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# The Study on the Influence of Diesel Fuel Oxygenates on Exhaust Emissions

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/62005

#### Abstract

The study discusses the use of oxygenated fuels in reduction of exhaust emissions from diesel engines. The study analyzes the physicochemical properties of oxygenated compounds in diesel fuels based on which 12 such compounds were selected for experimental research (glycol ethers, maleates, carbonates and alcohols). The study presents the results of investigations of the influence of oxygenated fuels on the exhaust emissions under dynamic homologation cycle chassis dynamometer conditions (diesel passenger vehicle, NEDC and FTP-75 cycles). The relationship among the content of individual oxygenated compounds, the conditions of the tests cycle and the exhaust emissions has been ascertained. The performed studies and experimental research have shown that the application of oxygenated fuels in diesel engines results in a significant reduction of the PM emission at a small increase in the emission of  $NO_x$ . Changes in the emission of CO and HC depend not only on the oxygen content in the fuel but also on the self-ignition quality of the applied oxygenated compounds. The application of oxygenated fuels does not influence the emission of CO<sub>2</sub>. Out of the analyzed oxygenated compounds, the most advantageous emission changes (reduction of the emission of PM, CO and HC at a small increase in the emission of  $NO_x$ ) are generated by the compounds of the glycol ethers group.

Keywords: Diesel engine, diesel fuel, oxygenates, exhaust emissions

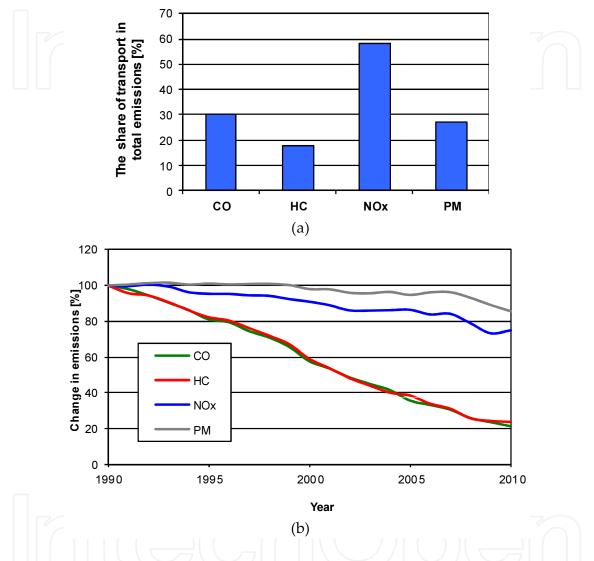
### 1. Introduction

An efficient transport system is one of the basic elements of every developed economy in the world. Transport is also a very important aspect of life for a large part of humanity, because it facilitates the daily movement of people. Access to transport is one of the main factors affecting the quality of life. In addition to the major benefits of transportation, there are also the adverse consequences, particularly pollution.

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Vehicles are a major source of air pollution in developed countries, including the European Union (EU) (Fig. 1a). It should be noted that in the past 20 years, the carbon monoxide (CO) and hydrocarbons (HC) emissions from transport have decreased significantly, while  $NO_x$  emissions, and in particular particulate matter (PM), have declined only slightly (Fig. 1b).



**Figure 1.** The share of transport in total emissions of major air pollutants in the European Union in 2009 (a) and change in emissions of these pollutants in the transport sector in 1990–2010 (b) [1]

The main sources of CO and HC emissions from transport are vehicles powered by gasoline engines. The share of vehicles with spark ignition (SI) and compression ignition (CI) engines in NO<sub>x</sub> emissions is similar, while vehicles with diesel engines are responsible for the majority of PM emissions. Particulate matter is among the most harmful of emissions from motor vehicles. In the report of the US Environmental Protection Agency on the dangers of exhaust gases of diesel engines [2], it has been demonstrated, on the basis of several dozen independent medical studies on humans and laboratory tests on animals, that airborne PM have carcinogenic effects and contribute in particular to the occurrence of lung cancers.

One of the reasons of the mentioned small reduction in PM emissions compared to other exhaust compounds is an increase in the number of sources of PM emissions, which means the number of vehicles powered by diesel engines is higher. From the middle of the past decade, more cars with diesel engines than SI were sold in the European Union. In 2012, the share of passenger vehicles with diesel engines among new cars was 56% [3]. The economic development of the countries in the European Union leads to an increase in the number of heavy vehicles, which typically use only diesel engines. This situation is well illustrated by the trends in demand for motor fuel. In 2000, the European Union had a similar demand for automotive gasoline and diesel fuels. At present, the demand for diesel fuel is twice that of gasoline, and taking into account the off-road oil consumption, it is nearly three times higher (Fig. 2). A similar situation also exists in Poland, but in this country, it is largely the result of popularity of liquefied petroleum gas (LPG). According to data from the Central Statistical Office [4], 3 925 thousand tons of gasoline and 12 219 thousand tons of diesel fuel have been sold in Poland in 2011.

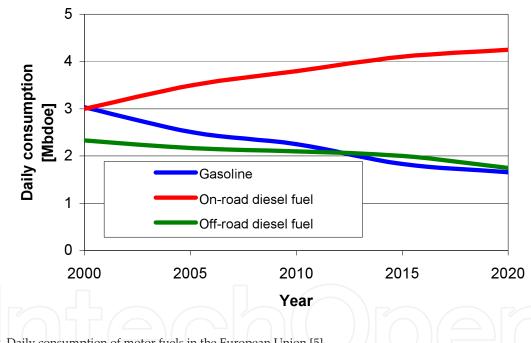


Figure 2. Daily consumption of motor fuels in the European Union [5]

The second reason for the similar level of PM emissions from transport sources continued over the years is lower PM emission reduction efficiency of vehicles compared to the gaseous components of the exhaust. Currently, getting acceptably low exhaust emissions from diesel engines requires numerous and varied measures, covering at least [6]:

- the optimization of the combustion process in the engine,
- utilization of systems that reduce the creation of harmful compounds in the operating processes of the engine (e.g., exhaust gas recirculation (EGR)),
- using effective exhaust aftertreatment systems,

- utilization of onboard diagnostics (OBD) to monitor the emission levels of harmful compounds by the vehicle,
- improving the fuel composition to reduce the creation of harmful exhaust compounds.

The basis for the development of eco-friendly motor fuels are research programs concerning the impact of fuel on emissions of toxic components, performance, durability, and other indicators for internal combustion engines. The first such program was AQIRP (Auto/Oil Air Quality Improvement Research Program) conducted in the US in 1989–1997. However, it only researched fuels for SI engines [7]. Evaluation of the impact of fuel emissions was also one of the elements of the JCAP program (Japan Clear Air Program) implemented in Japan in 1996–2001 [8]. In the years 1993–1996, the European Union conducted its EPEFE program (European Programme on Emissions, Fuels and Engine Technologies), usually abbreviated to Auto-Oil program [9]. On the basis of research [10], it was found that the greatest impact on the level of harmful exhaust emissions from diesel engines have the following parameters of diesel fuel (Fig. 3):

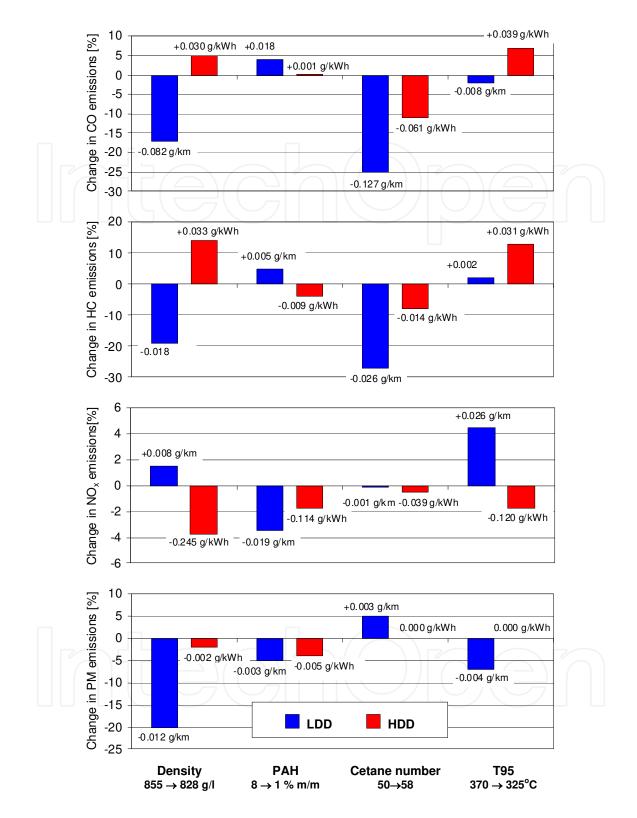
- cetane number,
- density,
- polycyclic aromatic hydrocarbons (PAH) content,
- fractional composition, particularly the amount of heavy hydrocarbons characterized by the T90, T95, and FBP temperatures,
- sulfur content.

