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INFLUENCES ON NO_2-EMISSIONS FROM DPF'S WITH PASSIVE REGENERATION

WPŁYW DPF Z PASYWNĄ REGENERACJĄ NA EMISJĘ NO_2

A b s t r a c t

NO_2 is much more toxic than NO. Due to the use of oxidation catalysts and catalytic coatings in the exhaust gas systems in the last decades and due to the use of low sulphur fuels the average NO_2 – portion in exhaust gases of vehicles increases. Diesel oxidation catalysts (DOC) and Pt – containing DPF-coatings are generally used to support the regeneration of particle filters, which can be a source of strongly increased NO_2 – production. The present paper shows some examples and summarizes the experiences in this matter elaborated at the Laboratories for IC-Engines & Exhaust Emissions Control (AFHB) of the University of Applied Sciences Biel-Bienne, Switzerland, during some research activities on engine dynamometers in the years 2010–2012. In general it can be stated: with a Pt – coated catalyst (DOC), or with catalytic surface filter (CSF) there is a maximum of NO_2/NO_x – ratio typically in the exhaust gas temperature range around 350°C, with higher Pt – content in the coating there is a higher potential for NO_2 – formation, lower NO_2 – production appears with: higher spatial velocity, higher S-content in fuel and with DOC/DPF used and/or soot loaded.

Keywords: *NO_2 non-legislated component, Diesel particle filter systems, DOC-DPF coating, DPF soot load*

S t r e s z c z e n i e

NO2 jest znacznie bardziej toksyczne niż NO. Na skutek stosowania w ostatnim czasie katalizatorów utleniających i powłok katalitycznych w układach wydechowych, a także na skutek stosowania paliw o niskiej zawartości siarki, średnia ilość NO2 w spalinach pojazdów wzrasta. Katalizatory utleniające dieslowskie (DOC) i powłoki DPF zawierające Pt są zwykle stosowane wspomagająco w regeneracji filtrów cząstek, co może być źródłem silnego wzrostu NO2. W niniejszej pracy przedstawiono kilka przykładów i podsumowano badania doświadczalne przeprowadzone przy zastosowaniu dynamometrów silnikowych, w Laboratoriach dla IC-Engines & Exhaust Emissions Control (AFHB) Uniwersytetu Nauk Stosowanych Biel-Bienne, w Szwajcarii, w latach 2010–2012. Ogólnie można stwierdzić:

– Przy katalizatorze (DOC) powlekanym platyną, lub przy filtrze (CSF) o powierzchni katalitycznej, maksymalny współczynnik NO_2/NO_x występuje zazwyczaj przy temperaturze spalin ok. 350°,
– Przy wyższej zawartości Pt w powłoce, możliwość powstawania NO2 jest większa,
– Mniejsze wytwarzanie NO_2 występuje przy: wyższej prędkości przestrzennej, wyższej zawartości S w paliwie i przy zastosowaniu DOC/DPF i/lub obciążeniu sadzą.

Słowa kluczowe: nieprzewidziany składnik NO_2, systemy filtracji cząstek w silnikach wysokoprężnych, powłoka DOC-DPF, obciążenie sadzą DPF

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Abbreviations

AFHB – Abgasprüfstelle FH Biel, CH
Air min – stoichiometric air requirement
BAFU – Bundesamt für Umwelt, (Swiss EPA)
BfE – Bundesamt für Energie
Cdpf – Catalytic DPF
CFPP – cold filter plugging point
CLD – chemiluminescence detector
CPC – condensation particle counter
CRT – Continuously regenerating trap
DC – Diffusion Charging sensor
DI – Direct Injection
DOC – Diesel oxidation catalyst
DPF – Diesel Particle Filter
ECU – electronic control unit
EMPA – Eidgenössische Material Prüf- und Forschungsanstalt, CH
FE – filtration efficiency
FI – fuel injection
FID – flame ionization detector
FL – full load
FOEN – Federal Office of Environment (BAFU), CH
FTIR – Fourier Transform Infrared Spectrometer
HD – heavy duty
ICE – internal combustion engines
LRV – Luftreinhalteverordnung, CH (OAPC)
NDIR – nondispersive infrared
NEM – non limited engine map
OAPC – Ordinance on Air Pollution Control
OEM – original equipment manufacturer
OP – operating point
PAH – Polycyclic Aromatic Hydrocarbons
RME – rapeseed oil methyl ester
SV – spatial velocity
TTM – Technik Thermische Maschinen, CH
ULSD – ultra low sulfur Diesel
VERT – Verification of Emission Reduction Technology (www.vert-certification.eu)

1. Introduction

NO_x are a complex mixture of diverse oxides of nitrogen, mainly NO and NO_2 in proportions varying with engine types and their operating conditions, nature of the exhaust control devices and measuring protocols. NO_x as a whole family is said to be easy to measure, as well as NO alone, which leads to express NO_2 by calculation according to equation $NO_x - NO = NO_2$.

In the present exhaust gas legislations for on-road vehicles the nitric oxides are measured in summary as volumetric NO_x-concentration and recalculated in the mass-emission by means of the density of NO_2, even if there is usually a relatively low NO_2 content in NO_x at engine-out.

As combined effect of: increasing fleet of Diesel vehicles with oxidation catalysts (DOC), use of low Sulfur fuels and of passive DPF regeneration systems an increase of atmospheric pollution with NO_2 and Ozone can be observed in the dense traffic areas, in spite of general reduction of NO [1–5].

An oxidation catalyst, which often is used as a key element of the DPF regeneration concept, can increase the NO_2- portion in the exhaust gas, which is of big concern, since NO_2 is more toxic than NO.

Some particulate filters technologies are especially problematic as they form NO_2 on purpose to regenerate the filter continuously. The process would be attractive as long as there would be a stoichiometric equilibrium between PM and NO_2, but the good operation of such DPF requires an excess of NO_2 and therefore emit a large excess of unconsumed NO_2.

Most known is the continuously regenerating trap CRT, a technology, which uses NO_2 as the only oxidizing agent to continuously burn the soot. This technology is used to retrofit buses in several European cities and it also is one of the reasons of locally increased NO_2-level [6].

