**Reduction of Emissions of Nitrogen Oxides from Traffic**

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**Abstract**—The value of emission factor was calculated in the older type of Diesel engine operating on an engine testing bench and then compared with the parameters monitored under similar conditions when the Envirox™ additive was applied. It has been found out that the additive based on CeO₂ nanoparticles reduces emission of NOₓ. The dependencies of NOₓ emissions on reduced torque, engine power and revolutions have been observed as well.

**Keywords**—Additive, air, cerium dioxide, emission factor, emissions, nanoparticles, nitrogen oxides

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**I. INTRODUCTION**

Air pollution significantly changes the natural characteristics of earth’s atmosphere and represents a serious problem. It reduces the value of assets, negatively affects the functions of ecosystems and imminently endangers human health. Contaminated air causes an increased incidence of deaths, diseases of mainly respiratory organs, reproduction and neurological disorders, cancers and diseases of circulatory system [1].

Apart from the quantitatively dominant pollutants, which include mainly CO₂, CO, SO₂, CH₄ and particulate matter (PM), air is polluted by other highly eco-toxic pollutants. The other pollutants include N₂O₃, N₂O₄, heavy metals, mainly Pb, Cd, Ni and Cr, platinum metals, mainly Pt, Pd and Ru, 1,3-butanediene, benzene, toluene, o-, m-, p-xylene, phenols, aldehydes, ketones, tar, persistent organic substances type polycyclic aromatic hydrocarbons, polychlorinated biphenyls and terphenyls, dibenzofuran, dibenzo-p-dioxines, etc. [2]. The biggest sources of air pollution are heating plants, thermal power plants and recently mainly traffic [3].

The requirement to reduce emissions from traffic is raised by the use of cars at the expense of public transport and permanently increasing ratio of road haulage transport to rail transport [4], [5].

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The paper is focused on evaluating the quantities of NOₓ emissions while applying conventional Diesel oil both without and with the additives on the basis of cerium dioxide nanoparticles (CeO₂).

**II. THE ANALYSIS OF CURRENT STATE**

The group of nitrogen oxides include nitrogen oxide NO, a colourless and odourless gas, and reddish brown nitrogen dioxide NO₂ of acrid smell, which are summarily referred to as NOₓ. Other nitrogen oxides occur in the atmosphere in smaller amounts and do not represent significant risk. They include dinitrogen trioxide N₂O₃, dinitrogen tetroxide N₂O₄, dinitrogen oxide N₂O₅ and dinitrogen pentoxide N₂O₅. Density of the two most significant nitrogen oxides is comparable with air [6].

NOₓ emissions are a serious problem, because they are linked to the burning of noble fuels (gas, Diesel oil), including biomass and their production is of a progressive nature. Cars are the primary source of up to 55 % of anthropogenic NOₓ, despite catalytic converters. There are high temperatures during fuel combustion in cars. Therefore the atmospheric nitrogen N₂ oxidises to so called high-temperature NOₓ [7].

NOₓ reacts with ammonia, moisture, and other compounds to form nitric acid vapour and related particles. Small particles can penetrate deeply into sensitive lung tissue and damage it, causing premature death in extreme cases. Inhalation of such particles may cause or worsen respiratory diseases such as emphysema, bronchitis it may also aggravate existing heart disease [8], [9].

NOₓ reacts with volatile organic compounds in the presence of sunlight to form ozone. Ozone can cause adverse effects such as damage to lung tissue and reduction in lung function mostly in susceptible populations (children, elderly, and asthmatics). Ozone can be transported by wind currents and cause health impacts far from the original sources [10].

The amount of emitted NOₓ is dependent on many factors. If driving style, terrain and current weather conditions are not considered, then the NOₓ emissions depend mainly on the following factors:

2) Principles of oxidation catalyst and its action [12].
3) The type and amount of biodiesel added to fuel [13].
4) The composition and quality of Diesel oil [11], [14].
5) The type and composition of additives added to fuel [15].

