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Will diesel technology survive?

21\textsuperscript{st} ETH Conference on Combustion Generated Nanoparticles
Zürich, June 19-22, 2017
Will diesel technology survive?

As an executive summary

only with

efficient particle filter and deNOx technologies!

21st ETH Conference on Combustion Generated Nanoparticles
Zürich, June 19-22, 2017
Will diesel technology survive?

1st part: 13:50-15:10

Impact of current diesel technologies

Coffee break 15:10-15:40

2nd part: 15:40-16:40

The future of diesel technologies

Goodbye: 16:50
Blue Technology: Not green enough yet

Year two after the VW scandal
Mean annual NO$_2$ levels: City of London

The NO$_2$ problem in central London is severe as in many European cities!
Mean annual NO$_2$ levels: City of London

From a Swiss perspective, the Brexit will not solve the NO$_2$ problem!

Swiss Limit
30 µg/m$^3$

EU Limit
Jan. 1$^{st}$, 2010
40 µg/m$^3$

Swiss Limit
30 µg/m$^3$
Blue Technology: Not green enough yet

Nitrogen chemistry of current on-road deNOx technologies

Best deNOx system on European roads
(Honor to whom honor is due!)

NOx-trap technology
(Not very efficient yet)

Urea-based SCR technology
(Substantial cold start problems)
Who knows John J. Mooney?
Who knows John J. Mooney?

• **How to meet the president?**
  
  2002 National Medal of Technology Award from National Science & Technology Foundation.

  Co-inventor of TWC (1 of the 10 most important inventions in car industry).

  In 1976-2001 TWC avoided 3, 3 & 30 billion tons of HC, NOx and CO emissions.

• **Good catalyst design:**
  
  results in money, honor & fame

Fig. 1: John J. Mooney & Carl D. Keith, Engelhard  
Fig. 2: Haren S. Gahndi, Ford Motor Company
The best deNO$_x$-system on European roads

Honor to whom honor is due
DeNO$_x$ on a Pd/Rh-TWC

Dynamometer set-up for time-resolved NO and NH$_3$ measurements

**Vehicle:**
- BMW 318 (1.8 l, 1995, Euro-1, mileage 70'000 km)

**Fuel:**
- 95 RON gasoline (specification CEF RF-08-A-85)

**Catalyst:**
- New, original spare part TWC
- Two-layered Pd-CeO$_2$-Al$_2$O$_3$/Rh-ZrO$_2$-Al$_2$O$_3$ structure
DeNO$_x$ on a Pd/Rh-TWC

Swiss made driving cycle to mimic highway driving

The Swiss highway cycle

- smooth and relaxed drive at 120 km/h
- unsteady and stressed drive in denser traffic
DeNO$_x$ on Pd/Rh-TWC

Pre-catalyst NO up to 200 mg s$^{-1}$ at transient highway driving

NO emission (BMW, 1.8 l, 1995, EURO-1)

Nitrogen monoxide (Ra cycle, pre-catalyst)

DeNO$_X$ on a Pd/Rh-TWC

Post catalyst less than 6 mg s$^{-1}$

NO emission (BMW, 1.8 l, 1995, EURO-1)
TWC-induced formation of ammonia

No ammonia before catalyst

Ammonia emissions (BMW, 1.8 l, 1995, EURO-1)
TWC-induced formation of ammonia

Relevant ammonia emissions post catalyst

Ammonia emissions (BMW, 1.8 l, 1995, EURO-1)

What’s going on the catalytic surface?

