Emissions of selected gas pollutants in the application of the additive Envirox™

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Abstract

The value of selected emission factors was monitored in the operation of an older type of engine testing bench using diesel and compared with the same parameters monitored under similar conditions with the addition of the additive, Envirox™. It was found that the additive based on CeO_2 nanoparticles reduces emissions of hydrocarbons C_xH_y, and NO_x, while emissions of CO_2 remain comparable or slightly lower and CO emissions even significantly increase. Dependence of tested emissions on reduced torque TM_R, engine power P and revolutions f was observed as well.
Keywords: additive, emission factor, nano-particle, environment, cerium dioxide, carbon mono-oxide, nitrogen oxide.

1 Introduction

Escalating activities of human society in order to ensure a higher standard of living brings along a number of negative externalities. Among the important, and by the lay and professional community strongly discussed externalities, belongs the increase of burden to the atmosphere through the implementation of industrial and agricultural activities, energy production, waste management and household management. To the increase in ambient air pollution also contributes a significant level of mobile assets, consisting primarily of passenger and goods transport [1].

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 nitrogen oxide and nitrogen dioxide (NO_x) by 30%, and volatile organic compounds (VOCs), about 24%. Besides the above, the quantitative aspect of the

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dominant pollutant is the traffic which is also producer of other, mainly health and eco highly harmful substances [2]. Emitted pollutants have often non-quantifiable impact on morbidity and mortality of the population, ecosystem function and value of social assets [3].

Because transportation is currently one of the world's most dynamically developing sectors, it is necessary, in accordance with the principles of sustainable development, to pay enormous attention to minimize emissions. This requirement is compounded by the use of personal automobiles at the expense of public transport and permanently increasing the ratio of road haulage transport relative to rail transport [1].

The submitted paper is devoted to the evaluation of the quantities of CO_2, CO, NO_x and VOCs in the form of unburned hydrocarbons C_xH_y emissions from fuels used in conventional diesel engines in comparison to the addition of fuel additive based on cerium dioxide (CeO_2).

2 The analysis of current state

The amount of pollutants emitted while driving a motor vehicle is dependent on many factors. If the typical way of driving for each driver is left aside, as well as the nature of terrain and weather conditions, the current emissions are dependent upon, in particular:

a) The type of engine and its technical parameters [4];
b) Principles of oxidation catalyst effect [5];
c) The type and amount of biodiesel added to the base fuel [6];
d) The composition and quality of used motor oil [7];
e) The type and composition of additives added to the basic fuel [8].

The calculation of the *i*-th pollutant emission is based on the knowledge of an emission factor Ef_m^i [g kg^{-1}] which is consistently with eqn (1) given by weight of the *i*-th pollutant per a unit mass of consumed fuel [9]:

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

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, n^d [mol] substance amount of dry exhaust gas, N_F [mol] substance amount of consumed fuel, and finally y_i^d molar fraction of the *i*-th pollutant in dry exhaust gasses.

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 [10]:

a) Refinery additives;
b) Safety increasing or legally required additives;
c) Additives for improvement of technical parameters and increase of fuel performance.

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

$$4\ CeO_2 + C = 2\ Ce_2O_3 + CO_2 \quad (3)$$

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

$$2\ Ce_2O_3 + 2\ NO = 4\ CeO_2 + N_2 \quad (5)$$

$$4\ Ce_2O_3 + 2\ NO_2 = 8\ CeO_2 + N_2 \quad (6)$$

CeO_2 regeneration catalyst is carried out in accordance with chemical formula (7).

$$2\ Ce_2O_3 + O_2 = 4\ CeO_2 \quad (7)$$

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%) present reduction of emissions of CO_2, CO, NO_x, C_xH_y and particulate matters. The additive is also compatible with all diesel common additives [11, 12].

