

Emissions of Selected Pollutants While Applying of Specific Additive EnviroxTM

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Abstract: - The value of selected emission factors was monitored in operation on older type of engine testing bench using diesel and being compared with the same parameters monitored under similar conditions with addition of additive EnviroxTM. It was found out that additive based on dispersed nanoparticles of cerium dioxide reduces emission of particulate matter, hydrocarbons and nitrogen oxides, while emissions of carbon dioxide remained comparable or slightly lower and carbon monoxide emissions even significantly increased. Dependence of tested emission on reduced torque, engine power and revolutions was observed as well.

Key-Words: - Additive, atmosphere, carbon oxides, cerium dioxide, diesel fuel, emission factor, nanoparticles, nitrogen oxides, particulate matter, pollutant.

1 Introduction

Escalating activities of human society aiming at ensuring a higher standard of living have brought a number of negative externalities. Among the important and by the lay and professional community strongly discussed externalities currently belongs the increase of burden to the atmosphere caused by industrial, agricultural and mining activities, energy production, waste management and household management. Mobile assets, including primarily transport of passengers and cargo have significantly contributed to the increase in ambient air pollution as well [1, 2].

It is estimated that transport contributes to overall air pollution by carbon monoxide (CO) and carbon dioxide (CO₂) emissions by 37%, a mixture of nitric oxide (NO) and nitrogen dioxides (NO₂), generally known as nitrogen oxides (NO_x) by 30%, and volatile organic compounds (VOCs), by approximately 24% [3].

Besides the facts mentioned above from the quantitative aspect of the dominant pollutants, traffic is also producer of other, mainly health and eco highly harmful substances. Furthermore, the waste generated during the operation, due to accidents and end of life vehicles contribute as indispensable part to the environmental contamination, including the troposphere [3].

Emitted pollutants have often non-quantifiable impact on population morbidity and mortality, ecosystem

functionality and value of social assets. [3, 4, 5].

As transportation is currently one of the world's most dynamically developing sectors it is necessary to pay enormous attention to the reduction of emissions. This requirement is highly supported by the use of cars at the expense of public transport and permanently increasing ratio of road haulage transport to rail transport [1, 6].

The submitted paper is focused on evaluating the quantities of CO₂, CO, NO_x, VOCs in the form of unburned hydrocarbons C_xH_y, and particulate matter (PM) emissions while applying conventional diesel fuels without and with the additive based on dispersed cerium dioxide (CeO₂) nanoparticles.

2 The Analysis of Current State

Besides undisputable advantages connected with an intensive development of transport there are number of new negative phenomena. The most important factors are higher accident rate, mortality in traffic accidents, changed scenery and morphology of landscape, barriers for wild and migrating animals, reduction of biodiversity, increased noise pollution, waste, vibrations, contamination of individual environmental elements caused by exhaust emissions, release of dangerous substances, use of spreading salt in roads in winter. And last but not least an appropriation of land is an important factor, especially the appropriation of agricultural land

resources for the construction and re-construction of road and highway network [3].

A number of other hazardous substances are produced apart from the quantitatively dominant pollutants, which include CO₂, CO, mix of nitrogen oxides NO_x, VOCs [2]. These are mainly nitrous oxide (N₂O), sulfur dioxide (SO₂), ozone (O₃), heavy metals particularly lead, cadmium, nickel, and chromium, platinum group metals as platinum, palladium and ruthenium, 1,3-butadiene, benzene, toluene, o-, m-, p-xylenes, phenols, aldehydes, ketones, tar, persistent organic substances such as polychlorinated biphenyls and terphenyls, polycyclic aromatic hydrocarbons, dibenzo-p-dioxins, dibenzofuranes etc. It should not be forgotten to include solid particles which are able to adsorb the number of contaminants on their surface thereby greatly increasing their hazard [3, 7, 8].

The dependence of contaminants concentration in the atmosphere on the time shows an exponential character especially in city areas with heavy traffic they reach the values to which only a few organisms are able to adapt [4].

Recently, considerable attention is devoted to the health effects of emissions of suspended PM. The danger lies mainly in its ability to bind a number of toxic inorganic and organic pollutants to the surface. The biggest problem represent particles smaller than 2.5 μm (PM_{2.5}) which cannot be captured in the upper respiratory tract. PM_{2.5} and smaller fractions therefore penetrate into the alveoli and as the efficiency of their removal is limited, inhalation causes serious health problems [1].

Epidemiological studies have attributed not only short but also chronic effects to PM, especially in the long term exposure, even at lower concentrations. Short-term effects are reflected in the form of mechanical damage to the cornea, difficult breathing, deterioration of health among asthmatic patients, and lung tissue damage leading to the fibrillation of lungs [1, 8]. Long-term effects can be seen in the increased incidence of bronchitis, cardiovascular and reproduction disorders and, in case of extreme exposure, cancer of mainly respiratory organs [9, 10].

The polycyclic aromatic hydrocarbons (PAHs) belong to highly toxic pollutants, which are adsorbed on suspended particulates. PAHs also include azaarenes, oxaarenes, thiaarenes and their derivatives, for example alkyl- oxo- or nitro- derivatives. These compounds originate from PAH by the substitution of carbon in a benzene cycles by the atoms of N, O, or S and may be identified and quantified in the PAHs fractions, because their physico-chemical properties are similar. Diesel engines of trucks are the main sources of emissions of PAHs. The low-molecular PAHs with two and three benzene cycles in a molecule are present

mostly in the gaseous form while the high-molecular PAHs with four and more benzene cycles in a molecule are bound mostly to the PM [3].

