Effects of a combined diesel particle filter-deNOx system on reactive nitrogen compounds emissions

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Catalytic diesel particle filters (DPFs) have evolved to a mature environmental technology over the last two decades. Two important filter families can be distinguished. They differ with respect to their oxidation potential and related to this their nitric oxide (NO) and nitrogen dioxide (NO2) emission characteristics. DPFs with high oxidation potential (hox-DPFs) convert NO to NO2, whereas low-oxidation potential DPFs (lox-DPFs) reduce NO2 (Fig. 1, R1). Hox-DPFs typically rely on noble metal catalysts, lox-DPFs on transition metal- or rare earth metal-catalysts.

\[
\begin{align*}
2 \text{NO} + \text{O}_2 & \rightleftharpoons \text{NO}_2 \\
2 \text{NH}_3 + \text{NO} + \text{NO}_2 & \rightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O} \\
4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 & \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \\
8 \text{NH}_3 + 6 \text{NO}_2 & \rightarrow 7 \text{N}_2 + 12 \text{H}_2\text{O} \\
\text{CO(NH}_2)_2 & \rightarrow \text{NH}_3 + \text{HNCO} \\
\text{HNCO} + \text{H}_2\text{O} & \rightarrow \text{NH}_3 + \text{CO}_2 \\
\text{H}_2\text{O} + 2 \text{NO}_2 & \rightarrow \text{HN}_2\text{O}_2 + \text{HN}_2\text{O}_3
\end{align*}
\]

Fig. 1. Reactive nitrogen compounds (RNCs) chemistry in combined DPF-deNOx systems

Diesel engines have improved considerably over the years, but their NO and NO2 emissions still affect air quality. In several European cities, ambient air NO2 levels frequently exceed the 40 \(\mu\text{g/m}^3\) threshold set by the EU parlament in 2010. NO2 is a strong oxidizing agent involved in the photochemical formation of ozone. At higher concentrations, NO2 induces skin and eye irritations and lung oedema. Long-term effects like asthma and chronic obstruction pulmonary disease are induced by lower NO2 doses.

The implementation of diesel oxidation catalysts (DOCs) and hox-DPFs, which support a substantial NO2 formation, additionally contribute to the persistently high
NO$_2$ levels in many urban environments and along roads. Recent developments of different deNO$_x$ technologies for diesel engines may help to improve the situation.

In this contribution, we will discuss the impact of a combined diesel particle filter-deNO$_x$ system (DPN) on the emissions of reactive nitrogen compounds (RNCs). The DPN consisted of a platinum-coated cordierite filter and a vanadia-based deNO$_x$ catalyst. The latter supported ammonia-based selective catalytic reduction (SCR) chemistry. Figure 1 displays some of the involved SCR chemistry. Both, NO and NO$_2$ are reduced with ammonia (NH$_3$) to dinitrogen (N$_2$) at different stoichiometries (Fig. 1, R2, R3 and R4). Ammonia is produced in situ, either from thermolysis of urea or from hydrolysis of isocyanic acid (HNCO) as shown in Fig. 1 (R5, R6). HNCO and NH$_3$ are both toxic and highly reactive intermediates and, if released, have to be considered as unwanted secondary emissions of the deNO$_x$ system.

We studied emissions of these RNCs and effects of changing urea feed factors ($\alpha$), exhaust temperatures, and residence times. The deNO$_x$ system was only part-time active and urea injection was stopped and restarted twice in the test cycle (Fig. 2, stages 4 and 8).

![Test cycle and exhaust temperatures before (dashed) and after (solid) a combined DPF-deNOx system](image)

Nevertheless, high mean NO conversion efficiencies of 80%, 95% and 97% were achieved at $\alpha$=0.8, 1.0, and 1.2, respectively, those for NO$_2$ were 43%, 87%, and 99%. HNCO emissions increased from 28 mg/h engine-out to 183, 245, and 258 mg/h at $\alpha$=0.8, 1.0 and 1.2. NH$_3$ emissions increased from <45 to 124, 1820, and 12700 mg/h, respectively, with maxima at highest temperatures and shortest residence times (<0.3 s). Most HNCO is released at intermediate residence times and intermediate temperatures of 300-400 °C.

The investigated DPN represents the most advanced converter system tested so far under the VERT protocol with high conversion efficiencies for particles, NO, NO$_2$, CO, and hydrocarbons. But the release of NH$_3$ and HNCO should be further minimized. Clearly there is a trade-off between deNO$_x$ efficiency and secondary emissions. Thus optimized conditions have to be established for different diesel engine applications. The DPN has the potential to lower NO$_x$- and particle-pollution, but risks of increased NH$_3$ and HNCO emissions have to be assessed as well.
Effects of a combined DPF-deNO$_x$ system on RNC emissions

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ETH Zurich, June 24-27, 2012
When DPFs meet deNO$_x$-technologies

Adverse health effects of diesel exhaust

Reactive nitrogen compounds

Impact of deNO$_x$-technologies on RNC emissions
Adverse health effects of diesel exhaust

DPFs are very efficient - not only for soot particles!