Parameter	Unit	Since 2000	Since 2005
Cetane number, min.	_	51	51
Sulfur content, max.	ppm	350	50/101)
PAH content, max.	% (m/m)	11	11
Density at 15°C, max.	kg/m <sup>3</sup>	845	845
Distillation, T95 max.	°C	360	360

Table 1. Specifications of diesel fuel according to the European Directive 98/70/EC

Auto-Oil program was the only program so far that so comprehensively encompassed the issues of the impact of fuel emissions of harmful exhaust compounds. The results of the Auto-Oil program were the basis for establishing the fuel specifications of the European Union, in force since 2000, contained in the European Directive 98/70/EC. The new requirements introduced by this directive significantly changed the parameters of diesel fuels affecting the level of exhaust emissions (Table 1). Through this, the potential of conventional diesel fuels in

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**Figure 3.** Effect of diesel fuel parameters on the exhaust emissions of the European LDD and HDD engines according to the Auto-Oil program [10]

reducing emissions was largely used up, so that further modification of the conventional fuel parameters is possible only to a limited extent. The sulfur content in fuels produced today is

nearly zero, and the PAH content has been reduced to about 2–3%. Excessive increase in cetane number would have an adverse impact on the process of combustion and emissions. A further change of composition in the direction of lighter fractions is also unjustified. So to even further exploit the potential of fuels to reduce exhaust emissions of diesel engines, unconventional modifications of their properties are necessary. It seems that one of the promising fields of this type of activity is the use of oxygenated fuels, namely the introduction of components that act as carriers of oxygen (oxygenates) into the composition of diesel fuels. Oxygenated fuels are successfully utilized in SI engines to provide lower emissions of CO and HC. Due to the nature of combustion in the diesel engine, namely an inhomogeneous air–fuel mixture and local oxygen deficiency regions, the emission benefits associated with the use of oxygenated fuels in diesel engines should be even greater. This chapter is dedicated to the issue of the impact of oxygenated fuels on exhaust emissions from diesel engines.

It should be noted that the introduction of low-emission diesel fuels involves a number of potential benefits, which cannot be provided by other solutions for reducing emissions. First of all, eco-friendly fuels immediately impact the whole fleet of vehicles, and their introduction into the market in sufficient quantities (as opposed to alternative fuels) can be done in a short time. Although the unit emission reduction is probably less than one achieved with modern engine technology or alternative fuels, because of the huge scale of fuel consumption, a quick global effect may be larger than what can be achieved by several other means. In addition, low-emission fuels can provide a reduction in emissions from older vehicles, which on the one hand are the largest source of harmful exhaust emissions, and on the other hand, reducing their harmfulness is technically impossible or not cost-effective through other means. Another advantage of the low-emission diesel fuels is their impact on reducing harmful exhaust emissions in circumstances when other measures are not effective (e.g. engine start-up and warm-up period).

# 2. Requirements for oxygenated compounds used as components of diesel fuels

Oxygen compounds used as components of oxygenated fuels must demonstrate properties that are required for all components of motor fuels. Not all oxygenates are suitable for use as an additive to diesel fuel. According to Murphy [11], potential oxygenated components must meet the following requirements:

- be able to mix with diesel fuel in the whole range of engine operating temperatures,
- low-temperature parameters of diesel fuel and oxygenated compounds mixtures must be suitable for the climate where they will be used,
- mixtures of diesel fuel and oxygenated compounds should not be susceptible to stratification as a result of contamination with water,
- oxygenated compounds should have a sufficiently high cetane number,

• oxygenated compounds should not have a too high volatility nor too low flash point.

Additional important requirements for potential oxygenates of diesel fuels should include:

- high oxygen content in the molecule allowing for small concentrations of oxygenated compounds to achieve sufficient amount of oxygen in the final fuel mixture; lower concentrations also have a lesser impact on the physical properties of fuel,
- no negative impact on fuel system components: no corrosive effect on metals or swelling effects on plastics (elastomers),
- low own toxicity of the oxygenated compound,
- competitive price and availability.

It should be noted that the fulfillment of these criteria will often depend on the amount of oxygenated compound added to the fuel composition.

The literature provides various proposals for chemical compounds to be used as oxygen compounds in fuels. Particularly, one paper [12] presents an analysis of the physicochemical properties of 71 potential oxygenated compounds. After initial selection on the basis of three parameters, such as oxygen content, density, and flashpoint temperature, 42 oxygenated compounds were addressed for further analysis, where they have been evaluated in terms of miscibility with diesel fuel and water tolerance. Seventeen compounds that at this stage rated positively were then tested for corrosive properties. Their toxicological properties, biodegradability, and impact on elastomers were also evaluated. Based on the analyses performed, eight most promising oxygenated compounds were chosen for further use in diesel fuels: tripropylene glycol monomethyl ether, 1-methoxy-2-propanol, dipropylene glycol monomethyl ether, 2-ethoxy ethyl acetate, 2-ethoxy ethyl ether, diethyl adipate, tributyrin, and dibutyl maleate.

Bertoli and Boulouchos [13] describe the analysis of 27 prospective oxygen compounds in terms of their compatibility with diesel fuel, their oxygen content, and calorific value. This analysis found that the best oxygenated compounds are diethylene glycol dimethyl ether, dibutoxymethane (butylal), and dipenthylether. Delfort et al. [14] show the applicability as fuel components of 18 oxygen compounds of chemical groups such as ethers, acetals, polyacetals, and carbonates. Murphy in his works [15, 16] pointed out the inappropriate fire safety and toxicology performance of some of oxygen compounds.

3. Analysis of exhaust emissions from a passenger car fueled with oxygenated fuels

#### 3.1. The essence of application of oxygenated diesel fuels

Fuel, as the integral element of combustion in the engine, has an immense effect on the composition and harmfulness of exhaust gases emitted by the engine. The changes of EU standard requirements for diesel fuels, implemented in 2000, 2005, and 2009, were directed

toward the reduction of the harmfulness of the exhaust gases emitted by the engines. At present, the modification of the conventional properties of diesel fuel that affect the emissions (cetane number, sulfur content, distillation, etc.) is possible to a limited extent only. Therefore, in order to take the maximum advantage of the fuel potential in exhaust emissions reduction, some more unconventional modifications of the fuel should be considered. The application of oxygenated compounds seems to be one of the more promising solutions in this field. The compounds particularly affect a very troublesome component of diesel engine exhaust – i.e., particulate matter. On the basis of physicochemical and environmental parameters, test results described in the literature, as well as price and availability, oxygen compounds belonging to chemical groups such as glycol ethers, maleates, and carbonates were selected for further experimental testing in this study. The study also includes butanol, whose mass production from biomass is being considered. Butanol is closer in terms of its properties to diesel fuel than the currently produced large-scale ethanol. The detailed characteristics of the oxygen compounds selected for testing are presented in Section 3.2.

The literature presents some test results of maleates as components of diesel fuel. Among them, there are works delivered by Stoner and Lizinger [17], who obtained reduction in PM and  $NO_x$  emissions at the same time by using diethyl maleate and dibutyl maleate. They also tested some glycol ethers, which, however, caused less favorable changes in emissions than maleates. Natarajan et al. [12] analyzed potential oxygenated compounds and, based on their physical and chemical properties, they selected eight of the most suitable oxygenates to be used in diesel fuel. Among them, there was dibutyl maleate. Further, they performed emissions tests in one mode of engine operation with the use of the selected components at the concentration, ensuring 7% of oxygen in the fuel [18]. Dibutyl maleate caused considerable decrease in PM emissions and, at the same time, considerable increase in  $NO_x$  emissions. Based on total PM emissions and other considerations, dibutyl maleate and tripropylene glycol monomethyl ether were identified as the most promising oxygenated compounds for future engine testing. These more extensive engine tests carried out in several engine operating modes confirmed high efficiency of the abovementioned oxygenates in PM emissions reduction and showed that these oxygenates had no unfavorable influence on  $NO_x$  emissions [19].

In the available bibliography, there are some examples of the results obtained in the tests of carbonates as diesel fuel components. Murayama et al. [20] carried out some extensive research on the influence of dimethyl carbonate on the combustion characteristics and emissions from a direct injection (DI) diesel engine. It was found that for the carbonate content in fuel of 10%, the smoke emission was lowered by 35–50%, and also that the extent of the smoke emission reduction was proportional to the oxygenate content. Moreover, it was found that the carbonate additive caused a significant decrease in the CO and HC concentrations in exhaust gases and a small increase in the NO<sub>x</sub> emissions. Also Akasaka and Sakurai presented in their paper [21] the reduction in smoke emission obtained with the use of an additive from the carbonate group (its name was not mentioned). The research on the influence of oxygenates on the PM emissions in the New European Driving Cycle (NEDC) with the use of the Audi A3 TDI (Euro 2) passenger car were carried out by Delfort et al. [14]. They tested 18 oxygenates, including 5 oxygenates from the chemical family of carbonates.

fuel and the oxygenated compound chemical structure were decisive for the reduction in the PM emissions. Their tests showed that at the same content of different oxygenates in fuel, the highest reduction in the PM emissions was obtained in case of the use of carbonates. Next, from among all tested carbonates, diethyl carbonate and diethoxy-2-ethyl carbonate were the most effective ones, which, when added to the fuel in amount of 5%, caused the reduction in the PM emissions in the NEDC by 17–18%. Substantial reduction in exhaust soot emissions for diesel fuel containing dimethyl carbonate was described by Kocis et al. [22]. They also discussed the potential paths of oxygenated compounds influence on soot production.

Glycol ethers are as often as not tested as diesel oxygenated compounds. The aforementioned research, carried out by Delfort et al. [14], showed their moderate efficiency in PM emission reduction. The research conducted by Hallgren and Heywood [23] also showed that glycol ethers decrease PM emissions. Moreover, this research proved that these oxygenates reduce mainly insoluble fraction (soot), whereas soluble organic fraction (SOF) remains intact. Yeh et al. [24] proved that glycol ethers cause not only a reduction in PM emissions but also a reduction in CO and HC emissions and an increase in NO<sub>x</sub> emissions. Favorable effects of glycol ethers on exhaust emissions were also described in papers delivered by Porai et al. [25] and Akasaka and Sakurai [21].