The SCR deNO_x-systems, a very important technology especially in the HD-segment, attain the best NO_x reduction rates when a half of NO_x is converted to NO_2 before entering the SCR-catalyst. In some operating conditions NO_2-slip is possible [7–13].

NO_2 is limited in the air protection legislation [14], i.e. Germany since 1.01.2010 restricted limit values: yearly average $< 40\ \mu g/m^3$. (Respiration of concentrations 10–100 $\mu g/m^3$ over longer time leads to durable health damages). Due to these efforts the reasons of NO_2-production were extensively investigated by the concerned industry [13–15]. It results that the lower spacial velocity and the higher content of Pt-coating increase NO_2.

Interesting results about durability of the catalytic coatings are given in [15]. The NO_2/NO_x ratio after DOC+cDPF, at certain operating condition of the engine, is reduced with the number of active regenerations, due to similar reduction of specific active surface of the washcoat. This can be represented with the following Table 1.

The objectives of the present paper are to verify some known influences on NO_2-formation and to add some specific new examples which are from interest in order to minimize the emissions of NO_2.

Table 1

Influence of number of active regenerations on NO_2/NO_x-ratio after DOC+cDPF; example from [15]

Number of active regenerations	0	100	200	300
NO_2/NO_x [%]	67	51	47	46

2. Test engines

The presented results are obtained on two Diesel engines: IVECO F1C version Euro4 and LIEBHERR D934S.

The IVECO engine is attached to a dynamic brake, which enables to perform all kind of dynamic testing.

Figure 1 shows the engines in the laboratory for IC-engines, University of Applied Sciences, Biel-Bienne and Table 2 summarizes the most important data.

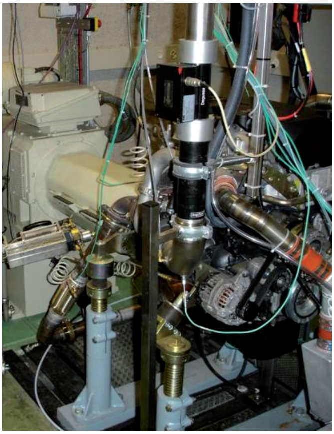


Fig. 1a. Iveco engine F1C in the engine room

Rys. 1a. Silnik Iveco F1C w maszynowni

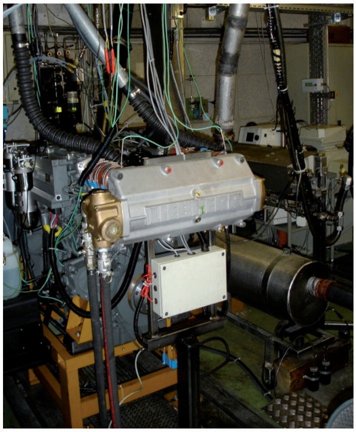


Fig. 1b. LIEBHERR engine D934 in the engine room

Rys. 1b. Silnik LIEBHERR D934 w maszynowni

Table 2

Data of the tested engines

Manufacturer	Iveco, Torino Italy	Liebherr Machines Bulle S.A., Bulle/Fribourg
Type	F1C Euro 4*)	D934 S
Displacement	3.00 Liters	6.36 Liters
RPM	max. 4200 rpm	2000 min^{-1}
Rated power	105 [kW] @ 3500 [min^{-1}]	111 kW
Model	4 cylinder in-line	4 cylinder in-line
Combustion process	direct injection	direct injection
Injection system	Bosch Common Rail (CR) 1600 bar	Bosch unit pumps
Supercharging	Turbocharger with intercooling	Turbocharger with intercooling
Emission control	cooled EGR**)	none (exhaust gas aftertreatment according to the requirements)
Development period	until 2005	2005

*) light duty and heavy duty.