Soot, \( O_2 \)

Toxicity

DPF

Toxicity?

\( CO_2, H_2O \)
Adverse health effects of diesel exhaust

Problem: Genotoxicity

- Diesel exhaust is genotoxic (contains mutagenic and carcinogenic compounds)
- Diesel exhaust classified as group 1 carcinogen inducing lung and bladder cancer in humans (IARC, WHO 2012)
- DPF remove genotoxic compounds up to 98%
Adverse health effects of diesel exhaust

All VERT-tested DPFs convert carcinogenic PAHs, most are rather efficient

Conversion of carcinogenic PAHs

Efficiency [%]
Adverse health effects of diesel exhaust

Problem: Trojan horse effect

- Nanoparticles penetrate cell membranes (alveoli, placenta, blood cells) acting like a Trojan horse
- DPF remove > 98% of nanoparticles
Adverse health effects of diesel exhaust

more than 40 VERT-tested DPFs. All approved systems are excellent particle filters

Mayer et al. MTZ, 2009, 70, 72-79
Adverse health effects of diesel exhaust

You have to zoom in to see differences

Mayer et al. MTZ, 2009, 70, 72-79
Adverse health effects of diesel exhaust

Problem: Reactive nitrogen compounds

- NO and NO₂ induce acute and chronic toxicity (oxidative stress, inflammatory responses, chronic obstructive pulmonary disease, COPD)
- hox-DFP increase NO₂ emissions
- deNOx technologies are needed!
Mean annual NO$_2$ levels of the City of London

EU Limit
Jan. 1$^{st}$, 2010
annual mean
$<$40 $\mu$g/m$^3$

Impact of deNOx-technologies on RNC emissions?

Urea-based SCR

$\text{CO(NH}_2\text{)}_2$

$\text{HNCO, NH}_3$

$\text{NO, NO}_2$

$\text{CO}_2, \text{N}_2, \text{H}_2\text{O}$

$\text{deNO}_x$
Urea-based SCR

At least two steps to decompose and hydrolyze urea

\[ 2 \text{NO} + \text{O}_2 \rightleftharpoons 2 \text{NO}_2 \] (1)

\[ 2 \text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O} \] (2)

\[ 4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \] (3)

\[ 8 \text{NH}_3 + 6 \text{NO}_2 \rightarrow 7 \text{N}_2 + 12 \text{H}_2\text{O} \] (4)

\[ \text{CO(NH}_2)_2 \rightarrow \text{NH}_3 + \text{HNCO} \] (5)

\[ \text{HNCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2 \] (6)
Reactive nitrogen compounds (RNCs)

What are reactive nitrogen compounds?

**Nitrogen dioxide**
- **Oxidation**
  - T < 400 °C

**Nitric oxide**
- **Oxidation**
  - T > 1000 °C

**Urea (Add Blue)**
- **Degradation**
  - T > 200 °C

**Isocyanic acid**
- **Hydrolysis**
  - T > 200 °C

**Nitrogen**

**Ammonia**
Reactive nitrogen compounds (RNCs)

What are reactive nitrogen compounds?
Reactive nitrogen compounds (RNCs)

What are reactive nitrogen compounds?

RNCs are:
- highly reactive
- short life time
- fast transformation
- acute toxicity
- difficult to detect
Urea-based SCR

They are also key molecules of the urea-based SCR chemistry.
The NH₃ problem

- NH₃ - a toxic air pollutant
- Eutrophication of soils and surface waters
- Involved in the formation of secondary aerosols

Risks

- On-board formation of NH₃
- NH₃ slip at transient engine operation
- Over dosage of urea
**Secondary pollutants of deNOx-technologies**

**The HNCO problem**

- Isocyanates are toxic
- Highly reactive, react with -OH, -NH₂, and -SH groups (molecules of life)
- Methyl isocyanate accident Bhopal, India (42 t released on 3.12.1984)

**Risks**

- On-board HNCO formation
- Over dosage of urea
- Reacts with other exhaust constituents to form secondary pollutants
The combined DPF-deNO$_x$ system – a chemical factory?

If a DPF is considered as a chemical reactor, a combined dePN is a factory!
Exhaust temperatures in the ISO 8178/4 C1 cycle

The deNOx-system is only part-time active (60-80%)

Urea-based deNOx-system active >200°C
DeNO$_x$ Efficiencies

High NO conversion efficiencies can be achieved!

Nitric oxide (NO)

engine-out

SCR only

DPF/SCR

86%  20.5 g h$^{-1}$
$^{(2.3 \text{ g kg}^{-1}_{\text{fuel}})}$

-14%

21%

94%  8.15 g h$^{-1}$
$^{(0.96 \text{ g kg}^{-1}_{\text{fuel}})}$
DeNO$_x$ Efficiencies

High efficiencies for NO$_2$ even with intense NO$_2$ formation in the DPF!