3 Problem solution

3.1 Applied methods and devices

Tests to determine emission levels were carried out on the engine testing bench of VOP-026 Šternberk electric eddy current brake Schenk 0900 kW, operating in the range of 0–6000 revolutions min^{-1}. Diesel NM-54 was used as the primary fuel which served as an alternative version for the comparative tests mixed with 2.5×10^{-4} volumes of additives. The concentrations of CeO_2 found in diesel fuel by inductively coupled plasma atomic emission spectroscopy was 7.6 ppm w/w which corresponds to Envirox^{TM} suppliers' requirement.

For the actual test a diesel engine was used, four stroke, naturally-aspirated engine Tatra T3 930-31 with direct injection, air-cooled, engine cylinder capacity of 1.9×10^4 cm^3, cylinder diameter/stroke 120/140 mm, OHV distribution 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 2.2×10^3 min^{-1} with a maximum torque of 1.13×10^3 N m at revolutions $1.4\times10^3 \pm 200$ min^{-1}.

Emission testing was performed by a combined device for analysis of combustion gas composition ECOM – JN, equipped by electrochemical sensor of an English company City Technology which enabled the determination of CO, NO, NO_2 and O_2 concentrations. Sensor types, ranges and uncertainty in determination of individual quantities are listed in table 1.

A 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 each pollutant sensors. It was possible to determine the concentration of CO and NOx by applying unheated tube between the probe and analyzer as possible combustion gas condensation in the traffic route did not affect their value.

Table 1: Ranges and uncertainties in determination of measured quantities.

Pollutant	Range (ppm)	Uncertainty of measurements	
		20 % range	100 % range
NO	$0 – 2.0\times10^3$	2 %	5 %
NO_2	$0 – 2.0\times10^2$	2 %	5 %
CO	$0 – 1.0\times10^4$	2 %	5 %
O_2	$0 – 2.1\times10^5$	2 %	5 %

CxHy content was tested by analyzer operating on the principle of flame ionization (FID). The principle uses the effect that the burning of hydrocarbons in the hydrogen flame of the combustion chamber of the analyzer burner gets ionized bond C-H. 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. Into the FID unit was the sample of gases transported through a tube heated vacuum pump analyzer.

Location of measuring point where the combustion gas velocity was measured with the Prandtl probe simultaneously with gas temperature measured with thermocouple is evident from fig. 1.

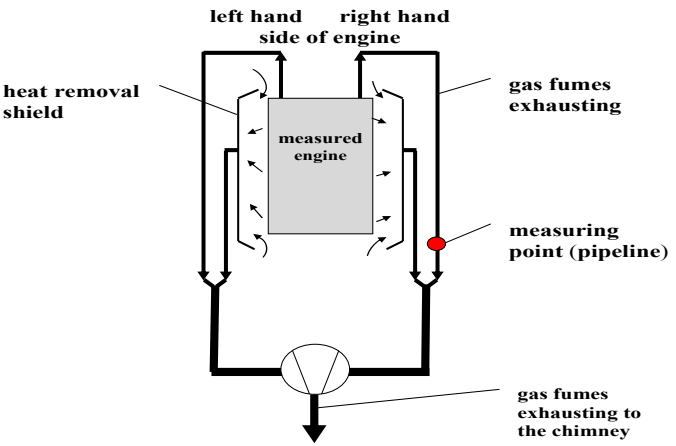

Figure 1: Location of sampling probes.

3.2 Outcomes and discussion

3.2.1 Mass balance

Calculation of emission factors was based on eqn (8) characterizing the combustion of fuel, also based on the carbon material balance, eqn (9), hydrogen (10), oxygen (11) and nitrogen (12), on the amount of substance entering into the combustion process N_V^d [mol] and on the process

of exiting n^d [mol] of the dry gas. eqn (13) eventually (14) and finally based on measurements of the concentration of contaminants and oxygen. Fuel combustion in the engine was considered under simplified conditions in the absence of trace amounts of polycyclic aromatic hydrocarbons, N_2O, NH_3, SO_2 etc.