The amount of pollutants emitted by a truck is dependent on many factors. If driving style, terrain and weather conditions are not considered, and then the quantity of produced emissions depends mainly on the following factors [2]:

- a) The type and technical parameters of engine [11, 12];
- b) Principles of oxidation catalyst [13, 14];
- c) The type and amount of biodiesel added to basic fuel [15, 16];
- d) The composition and quality of diesel oil [12, 17, 18];
- e) The type and composition of additives added to the basic fuel [19, 20].

The industry producing and supplying fuels operates with a number of additives that can be added to the diesel fuel. These can be divided into three main areas depending on their nature [21]:

- a) refinery additives;
- b) safety increasing or legally required additives
- c) additives for improvement of technical parameters and increase of fuel performance;

Refinery additives are added to fuels during the production and refining mostly for improvement of:

- α) flow characteristics of middle fractions in order to prevent freezing of fuel in winter;
- β) lubricating ability of fuel, used to compensate the loss of these capabilities in the production of fuels with low and ultra-low sulfur content;
- γ) cetane numbers in order to comply with requirements to provide the flashpoint without cost-intensive refining processes;

Safety increasing or legally required additives can be added at any stage of the delivery cycle. Conventional additives used for these purposes are:

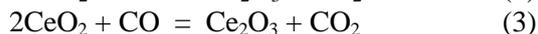
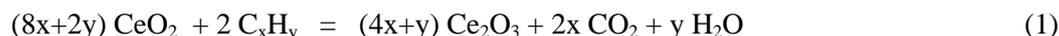
- α) dye used to color the fuel into the red for agricultural purposes;
- β) markers (for easy identification of fuel) that do not taint the fuel, but can be extracted and then identified by a simple laboratory or road test;

Additives for improvement of technical parameters and increase of performance in diesel are usually dispensed in a distribution terminal or later by the end user into the storage tank or directly into the fuel tank of a vehicle. Common additives in this category include:

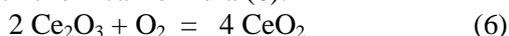
- α) antifoaming means of limiting foam;
- β) additives increasing cetane number and improving fuel ignition characteristics;
- γ) anti-corrosion additives preventing corrosion in storage reservoirs and tanks of vehicles;
- δ) detergents applied with an intention to maintain and ensure clean injectors.

The EnviroxTM is a dispersion of CeO₂ nanoparticles in aliphatic and cycloaliphatic hydrocarbons. This diesel

fuel additive should, according to promotional materials of Oxonica (now Energenics) Company, improve more than only the technical parameters of fuel [21]. Unlike conventional additives, Envirox™ is advertising efficiency throughout the combustion process, because most of the common ingredients decompose under the thermodynamic conditions prevailing in the engine combustion chamber. The Envirox™ enables engine to gain more energy from fuel and therefore reduce its



CeO₂ regeneration catalyst is carried out in accordance with chemical formula (6).



Statistically validated operational tests carried out by Oxonica Company provide evidence that the recommended dosage of 5 to 10 ppm w/w CeO₂ can achieve relevant reductions in fuel consumption (about 5-12%) while reducing the emissions of CO₂, CO, NO_x, C_xH_y and PM. The additive is also compatible with all common diesel additives [22, 24].

The calculation of the *i*-th pollutant emission is based on the knowledge of an emission factor Ef_m^i [g kg⁻¹]. The value of emission factor is given in accordance with formula (7) as the weight of the *i*-th pollutant per a unit

$$Ef_l^i = Ef_m^i \times \frac{m_F}{l} = Ef_m^i \times FC \times \rho_F = y_i^d \times \frac{M_i \times n^d}{M_F \times N_F} \times FC \times \rho_F \quad (8)$$

In equation (2) *FC* further indicates fuel consumption [dm³ km⁻¹], ρ_F [kg dm⁻³] fuel density and other symbols have the same meaning as in equation (7)

3 Applied Methods and Devices

Tests to determine emission levels were carried out on the VOP-026 Sternberk Company engine testing bench with the Schenk 0-900 kW electric eddy current brake operating in the range of 0-6.0×10³ [min⁻¹] revolutions. NM-54 Diesel was used as the primary fuel, which was mixed with 2.5×10⁻⁴ volumes of additives in an alternative version of comparative tests. The concentrations of CeO₂ found in diesel fuel with addition of Envirox™ by inductively coupled plasma atomic emission spectroscopy was 7.6 ppm w/w, which corresponds to suppliers' requirement.

Diesel engine with the following characteristics was used for the tests: Tatra T3 930-31 four-stroke, naturally aspirated engine with direct injection, air-cooled, engine cylinder capacity of 1.9×10⁴ cm³, cylinder

consumption, remove the residual soot deposits in engine combustion chamber while minimizing the formation of some contaminants [22]. Chemistry of combustion process is presented in equation (1) for the more efficient use of fuel energy, in equation (2) for the elimination of carbon deposits in engine combustion chamber and equations (2) – (5) for the reduction of pollutants in emissions [23].

mass of consumed diesel fuel *F* [2, 25]:

$$Ef_m^i = m_i \times m_F^{-1} = y_i^d \times \frac{M_i \times n^d}{M_F \times N_F} \quad (7)$$

where *m_i* [g] is the mass of the *i*-th pollutant, *m_F* [kg] weight of fuel, *M_i* molar molecular weight of the *i*-th pollutant [g mol⁻¹], *M_F* [kg mol⁻¹] molar molecular weight of fuel *F*, *n^d* [mol] or *N_F* [mol] substance amount of dry exhaust gas or consumed fuel, and finally *y_i^d* molar fraction of the *i*-th pollutant in dry exhaust gases.

