FOCUS ON THE EVOLUTION OF A LEAN NO$_x$-TRAP MODEL FOR NO/NO$_2$ DIFFERENTIATION

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01 THE NO$_2$ ISSUE
TOXICOLOGY AND ENVIRONMENT IMPACTS OF NO\textsubscript{x}

- **Nitrogen monoxide NO**

  ![Nitrogen monoxide]

  NO, not very soluble in water, causes irritations of respiratory system

- **Nitrogen dioxide NO\textsubscript{2}**

  ![Nitrogen dioxide]

  NO\textsubscript{2}, very soluble in water, reacts with water of the lungs to produce nitric acid which causes lesions and pulmonary oedema.
  
  NO\textsubscript{2} is 5 times more toxic than NO

- **Toxicology:**
  - NO, not very soluble in water, causes irritations of respiratory system
  - NO\textsubscript{2}, very soluble in water, reacts with water of the lungs to produce nitric acid which causes lesions and pulmonary oedema.
  - NO\textsubscript{2} is 5 times more toxic than NO

- **Environment impacts:**
  - Ozone formation in tropospheric layers which is a powerful greenhouse gas
  - Acid rains formation
  - Ground eutrophication
ZONES AND POPULATIONS TOUCHED BY NO₂

- **Sensible zones:**
  - Major cities
    - European capitals cities
    - Due to transport pollution
  - Industrial zones
    - European industrial centers
    - Thermal power station

- **At risk population:**
  - Children and infants
  - Asthmatic
  - People with respiratory system deficiency

[1]: Photo: European Space Agency/IUP Heidelberg
**NO\textsubscript{X} AND NO\textsubscript{2} LIMITATIONS IN EURO 6 STANDARDS**

### Euro 6 Emission Limits

<table>
<thead>
<tr>
<th>Category</th>
<th>Class</th>
<th>Reference mass (g/dl)</th>
<th>PI</th>
<th>CI</th>
<th>PI</th>
<th>CI</th>
<th>PI</th>
<th>CI</th>
<th>PI</th>
<th>CI</th>
<th>PI</th>
<th>CI</th>
<th>PI</th>
<th>CI</th>
<th>Number of particles ((#))</th>
<th>(#)</th>
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</thead>
<tbody>
<tr>
<td>M</td>
<td>All</td>
<td>1 009 500 100</td>
<td>68</td>
<td>60</td>
<td>80</td>
<td>170</td>
<td>5.0/4.5 5.0/4.5 5.0/4.5 5.0/4.5 6.0 × 10\textsuperscript{11}</td>
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<tr>
<td>N\textsubscript{1}</td>
<td>I  RM ≤ 1 305</td>
<td>1 009 500 100</td>
<td>68</td>
<td>60</td>
<td>80</td>
<td>170</td>
<td>5.0/4.5 5.0/4.5 5.0/4.5 5.0/4.5 6.0 × 10\textsuperscript{11}</td>
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<tr>
<td></td>
<td>II  1 305 &lt; RM ≤ 1 760</td>
<td>1 810 630 130</td>
<td>90</td>
<td>75</td>
<td>105</td>
<td>195</td>
<td>5.0/4.5 5.0/4.5 5.0/4.5 5.0/4.5 6.0 × 10\textsuperscript{11}</td>
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<tr>
<td></td>
<td>III  1 760 &lt; RM</td>
<td>2 270 740 160</td>
<td>108</td>
<td>82</td>
<td>125</td>
<td>215</td>
<td>5.0/4.5 5.0/4.5 5.0/4.5 5.0/4.5 6.0 × 10\textsuperscript{11}</td>
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<tr>
<td>N\textsubscript{2}</td>
<td>All</td>
<td>2 270 740 160</td>
<td>108</td>
<td>82</td>
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<td>215</td>
<td>5.0/4.5 5.0/4.5 5.0/4.5 5.0/4.5 6.0 × 10\textsuperscript{11}</td>
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</table>

- **Current limitations for EURO 6 standards:**
  - NO\textsubscript{X} limitations: 80mg/km for Diesel type engines
  - Combined mass of HC and NO\textsubscript{X}: 170mg/km

- **Hypothesis for future limitations:**
  - NO\textsubscript{2} limitation in percent of total NO\textsubscript{X}
  - Off-cycle