The best deNO$_x$-system on European roads
The TWC in theory

- TWC
  - Which three ways to go?

\[
\begin{align*}
\text{CO} & \quad + \quad \frac{1}{2} \text{O}_2 & \quad \iff & \quad \text{CO}_2 \\
\text{HC} & \quad + \quad \text{O}_2 & \quad \iff & \quad \text{H}_2\text{O} \quad + \quad \text{CO}_2 \\
\text{NO} & \quad + \quad \text{CO} & \quad \iff & \quad \frac{1}{2} \text{N}_2 \quad + \quad \text{CO}_2
\end{align*}
\]
The TWC in real world application

- The important role of H₂!
  - Which three ways to go?
  - A new try with H₂, water gas-shift-reactions and steam reforming

\[
\begin{align*}
\text{CO} + \frac{1}{2} \text{O}_2 & \rightleftharpoons \text{CO}_2 \\
\text{HC} + \text{O}_2 & \rightleftharpoons \text{H}_2\text{O} + \text{CO}_2 \\
\text{NO} + \text{CO} & \rightleftharpoons \frac{1}{2} \text{N}_2 + \text{CO}_2 \\
\text{H}_2 + \frac{1}{2} \text{O}_2 & \rightleftharpoons \text{H}_2\text{O} \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2 + \text{CO}_2 \\
\text{HC} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2 + \text{CO} + \text{CO}_2
\end{align*}
\]
The TWC in real world application

### Why NH₃ and N₂O?

- **Which three ways to go?**

- A new try incl. H₂, water gas-shift-reactions and steam reforming

- Another try with H₂, N₂O and NH₃

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + 1/2 O₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>HC + O₂</td>
<td>H₂O + CO₂</td>
</tr>
<tr>
<td>NO + CO</td>
<td>1/2 N₂ + CO₂</td>
</tr>
<tr>
<td>H₂ + 1/2 O₂</td>
<td>H₂O</td>
</tr>
<tr>
<td>CO + H₂O</td>
<td>H₂ + CO₂</td>
</tr>
<tr>
<td>HC + H₂O</td>
<td>H₂ + CO + CO₂</td>
</tr>
<tr>
<td>NO + H₂</td>
<td>1/2 N₂ + H₂O</td>
</tr>
<tr>
<td>NO + HC</td>
<td>N₂ + H₂O + CO₂</td>
</tr>
<tr>
<td>NO + 5/2 H₂</td>
<td>NH₃ + H₂O</td>
</tr>
<tr>
<td>3 NO + 2 NH₃</td>
<td>5/2 N₂ + 3 H₂O</td>
</tr>
<tr>
<td>2 NO + H₂</td>
<td>N₂O + H₂O</td>
</tr>
<tr>
<td>2 N₂O</td>
<td>2 N₂ + O₂</td>
</tr>
<tr>
<td>2 NH₃</td>
<td>N₂ + 3 H₂</td>
</tr>
</tbody>
</table>
### NOx-trap technology

The first GDI vehicle (Mitsubishi Carisma, 1.8L, Euro-3) with NOx trap technology

<table>
<thead>
<tr>
<th>Vehicle</th>
<th>Mitsubishi Carisma 1.8 GDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine code</td>
<td>4G93</td>
</tr>
<tr>
<td>Number and arrangement of cylinder</td>
<td>4 / in line</td>
</tr>
<tr>
<td>Displacement cm³</td>
<td>1834</td>
</tr>
<tr>
<td>Power kW</td>
<td>90 @ 5500 rpm</td>
</tr>
<tr>
<td>Torque Nm</td>
<td>174 @ 3750 rpm</td>
</tr>
<tr>
<td>Injection type</td>
<td>DI</td>
</tr>
<tr>
<td>Curb weight kg</td>
<td>1315</td>
</tr>
<tr>
<td>Gross vehicle weight kg</td>
<td>1750</td>
</tr>
<tr>
<td>Drive wheel</td>
<td>Front-wheel drive</td>
</tr>
<tr>
<td>Gearbox</td>
<td>M5</td>
</tr>
<tr>
<td>First registration</td>
<td>05.2001</td>
</tr>
<tr>
<td>Exhaust</td>
<td>EURO 3</td>
</tr>
</tbody>
</table>
NOx-trap chemistry

An ideal cycle to study converter chemistry at best conditions!

NOx-trap activity at steady driving

km/h

0.0E+00  2.5E+01  5.0E+01  7.5E+01

freeway
(94 km/h)

highway
(61 km/h)

extra-urban
(45 km/h)

urban
(26 km/h)

Velocity
NOx-trap chemistry

Extra fuel injections (FI) nearly every minute!