The majority of the published papers concerning the influence of oxygenates on exhaust emissions from diesel engines have reported the results of research conducted under stationary conditions, for one or more engine operating modes. From among the few investigations carried out under transient conditions, aforementioned research performed by Delfort et al. [14] and Yeh et al. [24] should be noted.

The detailed mechanism by which oxygenates reduce PM emissions has not been precisely defined so far. The literature contains contradictory results as to whether the oxygen content in fuel is the only important factor determining PM/smoke emissions, or whether oxygenate molecular structure or other variables also play important roles. Research carried out by Nabi et al. [26] with highly oxygenated diesel fuels containing glycol ethers and carbonates showed that smoke decreased linearly and depended entirely on the oxygen content in the fuel, regardless of the kind of the oxygenate. Another study with highly oxygenated diesel fuels by Mueller and Martin [27] indicates that overall oxygen content is not the only important parameter governing the soot reduction potential of a fuel, and that molecular structure effects may also be significant. Buchholz et al. [28] using selective labeling of carbon atoms in dibutyl maleate molecules proved that the molecular structure and distribution of oxygen within an oxygenated diesel fuel strongly influences the ability of the fuel to reduce PM emissions. In the recent study written by Boot et al. [29], it was shown that the oxygen content has a pronounced effect on PM reduction, but chemical structure effects can be almost of the same order.

The experimental results presented in the chapter were obtained within a research program investigating the effect of different synthetic oxygenates on exhaust emissions from diesel passenger cars. The objective of this study was to select the most promising oxygenate compounds as blending components in diesel fuel for further advanced testing and practical application. The research was carried out with oxygenates representing different chemical groups. All the emissions test were conducted over dynamic cycles in a chassis dynamometer (NEDC, FTP-75).

#### 3.2. Research methodology

#### 3.2.1. Scope of the research

The study was performed at the BOSMAL Automotive Research & Development Institute in Bielsko-Biała. They included measurements of toxic exhaust emissions (CO, HC,  $NO_x$ , and PM), CO<sub>2</sub> emissions, and fuel consumption on a chassis dynamometer in test cycles for passenger cars with a Euro 4 class diesel engine run on different oxygenated fuel variants. The conducted study was comparative; hence, measurements were also made for cars running on conventional diesel fuel, not containing oxygenated components. The research was staged and includes, in particular:

- 1. Preliminary studies (NEDC) aimed to determine the effect of each of the 12 researched oxygenated compounds on the exhaust emissions, thus indicating which of the tested fuel additives are most beneficial for reducing the engine exhaust toxicity. The results of the preliminary research were also used as the basis for determining the unit efficiency of oxygen contained in the fuel to reduce PM emissions as well as for the selection of oxygen compounds for further, more detailed analysis.
- 2. Investigation of the effect of oxygenates on exhaust emissions, depending on their content in the fuel (5 or 10% v/v, NEDC).
- **3.** Investigation of the effect of oxygenates on exhaust emissions, depending on the test cycle conditions (NEDC and FTP-75).

#### 3.2.2. Research fuels

The study used 12 different synthetic oxygenates representing four chemical groups, such as the glycol ethers, maleates, carbonates, and alcohols. Oxygenated compounds were used in concentrations of 5 and 10%. Selection of components was dictated primarily by their physicochemical properties (oxygen content, compatibility with diesel fuel, etc.) and the results of tests described in the literature, followed by price and availability. Physicochemical properties of the oxygen compounds used in the study are shown in Table 2. The oxygen content of the compounds used is in the range 21.6–53.3% m/m. Oxygen compounds were labeled in this work with the symbol PT-X-Y%, where X is the number of oxygen compound used in accordance with Table 2, and Y is its content by volume.

All research fuels were formulated based on Euro 5 grade diesel fuel. Due to the long duration of the research, and taking into account the aging processes of fuel (change in fuel properties during storage), diesel fuel used was purchased in two tranches, labeled in this work as ON I and ON II. The properties of diesel fuel in both tranches were similar; they have been shown in Tables 3 and 4.

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No.	1	2	3	4	5	6
Chemical	Ethylene glycol dimethyl	Diethylene glycol	Triethylene glycol	Tetraethylene	Diethylene glycol dibutyl	Dipropylene glyco
name	ether	dimethyl ether	dimethyl ether	glycol dimethyl ether	ether	dimethyl ether
Molecular	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	(CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub>	CH <sub>3</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub>	CH <sub>3</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>4</sub>	(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> C	CH <sub>3</sub> OC <sub>3</sub> H <sub>6</sub> OC <sub>3</sub> H <sub>6</sub> OO
formula		О	CH <sub>3</sub>	CH <sub>3</sub>	$H_2)_2O$	$H_3$
Molecular weight, amu	90.12	134.17	178.23	222.28	218.33	162.23
Oxygen content, % m/m	35.6	35.8	36.0	36.0	22.0	29.6
Boiling point, °C	85	162	220	275	256	175
Freezing point, °C	-69	-64	-40	-30	-60	-80
Flash point, °C	-6	51	113	141	120	65
Density @ 20°C, kg/m <sup>3</sup>	867	944	987	1010	884	903
Viscosity @ 20°C, mm²/s	0.5	1.2	2.5	4.1	2.3	1.12
Cetane number (calculated)	86	112	144	144	144	86
Vapor pressure @ 20°C, kPa	6.4	0.4	_	<0.001	<0.001	-
No.	7	8	9	10		12
Chemical name	Tripropylene glycol methyl ether	Diethyl maleate	Dibutyl maleate	Dimethyl carbonate	Diethyl carbonate	N-butanol
Molecular formula	CH <sub>3</sub> (OC <sub>3</sub> H <sub>6</sub> ) <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OCOCH= CHCOOC <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OCOCH = CHCOO(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	(CH <sub>3</sub> O) <sub>2</sub> CO	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> CO	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH
Molecular weight, amu	206.28	172.18	228.28	90.08	118.13	74.12
Oxygen content,	31.1	37.3	28.1	53.3	40.7	21.6

content,

% m/m						
Boiling	243	225	281	90	127	117
point, °C						
Freezing	-78	-10	-	3	-43	-90
point, °C						
Flash point,	121	_	>110	-	_	34
°C						$\square$
Self-ignition	227	350	<u> </u>	( - / /		343
temperature,						
°C						
Density @	963	1064	988	1069	975	810
20°C, kg/m <sup>3</sup>						
Viscosity @	5.5	-	-	0.56	0.78	3.64
20°C, mm²/s						
Cetane	58.3	56.8	43.8	10.3	13.8	10.2
number						
(calculated)						
Vapor	< 0.001	0.1 (14°C)	_	2.4	1.3	0.5
pressure						
@ 20°C, kPa						

Table 2. The properties of synthetic oxygenated compounds used in this research

		Unit	Value
Cetan	e number	_	51.8
Ceta	ne index	-	53.1
Densi	ty @ 20°C	kg/m <sup>3</sup>	831.2
Sulfu	r content	ppm	9.9
Oxyge	en content	% m/m	0.0
Viscosity	@ 20°C	mm²/s	4.283
	@ 40°C	mm²/s	2.773
Distillation	E250	% v/v	35.3
	E350	% v/v	97.6
	T95	С	341.6
	FBP	С	352.0
Aromatic	Total aromatics	% m/m	23.9
hydrocarbons	Monoaromatics	% m/m	21.4

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	Unit	Value
Diaromatics	% m/m	2.4
Tri + aromatics	% m/m	0.1
Total PAH	% m/m	2.5

Table 3. Specifications of the first batch of base diesel fuel (ON I) Unit Value 52.8 Cetane number \_ Cetane index 53.4 \_ Density @ 20°C kg/m<sup>3</sup> 827.7 Sulfur content 8.8 ppm Oxygen content % m/m 0.0 Viscosity @ 20°C mm<sup>2</sup>/s 4.096 @ 40°C mm<sup>2</sup>/s 2.607 Distillation E250 % v/v 38.1 E350 % v/v \_ T95 С 332.3 С FBP 343.7 Aromatic Total aromatics % m/m 20.7 hydrocarbons Monoaromatics % m/m 18.8

 Table 4. Specifications of the second batch of base diesel fuel (ON II)

Diaromatics

Tri+ aromatics

Total PAH

#### 3.2.3. Research conditions

#### 3.2.3.1. Research equipment description

The research was conducted in the Exhaust Toxicity Laboratory at the BOSMAL Automotive Research & Development Institute in Bielsko-Biała, which has the instrumentation to measure toxic exhaust emissions from vehicles powered by diesel engines and accredited by the TÜV. The course of research in the laboratory is controlled by the measurement management system AVL CESAR. The temperature and humidity at the level required by the testing procedure are maintained by a complete heating, ventilation, and air-conditioning (HVAC) system.

% m/m

% m/m

% m/m

1.7

0.2

1.9

The laboratory is equipped with a SCHENCK 500GS/60 chassis dynamometer (Fig. 4). Chassis dynamometer is a device designed to simulate the resistance of motion (rolling and aerodynamic) for a car moving forward on a flat road and the inertia of the vehicle.