**) in present tests engine was used with closed E(4) EGR.

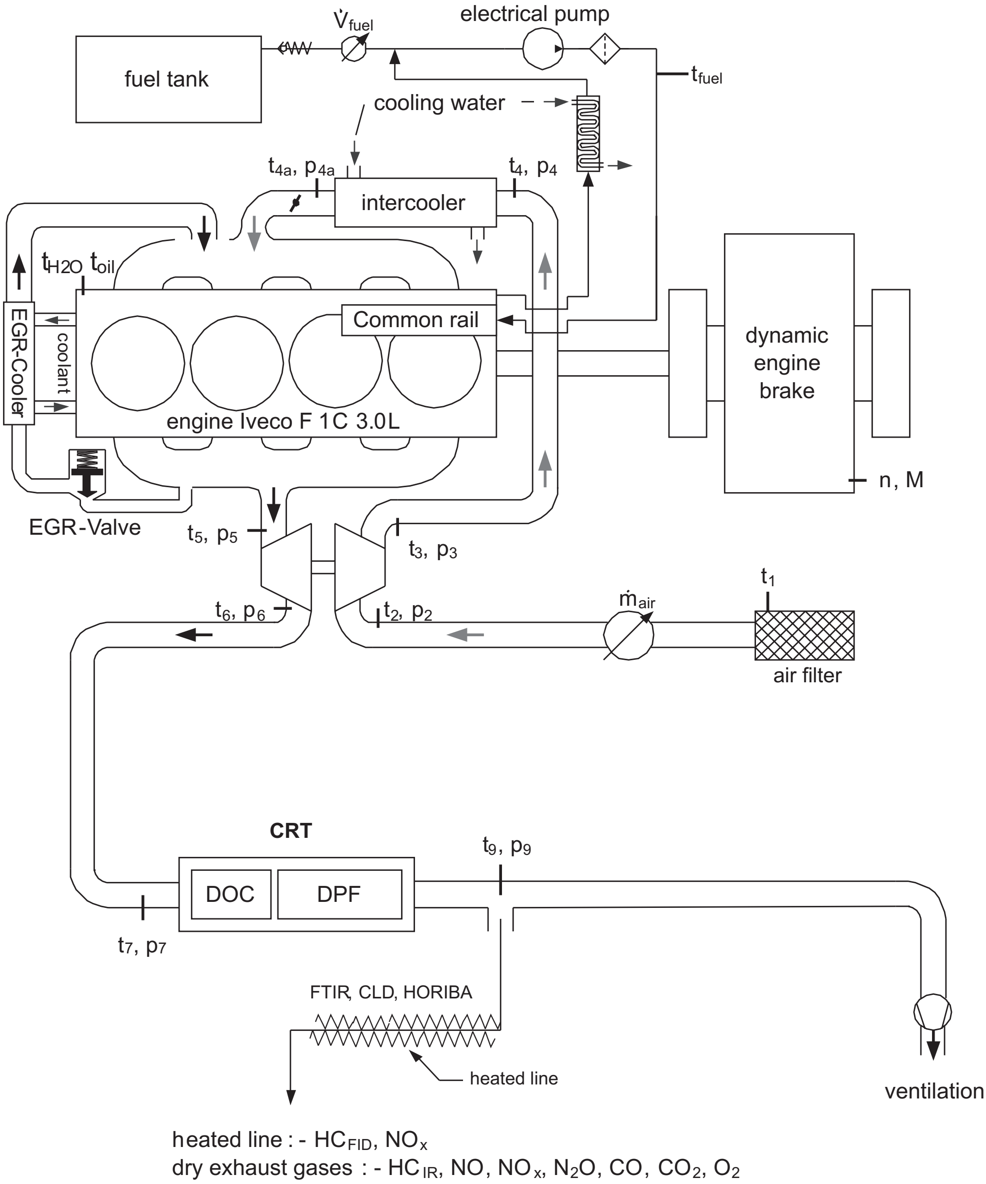


Fig. 2. Engine measuring set-up on the dynamic dynamometer

Rys. 2. Pomiary silnika z użyciem dynamometru dynamicznego

As fuel the Swiss market Diesel fuel according to SN EN 590, with $S < 10$ ppm w/w is used.

3. Measuring set-up & instrumentation

Figure 2 shows the scheme of installation, the measured control parameters and emissions in the exhaust of IVECO engine. The Euro4 version is equipped with EGR, which nevertheless was kept closed in the presented tests by means of the access to the engine ECU.

The installation and the control parameters of the LIEBHERR engine are nearly equal and are not represented separately. The used measuring systems for exhaust emissions are the same as for IVECO.

4. Test equipment for exhaust gas emissions

The measurement is performed according to the Swiss exhaust gas emissions regulation for heavy duty vehicles (Directive 2005/55/ECE & ISO 8178):

1. Volatile components:
   - Horiba exhaust gas measurement devices,
   - Type VIA-510 for CO_2, CO, HC_{IR}, O_2,
   - Type: Eco Physics CLD 822 for NO, NO_x,
   - Amluk exhaust gas measurement device Type FID 2010 for HC_{FID}.
2. FTIR (Fourier Transform Infrared) Spectrometer (AVL SESAM) with possibility of simultaneous, time-resolved measurement of 25 emission components – among others: NO, NO_2, NO_x, NH_3, N_2O, HCN, HNCO.

5. Test procedures

On both engine dynamometers stationary operating points (OP), so called steps-tests were performed. An example is given in Fig. 3.

All steps-tests were performed with a warm engine and for each research task always in the same sequence and with the same operating duration of the OP's.

Similar steptest were also performed on LIEBHERR engine at different engine speeds according to the size of the investigated DPF's.

In one test series on IVECO engine operating points with different exhaust gas temperatures, but with constant spatial velocity (SV = const) were driven.

On Iveco engine the dynamic testing was performed mostly with the ETC (European Transient Cycle), which was defined on the basis of the non limited engine operation map (NEM), for the engine version E3 (Fig. 4). The definition of ETC was not changed for the engine version E4 to keep a better comparability with the previous results.

Before the start of each dynamic cycle the same procedure of conditioning (a preliminary ETC) was used to fix as well as possible the thermal conditions of the exhaust gas aftertreatment system.