The calculation of the NOₓ emissions is based on the knowledge of an emission factor \( E_{\text{NO}_x} \) [g kg⁻¹] for...
\[ E_{f}^{NOx} = m_{NOx} \times m_{F}^{-1} = y_{NOx}^d \times \frac{M_{NOx} \times n^d}{M_{F} \times N_{F}} \] (1)

where \( m_{NOx} \) is the molar molecular weight \( NOx \) [g mol\(^{-1}\)], \( M_{F} \) [kg.mol\(^{-1}\)] molar molecular weight of fuel, \( n^d \) [mol] substance amount of dry exhaust gases, \( N_{F} \) [mol] substance amount of consumed fuel, and \( y_{NOx}^d \) molar fraction of \( NOx \) in dry exhaust gases.

There are number of additives that can be added to Diesel oil. These can be classified into three basic categories according to the character of their effects [17]:

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

Refinery additives are added to fuels during production and refinery mainly in order to improve:

a) Flow properties of middle fraction and ensure that fuel does not freeze in winter season.
b) Lubricating capabilities of fuel. Additives are used to compensate for the loss of these capabilities in the production of fuels with low and ultra-low content of sulphur.
c) Cetane number with the aim to meet the requirements for flash-point without cost demanding refinery procedures.

The safety increasing and legally required additives may be added in any phase of delivery cycle. Common additives used for these purposes are:

a) Dyes applied for red colouration of fuels in agriculture.
b) Markers for easy identification of fuels; markers do not colour the fuel, but can be extracted and then identified with the help of easy laboratory and road tests.

do the additives improving the technical parameters and increasing the engine performance are added into Diesel oil in doses, usually at a distribution terminal. They may also be applied later by an end user either into a storage tank or a car fuel tank. The common additives of this category include the following:

a) Anti-foam agents reducing foam formation.
b) Additives increasing the cetane number and improving the fuel ignition properties.
c) Anti-corrosion additives applied in storage tanks and car fuel tanks.
d) Detergents applied with the aim to maintain fuel injection nozzles clean.

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The Envirox™ Diesel oil additive should improve not only the technical parameters of fuel, but also bring a number of other advantages in comparison with conventional additives [17].

The Envirox™ is a dispersion of CeO2 nanoparticles in aliphatic and cyclo-aliphatic hydrocarbons. Unlike conventional additives, Envirox™ is advertising efficiency throughout all combustion process, because most of the common ingredients decompose under the thermodynamic conditions prevailing in the engine combustion chamber. The additive enables engine to gain more energy from fuel and thus reduce its consumption, remove the residual soot deposits in engine combustion chamber while minimizing the formation of some contaminants [18].

Chemistry of combustion process is presented in (2) for the more efficient use of fuel energy, in (3) for the elimination of carbon deposits in engine combustion chamber and (3)-(6) for the reduction of pollutants in emissions [2].

\[
\begin{align*}
(4x+2)CeO_2 + C_iH_j &= (2x+y)Ce_2O_3 + xCO_2 + yH_2O \\
4CeO_2 + C &= 2Ce_2O_3 + CO_2 \\
Ce_2O_3 + Co &= Ce_2O_4 + CO_2 \\
2Ce_2O_3 + 2NO &= 4CeO_2 + N_2 \\
4Ce_2O_3 + 2NO_2 &= 8CeO_2 + N_2
\end{align*}
\]

The regeneration of CeO2 catalyst is carried out in accordance with chemical (7):

\[
4Ce_2O_3 + O_2 = 2CeO_2
\]

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 (by 5-12%) while reducing the emissions of CO2, CO, NOx, CxHy and particulate matter. The additive is also compatible with all standard Diesel additives [18], [19].

III. PROBLEM SOLUTION

A. 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 0-6000 revolutions min\(^{-1}\). 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 oil by inductively coupled plasma atomic emission spectroscopy was 7.6 ppm w/w, which corresponds to Envirox™ suppliers' requirement.