The core elements of the dynamometer include:

- A set of rollers with individual ball bearings, combined with a system of clutches and a belt drive, powered by a DC motor,
- DC motor fitted with a thyristor control system,
- A set of rotating weights, used for mapping the inertial mass of the tested vehicle,
- A set of controls and measurement devices; the entire operation of the dynamometer (e.g. setting the inertial mass, characterization, calibration, etc.) is done via its own test bench control computer.

Dynamometer is equipped with a parameter adjustment system for the driver (Driver Guiding Unit LMC 68/40). The operation of this device consists in presenting (in advance) the required driving performance parameters as a function of time to the driver: speed, moving and stopping points for the vehicle, as well as the time to push the clutch down and shifting gears. In addition, the current time of the test as well as the number and total time of breaching the preset parameters of the drive cycle are given.



Figure 4. Chassis dynamometer SCHENCK 500GS/60 in BOSMAL Automotive Research & Development Institute

The measurement of toxic exhaust emissions during the driving tests was carried out with an exhaust collection and sampling system with a Venturi nozzle – "Quadro Venturi" (CFV-CVS)

of the AVL CEC-Q20 type, equipped with a full-flow exhaust dilution tunnel AVL CET-LD/20. A sample of the mixture of exhaust and air, in proportion to the flow rate of the mixture, is continuously taken and collected in a sampling bag during the driving test.

After completing the test, the contents of the measurement bags, which is a mixture of exhaust gases and ambient air, is directed to a set of analyzers, which determine the concentration of each of the gaseous exhaust components. In accordance with the procedure of measuring emissions from vehicles equipped with CI engines, the exception is the measurement of the concentration of HC, which is done by drawing a sample through a heated line directly from the dilution tunnel. The sample for measuring exhaust emissions of PM is also taken from the dilution tunnel using a particulate sampling system AVL CEP-LD/100. The concentration measurements of gaseous exhaust components was performed through a set of AVL CEB 600 exhaust gas analyzers, which includes the Rosemount NGA 2000 device.

#### 3.2.3.2. Drive cycle: NEDC

Most measurements of exhaust emissions are based on NEDC, introduced in the European Union on January 1, 2000, as a vehicle certification test. This cycle (Fig. 5) consists of two parts or phases (subtests): the UDC (Urban Driving Cycle) and the EUDC (Extra Urban Driving Cycle).

During the tests, the ambient temperature was 22–23°C, where the allowed temperature range for the test procedure is between 20 and 30°C. Before each test, the vehicle was conditioned in a laboratory environment. One test was performed per day. After each change of the fuel, the car also passed a whole cycle without the measurement of emissions to remove any residue of the previous fuel from the supply system, and the proper test was carried out the next day after reconditioning.

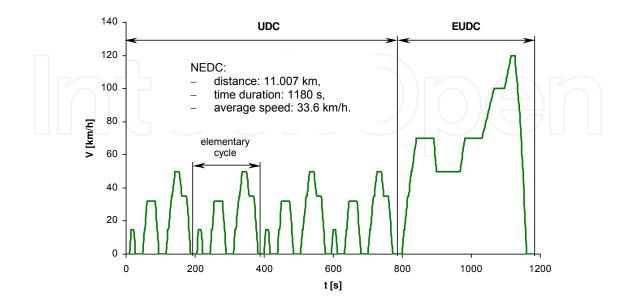


Figure 5. NEDC drive cycle according to the 98/69/EC directive

The intake of the analyzed exhaust gas starts immediately after starting the engine of the vehicle. The first phase (UDC) is composed of four elementary tests repeated in succession. Due to prior conditioning, the engine and the vehicle at the beginning of the UDC phase are at the ambient temperature, thus the start of the engine is cold, just as in real life at start-up after a long (e.g. overnight) parking. During the engine cycle, the temperature of the engine oil, engine coolant, and exhaust gases increases. The EUDC phase starts immediately after the end of the UDC phase, and therefore during the EUDC, the vehicle engine has warmed to operating temperature. In this phase, there are longer periods of operation of the engine at a constant speed and the vehicle speed reaches a value much higher than that in the UDC.

#### 3.2.3.3. Drive cycle: FTP-75

The American federal test FTP-75 (Federal Test Procedure) is used in the US for the measurement of exhaust emissions by light-duty type vehicles and has been in force since 1996. This test consists of three phases (Fig. 6):

- cold start phase,
- transient phase,
- hot start phase.

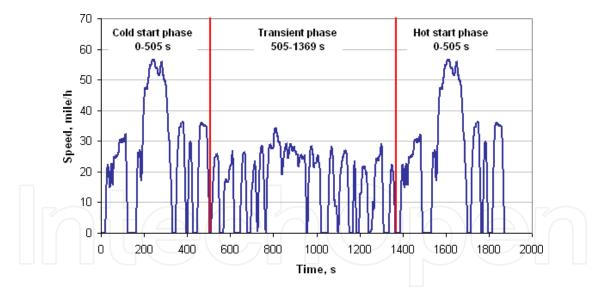


Figure 6. The result of an American FTP-75 drive cycle

A ten-minute break is made between the phases 2 and 3, during which the engine is switched off. The characteristics of the FTP-75 test are:

- distance traversed: 17.77 km,
- time duration: 1874 s,
- average speed: 43.1 km/h.

#### 3.2.3.4. Test vehicle

The study used a Fiat Panda 1.3 16v Multijet vehicle, which at the start of the research represented the level of technological advancement of vehicle technologies. The car was equipped with a turbocharged diesel engine fueled in a common rail system. The car had controlled EGR system and catalytic exhaust aftertreatment, and its exhaust emissions met the Euro 4 standard. Key parameters of the test vehicle are presented in Table 5.

Due to the necessity of frequent changes in the fuel type for the test vehicle, and to avoid contamination of the test fuel with the previous fuel remaining in the fuel system, the fuel supply system of the vehicle was modified. A portable external fuel tank with its own electric low-pressure pump was used, delivering fuel directly into the high-pressure pump nozzle. Thanks to this, the length of the low-pressure fuel lines (i.e. the distance between low-pressure pump and the high-pressure pump) has been reduced several times. Several elements with a large capacity (the factory-issued fuel tank, low-pressure pump and fuel lines leading to the high-pressure pump), which could retain the fuel of the preceding tests, have been eliminated from the fuel supply system.

Vehicle type	Passenger car
Dry weight	950 kg
Engine type	Diesel, 4-cylinder in-line
Displacement	1.3 dm <sup>3</sup>
Max. power	51 kW @ 4000 rpm
Max. torque	145 Nm @ 1500 rpm
Injection/combustion type	Direct injection common rail, turbocharged (intercooled)
Exhaust gas recirculation	Electronically controlled (closed-loop)
Emission control	Oxidation catalyst
Calibrated to	EURO 4

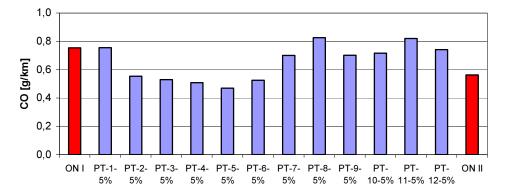
**Table 5.** Specifications of the test vehicle

#### 3.3. Preliminary studies of the effect of oxygenated compounds on exhaust emissions

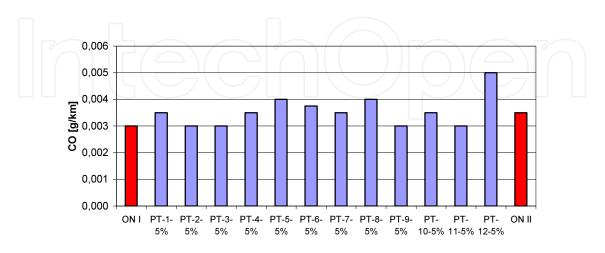
The aim of the research was to conduct a preliminary selection of oxygenates as fuel additives to ensure the most favorable changes in the composition of exhaust gases. These studies used 12 selected oxygenated compounds belonging to the following chemical groups: glycol ethers, maleates, carbonates, and alcohols. The preliminary studies testing the effectiveness of selected fuel oxygenates have been made under NEDC conditions, with a separate measurement of emission components in both its phases (UDC and EUDC). The emissions of CO, HC, NO<sub>x</sub>, PM, and CO<sub>2</sub> were measured. The oxygenated fuels used for the study were blended using two base diesel fuels: ON I and ON II. PT-1 to PT-6 fuels contained the ON I diesel fuel and the others, i.e. PT-7 to PT-12 the ON II diesel fuel. Vehicle emission test results of the researched individual oxygenated fuels should therefore be referred to the results obtained for the corresponding base diesel fuels.

#### 3.3.1. Carbon monoxide emissions

CO emission in the UDC phase (Fig. 7) was reduced when using most of the fuels containing glycol ethers, in particular for fuels containing oxygenated components 3–5. Note that these components had a very high cetane number and physical properties similar to those of diesel fuel. It appears that in the UDC phase conditions, so during engine warm-up, increased ability to self-ignition of fuel is essential to CO emission reduction. This is indicated by the result obtained for a fuel containing component 5 with a distinctly lower oxygen content than the components 3 and 4, as well as the results of studies on the effect of cetane number on emissions of CO made using fuels containing no oxygen [30, 31]. For fuels containing maleates and carbonates, the obtained CO emission levels were higher than for pure diesel. Maleates were characterized by a moderate amount of oxygen with a similar cetane number to that of diesel fuel, and for carbonates, low cetane number was compensated by a large oxygen content. Higher CO emissions have also been observed for the fuel containing *n*-butanol, which is a component with a low cetane number, relatively low oxygen content, and much lower boiling temperature than diesel fuel.