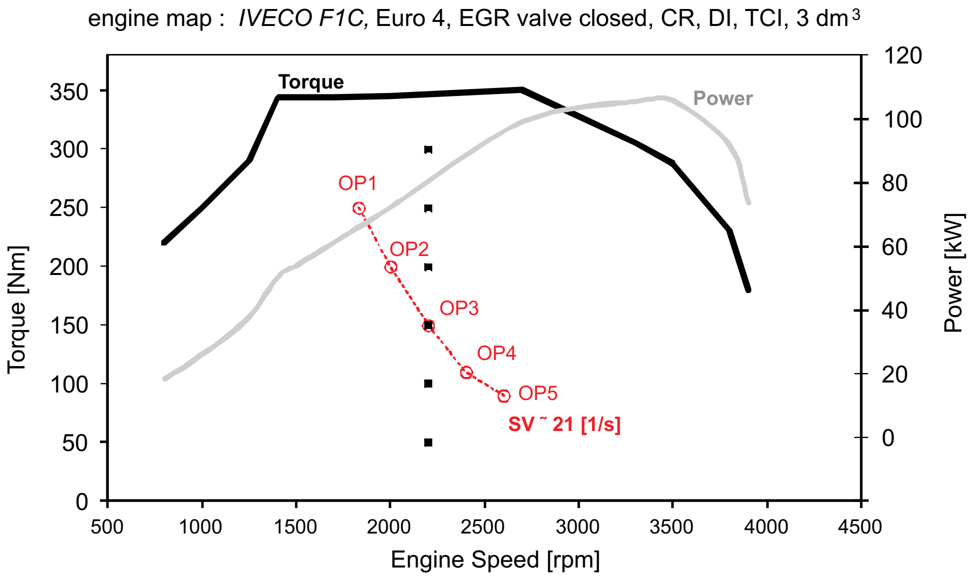


Fig. 3. Operating points in steptest and at SV = const on the IVECO engine

Rys. 3. Punkty robocze w teście krokowym i przy SV = const dla silnika IVECO

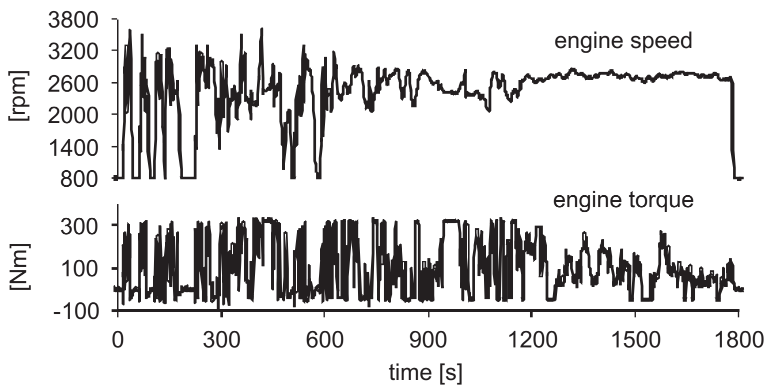


Fig. 4. Torque & speed in ETC IVECO F1C

Rys. 4. Moment i prędkość w ETC IVECO F1C

6. Tested DPF systems

The investigated DPF systems are represented in the Table 3.

Table 3

Data of the tested DPF systems with passive regeneration

DPF Syst. Nbr.	DOC Pt [g]	DOC Pd [g]	DPF Pt [g]	Regeneration	Active volume [m^3]	Summary Pt [g]
1	8.33	4.16	1.45	CRT	0.2	9.78
	SiC ø 144 mm x 102 mm		SiC ø 144 mm x 254 mm			
2	5.58	1.39	1.45	CRT	0.2	7.03
	SiC ø 144 mm x 102 mm		SiC ø 144 mm x 254 mm			
3	1.16	1.16	1.45	CRT	0.2	2.61
	SiC ø 144 mm x 102 mm		SiC ø 144 mm x 254 mm			
4	8.33	4.16	0	CRT	0.06	8.33
	SiC ø 144 mm x 102 mm		SiC ø 144 mm x 254 mm			
5	2.94	1.47	4.41	CRT	0.66	7.35
	SiC ø 229 mm x 152 mm		SiC ø 229 mm x 305 mm			
6	4.41	4.41	4.41	CRT	0.66	8.82
	SiC ø 229 mm x 152 mm		SiC ø 229 mm x 305 mm			
7	–		4.41	cDPF	0.44	4.41
			SiC ø 229 mm x 305 mm			
8	4.41	4.41	–	CRT	0.22	4.41
	SiC ø 229 mm x 152 mm		SiC ø 229 mm x 305 mm			
9	Pt/Pd/Rh		Pt/Pd/Rh	CRT	0.81	n/a
	Metal ø 283.5 mm x 130 mm		SiC ø 283.5 mm x 355 mm			
10	–		V_2O_5	cDPF	1.22	–
			SiC ø 275 mm x 584 mm			
11	3.8	–	V_2O_5 (14g/L)	CRT	0.24	3.8
	SiC ø 151 mm x 120 mm		SiC ø 151 mm x 300 mm			

The DPF's 1 to 8 were tested on IVECO engine: DPF's 1 to 4 are called "small" and DPF's 5 to 8 are called "big". DPF's 9 to 12 were investigated on LIEBHERR engine.

7. Results

7.1. DPF system coating

Figure 5 shows the time plots of exhaust gas temperature before DPF and of NO_2 in the steptest with different Pt- and Pd-content in the catalytic coating of the smaller DPF's. At a given load jump, with nearly identical temperature profile and with the same spatial velocity (SV) the higher content of the catalytic precious metals increases quicker the NO_2 to slightly higher values – see steps 3 & 4.

The bars in the lower part of this figure represent the NO_2/NO_x-ratio in the first four steps with the different coatings. DPF4 with the same coating of DOC, as DPF1, but with uncoated DPF-part has a significantly lower active volume (less residence time of gas in the proximity of catalytic substance) and shows respectively less NO_2-production.

In the 1st step with temperature below the light-off of the catalysts there is a lowering of NO_2 with DPF. This is a well known and repetitive effect, which is explained by partial decomposition of NO_2 to NO+O and a slight reduction with the present CO & HC.

Figure 6 compares the results of NO_2, NO_2/NO_x-ratio and $\Delta NO_2/NO_x$-ratio in stepstests with the bigger DPF's.

It is clearly to see, that the DPF6 with the highest Pt/Pd-content produces more intensely NO_2. The DPF8 with uncoated DPF-part and with the same DOC, as DPF6 produces the lowest values of NO_2 especially in the higher temperature range (higher steps). The DPF8 has the lowest active volume and especially at higher load-steps a high spatial velocity (see Fig. 10).

The Swiss DPF-quality systems VERT & OAPC consider the ratio $\Delta NO_2/NO_x$ according to the Swiss Norm SN 277 206 and indicate it in the results. The NO_2-producing DPF-systems are recommended not to be used in closed environments like in buildings, or in underground.

Figure 7 gives an example of results with the smaller DPF's in ETC. There is again a clear tendency of highest NO_2-values with the strongest catalytic coating of the DPF1.