To quantify the emission of *i*-th pollutants in relation to vehicle distance *l* [km] it is also possible to use the emission factor Ef_l^i [g km⁻¹] defined by equation (8), which was derived from equation (7) that was shown in our previous publication [2].

diameter/stroke 120/140 mm, over head valve called pushrod engine, and a compression ratio of 1:16. The engine had 12 cylinders in two separate lines at 90°. Rated engine output was 235 kW ± 10% at revolutions 2.2×10³ min⁻¹ with a maximum torque of 1.13×10³ N m at revolutions 1.4×10³ ± 200 min⁻¹.

It was necessary to know the concentration of combustion gas emissions in order to calculate the emission factor for the particular pollutants. The gas emission testing was performed by a combined device called ECOM-JN for analyzing the combustion gas composition, equipped with electrochemical sensor of the English Company City Technology, which enabled the determination of CO, NO, NO₂, and O₂ concentration. Ranges and uncertainty in the determination of individual quantities are listed in Table 1.

Sample of combustion gas was taken by a vacuum pump tube probe analyzer. The current air mass was led from the probe tube by unheated tube to filters and water separators analyzer and then to pollutant sensors. It was

possible to determine the concentration of CO and NO_x by applying unheated tube between the probe and analyzer as possible combustion gas condensation on the way did not affect their values.

Table 1 Ranges and uncertainties in determination of measured quantities

Pollutant	Range [ppm]	Uncertainty of measurement	
		20 % range	100 % range
NO	0-2.0×10 ³	2 %	5 %
NO ₂	0-2.0×10 ²	2 %	5 %
CO	0-1.0×10 ⁴	2 %	5 %
O ₂	0-2.1×10 ⁵	2 %	5 %

C_xH_y content was tested by analyzer operating on the principle of flame ionization detector (FID). The principle is based on the effect that the C-H bond gets ionized during the burning of hydrocarbons in the hydrogen flame of the analyzer burner combustion chamber. If the electrodes placed in the burner are energized, the value of flowing current is proportional to the number of free ions including organic matter content in the sample. The sample of gases was transported into the FID unit through a heated tube of analyzer vacuum pump.

The manual gravimetric method was used to measure the concentration of PM. The method consists in inserting the probe into the measuring point and extracting the dusty air mass sample, so that there was the same rate of bearing air mass (so-called isokinetic sampling) in its aperture and around the probe. Extracted and measured volume of sampled air mass has been deprived of solid additives on a special filter and later, in the prescribed manner, the weights of the captured particles were determined. An extraction set with zero sampling probe was used for the measurement, with a filter assembly positioned outside the pipe. Setting the isokinetic sampling with zero probe was achieved by regulation of exhaust gas quantity so that the pressure differential at zero probe reached zero. The planar filter used by the Amersil-filpap of Steti Company is manufactured from 100 % borosilicate glass microfibers without organic bonding agents. The paper is resistant to temperatures up to 770 K and is able to retain greater amount of impurities before any increase in resistance to the passage of filtered media.

Measurement of ventilation parameters was carried out according to standard operating procedure [26]. The "L" shaped Prandtl probe of 8 mm diameter was used to measure the rate of combustion gases. The probe was fixed in the middle section of the measuring extension.

The diagram of the location of measuring point

results from Figure 1 where the combustion gas velocity was measured with the Prandtl probe with gas temperature measured with K (NiCr-Ni) thermocouple simultaneously.

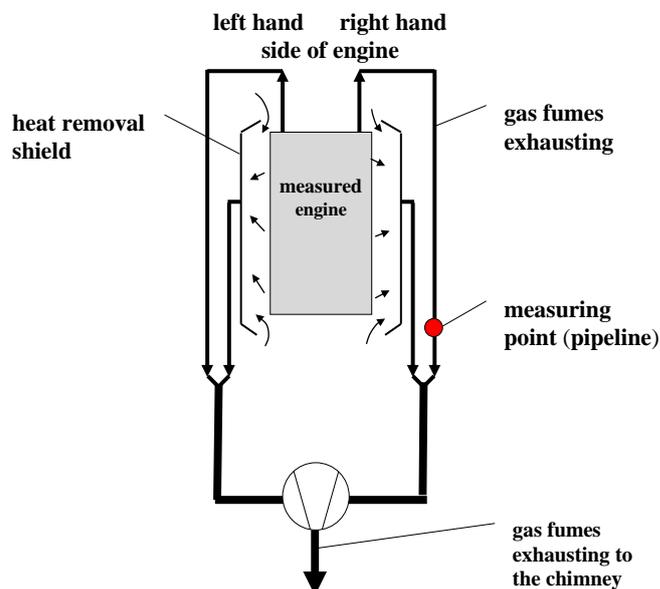


Fig. 1 Diagram of the location of measuring point

The Figure 2 demonstrates real sample collection point in the VOP-026 Sternberk Company.



Fig. 2 Real sample collection point in the VOP-026 Sternberk Company

4 Outcomes and Discussion

3.2.1 Mass balance

Calculation of emission factors was based on equation (9) characterizing the fuel combustion, further based on the carbon mass balance equation (10),

hydrogen mass balance equation (11), oxygen mass balance equation (12), and nitrogen material balance equation (13), on the substance amount of the dry air components N^d [mol] entering into combustion process or the dry gases n^d [mol] exiting the process according to relation (14) or (15), and finally based

on measurements of the concentration of particular contaminants and oxygen coming out of combustion process. Fuel combustion in the engine and material balance was considered under simplified conditions in the absence of trace amounts of N_2O , NH_3 , SO_2 , H_2S , polycyclic aromatic hydrocarbons, etc.