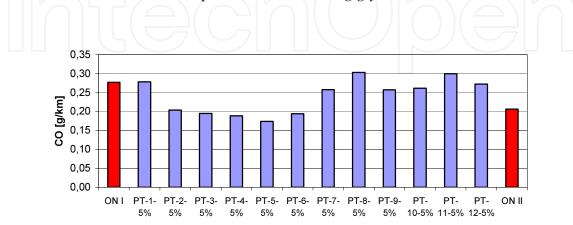
**Figure 7.** CO emissions during the UDC for conventional diesel fuels (ON I and ON II) and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v; PT-1-5% to PT-6-5% were formulated on the basis of diesel fuel ON I and PT-7-5% to PT-12-5% were based on the ON II fuel



**Figure 8.** CO emissions during the EUDC for conventional diesel fuels and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v

In the EUDC phase, the CO emissions are reduced to very low values (Fig. 8), mainly due to a stabilized thermal state of the engine and the effective operation of the catalytic converter. All fuels, except PT-12-5%, showed a similar level of emissions.

Very large disparities in CO emissions between phases UDC and EUDC (a difference of more than two orders of magnitude) mean that the average CO emissions in the NEDC (Fig. 9) are determined by the UDC phase. Therefore, the best performance over the NEDC was reported for the same fuel as for the UDC phase, thus containing glycol ethers.



**Figure 9.** The average emissions of CO in the NEDC (UDC + EUDC) for conventional diesel fuels and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v

#### 3.3.2. Hydrocarbons emissions

Same as for CO, the UDC phase saw a significantly lower HC emission for most of the oxygenated fuels (Fig. 10). Again, the relationship of fuel cetane number and the levels of emission reduction has been noted. When using fuels containing maleates, carbonates, and *n*-butanol, a slightly higher emission of HC has been observed than for neat diesel fuel.

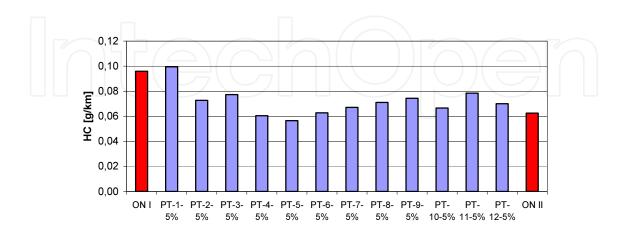
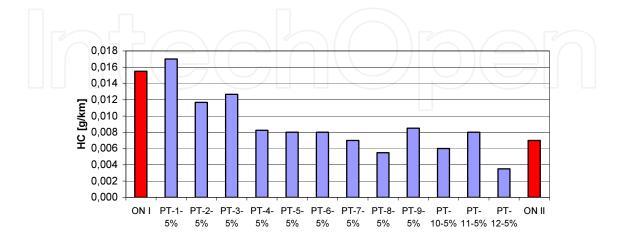


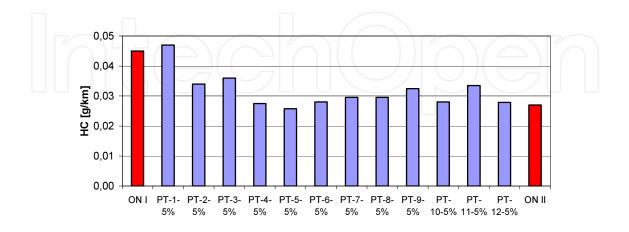
Figure 10. HC emissions during the UDC for conventional diesel fuels and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v

HC emissions in the EUDC phase are roughly an order of magnitude lower than in the UDC phase (Fig. 11), which is the result of steady thermal state of the engine, the effective operation of the catalytic converter and less dynamic changes in the operating conditions of the engine. For all oxygenated fuels, the HC emissions were reduced, or at least maintained at the level similar to that of diesel fuel (PT-1-5%, PT-9-5%, PT-11-5%).

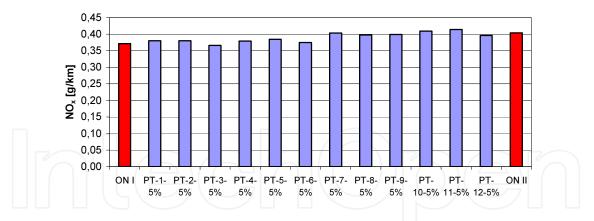


**Figure 11.** CO emissions during the EUDC for conventional diesel fuels and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v

The average HC emission in the NEDC test (Fig. 12) is determined mainly by the UDC phase. Generally, it can be said that all tested glycol ethers, with the exception of the compound number 1, produced a significant (approximately 30%) reduction in HC emissions. The said ether has a lower cetane number and physical properties (viscosity, boiling point) greatly deviating from the characteristics of diesel fuel. In contrast, other fuels containing oxygenated compounds cause HC level to remain similar to or slightly higher than that of diesel fuel (fuels containing components 9 and 11).



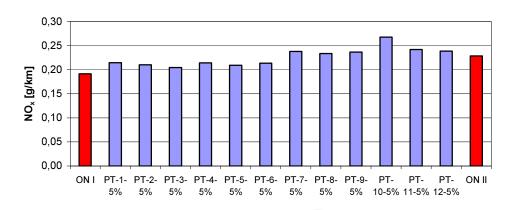
**Figure 12.** The average emissions of HC in the NEDC (UDC + EUDC) for conventional diesel fuels and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v



**Figure 13.** NO<sub>*x*</sub> emissions during the UDC for conventional diesel fuels and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v

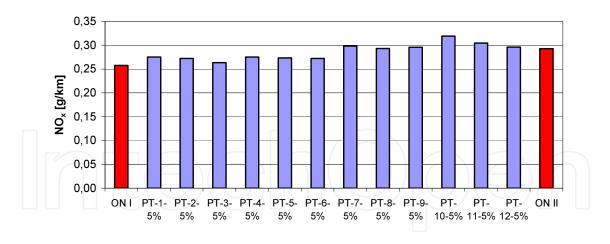
#### 3.3.3. Nitrogen oxides emissions

In the UDC phase, a very slight difference, not exceeding a few percent, was found in  $NO_x$  emissions for various fuels (Fig. 13). In the EUDC phase, for all the tested oxygenated fuels slightly higher  $NO_x$  emissions than for diesel fuel were observed (Fig. 14), but these differences can be considered minor.



**Figure 14.** NO<sub>*x*</sub> emissions during the EUDC for conventional diesel fuels and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v

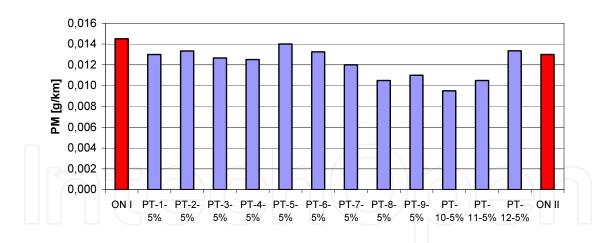
The average NO<sub>x</sub> emission in the NEDC for most oxygenated fuels was slightly (only a few percent) higher than the recorded emissions when powered by diesel fuel alone (Fig. 15); for other oxygenated fuels, the emission values remained in line with diesel fuel. These results confirm the limited impact of fuel on the engine NO<sub>x</sub> emission level (downstream the outlet valve). It should be added that the highest NO<sub>x</sub> emissions were observed for fuel with the highest oxygen content, which may be explained by a better availability of oxygen in the zone where nitrogen oxides are created according to the *prompt* mechanism as well as by locally leaner air–fuel mixture, allowing for burning more fuel and achieving higher local temperatures in the combustion chamber. One can assume that the smaller intensity of the formation of NO<sub>x</sub> was the effect of a high cetane number of fuels containing the components 1–6. This was confirmed in studies using fuels containing no oxygen [31].



**Figure 15.** The average NO<sub>x</sub> emissions in the NEDC (UDC + EUDC) for conventional diesel fuels and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v

#### 3.3.4. Particulate matter emissions

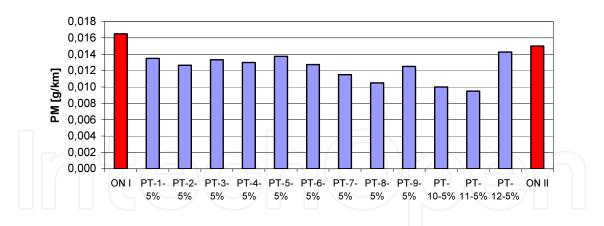
PM emissions in the UDC phase was lower for all oxygenated fuels (Fig. 16), except PT-12-5% containing *n*-butanol. It may be noted that the largest reduction in PM emissions was observed for fuels with the highest oxygen content. Among fuels with a similar oxygen content, the most effective in emission reduction were components with lower cetane number. It can also be pointed out that physical properties of the PT-1-5% component, deviating from those of the diesel fuel, were not an obstacle in PM emission reduction.



