Emissions of Selected Pollutants While Applying of Specific Additive Envirox™

Frantisek BOZEK[1], Jiri HUZLIK[2], Jaromir MARES[1], Hana MALACHOVA[1]
[1] Civil Protection Department
University of Defence
65 Kounicova, 662 10 Brno
CZECH REPUBLIC
frantisek.bozek@unob.cz http://www.vojenskaskola.cz
[2] Transport Research Centre
2557/33a Lisenska, 636 00 Brno-Lisen
CZECH REPUBLIC
jiri.huzlik@cdv.cz http://www.cdv.cz

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 Envirox™. 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 (CO_2) emissions by 37%, a mixture of nitric oxide (NO) and nitrogen dioxides (NO_2), 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 CO_2, 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 (CeO_2) 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 bio-diversity, 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

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 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].

$$(8x+2y)\,CeO_2 + 2\,C_xH_y = (4x+y)\,Ce_2O_3 + 2x\,CO_2 + y\,H_2O \quad (1)$$

$$4\,CeO_2 + C = 2\,Ce_2O_3 + CO_2 \quad (2)$$

$$2CeO_2 + CO = Ce_2O_3 + CO_2 \quad (3)$$

$$2\,Ce_2O_3 + 2\,NO = 4\,CeO_2 + N_2 \quad (4)$$

$$4\,Ce_2O_3 + 2\,NO_2 = 8\,CeO_2 + N_2 \quad (5)$$

CeO_2 regeneration catalyst is carried out in accordance with chemical formula (6).

$$2\,Ce_2O_3 + O_2 = 4\,CeO_2 \quad (6)$$

Statistically validated operational tests carried out by Oxonica Company provide evidence that the recommended dosage of 5 to 10 ppm w/w CeO_2 can achieve relevant reductions in fuel consumption (about 5-12%) while reducing the emissions of CO_2, 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 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].

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

In equation (2) *FC* further indicates fuel consumption [dm^3 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 0-6.0×10^3 [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 CeO_2 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 1.9×10^4 cm^3, cylinder 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 2.2×10^3 min^{-1} with a maximum torque of 1.13×10^3 N m at revolutions 1.4×10^3 ± 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, NO_2, and O_2 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.

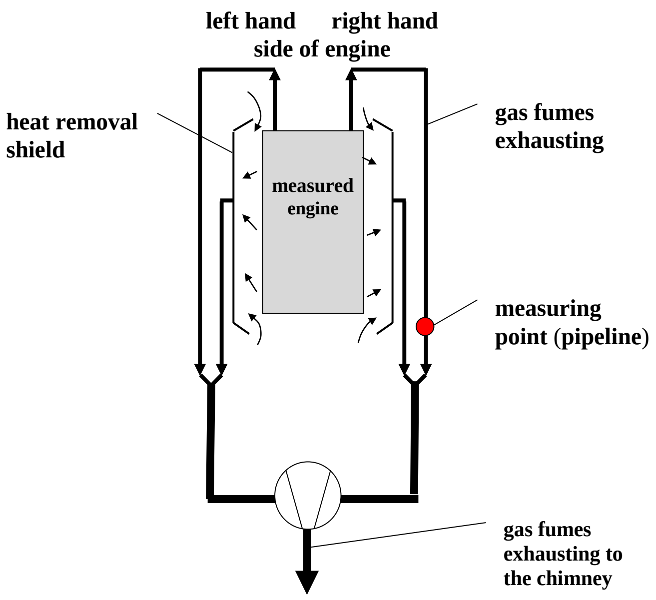

Fig. 1 Diagram of the location of measuring point

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

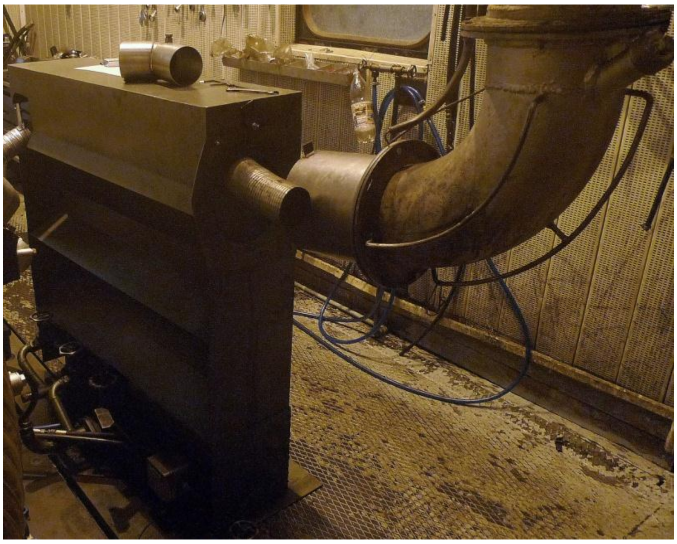

Fig. 2 Real sample collection point in the VOP-026 Sternberk Company

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.

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

$$a\times(N_F - n_F) = n_{CO_2} + n_{CO} \qquad (10)$$

$$b\times(N_F - n_F) = 2n_{H_2O} \qquad (11)$$

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

$$2(N_{N_2} - n_{N_2}) = n_{NO_2} + n_{NO} \qquad (13)$$

$$N^d = N_{N_2} + N_{O_2} + N_{CO_2} \qquad (14)$$

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

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).

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

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

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

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

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).

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

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

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].

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

$$y^d_{CO_2} = \frac{Y^d_{O_2} - y^d_{O_2} - \left[\omega \times \left(1 - Y^d_{O_2}\right) + \frac{1 + Y^d_{O_2}}{2}\right] \times y^d_{CO} - \left(1 - \frac{Y^d_{O_2}}{2}\right) \times y^d_{NO_2} - \frac{y^d_{NO}}{2} - Y^d_{O_2} \times y^d_F}{1 + \omega \times \left(1 - Y^d_{O_2}\right)} \qquad (22)$$

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 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.

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

$$\frac{n}{n^d} = 1 + \frac{N_{H_2O}}{N^d} \times \frac{N^d}{n^d} + y^d_{H_2O} \qquad (24)$$

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

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

After substitution in the equation (24) for $\frac{N_{H_2O}}{N^d_V} = Y^d_{H_2O}$ from equation (17), for $\frac{N^d_V}{n^d}$ from mass balance with help of formula (20), and for $y^d_{H_2O}$ from equation (21) the conversion factor $\delta = n \times \left(n^d\right)^{-1}$ 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.

$$B = \frac{\beta}{2} \times \left(1 - Y^d_{O_2}\right) - Y^d_{H_2O} \qquad (26)$$

$$X = \frac{\beta}{2} + \omega \times Y^d_{H_2O} \qquad (27)$$

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

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

3.2.4 Calculations of water vapor concentrations

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

$$Y^d_{H_2O} = x^d_{H_2O} \times \frac{M^d_{Air}}{M_{H_2O}} = \frac{\varphi \times p^{SAT}_{H_2O}}{p^{STC} - \varphi \times p^{SAT}_{H_2O}} \qquad (29)$$

where the symbol $x^d_{H_2O}$ represents the specific humidity of the air, M^d_{Air} [g mol^{-1}] molar molecular weight of dry air, M_{H_2O} [g mol^{-1}] molar molecular weight of water, φ [%] relative humidity of the air, $p^{SAT}_{H_2O}$ [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].

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

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:

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

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

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

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}]