CO₂ emissions at steady driving

km/h

freeway
(94 km/h)

highway
(61 km/h)

extra-urban
(45 km/h)

urban
(26 km/h)

ppm

32 FI

25 FI

10 FI

9 FI

1/37s

1/47s

1/122s

1/136s
Extra fuel injections result in extra CO emissions, but only in phase 1!

CO and CO$_2$ emissions

<table>
<thead>
<tr>
<th>ppm CO</th>
<th>ppm CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(94 km/h)</td>
<td>(61 km/h)</td>
</tr>
<tr>
<td>32 FI</td>
<td>25 FI</td>
</tr>
<tr>
<td>1/37s</td>
<td>1/47s</td>
</tr>
</tbody>
</table>

fuel-rich
Extra fuel injections result in extra CO and NH₃ emissions but only in phase 1!

**NH₃ & CO emissions**

<table>
<thead>
<tr>
<th>NH₃ ppm</th>
<th>CO ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0E+03</td>
<td></td>
</tr>
<tr>
<td>2.0E+03</td>
<td></td>
</tr>
<tr>
<td>1.0E+03</td>
<td></td>
</tr>
<tr>
<td>0.0E+00</td>
<td></td>
</tr>
</tbody>
</table>

- (94 km/h) fuel-rich
- (61 km/h)
- (45 km/h)
- (26 km/h)

**NOx-trap chemistry**
NOx trap at work: extra fuel injections result in extra NO emissions

NO and CO₂ emissions

CO₂ and NO peaks correlated
NOx trap at work: extra fuel injections result in extra NO and NO\textsubscript{2} emissions

NO\textsubscript{x}-trap chemistry
NOx-trap chemistry

NO₂ proportions lowest during extra fuel injections and high temperatures

NO₂ proportion in NOₓ

<table>
<thead>
<tr>
<th>Speed (km/h)</th>
<th>NO₂ Proportion (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>94</td>
<td>6</td>
</tr>
<tr>
<td>61</td>
<td>22</td>
</tr>
<tr>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td>26</td>
<td>38</td>
</tr>
</tbody>
</table>

The graph shows the proportion of NO₂ in NOₓ over time, with arrows indicating the percentage at different speeds.
Not funny, extra fuel injections also result in extra $N_2O$ emissions.

**N$_2$O and CO$_2$ emissions**

<table>
<thead>
<tr>
<th>ppm</th>
<th>(94 km/h)</th>
<th>(61 km/h)</th>
<th>(45 km/h)</th>
<th>(26 km/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ppm</th>
<th>32 FI</th>
<th>25 FI</th>
<th>11 FI</th>
<th>9 FI</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/37s</td>
<td>1/47s</td>
<td>1/122s</td>
<td>1/136s</td>
<td></td>
</tr>
</tbody>
</table>
NOx-trap chemistry

How much fuel penalty per injection

Extra CO₂ at 26 km/h (urban driving)

4.6% extra fuel per cycle
NOx-trap chemistry

How much deNOx activity per injection

deNO activity at 26 km/h

η: + 2% NO (no net NO conversion)
NOx-trap chemistry

How much deNOx activity per injection

deNO and deNO$_2$ activity at 26 km/h

\[ \eta: +2\% \text{ NO} \quad \text{no net NO conversion} \]

\[ \eta: -14\% \text{ NO}_2 \]
How much fuel penalty per injection

CO₂ at 94 km/h (motorway)

12.4% extra fuel per cycle
NOx-trap chemistry

How much deNOx activity per injection

deNO activity at 94 km/h

η: - 26% NO
NOx-trap chemistry

How much deNOx activity per injection

deNO and deNO$_2$ activity at 94 km/h

$\eta$: - 26% NO

$\eta$: - 42% NO$_2$
NOx-trap technology

Low NO\textsubscript{x} storage capacity, not very sulfur tolerant, its more a SO\textsubscript{x} than a NO\textsubscript{x} trap

**NOx-trap cycle**

\( \lambda > 1 \) (lean) \hspace{1cm} T: 150-450 °C

1. NO- & NO\textsubscript{2}-oxidation to NO\textsubscript{3}\textsuperscript{-}
2. Store as Ba(NO\textsubscript{3})\textsubscript{2}
Low NO$_x$ storage capacity, not very sulfur tolerant, it's more a SO$_x$ than a NO$_x$ trap.