$$e/2 N_2 + C_a H_b O_c + [a \times (1-z/2) + b/4 - c/2 + d \times (1-w/2)] O_2 = a \times (1-z) CO_2 + a \times z CO + (b/2) H_2O + d \times (1-w) NO_2 + e \times w NO \quad (9)$$

$$a \times (N_F - n_F) = n_{CO_2} + n_{CO} \quad (10) \quad b \times (N_F - n_F) = 2n_{H_2O} \quad (11)$$

$$2(N_{O_2} - n_{O_2}) + c \times (N_F - n_F) = n_{H_2O} + 2n_{CO_2} + n_{CO} + 2n_{NO_2} + n_{NO} \quad (12)$$

$$2(N_{N_2} - n_{N_2}) = n_{NO_2} + n_{NO} \quad (13) \quad N^d = N_{N_2} + N_{O_2} + N_{CO_2} \quad (14)$$

$$n^d = n_{N_2} + n_{O_2} + n_{CO_2} + n_{CO} + n_F + n_{NO_2} + n_{NO} \quad (15)$$

In the equations (10) - (15) N [mol] with the corresponding subscript represents amount of substance in the process of entering gases N_2 , O_2 , and CO_2 , or fuel F n [mol] with corresponding subscript represents amount of substance from the combustion process exiting exhaust gases, i.e. N_2 , O_2 , CO_2 , CO , NO_2 , NO , and fuel F as hydrocarbons (C_xH_y) and finally superscript d indicates that these are dry gases.

To simplify the record of other relations a substitution (16) was introduced where symbols a , b , c are stoichiometric coefficients in equation (9).

$$\omega = \frac{b-2c}{4a} = \frac{\beta}{4} - \frac{\gamma}{2} \quad (16)$$

Molar fractions Y_i^d and y_i^d of i -th element in dry inlet air or exiting gas are defined by relations (17) or (18):

$$Y_i^d = N_i \times (N^d)^{-1} \quad (17)$$

$$y_i^d = n_i \times (n^d)^{-1} \quad (18)$$

where N_i [mol] represents the substance amount of i -th component in the inlet wet air, n_i [mol] substance amount of i -th component in wet output, N_V^d [mol] is the substance amount of dry gases entering into the combustion process and n^d [mol] is the substance amount of dry gases exiting the process.

Based on the mass balance equations with the acceptance of relations (16) - (18) an equation (19) and (20) can be derived. These equations are needed to calculate emission factors. The meaning of symbols used in these equations is in respect of previous signs in equations (10) - (18).

$$\frac{n^d}{N_F} = \frac{a \times [1 + \omega \times (1 - Y_{O_2}^d)]}{Y_{O_2}^d - y_{O_2}^d + (1 - Y_{O_2}^d) \times \frac{y_{CO}^d}{2} - \left(1 - \frac{Y_{O_2}^d}{2}\right) \times y_{NO_2}^d - \frac{y_{NO}^d}{2} + [a \times (1 + \omega) - (1 + a\omega) \times Y_{O_2}^d] \times y_F^d} \quad (19)$$

$$n^d = N^d \times \frac{1 + \omega \times (1 - Y_{O_2}^d)}{1 + \omega \times (1 - y_{O_2}^d) - \frac{y_{CO}^d}{2} + (1 - \omega) \times \frac{y_{NO_2}^d}{2} - \omega \times \frac{y_{NO}^d}{2} - (1 + \omega) \times y_F^d} \quad (20)$$

3.2.2 Molar fraction of unmonitored components

As the concentration of water vapor and carbon dioxide in combustion gases were not monitored, it was necessary to express their molar fractions from the mass balance. Equations (21) and (22) were obtained with

help of relations (19) and (20) for the molar fraction $y_{H_2O}^d$, and $y_{CO_2}^d$ respectively, as it was presented earlier in Proceedings of WSEAS international conference on Waste Management, Water Pollution, Air Pollution, Indoor Climate in Iasi as well [23].

$$y_{H_2O}^d = \frac{\beta}{2} \times \frac{Y_{O_2}^d - y_{O_2}^d + (1 - Y_{O_2}^d) \times \frac{y_{CO}^d}{2} - \left(1 - \frac{Y_{O_2}^d}{2}\right) \times y_{NO_2}^d - \frac{y_{NO}^d}{2} - Y_{O_2}^d \times y_F^d}{1 + \omega \times (1 - Y_{O_2}^d)} \quad (21)$$

$$y_{CO_2}^d = \frac{Y_{O_2}^d - y_{O_2}^d - \left[\omega \times (1 - Y_{O_2}^d) + \frac{1 + Y_{O_2}^d}{2} \right] \times y_{CO}^d - \left(1 - \frac{Y_{O_2}^d}{2} \right) \times y_{NO_2}^d - \frac{y_{NO}^d}{2} - Y_{O_2}^d \times y_F^d}{1 + \omega \times (1 - Y_{O_2}^d)} \quad (22)$$

3.2.3 Conversion of concentrations of moist air constituents.

Amount of consumed fuel can be calculated from the volume velocity flowing wet exhaust gases in the sampling extension. To convert concentrations

$$n = n_{N_2} + n_{O_2} + N_{CO_2} + N_{H_2O} + n_{CO_2} + n_{CO} + n_{H_2O} + n_F + n_{NO_2} + n_{NO} = n^d + N_{H_2O} + n_{H_2O} \quad (23)$$

$$\frac{n}{n^d} = 1 + \frac{N_{H_2O}}{N^d} \times \frac{N^d}{n^d} + y_{H_2O}^d \quad (24)$$