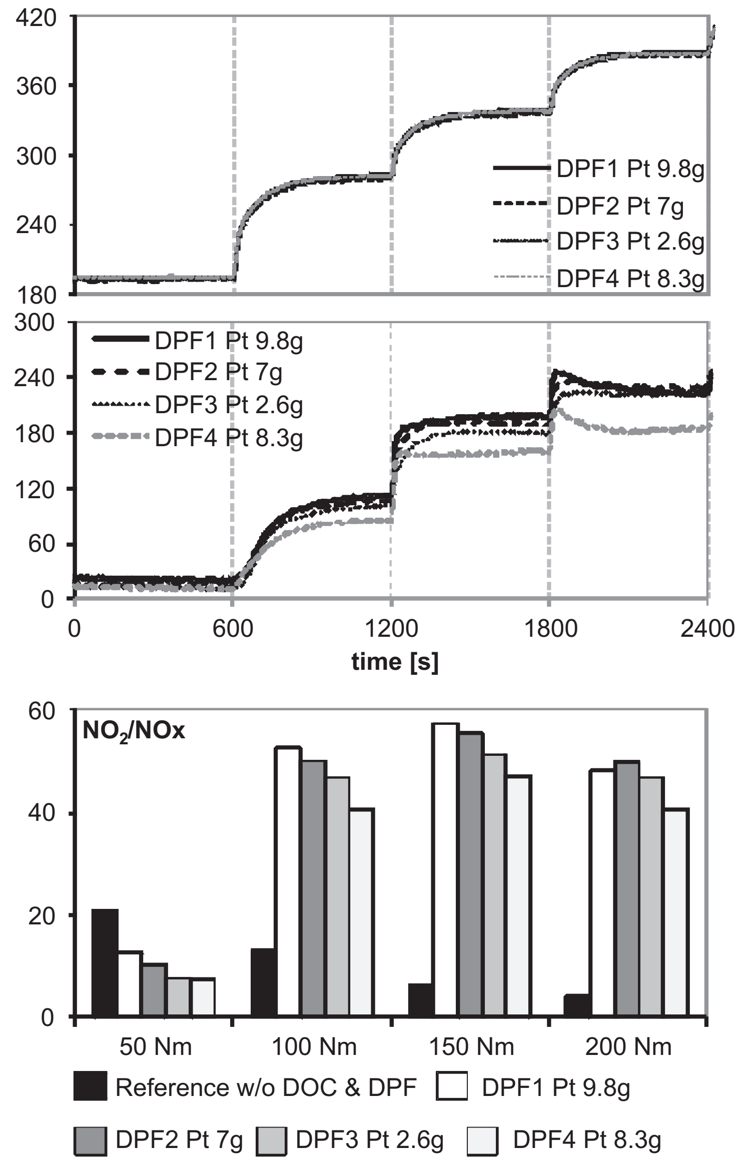
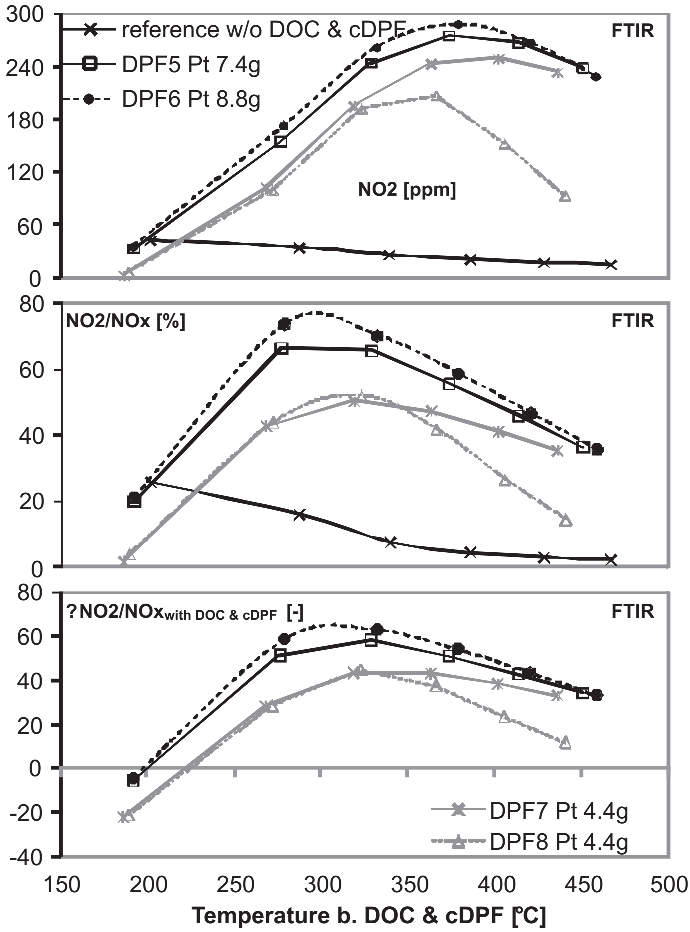


Fig. 5. NO_2-production in step-test with different content of Pt in the catalytic coating, smaller DPF's, Iveco engine F1C

Rys. 5. Wytwarzanie NO_2 w teście krokowym przy różnych zawartościach Pt w powłoce katalitycznej, mniejsze DPF-y, silnik IVECO F1C



> $\Delta NO_2 = NO_{2\text{with DOC \& cDPF}} - NO_{2\text{without DOC \& cDPF}}$

> $\Delta NO_2/NOx_{\text{with DOC \& cDPF}}$

> average values, 60 s

Fig. 6. NO_2 & ΔNO_2 versus temperature with different Pt-content and different active volume of the bigger DPF's, Iveco F1C

Rys. 6. NO_2 i ΔNO_2 w funkcji temperatury przy różnych zawartościach Pt i różnej aktywnej objętości większego DPF, Iveco F1C

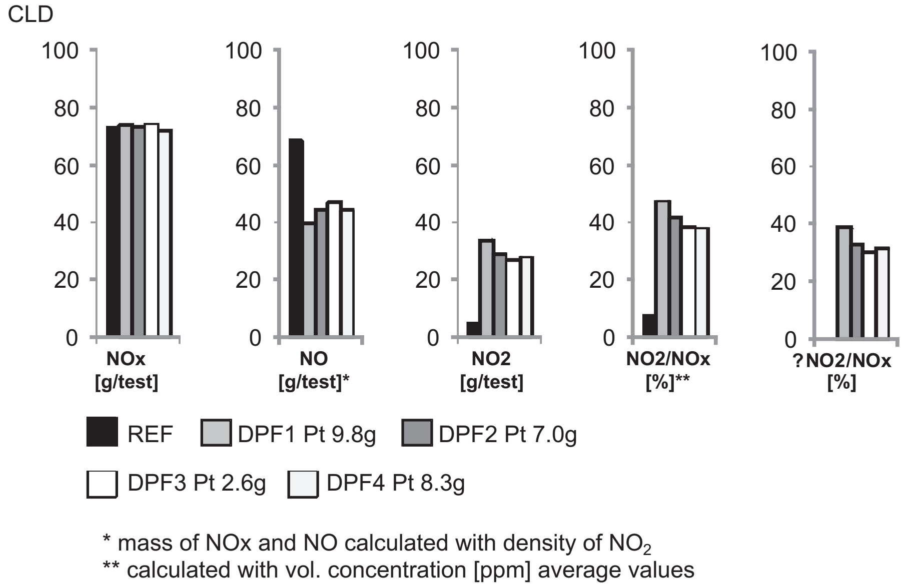


Fig. 7. NO_x, NO & NO_2 in ETC with different Pt-content, smaller DPF's, Iveco F1C