**NOx-trap technology**

**NOx-trap cycle**

1. NO- & NO$_2$-oxidation to NO$_3^-$
2. Store as Ba(NO$_3$)$_2$
3. Post injections of fuel
4. NO$_3^-$ reduction with H$_2$, HC etc.

\[ \lambda > 1 \ (\text{lean}) \quad \text{T: 150-450 °C} \]
\[ \lambda < 1 \ (\text{rich}) \quad \text{T: 200-500 °C} \]

Similar chemistry in the NO$_x$ trap with secondary formation of N$_2$O and NH$_3$. 
Impact of deNOx-technologies on RNC emissions?

Urea-based SCR

Currently the most efficient deNOx system for diesel engines
Urea-based SCR

At least two steps to decompose and hydrolyze urea

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

Per ton of NO to be reduced, one needs at least 1 ton of urea!
Exhaust temperatures in the ISO 8178/4 C1 cycle

Urea-based deNO$_x$-systems are active only for about 60-80% of the operating time

DeNO$_x$-system active >200°C
Impact of deNOx-technologies on RNC emissions?

Urea-based SCR

Currently the most efficient deNOx system for diesel engines
DeNO$_x$ Efficiencies: A best case scenario

Highest NO emissions at highest loads and temperatures (IVECO, 3.0 L, 100 kW, V-SCR)

Nitric oxide (NO)

engine-out

Heeb et al. Atm. Env. 45 (2011) 3203-3209

DeNO\textsubscript{x} Efficiencies: A best case scenario

High NO conversion efficiencies can be achieved at alpha = 1.0!

Nitric oxide (NO)

<table>
<thead>
<tr>
<th>scenario</th>
<th>NO \text{conversion efficiency}</th>
<th>NO \text{mass flow rate}</th>
</tr>
</thead>
<tbody>
<tr>
<td>engine-out</td>
<td></td>
<td>142 g h\textsuperscript{-1} (16.2 g kg\textsubscript{fuel}\textsuperscript{-1})</td>
</tr>
<tr>
<td>SCR only</td>
<td></td>
<td>20.5 g h\textsuperscript{-1} (2.3 g kg\textsubscript{fuel}\textsuperscript{-1})</td>
</tr>
<tr>
<td>DPF/SCR</td>
<td></td>
<td>8.15 g h\textsuperscript{-1} (0.96 g kg\textsubscript{fuel}\textsuperscript{-1})</td>
</tr>
</tbody>
</table>

Heeb et al. Atm. Env. 45 (2011) 3203-3209
DeNO\textsubscript{x} Efficiencies: A best case scenario

Low engine-out NO\textsubscript{2} emissions, only 3% on average

Nitrogen dioxide (NO\textsubscript{2})

engine-out

\begin{center}
\begin{tabular}{c|c|c|c|c|c|c|c|c}
\hline
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\
\hline
\hline
NO\textsubscript{2} [g h\textsuperscript{-1}] & 10.9 g h\textsuperscript{-1} & (1.25 g kg\textsubscript{fuel}\textsuperscript{-1}) \\
\hline
\end{tabular}
\end{center}

\textsim 3\% NO\textsubscript{2} und 97\% NO Anteile
DeNO\textsubscript{x} Efficiencies: A best case scenario

High deNO\textsubscript{2} efficiencies can be achieved at \( \alpha = 1.0 \)!

Nitrogen dioxide (NO\textsubscript{2})

- Engine-out
  - \( \alpha = 1.0 \)
    - >99%
    - 10.9 g h\(^{-1}\)
      - (1.25 g kg\(_{\text{fuel}}\)\(^{-1}\))
    - SCR only
    - DPF/SCR

- SCR only
  - \( \alpha = 1.0 \)
    - >99%
    - n.d.
    - 86%
    - 1.54 g h\(^{-1}\)
      - (0.18 g kg\(_{\text{fuel}}\)\(^{-1}\))

- DPF/SCR
  - \( \alpha = 1.0 \)
    - 91%
    - 92%

~3% NO\textsubscript{2} und 97% NO Anteile
Secondary pollutants of DeNO$_x$-technologies

Not much engine-out ammonia!