$$e/2\ N_2 + C_aH_bO_c + [a\times(1-z/2)+b/4-c/2+d\times(1-w/2)]\ O_2 =$$

$$= a\times(1-z)\ CO_2 + a\times z\ CO + (b/2)\ H_2O + d\times(1-w)\ NO_2 + e\times w\ NO \quad (8)$$

$$a\times\left(N_F - n_F\right) = n_{CO_2} + n_{CO} \quad (9)$$

$$b\times\left(N_F - n_F\right) = 2n_{H_2O} \quad (10)$$

$$2\left(N_{O_2} - n_{O_2}\right) + c\times\left(N_F - n_F\right) = n_{H_2O} + 2n_{CO_2} + n_{CO} + 2n_{NO_2} + n_{NO} \quad (11)$$

$$2\left(N_{N_2} - n_{N_2}\right) = n_{NO_2} + n_{NO} \quad (12)$$

$$N_V^d = N_{N_2} + N_{O_2} + N_{CO_2} \quad (13)$$

$$n^d = n_{N_2} + n_{O_2} + N_{CO_2} + n_{CO_2} + n_{CO} + n_F + n_{NO_2} + n_{NO} \quad (14)$$

In eqns (9)–(14) N [mol] with the corresponding subscript represents amount of substance in the process of entering gases N_2, O_2 and CO_2 and n [mol] subscript represents amount of substance in the process of exiting exhaust gases, i.e. N_2, O_2, CO_2, CO, NO_2, NO and fuels F.

To simplify the record of other formulas a substitution (15) was introduced where symbols a, b, c are stoichiometric coefficients in eqn (8).

$$\omega = \frac{b-2c}{4a} = \frac{\beta}{4} - \frac{\gamma}{2} \quad (15)$$

Molar fractions Y_i^d a y_i^d of i-th component in dry inlet air or combustion gas are defined by relations (16) or (17):

$$Y_i^d = N_i \times (N_V^d)^{-1}, \quad (16)$$

$$y_i^d = n_i \times (n^d)^{-1} \quad (17)$$

where N_i [mol] is the amount of substance of i-th component in the inlet n_i [mol] is the amount of substance of i-th component in output, symbol N_V^d [mol] has the same meaning as in eqn (13) and the symbol n^d [mol] as in eqn (14).

Based on the mass balance relations with the acceptance of relations (15)-(17) eqn (18) and (19) can be derived. These are needed to calculate emission factors for i-th pollutant. The meaning of symbols used in these eqns is in respect of previous signs in eqns (9)-(17).

$$\frac{n^d}{N_F} = \frac{a\times\left[1+\omega\times\left(1-Y_{O_2}^d\right)\right]}{Y_{O_2}^d - y_{O_2}^d + \left(1-Y_{O_2}^d\right)\times\frac{y_{CO}^d}{2} - \left(1-\frac{Y_{O_2}^d}{2}\right)\times y_{NO_2}^d - \frac{y_{NO}^d}{2} + \left[a\times(1+\omega) - (1+a\omega)\times Y_{O_2}^d\right]\times y_F^d} \quad (18)$$

3.2.2 Molar fraction of unmonitored components

Because the concentration of water vapor and CO_2 in combustion gases were not monitored, it was necessary to express the molar fractions from the mass balance. After adjustment formula (20) was obtained for the molar fraction of water and formula (21) for the molar fraction of carbon dioxide.

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

$$y_{H_2O}^d = \frac{\beta}{2}\times\frac{Y_{O_2}^d - y_{O_2}^d + \left(1-Y_{O_2}^d\right)\times\frac{y_{CO}^d}{2} - \left(1-\frac{Y_{O_2}^d}{2}\right)\times y_{NO_2}^d - \frac{y_{NO}^d}{2} - Y_{O_2}^d\times y_F^d}{1+\omega\times\left(1-Y_{O_2}^d\right)} \quad (20)$$

$$y_{CO_2}^d = \frac{Y_{O_2}^d - y_{O_2}^d - \left[\omega\times\left(1-Y_{O_2}^d\right) + \frac{1+Y_{O_2}^d}{2}\right]\times y_{CO}^d - \left(1-\frac{Y_{O_2}^d}{2}\right)\times y_{NO_2}^d - \frac{y_{NO}^d}{2} - Y_{O_2}^d\times y_F^d}{1+\omega\times\left(1-Y_{O_2}^d\right)} \quad (21)$$