Diesel engine with the following characteristics was used for the test: Tatra T3 930-31 four stroke, direct injection naturally-aspirated engine, 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 2.2×10³ min⁻¹ revolutions with a maximum torque of 1.13×10⁵ N m at 1.4×10³ ± 200 min⁻¹ revolutions.

The measurement of NO and NO₂ emissions was performed by a combined device called ECOM–JN for analysing the combustion gas composition, equipped with electrochemical sensor, which enabled the determination of the concentrations of CO₂ and O₂, which are necessary for calculating the NOₓ emission factor.

Sample of combustion gas was taken by a tube probe of underpressure analyser pump. The current air mass was led from the tube probe by unheated tube to filters and moisture separator of analyser and then to pollutant sensors. It was possible to determine the concentration of CO and NOₓ by applying the unheated tube between the probe and the analyser as possible combustion gas condensation on the way did not affect their concentration.

The C₂H₆ content, which is also necessary for calculating the NOₓ emission factor, was tested by analyser operating on the principle of flame ionization detection (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 analyser 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 underpressure analyser pump.

\[ \frac{e}{2} N₂ + C₄H₁₀ \rightarrow CO₂ + [a \times (1 - z / 2) + b / 4 - c / 2 + d \times (1 - w / 2)] O₂ \]
\[ = a \times (1 - z) CO₂ + a \times z CO + (b / 2) H₂ O + d \times (1 - w) NO₂ + e \times \text{wNO} \]
\[ a \times (N_F - n_F) = n_{CO₂} + n_{CO} \]
\[ 2(N_{O₂} - n_{O₂}) + c \times (N_F - n_F) = \]
\[ n_{H₂O} + 2n_{CO₂} + n_{CO} + 2n_{NO₂} + n_{NO} \]
\[ N_F = N_{N₂} + N_{O₂} + N_{CO₂} \]
\[ b \times (N_F - n_F) = 2n_{H₂O} \]
\[ 2(N_{N₂} - n_{N₂}) = n_{NO₂} + n_{NO} \]
\[ n^d = n_{N₂} + n_{O₂} + n_{CO₂} + n_{CO} + n_{P} + n_{NO₂} + n_{NO} \]

\[ \text{Molar fractions } Y_i^d \text{ and } y_i^d \text{ of } i\text{-th element in dry inlet air and exhaust gas are defined by relations (17) and (18) respectively:} \]
\[ Y_i^d = N_i \times (N_i^d)^{-1} \]
\[ y_i^d = n_i \times (n_i^d)^{-1} \]

where \( N_i \) [mol] represents the substance amount of \( i\)-th component in the inlet air, \( n_i \) [mol] the substance amount of \( i\)-th component in output, and symbols \( N_i^d \) [mol] and \( n_i^d \) [mol] have the same meanings as in (13) and (14).
Equations (18) and (19) necessary for the calculation of emission factor $E_{fr}^{NO_x}$ may be derived from the basis of mass balance while accepting relations (15) – (17).

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

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

2. Molar Fractions of Unmonitored Components

As the concentration of water vapour and CO$_2$ in exhaust gases were not monitored, it was necessary to express their concentration from the mass balance. After modification, the relation (20) has been obtained for the molar fraction in dry combustion gases $y_{H_2O}^d$ and the relation (21) for the molar fraction $y_{CO_2}^d$, which were then used for calculating the emission factor $E_{fr}^{NO_x}$.

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

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

3. Calculation of Fuel Composition

The stoichiometric coefficients in (8) can be set if the relative proportion $\psi_i$ of each $i$-th fuel component is known. It is clear that the relations (22) and (23) are valid:

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

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

And the relation (24) is valid for the molecular weight of fuel $\mu_F$ related to one carbon atom:

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

where $\psi_C$, $\psi_H$ and $\psi_O$ represent the relative contents of carbon, hydrogen and oxygen in fuel; $A_C$, $A_H$ and $A_O$ [g mol$^{-1}$] corresponding molar atomic weights; and constants $\beta$ and $\gamma$ have the same meaning as in (15).