Ammonia (NH$_3$)

engine-out

![Graph showing ammonia emissions](image)
Secondary pollutants of DeNO$_x$-technologies

Substantial ammonia emissions with active SCR at alpha = 1.0!

Ammonia (NH$_3$)

- **engine-out**
  - $\alpha = 1.0$
  - $<30$ mg h$^{-1}$
  - $<3$ mg kg$_{fuel}^{-1}$

- **SCR only**
  - $\alpha = 1.0$
  - $1870$ mg h$^{-1}$
  - $(210$ mg kg$_{fuel}^{-1})$

- **DPF/SCR**
  - $\alpha = 1.0$
  - $1790$ mg h$^{-1}$
  - $(210$ mg kg$_{fuel}^{-1})$
Some isocyanic acid in engine-out exhaust!

Isocyanic acid (HNCO)
Secondary pollutants of DeNO$_x$-technologies

Considerable amounts of isocyanic acid emissions with active SCR!

Isocyanic acid (HNCO)

<table>
<thead>
<tr>
<th>Engine-out</th>
<th>SCR only</th>
<th>DPF/SCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha = 1.0$</td>
<td>$\alpha = 1.0$</td>
<td>$\alpha = 1.0$</td>
</tr>
</tbody>
</table>

Heeb et al. Atm. Env. 45 (2011) 3203-3209
The visible effect of an SCR-system

7 m³ exhaust (only 3 minutes of a Euro-III engine (6.1 L, 105 kW))

For years thousands of Euro-III, -IV, -V HDVs without filters!
The visible effect of a particle filter

7 m$^3$ exhaust (3 minutes of an Euro-III engine (6.1 L, 105 kW)

At least Euro-VI HDVs now have both filters and deNOx!
Blue Technology: Not green enough yet

VW IM ABGAS-TEST

Und?

Software-Problem!
Blue Technology: Not green enough yet

We have some severe hardware problems too!

not only

Software-Problem!
Blue Technology: Not green enough yet

“Will blue technology be green enough in the future?”

There’s quite some work ahead of us, especially at urban driving conditions!

Year two after the VW scandal!
Blue Technology: Not green enough yet

A combined effort with many important contributions

• **VERT team:** Andreas Mayer, TTM, Niederrohrdorf
  Jan Czerwinski, Sandro Napoli, Tobias Neubert, Thomas Hilfiker, Samuel Bürki, Pierre Comte,
  Markus Kasper, Adrian Hess, Thomas Mosimann, Matter Aerosols, Wohlen
  Hans Jaeckle, Urs Debrunner, Oliver Schumm, Intertek Caleb Brett, Schlieren.

• **Empa colleagues:** Brigitte Buchmann, Thomas Bührer, Lukas Emmenegger, Anna-Maria Forss,
  Urs Gfeller, Maria Guecheva, Peter Graf, Roland Graf, Erika Guyer, Regula Haag, Peter
  Honnegger, Judith Kobler, Martin Kohler, Peter Lienemann, Alfred Mack, Peter Mattrel,
  Martin Mohr, Joachim Mohn, Christof Moor, Andreas Paul, Peter Schmid, Cornelia Seiler,
  Andrea Ulrich, Heinz Vonmont, Thomas Walter, Max Wolfensberger, Daniela Wenger,
  Adrian Wichser, Simon Wyss, Markus Zennegg, Kerstin Zeyer,

• **Governement:** Peter Bonsak, Philipp Hallauer, Giovanni D'Urbano, Felix Reutimann, Max Wyser,
  Gerhard Leutert, Martin Schiess, Swiss Fed. Office for Environment, Bern
  Thomas Gasser, Heinz Berger, Gerhard Stucki, Swiss Federal Road Office

• **Filter- & catalyst manufacturers:** >50 diesel particle filters, 4 deNOx-systems