Rys. 7. NO_x, NO & NO_2 w ETC przy różnych zawartościach Pt, mniejsze DPF, Iveco F1C

7.2. DPF system size

Figures 8 and 9 represent an extreme influence of DPF-system size on NO_2. The smaller DPF4 has uncoated DPF-part and due to that, the smallest active volume.

Both comparisons: in steptest (Fig. 8) and in ETC (Fig. 9) are at approximately the same exhaust gas temperatures, but the bigger DPF6 has 10 times lower spacial velocity (SV). The summary amount of precious metals Pt/Pd in the coating of both DPF-systems is similar and so it can be concluded, that the lower SV of the bigger DPF6 is the mayor factor of increased NO_2-production.

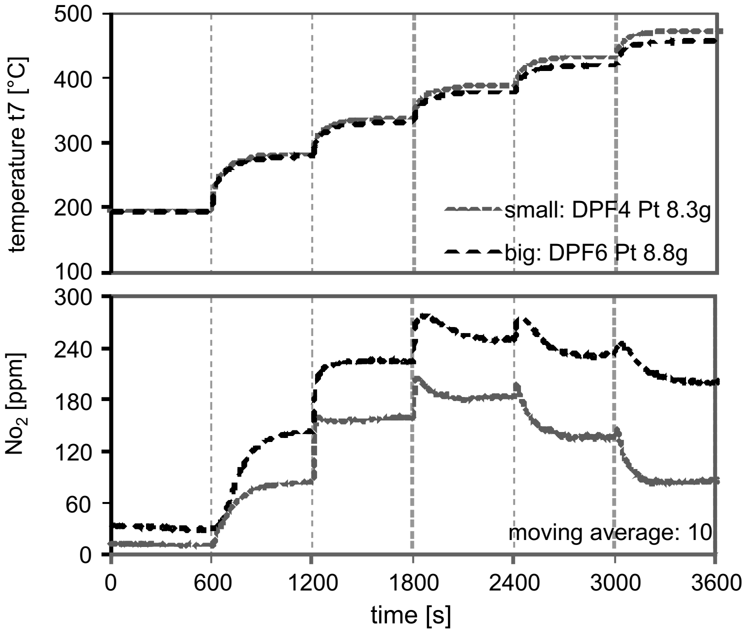


Fig. 8. NO_2 in step-test with different DPF size, Iveco F1C

Rys. 8. NO_2 w teście krokowym przy różnych wielkościach DPF, Iveco F1C

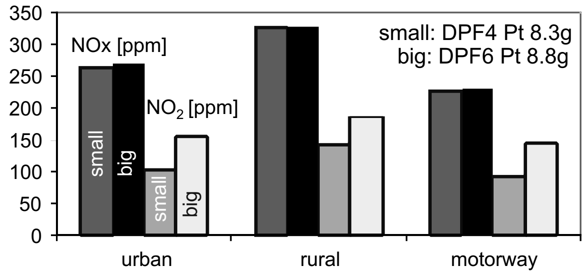


Fig. 9. NO_x & NO_2 in ETC with different DPF size, Iveco F1C

Rys. 9. NO_x i NO_2 w ETC przy różnych wielkościach DPF, Iveco F1C

7.3. Spatial Velocity (SV)

SV is the ratio of the volumetric exhaust gas flow to the reference volume of the aftertreatment device. Here the summary catalytically active volume was considered. The reciprocal value of SV is the residence time of gas element in this device. Higher spatial velocity means shorter residence time.

A trial was performed with different operating points of the engine, but with a constant SV (see operating points in Fig. 3). The value of SV = 21 1/s was chosen, as representative for the highest NO – NO_2 conversion in the steptests.

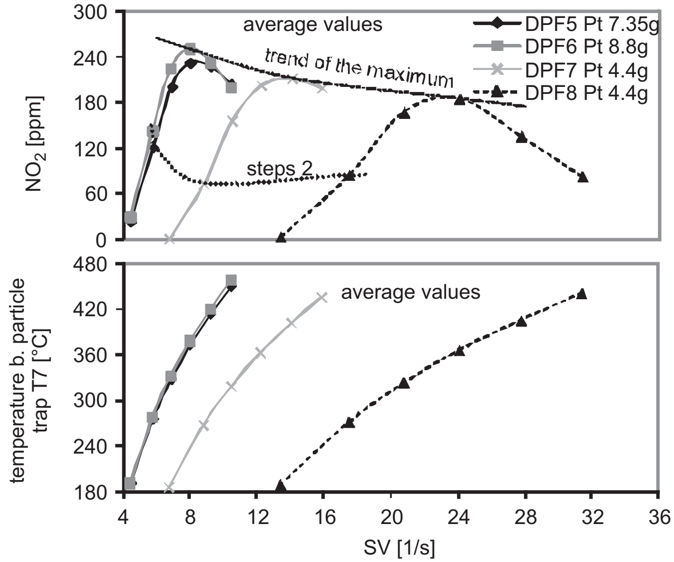


Fig. 10. NO_2 in step-test, dependent on exhaust temperature and spacial velocity; DPF's big, Iveco F1C

Rys. 10. NO_2 w teście krokowym, zależne od temperatury spalin i prędkości przestrzennej; DPF duże, Iveco F1C

Table 4 summarizes the results: the exhaust gas mass flow, exhaust gas temperature and the NO_x-emissions are connected to the engine OP. The NO_2/NO_x-ratio has a maximum at t_7 = 336°C, but the absolute values of NO_2 depend also on NO_x.