The relation (25) for constant $\gamma$ is derived using (22) and (23) and (26) for constant $\omega$ after substituting $\gamma$ into relation (15):

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

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

After substituting from relations (22) and (23) into formula (24) it applies (27) for $\mu_F$, from which it is possible to express easily the stoichiometric coefficients $a$, $b$, $c$ of (8).

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

4. Calculation of Emission Factor

It is possible to calculate the emission factor for NO$_x$, $E_{fr}^{NO_x}$ according to relation (28), which was deduced by substituting $n^d \times (Np)^{-1}$ from formula (18) in (1) ad by applying the relation (27) for $\mu_F = M_F \times a^{-1}$. 

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The calculated values of emission factors for NOx under the changing conditions of engine operation when NM-54 Diesel oil was used both with and without additives are presented in Table 1. It is apparent that the NOx emissions have been reduced by approx. 7.5% in total when additives were applied.

The total reduction of CO2 emissions in case the additive was dosed into Diesel oil was 0.3%, which was insignificant and corresponded to the fuel consumption slightly decreased by approx. 1.5% and recorded during the whole process of measuring. Therefore it may be stated that the balance of carbon in combustion gases ranges within the uncertainty of measurement. It has also been found out that saving in fuel of carbon in combustion gases ranges within the uncertainty of measuring. Therefore it may be stated that the balance by approx. 1.5% and recorded during the whole process and corresponded to the fuel consumption slightly decreased.

The fact that the declared reduction in fuel consumption and thus the reduction in CO2 emissions have not been proved may partially be explained by shorter time of sampling after the additive was applied in the fuel. It may also have been caused by an old type of engine produced in 1986, in case of which the above mentioned effect need not be fully displayed. Therefore further testing is planned for a newer type of engine with the sampling period after 200 hours of engine operation at minimum with the fuel containing the tested additive.

At the same time the dependencies of emission factor for NOx on the reduced torque TMR, engine power P and revolutions r have been monitored. The example in Fig. 2 illustrates the graphical dependence of emission factors for NOx as a function of TMR. In accordance with theoretical expectations it may be stated that after an initial slight increase the emissions of NOx then decrease with the increasing TMR due to more efficient fuel combustion. Format of the trend line was evaluated by linear regression through the polynomial of second degree with the corresponding regression and reliability value R.

The increase in NOx emissions at high TMR while using the additive as opposed to the emissions of clear Diesel oil is difficult to be explained.
Similarly the decrease in NOx emissions was monitored at the increased engine performance. On the contrary the emission factor NOx is the highest at engine revolutions
\( \approx 1900 \text{ min}^{-1} \), which is in contradiction to theory. Therefore it will be reasonable to verify the findings in further experiments under the conditions mentioned above and with a newer type of engine.

IV. CONCLUSION

The methodology of measuring and calculation of NOx emissions in engine exhaust gases has been developed. It has been discovered that the Envirox™ additive based on dispersed CeO2 nanoparticles reduces the value of the NOx emission by approx. 7.5%, which is in compliance with the findings of the Oxonica company [19]. The above mentioned methodology may also be applied for determining the emission factors of CxHy, CO, CO2 [2] and particulate matter [20]. However, the declared decrease in fuel consumption by 5–12% has not been verified. The maximum fuel savings of approx. 3% was monitored only under optimum conditions of engine operation, and was accompanied by the reduction in CO2 emissions by approx. 2.5%.

At the same time dependencies of the emission factor for NOx were monitored on reduced torque, engine power and engine revolutions. Beside one exception the mentioned functions were in accordance with theoretical expectations. Disagreements with the data reported by Oxonica on fuel consumption as well as the dependencies of the emission factor NOx on the selected engine characteristics will have to be verified in further tests on a newer type of engine and after sufficiently long period of engine operation with the Envirox™ additive.

REFERENCES


