends containing 50% diesel fuel and 50% butanol effectively reduce soot emissions from a modern diesel engine. For low load (BMEP = 0.4 MPa) the soot emission reduction was 50%. At high load (BMEP = 1.2 MPa) the reduction was even greater, reaching 80%. In addition, it has been shown that all butanol isomers had a similar effectiveness in reducing soot emissions at low load. At high load, there were already clear differences between the individual isomers. The most effective was n-butanol (soot reduction by 80%). The least effective was sec-butanol, which reduced soot emissions by 50%. The authors of [79] showed that with lower butanol additions (20%), regardless of the type of isomer, a similar reduction in soot emissions was obtained (by about 35%). Only when the content of butanol was higher, the differences in the effectiveness of the various isomers appeared. Iso-butanol was the most effective (soot reduction by maximum of 85%), and the least effective was tert-butanol (soot reduction by maximum of 68%). The authors of [80] showed that the concentration of PM in exhaust gas decreases linearly with the increase in butanol content in diesel fuel in the tested range of 10% to 30% *v/v*. Dogan [81] showed a similar dependence in the scope of 5% to 20% butanol content and smoke opacity. In Lauperta et al. [82,83], the beneficial effect of butanol addition to diesel fuel on PM emissions from a Euro 6 passenger car was confirmed.

The effect of butanol on PM emissions was also investigated for heavy-duty engines. The tests described in [84] showed that when using a mixture containing 40% n-butanol, smoke emissions close to zero were achieved, even using high levels of exhaust gas recirculation (EGR) to reduce NO_x emissions. Tipanluisa et al. [85] tested the influence of

n-butanol/diesel blends on performance and emissions of a heavy-duty diesel engine over the World Harmonized Steady-State Cycle (WHSC). They observed significant reductions in PM emissions for fuel blends that contained 10% and 20% of butanol. At 10% butanol concentration, PM emissions decreased by 22–88%, while at 20%, they decreased by 15–87%, as compared to neat diesel fuel.

5. Conclusions

The harmful effects on human health of diesel particulate matter are indisputable at present. The tests showed that oxygenated compounds in diesel fuel significantly reduce PM even at a low concentration of 5% *v/v*. The most effective oxygenates, i.e., diethyl carbonate and diethyl maleate, reduced PM emissions in the NEDC cycle by 32% and 25%, respectively. This is a very good result, especially taking into account the simplicity of the solution, which is a 5% addition of a given substance to the fuel. At a concentration of 5%, oxygenates from the group of glycol ethers provided a lower reduction in PM emissions (by about 15%). Thus, in the case of glycol ethers, it is recommended to double their content in fuel, i.e., from 5% to 10%, as according to the obtained results, it also doubles the effectiveness of PM emissions reduction.

The analysis of the mechanism of the influence of fuel oxygenates on particulate matter (soot) emissions showed that the main determinant of the effectiveness of PM reduction is the oxygen content in fuel, but other factors also play a role. According to the results described in this article (Figure 5), 1% of oxygen in the fuel resulted in an average reduction of PM emissions by 7% to 10%. During the tests, the content of oxygenated compounds did not exceed 10%, so that the physical properties of the fuel did not change significantly compared to neat diesel fuel. Hence, it can be assumed that the observed effect of reducing PM emissions was mainly due to the presence of oxygen.

The effective action of oxygenated compounds on PM emissions, even at low concentrations, allows their use in serial combustion engines without the need for structural changes. It can also be used as a method of PM emissions reduction from older vehicles/engines that are still in operation but where retrofitting them is not profitable. For vehicles with DPFs, the effect of oxygenated fuels “at the end of the exhaust pipe” will be less [86]. However, even in this case, the benefit will be the lower frequency of DPF regeneration, which is not neutral to the environment.