It is obvious from mass balance that for molar fraction y_i of i -th constituent in wet emissions is valid the equation (25):

$$y_i = y_i^d \times \frac{n^d}{n} \quad (25)$$

After substitution in the equation (24) for $\frac{N_{H_2O}}{N^d} = Y_{H_2O}^d$ from equation (17), for $\frac{N^d}{n^d}$ from mass balance with help of formula (20), and for $y_{H_2O}^d$ from

$$\delta = \frac{n}{n^d} = 1 + \frac{\beta}{2} \times \frac{B \times \left(\frac{y_{CO}^d}{2} - \frac{y_{NO_2}^d}{2} + y_F^d - 1 \right) + X \times \left(1 - y_{O_2}^d - \frac{y_{NO_2}^d}{2} - \frac{y_{NO}^d}{2} - y_F^d \right)}{\omega \times B + X} \quad (28)$$

3.2.4 Calculations of water vapor concentrations

Concentration of water vapor $Y_{H_2O}^d$ converted into dry air, which is needed to calculate the conversion factor δ from equation (28) can be expressed by formula (29):

$$Y_{H_2O}^d = x_{H_2O}^d \times \frac{M_{Air}^d}{M_{H_2O}} = \frac{\varphi \times p_{H_2O}^{SAT}}{p^{STC} - \varphi \times p_{H_2O}^{SAT}} \quad (29)$$

where the symbol $x_{H_2O}^d$ represents the specific humidity of the air, M_{Air}^d [g mol⁻¹] molar molecular weight of dry

$$\ln p_{H_2O}^{SAT} = C_8 \times T^{-1} + C_9 + C_{10} \times T + C_{11} \times T^2 + C_{12} \times T^3 + C_{11} \times \ln T \quad (30)$$

3.2.5 Calculation of fuel composition

Stoichiometric coefficients in equation (9) can be set if the relative proportion ψ_i of each i -th fuel component is known. It is clear that relations (31) and (32) are valid:

$$\beta = \frac{\psi_H \times A_C}{\psi_C \times A_H} \quad (31) \quad \gamma = \frac{\psi_O \times A_C}{\psi_C \times A_O} \quad (32)$$

of dry gas emission into concentrations in wet combustion gas at the place of measurement of dynamic pressure by Prandtl tube is valid relation (23) and the adjustment relation (24) where symbols have the same meaning as above.

equation (21) the conversion factor $\delta = n \times (n^d)^{-1}$ for concentration conversion of the i -th component from dry to wet gases could be derived and is given by equation (28) in which a substitution (26) and (27) was introduced to simplify the final relation.

$$B = \frac{\beta}{2} \times (1 - Y_{O_2}^d) - Y_{H_2O}^d \quad (26)$$

$$X = \frac{\beta}{2} + \omega \times Y_{H_2O}^d \quad (27)$$

Formula (28) enables to calculate the conversion factor δ by using the measured values of pollutants concentrations.

air, M_{H_2O} [g mol⁻¹] molar molecular weight of water, φ [%] relative humidity of the air, $p_{H_2O}^{SAT}$ [Pa] the partial pressure of saturated water vapor at temperature T [K] and finally $p^{STC} = 1.013 \times 10^5$ [Pa] pressure at standard conditions. In accordance with the literature [27], it is possible to calculate the partial pressure of saturated water vapor in the temperature interval from 273 to 473 K according to equation (30), where symbols C_8, C_9, C_{10}, C_{11} , and C_{12} mean tabulated constants for air temperature T [K].

The molecular weight of fuel μ_F related to one carbon atom is given by equation (33):

$$\mu_F = A_C + \beta \times A_H + \gamma \times A_O = \frac{100 \times A_C}{\psi_C} \quad (33)$$

where ψ_C, ψ_H a ψ_O means a relative content of carbon, hydrogen and oxygen in the fuel, A_C, A_H a A_O [g mol⁻¹]

corresponding molar atomic weights and constants β and γ have the same meaning as in equation (16).

The formula (34) for constant γ was derived using equations (31) and (32) and the formula (35) for constant ω after substituting γ into relation (16):

$$\gamma = \frac{\psi_o \times (A_C + \beta \times A_H)}{(100 - \psi_o) \times A_O} \quad (34)$$

$$\omega = \frac{\beta}{4} - \frac{\psi_o \times (A_C + \beta \times A_H)}{2 \times (100 - \psi_o) \times A_O} \quad (35)$$

After substituting from relations (31) and (32) into formula (33) it applies equation (36) for μ_F from which

$$Ef_m^i = \frac{y_i^d \times \frac{M_i}{\mu_F} \times [1 + \omega \times (1 - Y_{O_2}^d)]}{Y_{O_2}^d - y_{O_2}^d + (1 - Y_{O_2}^d) \times \frac{y_{CO}^d}{2} - \left(1 - \frac{Y_{O_2}^d}{2}\right) \times y_{NO_2}^d - \frac{y_{NO}^d}{2} + [a \times (1 + \omega) - (1 + a\omega) \times Y_{O_2}^d] \times y_F^d} \quad (37)$$

Equation (38) is valid for the emission factor Ef_t^{PM} [g h⁻¹] of particulate matter in mass units related to time unit t [h]:

$$Ef_t^{PM} = \frac{m_t^{PM}}{t} = \frac{m_t^{PM} \times V_t^{STC}}{V_t^{STC} \times t} = c_{PM}^{STC} \times V_t^{STC} \quad (38)$$

where m_t^{PM} [g h⁻¹] represents the mass of captured PM matter in time unit t , V_t^{STC} [m³ h⁻¹] means the volume of exhaust gases under standard conditions (STC) released during time unit t , and finally c_{PM}^{STC} [g m⁻³] is the concentration of PM in combustion gas at standard conditions.

$$V_t^{STC} = \frac{m_t^F \times V^*}{y_{CO_2}^d + y_{CO}^d + a y_F^d} \times \left[\frac{1}{\mu_F \times t} + \beta \times \frac{B \times (y_{CO}^d - y_{NO_2}^d + 2y_F^d - 2) + X \times (2 - 2y_{O_2}^d - y_{NO_2}^d - y_{NO}^d - 2y_F^d)}{4 \times (\mu_F \times t) \times (X + \omega \times B)} \right] \quad (40)$$