**Figure 16.** PM emissions during the UDC for conventional diesel fuels and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v

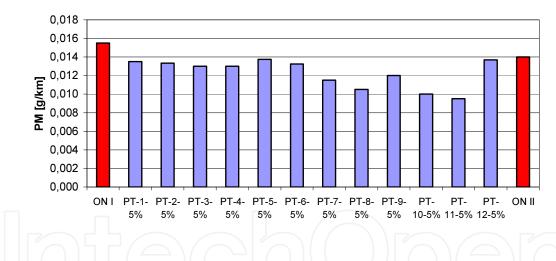
During the EUDC phase, the impact of oxygenated fuels on emissions of PM was even more favorable and clear (Fig. 17) than in UDC. Classification of oxygenates in terms of efficacy was similar to the one in the UDC phase, where the most effective component (11) lowered PM emissions by 40%.

PM emission level when running on diesel fuel was higher in the EUDC phase than in the UDC phase, whereas for oxygenated fuels, it was roughly similar in both phases, and therefore the



**Figure 17.** PM emissions during the EUDC for conventional diesel fuels and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v

application of oxygenated fuels resulted in a greater reduction in PM emissions in the EUDC phase. On average, over the whole NEDC, oxygenated fuels achieved at least a few percent of reduction in PM emissions (Fig. 18).

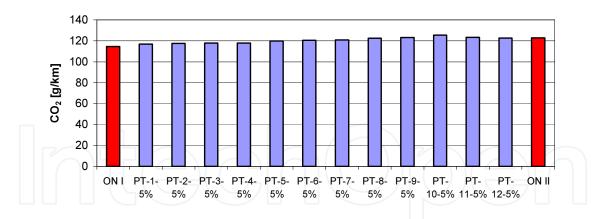


**Figure 18.** The average PM emissions in the NEDC (UDC + EUDC) for conventional diesel fuels and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v

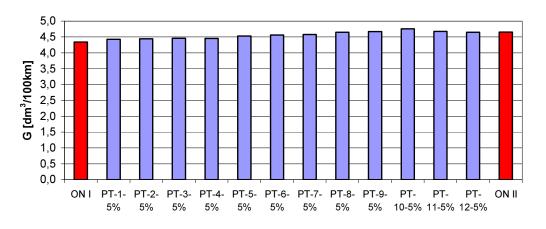
Glycol ethers, which for the previously analyzed exhaust gas components cause the most favorable changes, were less effective for PM emissions. The greatest reduction in PM emissions was obtained for carbonates and for maleates. The use of *n*-butanol resulted in the lowest reduction in PM emissions of the tested fuels with oxygenated compounds.

#### 3.3.5. CO<sub>2</sub> emissions and fuel consumption

 $CO_2$  emissions (Fig. 19) and fuel consumption (Fig. 20) in the NEDC was only slightly higher – in the range of measurement uncertainty – for oxygenated fuel.



**Figure 19.** The average  $CO_2$  emissions in the NEDC (UDC + EUDC) for conventional diesel fuels and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v

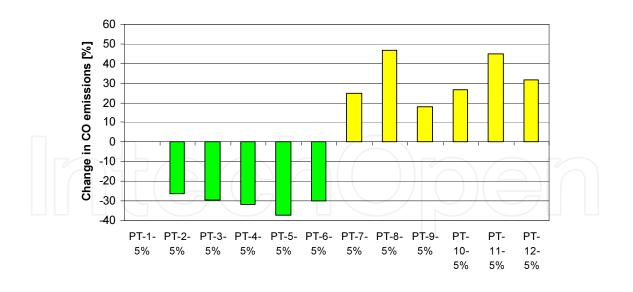


**Figure 20.** The average fuel consumption in the NEDC (UDC + EUDC) for conventional diesel fuels and oxygenated fuels containing individual oxygenates at a concentration of 5% v/v

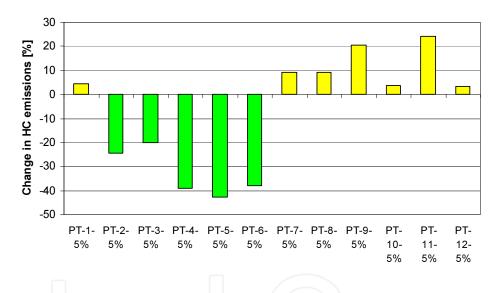
#### 3.3.6. A summary of preliminary results

Figures 21–24 show the percentage changes in exhaust emissions of the test vehicle in the NEDC by using fuels containing individual oxygenates at a concentration of 5% v/v. The results indicate that some of the oxygenated fuels caused a reduction of CO and HC, and all the fuel types tested caused a reduction of emissions of PM and an increase in NO<sub>x</sub> emissions.

It should be emphasized that the scale of emission changes of individual exhaust components caused by the different oxygenated fuels varied. It was generally found that fuels containing oxygenated compounds from the group of glycol ethers resulted in the largest, of up to 40%, reduction in emissions of CO and HC with an increase of several percent in NO<sub>x</sub> emission and a moderate reduction of PM emission. Fuels containing carbonates provided the greatest, even by more than 30%, reduction in PM emissions; however, they also increased the emissions of other toxic components of exhaust gases. The advantages of fuels containing maleates were no increase in NO<sub>x</sub> and PM reduction greater than when using glycol ethers, although using maleates increased emissions of CO and HC. The effect of oxygenated fuel containing n-



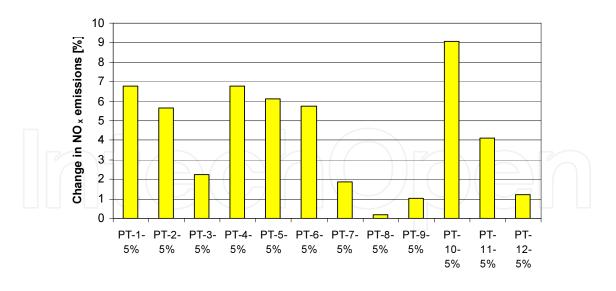
**Figure 21.** The percentage change in CO emissions in the NEDC (UDC + EUDC) for oxygenated fuels containing individual oxygenates at a concentration of 5% v/v with respect to regular diesel fuel



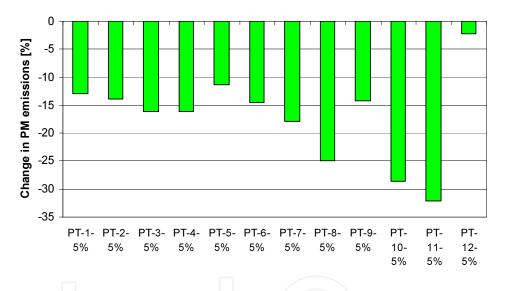
**Figure 22.** The percentage change in HC emissions in the NEDC (UDC + EUDC) for oxygenated fuels containing individual oxygenates at a concentration of 5% v/v with respect to regular diesel fuel

butanol on the exhaust emissions is rated as unfavorable, because it resulted in a significant increase in CO emissions at a much lower decrease in PM emissions than for other fuels used.

The literature on the influence of oxygenates on the PM emissions for CI engines contains diverging opinions on whether the reduction in PM emissions depends only on the amount of oxygen introduced to the fuel [21, 26, 32, 33], or also on the type of the oxygenated compound, which is to be used [17, 23, 27, 29]. This divergence of opinion is based on the fact that very few papers [14, 24] present the results of using a wide variety of oxygenates under identical measurement conditions. Comparison of the change of PM emissions in the NEDC shown in Fig. 25 to the oxygen content in the individual oxygenated fuels indicates that 1% of the oxygen contained in the fuel corresponds in most of the cases to a reduction in emissions



**Figure 23.** The percentage change in NO<sub>x</sub> emissions in the NEDC (UDC + EUDC) for oxygenated fuels containing individual oxygenates at a concentration of 5% v/v with respect to regular diesel fuel



**Figure 24.** The percentage change in PM emissions in the NEDC (UDC + EUDC) for oxygenated fuels containing individual oxygenates at a concentration of 5% v/v with respect to regular diesel fuel

of PM in the NEDC by 7–10%. It can be concluded that the oxygen content of fuel is a very important, but not the only, parameter determining the level of reduction of PM emissions.

In assessing the impact of individual oxygenates on the exhaust emission, what should be taken into account, first of all, are the changes in the emission of PM and  $NO_x$ , including the mutual relation of these changes (i.e.  $PM/NO_x$  trade-off), due to the fact that they are, on the one hand, the most harmful components, and on the other, the most difficult to remove from the exhaust gas. The effect on emissions of CO and HC should only be taken into account in the longer term, particularly if the impact is significant. On this basis, six oxygenates (shown in the Table 6), which resulted in the most favorable changes in exhaust emissions during preliminary tests described in this chapter, were selected for further, more detailed studies.

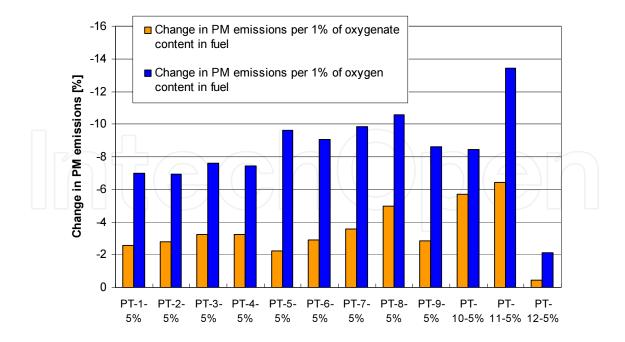


Figure 25. The relative effect of oxygen compounds and oxygen content of the fuel on PM emissions in the NEDC

Oxygenate no.	Chemical name	
3	Triethylene glycol dimethyl ether	
4	Tetraethylene glycol dimethyl ether	
5	Diethylene glycol dibutyl ether	
6	Dipropylene glycol dimethyl ether	
8	Diethyl maleate	
11	Diethyl carbonate	

Table 6. Oxygen compounds selected for further, more detailed analysis

#### 3.4. Evaluation of the impact of oxygenated compounds based on their content in the fuel

The relationship between the changes in emissions and the content of oxygenated compounds in the fuel is a key issue from the point of view of rational use of oxygenates. Recognition of these relationships also provides additional data for the analysis of the mechanisms of the effect of oxygenates on emissions of toxic exhaust components. The literature reports on the relationship between PM emissions and the oxygen content in the fuel, which is usually defined as approximately linear [20, 26]. Figure 26 shows the results of the influence of the six selected oxygenates used at concentrations of 5 and 10% v/v on the change in emissions of CO, HC, NO<sub>x</sub>, and PM in the NEDC.