Nitrogen dioxide (NO$_2$)

<table>
<thead>
<tr>
<th></th>
<th>engine-out</th>
<th>SCR only</th>
<th>DPF/SCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$ [g h$^{-1}$]</td>
<td>10.9 (1.25 g kg$^{-1}$$_{\text{fuel}}$)</td>
<td>&gt;99% n.d.</td>
<td>86% 1.54 g h$^{-1}$ (0.18 g kg$^{-1}$$_{\text{fuel}}$)</td>
</tr>
<tr>
<td></td>
<td>3.E+01</td>
<td></td>
<td>91% 92%</td>
</tr>
</tbody>
</table>
Secondary pollutants of deNOx-technologies

Ammonia ($\text{NH}_3$)

Substantial ammonia emissions with active SCR!

- **Engine-out**
  - $<$30 mg h$^{-1}$
  - ($<$3 mg kg$^{-1}_{\text{fuel}}$)

- **SCR only**
  - 1870 mg h$^{-1}$
  - (210 mg kg$^{-1}_{\text{fuel}}$)

- **DPF/SCR**
  - 1790 mg h$^{-1}$
  - (210 mg kg$^{-1}_{\text{fuel}}$)
Secondary pollutants of deNOx-technologies

Ammonia formation in a Pd/Rh-TWC (BMW, 1.8 l, Euro-1)

No ammonia before catalyst

Ammonia formation tendencies (Ra cycle, pre-catalyst)
How much NH₃ emissions have we already accepted from the TWC technology?

Ammonia formation in a Pd/Rh-TWC (BMW, 1.8 l, Euro-1)

Heeb et al. Atm. Env. 42 (2008) 2543-2554
Secondary pollutants of deNOx-technologies

Substantial ammonia emissions with active SCR!

Ammonia ($\text{NH}_3$)

- **Engine-out**
  - $<30 \text{ mg h}^{-1}$
  - $<3 \text{ mg kg}_{\text{nal}}^{-1}$
- **SCR only**
  - $1870 \text{ mg h}^{-1}$
  - $210 \text{ mg kg}_{\text{nal}}^{-1}$
- **DPF/SCR**
  - $1790 \text{ mg h}^{-1}$
  - $210 \text{ mg kg}_{\text{nal}}^{-1}$

5 g/h
1.4 g/h
0.5 g/h

Heeb et al. Atm. Env. 42 (2008) 2543-2554
Livingston et al. Atm. Env. 43 (2009) 3326-3333
Secondary pollutants of deNOx-technologies

Increased isocyanic acid emissions with active SCR!

Isocyanic acid (HNCO)

- engine-out
- SCR only
- DPF/SCR

Heeb et al. Atm. Env. 40 (2011) 3203-3209
Swiss National Accident Insurance (SUVA): Exposure limits at workplaces

Maximum tolerable workplace concentration 0.02 mg/m³ not to be exceeded for 15 min

**MTWC of isocyanates**

<table>
<thead>
<tr>
<th>Stoff [CAS-Nummer]</th>
<th>MAK-Wert ml/m³ (ppm)</th>
<th>Kurzzeitgrenzwerte ml/m³ (ppm)</th>
<th>Zeitl. Begrenzung (Häufigkeit x Dauer in min./Schicht)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isocyanate (Monomere und Präpolymere) (als Gesamt-NCO gemessen)</td>
<td>0,02</td>
<td>0,02</td>
<td>15 min</td>
</tr>
</tbody>
</table>
Secondary pollutants of deNOx-technologies

Isocyanic acid emissions 70-85 x above MTWC

Isocyanic acid (HNCO)

engine-out

SCR only

DPF/SCR

Heeb et al. Atm. Env. 40 (2011) 3203-3209
The combined DPF-deNO$_x$ system – a chemical factory?

If a DPF is considered as a chemical reactor, a combined dePN is a factory!

Are DPN systems the ultimate solution?

**VERT-goals:**
- Benefit/risk assessment of converter technologies
- Effectiveness on regulated pollutants
- Effects on toxic exhaust gas constituents
- Potential for secondary emissions (poisoning)
The VERT approach is also suitable for benefit/risk assessments of DPN systems.

**Requirements for combined systems**

**Approved DPNs should:**

- Reduce PM- & PN-emissions (>98%)
- Reduce genotoxic compounds (a.m.a.p.)
- Have low risks of secondary emissions
- Reduce NO and NO₂ emissions (">? %)

Combined systems are considered as DPFs with additional features. They have to fulfill the same VERT standards as DPFs.
When DPFs meet deNO$_x$-technologies

DPFs are now BAT to detoxify diesel exhaust. Combinations with appropriate deNO$_x$-technologies will be the future!
Effects of a combined DPF-deNO\textsubscript{x} system on RNC emissions

A combined effort with many important contributions

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