Table 4

Operating points and results at SV = const.; DPF2, Iveco F1C

OP		1	2	3	4	5
n	[1/min]	1830	2000	2200	2400	2600
M	[Nm]	250	200	150	110	90
$\dot{m}_{exh}$	[kg/h]	228	245	267	277	290
T_7	[°C]	434	384	336	297	278
Δp_7	[Pa]	8400	8600	8600	7800	8100
$\dot{V}_{exh}$	[m³/h]	438	437	442	432	435
SV	[1/s]	21	21	21.3	20.8	20.9
NO_2	[ppm]	295	268	186	115	87
NOx	[ppm]	778	529	330	241	204
NO_2/NOx	[%]	38	51	56	48	43

It can be summarized, that on an engine there is no liberty to separate the parameters: engine-out NO_x-emission and exhaust gas temperature. This trial confirms nevertheless the maximum intensity of NO_2-production in the temperature range around 350°C.

Figure 10 shows the NO_2-emissions in steptests with the bigger DPF-systems dependent on spatial velocity and exhaust gas temperature DPF's 5 & 6 with the biggest active volume have the lowest range of SV during the steptest. They reach also the highest maximum values of NO_2.

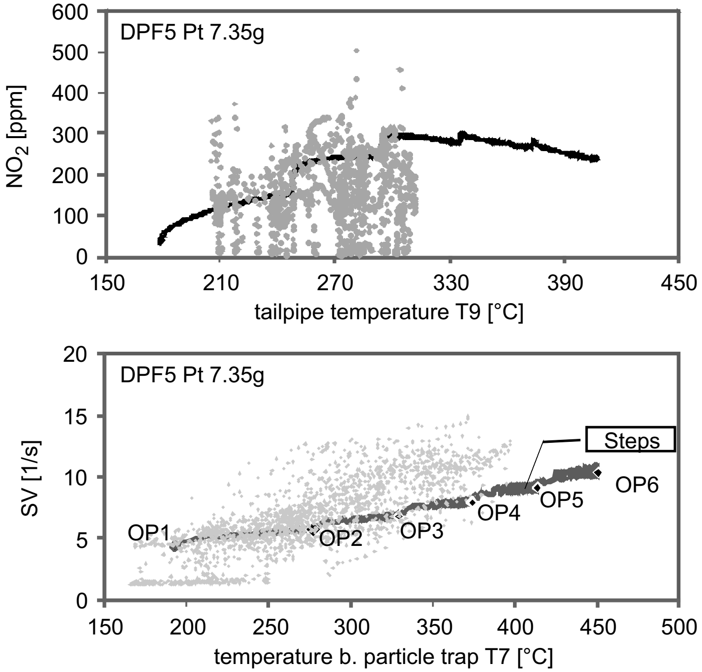


Fig. 11. Comparison of NO_2, t_{exh} & SV in step-test and in ETC, DPF5; Iveco F1C

Rys. 11. Porównanie NO_2, t_{exh} i SV w teście krokowym i w ETC, DPF5; Iveco F1C

The temperatures of NO_2-maximum depend slightly on the SV-range: at higher SV (24 1/s) ≈ 360°C, at lower SV (8 1/s) ≈ 380°C. The represented points in the diagrams are averages of the last 60 s of each step.

Interesting is the comparison of parameters, which influence the NO_2-production in both used testing methods: steptest and ETC (Fig. 11). The step tests with 10 min step duration represent a stationary testing, where the engine attains the emission- and the thermal stability and the exhaust system attains nearly the thermal stability. In opposite to that in a transient test, like ETC, neither the engine, nor the exhaust treatment system attain a thermal stability. The range of tailpipe temperature in ETC starts at higher values than the step test, this because of conditioning before ETC (upper part of Fig. 11). The maximal tailpipe temperatures are higher in steptest, because of longer operation at high OP's and enough time to warm-up the exhaust system. In ETC also high OP's are realized, but only in transient way and there is no time to heat-up the system like in steptest.

Any given constant value of tailpipe temperature in ETC represents a big number of different instantaneous operating points of the engine and also different values of NO_2.

The spatial velocity in ETC varies also in a larger spectrum, than in steps (see lower part of Fig 11), which is a result of strong variations of: exhaust mass flow, exhaust temperature (T_7 before DPF) and backpressure parameters influencing the instantaneous volumetric flow of exhaust gases.

The lowest temperatures before DPF (T_7) are in ETC lower than at tailpipe (T_9). This is because the engine has transitory operation conditions in idling, or in braking mode, while the exhaust system is still warmer due to the conditioning and the thermal inertia.

Summarizing it can be stated, that the parameter which influence the NO_2-formation – temperatures of exhaust gas and of exhaust system, spatial velocity and engine-out emissions (NO_x/NO_2) – vary very much in the transient test cycle.

The resulting instantaneous NO_2 is an effect of overlapping of several influences connected with those parameters.

The conditioning before testing plays important role for the temperature level of the exhaust system and for the repetitivity of emission results.

7.4. Sulfur in fuel

Several attempts of soot loading and regenerations were performed with DPF-systems on Liebherr engine. Fig. 12 shows a comparison of NO_2/NO_x-ratios obtained in steps tests with different sulfur content (ULSD < 10 ppm S and HSD ≈1250 ppm S) and with different coatings. With Pt-coating (DPF 9) there is a significant production of NO_2 with sulfur-free fuel (ULSD). With V-coating (DPF10) this problem does not exist, but there are some strict limits of high temperature operation with V-coating. Nevertheless, there are some important progresses in development and the V-based coatings can be still regarded as an important option to lower NO_2.

With HSD the NO_2-production did not appear even with strong Pt-coatings, because there was a preference of oxidation of sulfur in the catalyst.