Analyzing these results reveals different impacts of fuels containing components from different chemical groups. In particular, the different impact on emissions between fuels containing glycol ethers (components 3–6), maleates, or carbonates (components 8 and 11).

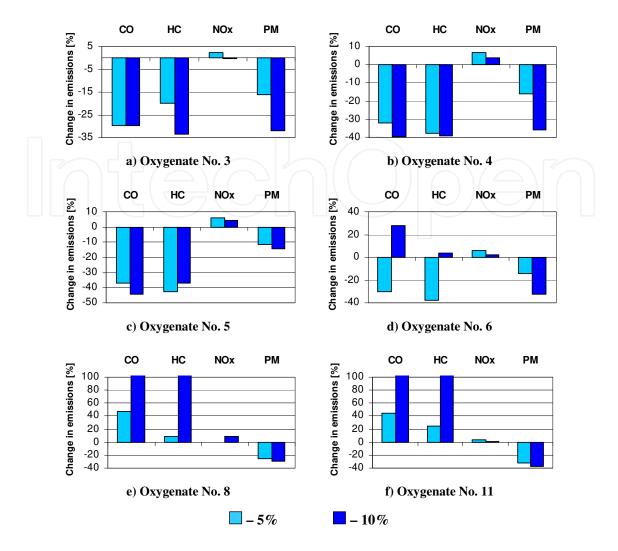


Figure 26. The impact of oxygenate content on the change in exhaust emissions over the NEDC

In the case of glycol ethers, it can generally be said that the amount of oxygenated compounds, and thus the amount of oxygen in the fuel, affects PM emissions the most. The reduction of this emission is generally proportional to the content of the oxygenated component/oxygen. Doubling the content of components 3, 4, and 6 resulted in twice the reduction in PM emissions. Increasing the content of the oxygenated components also resulted in the reduction of  $NO_x$  emission compared to fuels containing a smaller amount of the oxygenate. Taking into account the PM/NO<sub>x</sub> relationship, an increase in the levels of these oxygenated components from 5 to 10% produced clearly beneficial effects.

For fuels containing components 8 and 11, doubling the oxygenated component content in the fuel did not cause a significant reduction in PM emissions. At 5% content, the glycol ethers were clearly less effective in reducing PM emission than diethyl maleate and diethyl carbonate. At 10% content, the efficiency of the best components from all tested chemical groups was similar – PM reduction of 30–40%. For most of these fuels, favorable  $NO_x$  emission values at a higher content of oxygenated component were also reported.

In relation to CO and HC, it can be generally stated that the oxygenated compounds from the group of glycol ethers were effective in reducing CO and HC emissions in NEDC, while increasing the concentration of the individual oxygenates caused various effects. For component 3, a significant reduction in HC emissions at the same level of CO emission (Fig. 26a) was achieved. For component 4, CO emission was decreased by an additional 8 percentage points, with the same level of HC emission (Fig. 26b). For component 5, CO emission was reduced by a few extra percentage points (Fig. 26c), while increasing emissions of HC in a similar range. For component 6, an increase in CO and HC emissions was reported (Fig. 26d) at higher concentrations of oxygenated components.

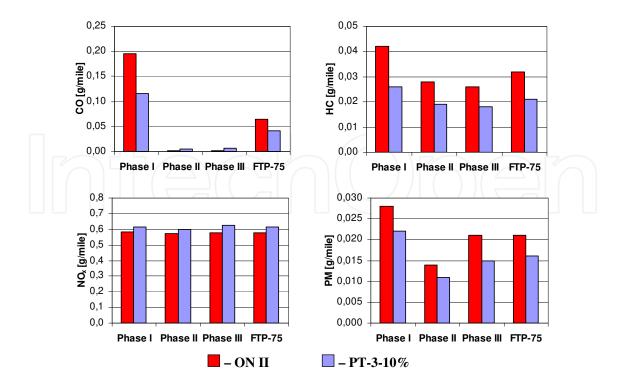
Emissions of CO and HC for fuels containing components 8 and 11 (Fig. 26e and f) were clearly higher than for neat diesel, and increasing the oxygen content of the fuel greatly increased this unfavorable phenomenon. For a content of 10% of the oxygenated components 8 and 11, CO and HC emissions were over 100% higher than for neat diesel.

In the light of these results, it can be concluded that the use of oxygenated components in the concentration of 10% is preferred especially for components 3 and 4, where the higher content in the fuel meant significantly lower emissions of PM, and the same or more favorable emission levels of other toxic exhaust components as for the 5% content.

#### 3.5. The effect of oxygenates on exhaust emissions in the conditions of different test cycles

The level of exhaust emissions for a vehicle of given emission class largely depends on the operating conditions of its engine, in particular parameters such as speed, load, thermal state, as well as the dynamics of changes in these operating conditions. To assess the impact of engine operating conditions on the reduction in exhaust emissions as a result of addition of oxygenated compounds, the previously performed emission tests in the NEDC regime were followed up with the same type of research carried out for the FTP-75 cycle. Despite being the most widely used worldwide cycles in research of exhaust emissions, the conditions of performing these two cycles are significantly different. Both drive cycles are described in more detail in Section 3.2, but at this point, it should be emphasized that the FTP-75 cycle is more dynamic than NEDC. It is characterized by a more aggressive acceleration, smaller share of engine idling and maximum speed for the cycle (which is slightly lower than for the NEDC) reached in its early stages already.

Figure 27 shows, as an example of the tests performed, a comparison of the results of measurements of exhaust emissions in the individual phases and the average over the FTP-75 cycle for the test vehicle powered by diesel fuel and oxygenated fuel PT-3-10%. It can be seen that the high CO emission occurs only in the first phase of the FTP-75 cycle. In further phases, the engine thermal condition is stabilized, and the emission significantly reduced. HC emissions are also highest in the first phase, but the decrease in emissions in subsequent phases is not as significant as for CO. This can be related to different efficiencies of catalytic converter in relation to CO and HC emission reduction. It should be pointed out that the exhaust gas temperature in the different phases of the FTP-75 cycle was lower than in the EUDC phase of the NEDC. NO<sub>x</sub> emissions during all phases reached similar values, while for PM emissions,



**Figure 27.** Exhaust emissions in the various phases and the average over the FTP-75 cycle for the test vehicle powered by diesel fuel and oxygenated fuel PT-3-10%

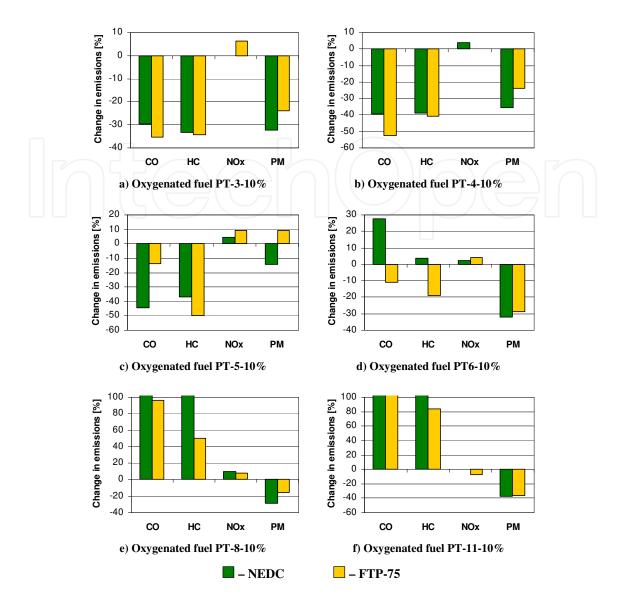
there is a clear dependence on the thermal state and the engine load in the different phases of the FTP-75 cycle.

Figure 28a–f compares the change in exhaust emissions over the NEDC and FTP-75 test cycles as a result of application of oxygenated fuels: PT-3-10%, PT-4-10%, PT-5-10%, PT-6-10-%, PT-8-10%, and PT-11-10%, respectively. Analysis of the results indicates that when there was a significant change in emissions (over 10%), then the direction of emission changes caused by the use of the oxygenated fuel was the same for both test cycles. For most oxygenated fuels, a similar scale of changes in CO and HC emissions was achieved in both test cycles. Changes in NO<sub>x</sub> emissions for all oxygenated fuels in both cycles were small – less than 10%. Thus, only PM emissions can point to a clear link between the level of emission changes caused by the use of oxygenated fuels and the conditions of the test cycle. For all the examined oxygenated fuels, and for most significantly, a greater reduction in PM emissions was achieved in the NEDC than the FTP-75 cycle conditions. Larger maximum load on the engine found in the EUDC phase is thought to have been a significant factor.