Some opinions indicate [87,88] that alternatives to the currently widely used bio-diesel (fatty acid methyl esters—FAME) should be sought. Due to their properties, oxygenated compounds can be components of tailor-made fuels for modern, low-emission engines. Moreover, they can be produced as renewable fuels, in environmentally friendly technologies, such as biomass fermentation (butanol) or in currently developed Power-to-Liquid technologies. In the view of already limited possibilities of modifying conventional parameters of diesel fuels (density, PAHs content, sulfur content, etc.) the use of oxygenated compounds is a promising way to trade on the potential of fuels in PM emissions reduction.

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Appendix A

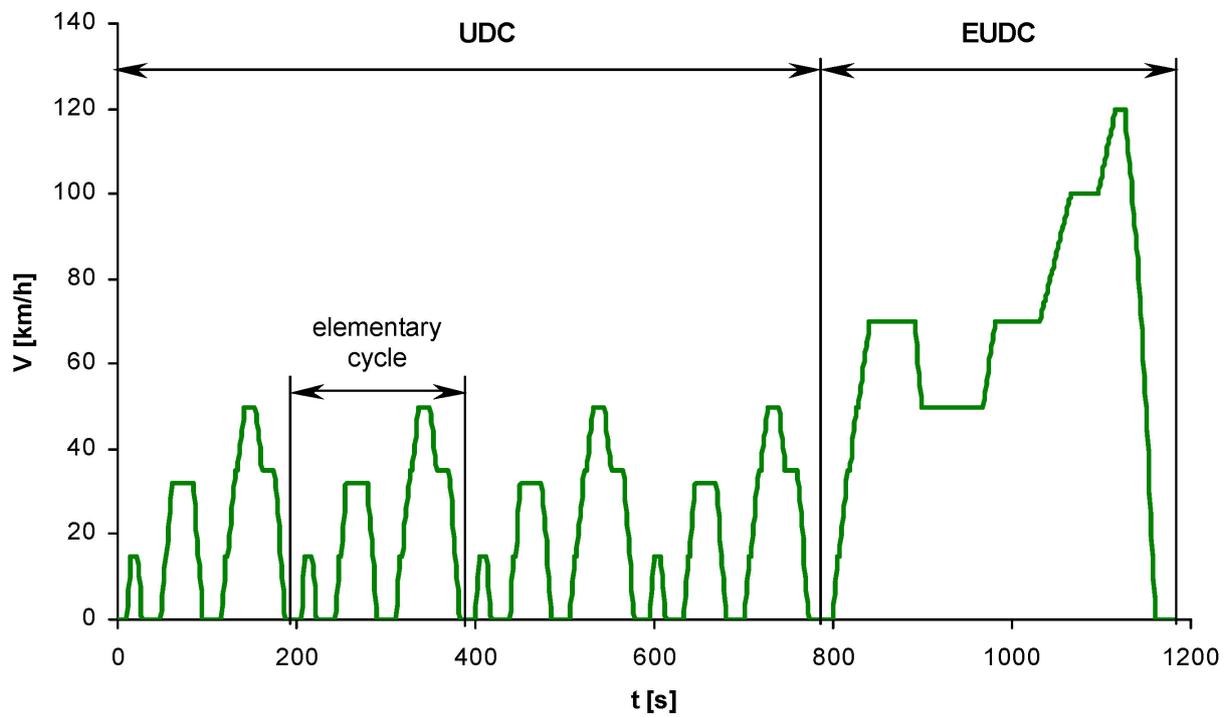


Figure A1. The New European Driving Cycle (NEDC); distance: 11.007 km, duration: 1180 s, average speed: 33.6 km/h; NEDC consists of two phases: UDC (Urban Driving Cycle) and EUDC (Extra Urban Driving Cycle).