7.5. DPF soot load

Figure 13 shows the regeneration attempts of a passive catalytic system (DPF 11) with different soot load. In the steptest with unloaded DPF (reg. nr. 2) the NO_2-production is most intense and in the largest range of operating load steps. The variants with soot-loaded DPF have two reasons for lower NO_2: less NO_2-formation due to masking of catalytic surface and NO_2 consumption for soot oxidation.

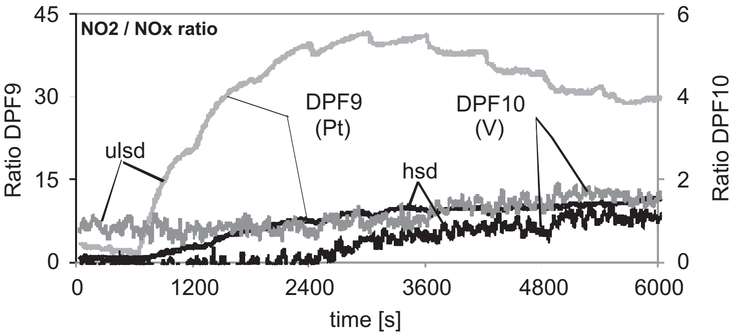


Fig. 12. Influence of high sulfur Diesel fuel (HSD) on the NO_2/NO_x-ratio with different coatings (Pt or V); Liebherr D 934S

Rys. 12. Wpływ oleju napędowego o dużej zawartości siarki (HSD) na współczynnik NO_2/NO_x przy różnych powłokach (Pt albo V); Liebherr D 934S

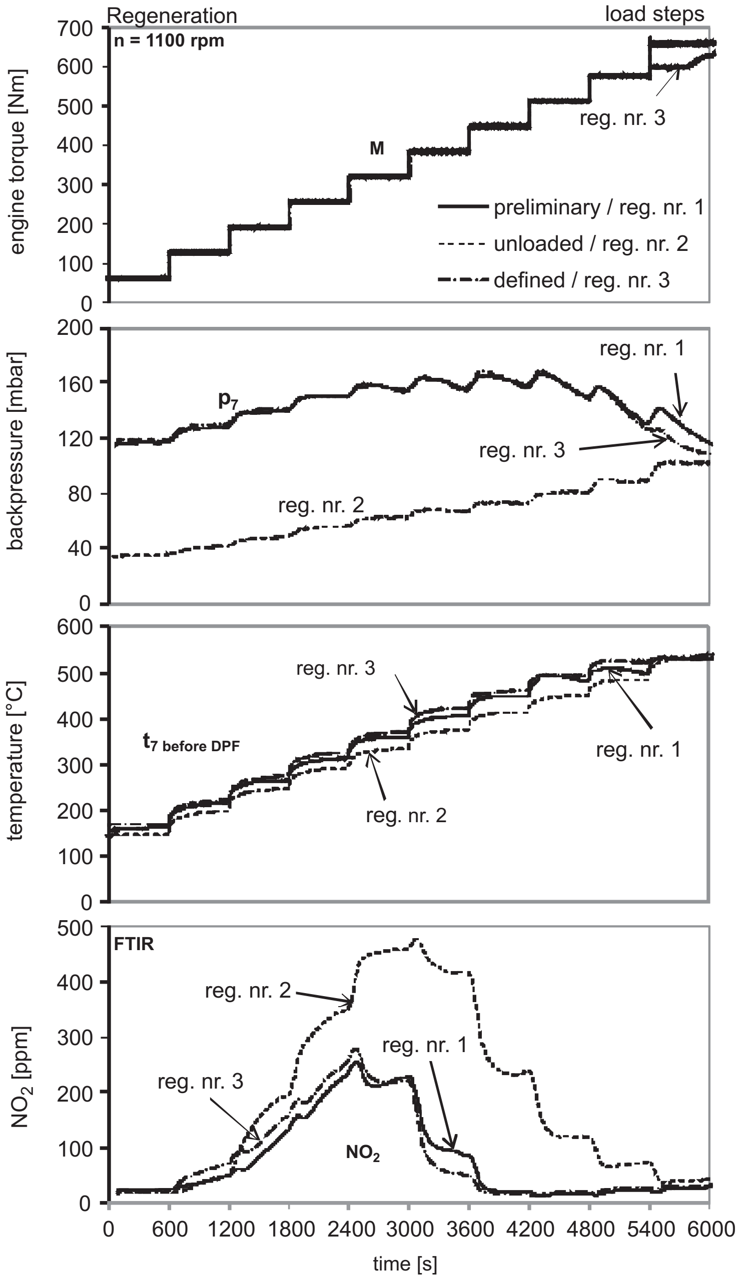


Fig. 13. Effect of different soot loading history on NO_2-emmissions during the regeneration procedure, DPF11; Liebherr D 934S

Rys. 13. Wpływ różnych obciążeń sadzą na emisję NO_2 podczas regeneracji, DPF11; Liebherr D 934S

8. Conclusions

Several examples and influences on NO_2-formation in the catalytically active Diesel particle filter systems were presented in this work. The conclusions can be given with following statements:

1) with presence of Pt-coating in DOC, in DPF, or in both, there is an oxidation NO-NO_2 and a typical maximum of the NO_2/NO_x-ratio in the temperature range around 350°C,
2) with higher Pt-content in the coatings, there is a higher potential of NO_2-formation (larger temperature range and higher maximum values),
3) in the low-temperature range (low-load engine operation) the catalysts are below the light-off temperature and the DPF's reduce slightly NO_2; the absolute values of NO_2 & NO_x are low in these operating conditions and the NO_2/NO_x-ratio gives an exagerated picture of the NO_2-differences,
4) the bigger size, or bigger active volume of the after treatment system causes a lower spatial velocity, longer residence times and a more intense NO_2-production,
5) the higher sulfur content in fuel inhibits the NO – NO_2 oxidation and gives preference to the SO – SO_2 oxidation; the Vanadium-based coatings have potential of lowering NO_2,
6) with used and/or soot-loaded DPF (DOC) there is less production of NO_2; the reasons are: masking, or ageing of the catalytic coating and use of NO_2 for soot oxidation.

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