#### 4. Conclusions

1. The use of oxygenated fuels has a significant impact on the level of exhaust emissions from diesel engines without particulate filters. This effect is significant even at low oxygenate content in the fuel (5% v/v).

The Study on the Influence of Diesel Fuel Oxygenates on Exhaust Emissions 71 http://dx.doi.org/10.5772/62005



**Figure 28.** Comparison of changes in exhaust emissions as a result of application of oxygenated fuels over the NEDC and the FTP-75 cycle conditions

- 2. When using oxygenated fuels, irrespective of the component, a significant reduction in PM emissions and a slight increase in NO<sub>x</sub> emissions were found in the both NEDC and FTP-75 cycle. Changes in CO and HC emissions depend on the type of oxygenated compound used.
- **3.** The main parameter that determines the degree of reduction in PM emissions is the oxygen content in the fuel. After using various oxygenates at a concentration of 5% v/v, it was found that 1% of the oxygen present in the fuel caused the PM emissions of a Euro 4 class vehicle in NEDC to be reduced by 7–10%.
- **4.** The type of an effect that oxygenated fuels have on CO and HC emissions is related to oxygen content to a lesser extent, and mainly depends on their autoignition properties.

Fuels containing glycol ethers cause a reduction of CO and HC emission, while fuels containing maleates, carbonates or butanol cause its growth.

- 5. Increasing the concentration of oxygenates in the fuel from 5 to 10% v/v causes different effects for different components. The most favorable changes in emissions were observed for glycol ethers where increased concentration was usually followed by a further significant reduction in PM emissions, and, to a lesser extent, reductions in CO and HC emissions. For maleates and carbonates, changes were less favorable, because a slight decrease in PM emissions was accompanied by a significant increase in CO and HC emissions.
- 6. The effect of the test conditions (NEDC/ FTP-75 cycle) on changes in exhaust emissions occur primarily for PM where a greater reduction was achieved in the NEDC. Changes in NO<sub>x</sub> emissions for all fuels in both cycles do not exceed 10%.
- 7. The slight increase in  $NO_x$  emissions and substantially lower PM emissions associated with the use of oxygenated fuels should be judged as a favorable change in the correlation of PM/NO<sub>x</sub> emissions (the PM/NO<sub>x</sub> trade-off). In this situation, there is a possibility for reducing the exhaust emissions of both aforementioned components at the same time.

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#### References

- [1] European Environment Agency, www.eea.europa.eu, access on 15 June 2015.
- [2] United States Environmental Protection Agency (EPA): Health Assessment Document For Diesel Engine Exhaust, Waszyngton, 2002.
- [3] European Automobile Manufacturers' Association (ACEA), www.acea.be, access on 15 June 2015.
- [4] Główny Urząd Statystyczny: Gospodarka paliwowo-energetyczna w latach 2011, 2012, Warszawa 2013 (Polish Central Statistic Office: Energy Statistics 2011, 2012, Warsaw 2013).
- [5] Benazzi E.: Gasoline and Diesel Imbalances in the Atlantic Basin. Petroleum Technology Quarterly, nr 2/2011.

- [6] Merkisz J., Kozak M.: Internal Combustion Engines at the Beginning of the Third Millennium. International Scientific Conference: Development of Design of Internal Combustion Engines and Quality of Fuels to Meet Future Levels, Kraków 20-21.06.2011.
- [7] Rutherford J.A.: Effects of Gasoline Properties on Emissions of Current and Future Vehicles – T50, T90, and Sulfur – Auto/Oil Air Quality Improvement Research Program. SAE Paper 952510, 1995.
- [8] Tsuda H., Ito T., Nakamura K.: Japan Clear Air Program (JCAP) Program Objectives and Design. SAE Paper 1999-01-1481.
- [9] MacKinven R., Hublin M.: European Program on Emissions, Fuels and Engine Technologies Objectives and design. SAE Paper 961065, 1996.
- [10] Rickeard D.J., Bonetto R., Singer M.: European Programme on Emissions, Fuels and Engine Technology (EPEFE) – Comparison of Light and Heavy Duty Diesel Studies. SAE Paper 961075, 1996.
- [11] Murphy M.: Oxygenate Compatibility with Diesel Fuels. SAE Paper 2002-01-2848.
- [12] Natarajan M. et al.: Oxygenates for Advanced Petroleum-Based Diesel Fuels: Part 1. Screening and Selection Methodology for the Oxygenates. SAE Paper 2001-01-3631.
- [13] Bertola A., Boulouchos K.: Oxygenated Fuels for Particulate Emissions Reduction in Heavy-Duty DI-Diesel Engines with Common Rail Fuel Injection. SAE Paper 2000-01-2885.
- [14] Delfort B., Durand I., Jaecker-Voirol A., Lacome T., Paille F., Montagne X.: Oxygenated Compounds and Diesel Engine Pollutant Emissions Performances of New Generation of Products. SAE Paper 2002-01-2852.
- [15] Murphy M., Lanning L.: Vapor Pressures of Diesel Fuel Oxygenate Blends. SAE Paper 2002-01-2850.
- [16] Murphy M.: Safety and Industrial Hygiene Issues Related to the Use of Oxygenates in Diesel Fuels. SAE Paper 1999-01-1473.
- [17] Stoner M., Litzinger T.: Effects of Structure and Boiling Point of Oxygenated Blending Compounds in Reducing Diesel Emissions. SAE Paper 1999-01-1475.
- [18] Gonzalez M.A., Piel W., Asmus T., Clark W., Garbak J., Liney E., Natarajan M., Neageli D.W., Yost D., Frame E.A., Wallace J.P.: Oxygenates Screening for Advanced Petroleum-Based Diesel Fuels: Part 2. The Effect of Oxygenate Blending Compounds on Exhaust Emissions. SAE Paper 2001-01-3631.
- [19] Gonzalez M.A., Clark W., Wolf L.R., Garbak J.A., Wright K.J., Natarajan M., Yost D.M., Frame E.A., Kenney T.E., Ball J.C., Wallace J.P., Hilden D.L., King D.: Impact of Engine Operating Conditions on Low-NO<sub>x</sub> Emissions in a Light-Duty CIDI Engine Using Advanced Fuels. SAE Paper 2002-01-2884.

- [20] Murayama T. et al.: Simultaneous Reductions of Smoke and NO<sub>x</sub> from a DI Diesel Engine with EGR and Dimethyl Carbonate. SAE Paper 952518, 1995.
- [21] Akasaka Y., Sakurai Y.: Effects of Oxygenated Fuel and Cetane Improver on Exhaust Emission from Heavy-Duty DI Diesel Engines. SAE Paper 942023, 1994.
- [22] Kocis D., Song H., Lee H., Litzinger T.: Effects of Dimethoxymethane and Dimethylcarbonate on Soot Production in an Optically-accessible DI Diesel Engine. SAE Paper 2000-01-2795.
- [23] Hallgren B., Heywood J.: Effects of Oxygenated Fuels on DI Diesel Combustion and Emissions. SAE Paper 2001-01-0648.
- [24] Yeh L., Rickeard D., Duff J., Bateman J., Schlosberg R., Caers R.: Oxygenates: An Evaluation of their Effects on Diesel Emissions. SAE Paper 2001-01-2019.
- [25] Porai P., Chandrasekaran S., Subramaniyam S., Jancirani J., Sahoo B.: Combustion and Performance of a Diesel Engine with Oxygenated Diesel Blend. SAE Paper 2004-01-0082.
- [26] Nabi M., Minami M., Ogawa H., Miyamoto N.: Ultra Low Emission and High Performance Diesel Combustion with Highly Oxygenated Fuel. SAE Paper 2000-01-0231.
- [27] Mueller C.J., Martin G.C.: Effects of Oxygenated Compounds on Combustion and Soot Evolution in a DI Diesel Engine: Broadband Natural Luminosity Imaging. SAE Paper 2002-01-1631.
- [28] Buccholz B.A., Mueller C.J., Upatnieks A., Martin G.C., Pitz W.J., Westbrook, C.K.: Using Carbon-14 Isotope Tracing to Investigate Molecular Structure Effects of the Oxygenate Dibutyl Maleate on Soot Emissions from a DI Diesel Engine. SAE Paper 2004-01-1849.
- [29] Boot M., Frijters P., Klein-Douwel R., Baert R.: Oxygenated Fuel Composition Impact on Heavy-Duty Diesel Engine Emissions. SAE Paper 2007-01-2018.
- [30] Bielaczyc P., Kozak M., Merkisz J.: Effects of Fuel Properties on Exhaust Emissions From the Latest Light-Duty DI Diesel Engine. Advanced Emission Aftertreatment Systems. SAE International, SP-1796, 2003.
- [31] Kozak M.: Wpływ wybranych parametrów paliwa na emisję toksycznych składników spalin z silników o zapłonie samoczynnym. Praca doktorska, Politechnika Poznańska, Poznań 2004. (Kozak M.: The Influence of Some Diesel Fuel Properties on Exhaust Emissions from Diesel Engines. PhD Thesis, Poznan University of Technology, Poznan 2004).
- [32] Miyamoto N., Ogawa H., Nurun N., Obata K., Arima T.: Smokeless, Low NO<sub>x</sub>, High Thermal Efficiency, and Low Noise Diesel Combustion with Oxygenated Agents as Main Fuel. SAE Paper 980506, 1998.

[33] Tree D., Svensson K.: Soot Processes in Compression Ignition Engines. Progress in Energy and Combustion Science vol. 33 (2007).







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