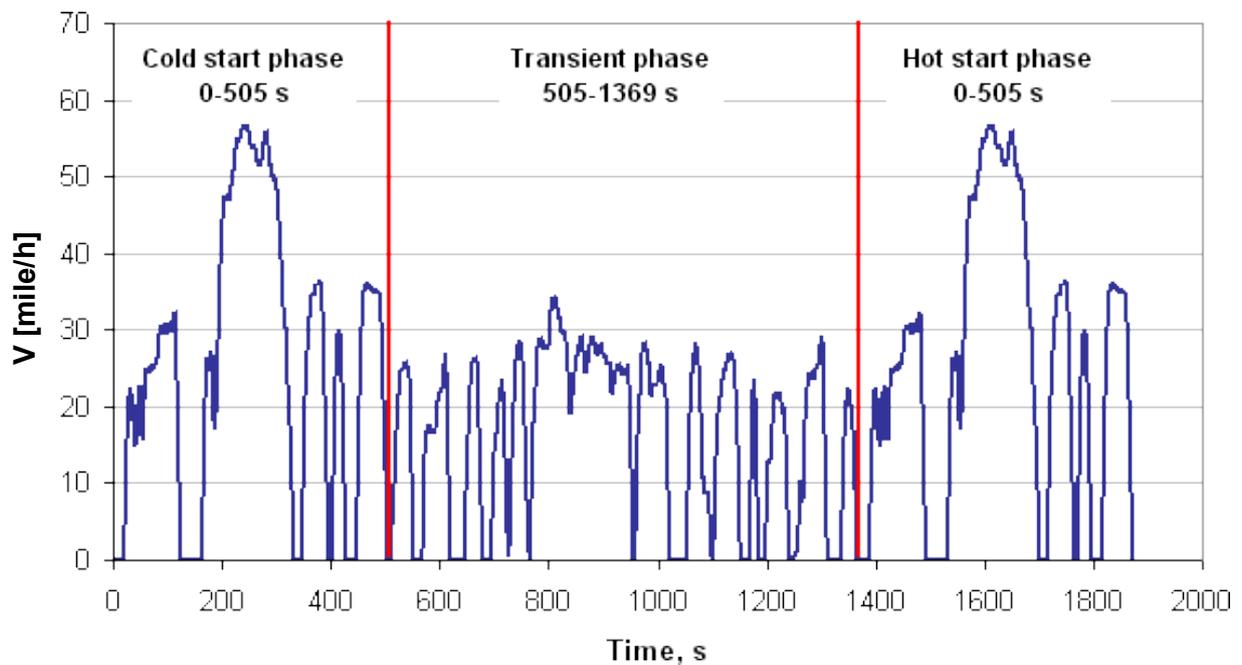


Figure A2. US Environmental Protection Agency Federal Test Procedure FTP-75; distance: 17.77 km, duration: 1874 s, average speed: 43.1 km/h; FTP-75 consists of three phases: cold start phase, transient phase and hot start phase.