Substituting for V_t^{STC} in the equation (38) it can be calculated emission factor Ef_t^{PM} for PM in mass units related to time unit t . The relation (41) follows from equation (7), from which it is possible with the known value of emission factor Ef_t^{PM} and the measured or according to relation (39) calculated fuel consumption m_t^F per time unit t to express an emission factor Ef_m^{PM} as the weight of the PM related to the unit of consumed fuel mass.

$$Ef_m^{PM} = \frac{m_t^{PM}}{m_t^F} = \frac{m_t^{PM}}{t} \times \frac{t}{m_t^F} = Ef_t^{PM} \times \left(\frac{m_t^F}{t} \right)^{-1} \quad (41)$$

Calculated values of emission factors for gaseous pollutants under varying conditions of engine operation

it is possible to express easily the stoichiometric coefficients a, b, c of equation (9).

$$\mu_F = \frac{M_F}{a} = \frac{100 \times (A_C + \beta \times A_H)}{100 - \psi_o} \quad (36)$$

3.2.6 Calculation of emission factors

Emission factors for the i -th contaminant can be calculated according to equation (37) obtained by substitution of $n^d = n^d \times (N_F)^{-1}$ from equation (19) in relation (7) and application of equation (36) for $a = M_F \times (\mu_F)^{-1}$.

It is evident that it will be necessary to estimate V_t^{STC} for calculating the emission factor Ef_t^{PM} . The relation (39) below derived from mass balance is valid for $m_t^F \times t^{-1}$, which represents the amount of consumed fuel per time unit t , while accepting the mass balance for consumed fuel and the equation for molar volume of ideal gas V^* [mol] under standard conditions.

$$\frac{m_t^F}{t} = M_F \times \left(\frac{y_{CO_2} + y_{CO}}{a} + y_F \right) \times \frac{V_t^{STC}}{V^*} \quad (39)$$

Assuming the validity of equations (28) and (36), the formula (40) for V_t^{STC} follows from relation (39):

in the use of diesel NM-54 with or without additives are presented in Table 2. From there it is obvious that the application of additives compared to clear diesel fuel amounted total decrease in emissions of C_xH_y about 12% and NO_x emissions of ca 8.5%, while emissions of CO markedly increased by approximately 22.5%. Differences of emission factors of CO₂, were for both alternatives statistically insignificant. Summary reduction of CO₂ emissions after applying additives by about 0.3% roughly correlates with the slightly, about 1.5%, reduced fuel consumption during the entire measurement. The actual value of fuel consumption depends on engine operating conditions. Fuel savings of a maximum about 3% was observed in the application of additives when reduced torque $TM_R \in \langle 890; 1030 \rangle$ N m, engine power $P \in \langle 186; 214 \rangle$ kW and at engine revolution from range $r \in \langle 1800, 2200 \rangle$ min⁻¹. Due to the

significant increase of CO concentrations in the combustion gas, the carbon balance in the combustion gas varies within the measurement errors.

Oxonica Company engaged in long-term tests in urban and suburban transport, with an additive EnviroxTM, advertises, depending on operating

conditions and type of engine in the application of additive reduction of C_xH_y emissions within 6-14%, 1-7% of CO and NO_x by 11%. Reduction of CO₂ emissions should be in accordance with a reduction in fuel consumption, which is declared by the company to be in an interval of 5-12% [24].

Table 2 The characteristics of the engine and emission factors for gaseous pollutants with and without additives

ML [%] motor load, r [min⁻¹] engine revolutions, TM_R [N m] reduced torque, T_{CG} [K] temperature of combustion products, T_{EP} [K] temperature of exhaust pipe, P [kW] engine power, FC [kg kWh⁻¹] fuel consumption, Ef_m^i [g kg⁻¹] emission factor for the i -th gaseous contaminant.

Test		ML	r	TM_R	T_{CG}	T_{EP}	P	FC	$Ef_m^{C_xH_y}$	Ef_m^{CO}	$Ef_m^{NO_x}$	$Ef_m^{CO_2}$
Fuel	No	[%]	[min ⁻¹]	[N m]	[K]	[K]	[kW]	[kg kWh ⁻¹]	[g kg ⁻¹]			
NM-54	1	100.0	2200	891.0	793	853	205.3	0.244	2.38	23.01	49.80	3 084
	2	100.0	1399	1100.0	769	828	161.2	0.213	2.17	24.45	31.86	3 082
	3	60.1	1803	993.0	773	833	187.5	0.226	2.42	27.66	48.41	3 076
	4	54.4	1799	821.6	663	720	154.8	0.220	2.89	26.40	56.63	3 077
	5	50.0	1799	616.1	593	629	116.1	0.231	3.97	26.97	56.83	3 073
	6	46.8	1800	408.4	527	550	77.0	0.264	5.64	28.78	51.43	3 065
	7	100.0	2199	932.3	764	821	214.7	0.235	3.01	27.77	36.18	3 074
NM-54 + Envirox	1	100.0	2201	927.8	780	840	213.8	0.236	4.63	48.98	41.81	3 036
	2	100.0	1399	1109.2	771	836	162.5	0.214	3.29	35.01	34.60	3 062
	3	63.4	1799	1022.3	767	826	192.6	0.219	2.01	26.62	43.21	3 079
	4	57.2	1799	817.7	673	721	154.0	0.219	1.54	23.16	49.09	3 086
	5	53.3	1801	616.3	595	633	116.2	0.227	1.90	22.98	47.81	3 085
	6	50.3	1801	408.0	520	549	76.9	0.260	3.17	25.48	44.35	3 077
	7	100.0	2201	934.6	772	832	215.4	0.233	3.25	45.17	45.81	3 046

Calculated values of emission factor Ef_m^{PM} for PM under same varying conditions of engine operation as for gaseous emission factors in the use of diesel NM-54 with or without additive EnviroxTM are presented in Table 3 together with the measured concentrations of pollutants and the concentration of oxygen. It is evident that the PM emissions decreased by about 17% when the additive was applied to the diesel fuel. Such a decrease even slightly exceeds the value interval stated by the Oxonica Company. This company carried out long-term tests in urban and suburban transport and it advertises that the EnviroxTM additive reduces PM emissions from 9 to 16% [24] depending on different operating conditions and the type of engine.