3.2.3 Calculation of fuel composition

Stoichiometric coefficients in eqn (8) can be determined if the relative proportion ψ_i of each i-th fuel components is known. It is clear that relations (22) and (23) stand good:

$$\beta = \frac{\psi_H \times A_C}{\psi_C \times A_H} \quad (22)$$

$$\gamma = \frac{\psi_O \times A_C}{\psi_C \times A_O} \quad (23)$$

It is obvious that the molecular weight of fuel μ_F related to one carbon atom is given by eqn (24):

$$\mu_F = A_C + \beta\times A_H + \gamma\times A_O = 100\times A_C\times\psi_C^{-1} \quad (24)$$

where ψ_C, ψ_H and ψ_O means a relative content of carbon, hydrogen and oxygen in the fuel, A_C, A_H and A_O [g mol^{-1}] corresponding molar atomic weights and constants β and γ have the same meaning as in eqn (15).

Using eqn (22) and (23) was derived the formula (25) for constant γ and after substitution into relation (15) the eqn (26) for constant ω:

$$\gamma = \frac{\psi_O \times \left(A_C + \beta \times A_H\right)}{\left(100 - \psi_O\right) \times A_O} \tag{25}$$

$$\omega = \frac{\beta}{4} - \frac{\psi_O \times \left(A_C + \beta \times A_H\right)}{2 \times \left(100 - \psi_O\right) \times A_O} \tag{26}$$

After substituting from relations (22) and (23) into formula (24) applies for μ_F eqn (27) from where it is possible easy to directly express stoichiometric coefficients *a*, *b*, *c* of eqn (8).

$$\mu_F = \frac{M_F}{a} = \frac{100 \times \left(A_C + \beta \times A_H\right)}{100 - \psi_O} \tag{27}$$

3.2.4 Calculation of emission factors

Emission factors for the *i*-th contaminant were calculated according to eqn (28) which was obtained by substitution of $n^d \times (N_F)^{-1}$ from relation (18) in eqn (1) and by application of eqn (27) for $\mu_F = M_F \times a^{-1}$.

$$Ef_m^i = \frac{y_i^d \times \frac{M_i}{\mu_F} \times \left[1 + \omega \times \left(1 - Y_{O_2}^d\right)\right]}{Y_{O_2}^d - y_{O_2}^d + \left(1 - Y_{O_2}^d\right) \times \frac{y_{CO}^d}{2} - \left(1 - \frac{Y_{O_2}^d}{2}\right) \times y_{NO_2}^d - \frac{y_{NO}^d}{2} + \left[a \times (1 + \omega) - (1 + a\omega) \times Y_{O_2}^d\right] \times y_F^d} \tag{28}$$

Calculated values of emission factors under varying conditions of engine operation 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 about 8.5%, while emissions of CO notably increased by approximately 22.5%. Differences of emission factors of CO_2 were for both alternatives statistically insignificant. Summary reduction of CO_2 emissions after applying additives by about 0.3% roughly correlates with the slightly (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% were 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 revolutions $f \in \langle 1800; 2200 \rangle$ min^{-1}. Due to the significant increase in concentrations CO in the combustion products the carbon balance of the burnt process varies within the measurement errors.

Oxonica company, engaged in long-term tests in urban and suburban transport with an additive Envirox^{TM}, advertises, depending on operating conditions and type of engine in the application of an additive, reduction of C_xH_y emissions within 6-14%, 1-7% of CO and NO_x by 11%. Reduction of CO_2

Table 2: Parameters of the engine and emission factors for selected pollutants with and without additive.

Test	ML	f	TM_R	T_{CG}	T_{EP}	P	FC	$Ef_m^{C_xH_y}$	Ef_m^{CO}	$Ef_m^{NO_x}$	$Ef_m^{CO_2}$
No	[%]	[min^{-1}]	[N m]	[K]	[K]	[kW]	[kg kWh^{-1}]	[g kg^{-1}]	[g kg^{-1}]	[g kg^{-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^{TM}											
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

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% [12].