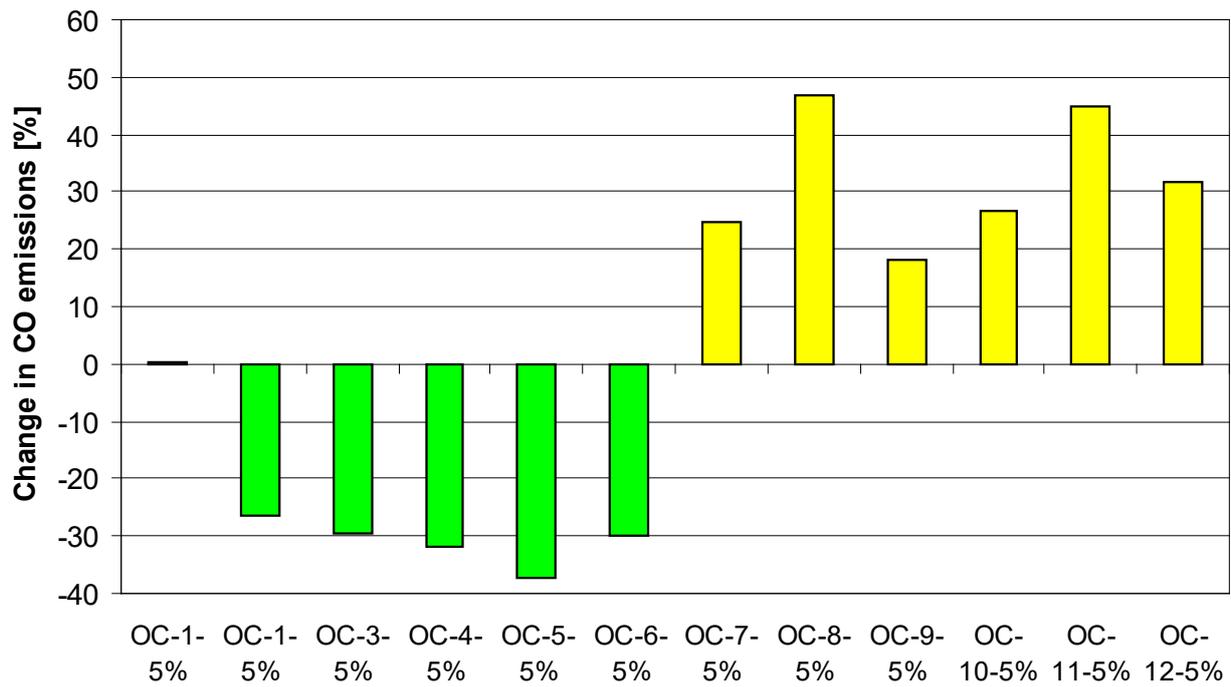


Figure A3. Percentage changes in CO emissions over the NEDC from a test car with fuels containing individual oxygenates at a concentration of 5% *v/v* compared to running on conventional diesel fuel.