Results obtained by our measurement are consistent with data reported by the company for C_xH_y, NO_x solely, and for PM emissions partially. The fact that there is not declared reduction of fuel consumption and hence reduction of CO₂ emissions and that CO emission factor even strongly increased can be partially explained by short-term sampling of the addition of additives to fuel. Moreover, increased production of CO could have been slightly caused by oxidation of carbon residue in the

engine chamber. Also, it could have been caused by an older type of engine made in 1986 where the mentioned effect need not appear sufficiently. For these reasons, the additional verification tests are planning for not only identical but also newer type of engine with a sampling period of at least 200 engine hours of the operation with fuel containing the investigated additive.

Simultaneously, the dependence of emission factor values were monitored as a function of reduced torque TM_R , engine power P and engine revolutions r .

In compliance to theoretical assumptions, the majority of gaseous emissions after an initial slight increase tend to decrease with increasing TM_R and reach a minimum of around 190 kW engine power. The example in Figure 3 illustrates the graphical dependence of the $Ef_m^{NO_x}$ as a function of TM_R . Format of the trend line was evaluated by linear regression second degree polynomial, with the corresponding regression equation with reliability value R are included within the graph. Maximum of CO₂ emissions was observed in power around 190 kW, when the fuel consumption is minimal, from unknown reasons yet.

Table 3 Engine parameters, concentration of pollutants and PM emission factor with and without Envirox™ additive ML [%] motor load, r [min^{-1}] engine revolutions, TM_R [N m] reduced torque, T_{CG} [K] temperature of combustion products, T_{EP} [K] temperature of exhaust pipe, P [kW] engine power, FC [kg h^{-1}] fuel consumption, and Ef_m^{PM} [g kg^{-1}] emission factor for the PM.

Test		ML	r	TM_R	T_{CG}	T_{EP}	P	FC	O_2	CO	NO_x	C_xH_y	PM	Ef_m^{PM}
Fuel	No	[%]	[min^{-1}]	[N m]	[K]	[K]	[kW]	[kg h^{-1}]	[%]	[ppm]	[ppm]	[ppm]	[mg m^{-3}]	[g kg^{-1}]
NM-54	1	100.0	2200	891	793	853	205.3	50.0	7.4	1147.2	1402.3	19.1	11.5	0.34
	2	100.0	1399	1100	769	828	161.2	34.4	8.1	1159.7	1410.5	16.5	9.1	0.31
	3	60.1	1803	993	773	833	187.5	42.3	8.4	1275.0	2083.0	18.0	8.4	0.34
	4	54.4	1799	821.6	663	720	154.8	34.0	11.0	965.0	1932.5	17.0	4.2	0.40
	5	50.0	1799	616.1	593	629	116.1	26.8	13.3	760.0	1495.0	18.0	4.9	0.54
	6	46.8	1800	408.4	527	550	77.0	20.3	15.3	602.0	1004.0	19.0	4.2	0.76
	7	100.0	2199	932.3	764	821	214.7	50.4	8.6	1262.0	1535.0	22.0	14.5	0.43
NM-54 + Envirox™	1	100.0	2201	927.8	80	840	213.8	50.5	7.7	2391.4	1905.4	36.4	11.8	0.66
	2	100.0	1399	1109.2	771	836	162.5	34.8	7.2	1770.7	1633.9	26.8	16.3	0.47
	3	63.4	1799	1022.3	767	826	192.6	42.2	8.0	1262.2	1912.7	15.3	11.3	0.29
	4	57.2	1799	817.7	673	721	154.0	33.7	11.0	846.6	1675.1	9.0	6.0	0.21
	5	53.3	1801	616.3	595	633	116.2	26.4	13.2	658.7	1279.6	8.8	8.0	0.26
	6	50.3	1801	408	520	549	76.9	20.0	15.3	531.7	863.9	10.7	8.6	0.43
	7	100.0	2201	934.6	772	832	215.4	50.2	7.9	2165.1	2049.9	25.1	11.0	0.46

Also decline in value of emission factors at the speed of $r \approx 1900 \text{ min}^{-1}$ is consistent with the theory because these conditions lead to efficient use of fuel. In contrast to this theory is the growth in CO_2 emissions when

applying fuel additives, the increase in C_xH_y emissions, if the diesel fuel was used without additive and NO_x emissions in both alternatives of test in the area of revolutions around 1900 min^{-1} .