ML [%] motor load, f [min^{-1}] engine revolutions, TM_R [N m] reduced torque, T_{CG} [K] temperature of combustion products, T_{EP} 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 contaminant.

Results obtained by us are in compliance with data reported by the Oxonica company solely for C_xH_y and NO_x emissions however for contaminants CO_2 and CO are markedly different. The fact that there is no declared reduction of fuel consumption and hence reduction of CO_2 and that CO emission factor even strongly increased may be partially explained by short-term sampling after the addition of Envirox^{TM} into diesel fuel. Moreover, increased production of CO could have been caused by oxidation of carbon residue in the engine. Also it could have been caused by an older type of engine with production year 1986, in which the mentioned effect does not sufficiently appear. For these reasons, there are planned additional verification tests for the newer engine type with a sampling period of at least 200 engine hours of the engine operation with fuel containing the investigated additive.

At the same time the dependence of emission factor values were monitored as a function of TM_R reduced torque, engine power P and engine revolutions f. According to theoretical assumptions, the majority of emissions after an initial

slight increase tend to decrease with increasing TM_R and reach a minimum of around 180 kW engine power. The example in fig. 2 illustrates the graphical dependence of the emission factor values for 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 and they are included within the graph. For yet unknown reasons the maximum of CO_2 emissions was observed in engine power around 180 kW, when the fuel consumption is on the minimal.

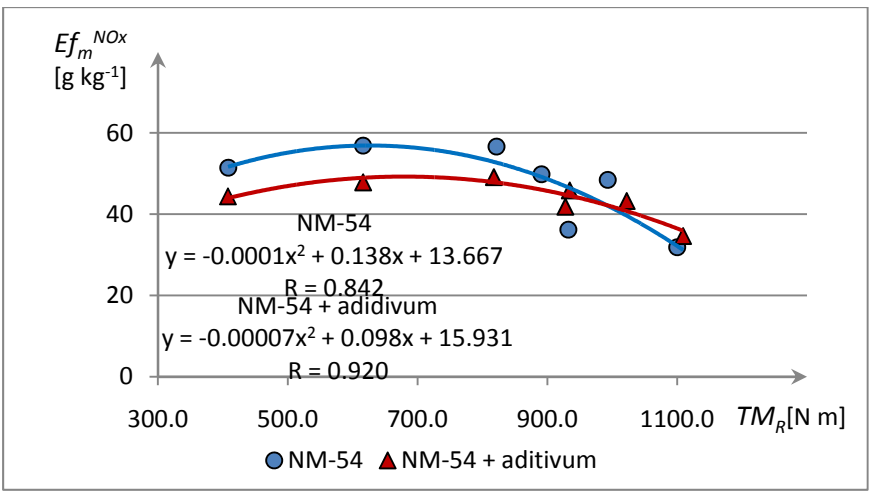

Figure 2: The dependence of emission factor $Ef_m^{NO_2}$ on reduced torque TM_R for both test alternatives.

Also decline in value of emission factors at the engine revolutions of $f \approx 1900$ 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 clear diesel fuel was used and NO_x emissions in both alternatives of test in discussed area of engine revolutions. Therefore it will be meaningful to verify these gaps with additional planned experiments under conditions listed above.

4 Conclusions

A methodology was developed for measuring and calculating emissions determination of C_xH_y, NO_x, CO and CO_2 in the engine exhaust. With its use it was found that the additive Envirox^{TM} based on dispersed nanoparticles of CeO_2 reduces the value of emission factors for C_xH_y by approximately 12% and NO_x by around 8.5%. Nevertheless the 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 about 3% were found out only

under optimum conditions of engine operation with a corresponding decrease in CO_2 emissions by only circa 1%. In contrast with announced lower amount of CO emissions an increase of almost 23% was observed.

At the same time was monitored dependence 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 newer type of engine and after sufficiently long period of engine operation with the addition of Envirox™ fuel efficiency additive.

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