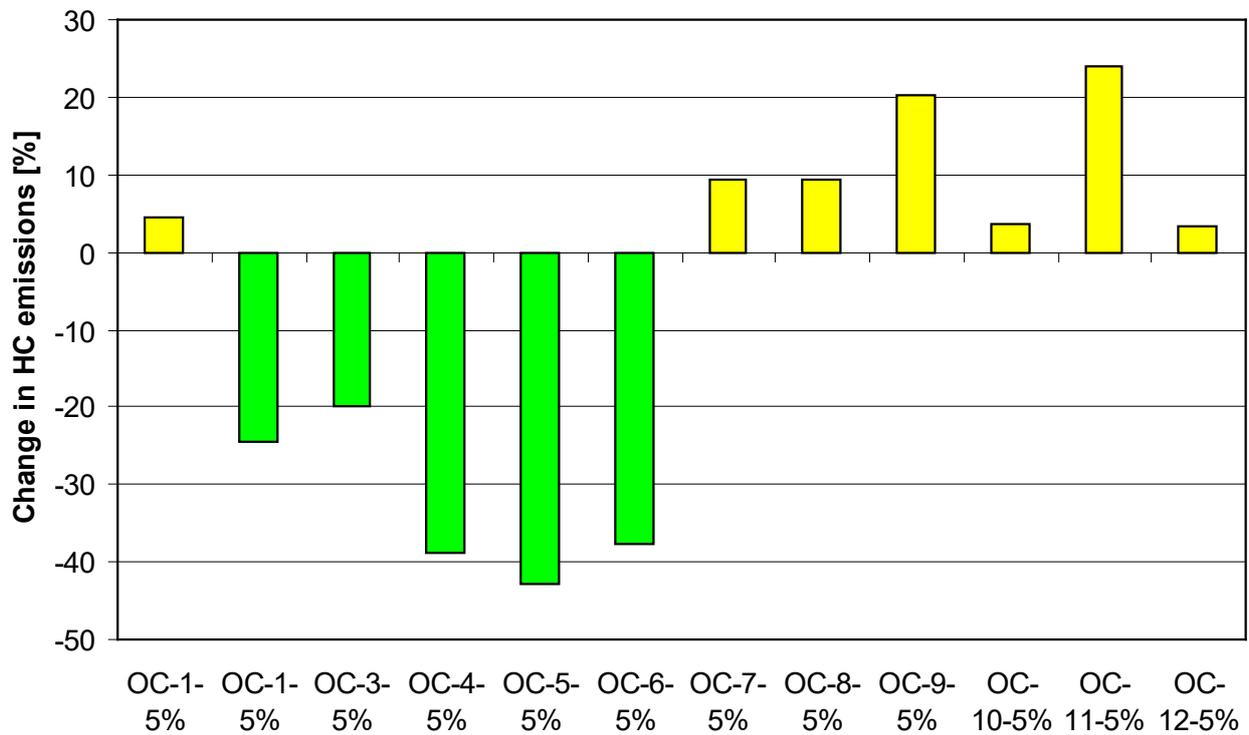


Figure A4. Percentage changes in HC emissions over the NEDC from a test car with fuels containing individual oxygenates at a concentration of 5% *v/v* compared to running on conventional diesel fuel.

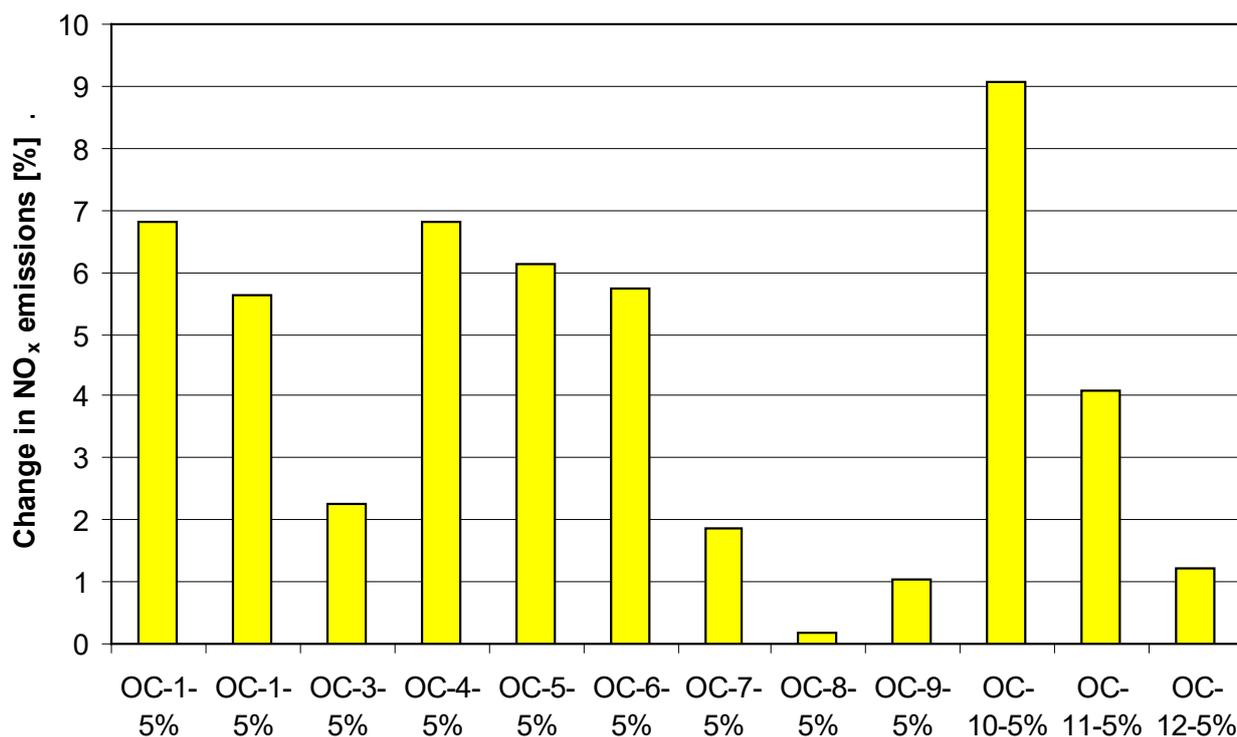


Figure A5. Percentage changes in NO_x emissions over the NEDC from a test car with fuels containing individual oxygenates at a concentration of 5% *v/v* compared to running on conventional diesel fuel.

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