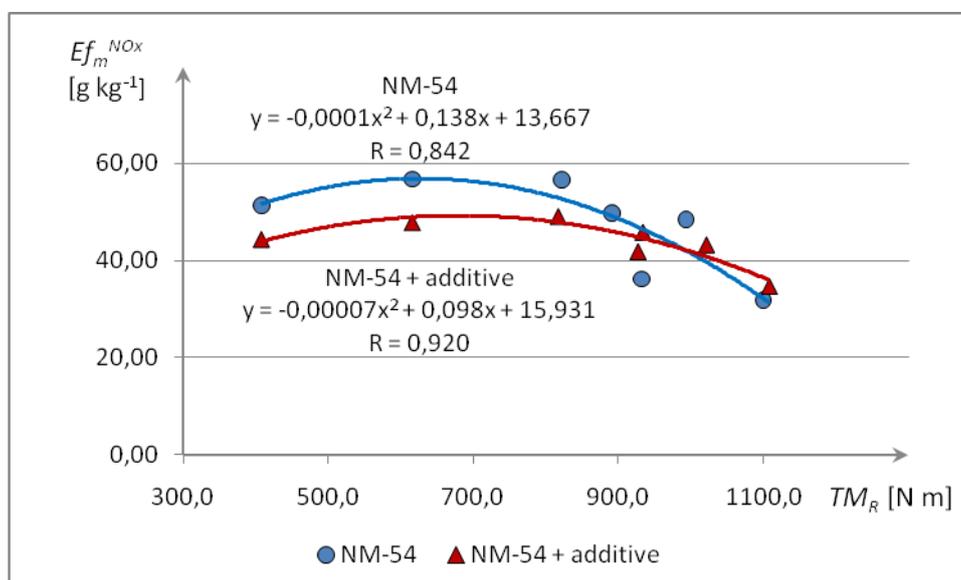


Fig. 3 The dependence of NO_x emission factor $Ef_m^{NO_x}$ on reduced torque TM_R for both test alternatives

The functions of the PM emission factor on the reduced torque TM_R , revolutions r and engine power P was observed as well. Dependencies show a minimum PM pollution in the interval of $TM_R \in \langle 700; 1000 \rangle$ N m, $r \in \langle 1750; 1900 \rangle \text{ min}^{-1}$, and $P \in \langle 140; 200 \rangle$ kW which is roughly in compliance with theoretical expectations

and observed reduced fuel consumption in dependence on considered parameters. The example in Figure 4 illustrates the graphical dependence of emission factor Ef_m^{PM} as a function of engine power P . Format of the trend line was evaluated by linear regression through the polynomial of second degree with the corresponding

regression equation and reliability coefficient R , analogically as in case of dependence NO_x emission factor $Ef_m^{\text{NO}_x}$ on reduced torque TM_R .

The increase PM emissions at engine revolutions $r \approx 1800 \text{ min}^{-1}$ while using diesel fuel without additives is an exception difficult to be explained.

Therefore it will be meaningful to verify these gaps with additional planned experiments under conditions listed above, i.e. after sufficiently long period of engine operation with the addition of EnviroxTM additive and on the identical and newer type of engine at the same time.

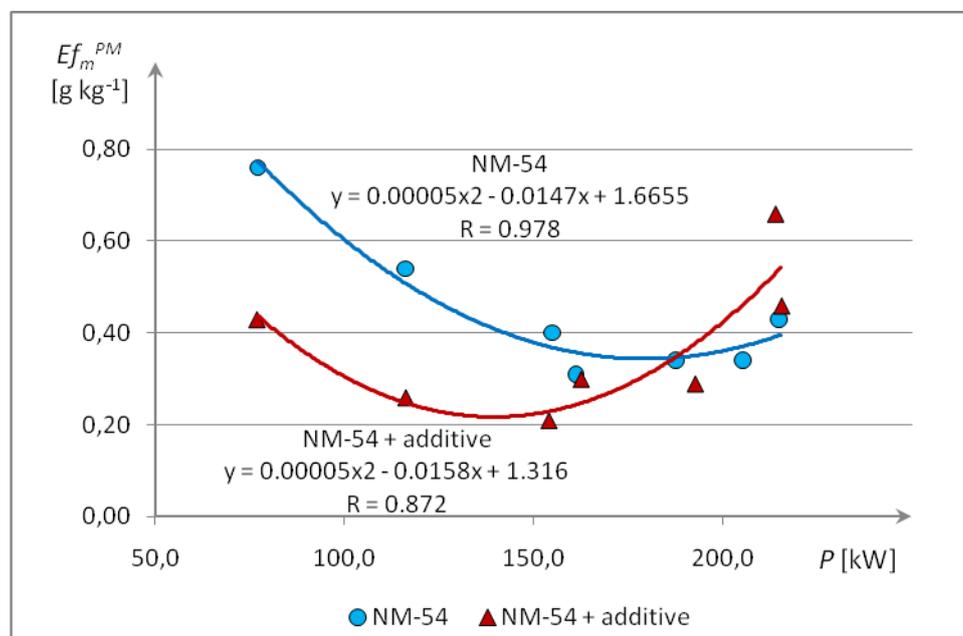


Fig. 4 The dependence of PM emission factor Ef_m^{PM} on engine power P for both test alternatives

4 Conclusions

A methodology was developed for measuring and calculating emissions determination of C_xH_y , NO_x , CO , CO_2 , and PM in the engine exhaust. By using it, it was found that the additive EnviroxTM based on dispersed nanoparticles of CeO_2 reduces the value of emission factors of C_xH_y by approximately 12%, NO_x by about 8.5% and PM by 17%. Nevertheless, reduction of CO_2 corresponding with lower fuel consumption in the range 5-12% declared by Oxonica Company could not be established. Maximum fuel savings of around 3% were found only under optimum conditions of engine operation, with a corresponding decrease in CO_2 emissions by only about 1%. Contrary to announced lower amount of CO emissions an increase of almost 23% was observed.

At the same time, there were monitored dependencies of emission factors on reduced torque, engine power and engine revolutions. With some exceptions the referred functions were in accordance with theoretical expectations.

The divergence between CO_2 a CO emissions production and the data stated by Oxonica Company as well as data collected in some dependency of

emission factors on selected engine characteristics will be necessary to verify with further tests on identical and new type of engine at the same time and after sufficiently long period of engine operation with the addition of EnviroxTM additive.

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