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NO₂ FORMATION IN COMBUSTION CHAMBER

- NO₂ formation Mechanisms [3]
  - Thermal formation of NO
    \[ N₂ + O₂ = 2NO \] (1)
  - NO₂ formation
    \[ NO + HO₂ \rightarrow NO₂ + OH \] (2)
    \[ NO₂ + O \rightarrow NO + O₂ \] (3)
  - Reaction (2) favored for Diesel engines
  - Reaction (3) inhibited by cold point on the combustion chamber
  - NO₂ principally produce at low engine speed and load

[3]: Automotive and pollution, P.Degobert; Society of Automotive Engineers, 31/12/1995, Book
EXEMPLE OF NO₂ EMISSIONS (ENGINE OUT) ON NEDC CYCLE

- Engine bench test

NO₂ / NOx rate engine out for NEDC cycle

\(\text{NO₂ / NOx rate } (\%)\)

\(\text{Time (sec)}\)

\(\text{Speed (m/s)}\)
02

MODELING OF THE NO$\textsubscript{x}$-TRAP
PRESENTATION OF THE LEAN NO$_x$-TRAP MODEL

- **Modeling hypothesis**
  - Homogeneous flooding of the monolith (monolith behavior is 1D)
  - Multi 0D modeling
  - Gas considered like perfect gas
  - Gas properties = air properties (viscosity, heat capacity, molar mass,…)
  - Conduction and radiation neglected
  - No pressure loss through the monolith (pressure is the same all along a canal)
  - Quasi-steady state approximation (QSSA) for gaseous concentrations mass balance

**Different steps of calculation for a canal:**

For the PSR number $i$, reactions rates calculation

Pollutants mass balances and thermal balances resolution

Calculations results = input of the PSR number $i+1$

\[
\frac{dC}{dt} \ll \frac{dT}{dt}, \quad \frac{dC^*}{dt}
\]
- **Reaction rate:**

\[
    r_j (z, t) = k_j^0 \exp \left( \frac{-E_{a_j}}{R G P T_g (z, t)} \right) \sum_{i=\text{products}} \left( C_{ij} (z, t) \right)^{n_{ij}}
\]

- **Mass balance on pollutants:**

\[
    \frac{d}{dt} (C_i (z, t)) = -\rho_u \sum_{j=\text{reactions}} n_{ij} r_j (z, y) - \frac{V_e C_i (z, t) - V_e C_i (z - 1, t)}{dz}
\]

- **Mass balance on adsorbed species:**

\[
    \frac{d}{dt} (C_k^* (z, t)) = -\rho_u \sum_{l=\text{reactions}} n_{kl} r_l (z, y)
\]

  **QSSA:**

\[
    \frac{d}{dt} (C_i (z, t)) = 0
\]

- **Thermal balance (gas):**

\[
    \frac{dT_g}{dt} = \frac{1}{\epsilon_m C_p \rho_g} \left[ -\frac{V_e \rho_g}{dz} \left( T_g (z) C_{pg} (z) - T_g (z - 1) C_{pg} (z - 1) \right) + h_m \frac{dS}{dV} (T_g (z) - T_s (z)) \right]
\]

- **Thermal balance (solid):**

\[
    \frac{dT_s}{dt} = \frac{h_m dS (T_g (z) - T_s (z)) \pm h_{ext} dS_{ext} (T_{ext} - T_s (z)) - \rho_s \sum_{i=\text{species}} r_i \Delta H_i dV}{(1 - \epsilon_m) C_{papp} \rho_{app} dV}
\]
LNT MODEL ON MATLAB / SIMULINK

Environment Var:
(Speed, Ext Temp, …)

Gas in composition:
(Flow, Conc, Temp, …)

Local Var in:
(Tmat, init state, …)

Pressure out

Evolution of the gas inside catalyst

Gas out composition:
(Flow, Conc, Temp, …)

Local Var out:
(Tmat, init state, …)

Pressure in

Variables in defined in Matlab workspace

- S-Function: C language
- Reactions rates and balances written in the S-Function

Variables out to Matlab workspace
GLOBAL KINETIC STUDY
### BASIC SCHEME

- **The study is based on the scheme given by L.Cao & al. [4]:**
  - Reversible NO oxidation on Pt:
    \[
    NO + \frac{1}{2}O_2 = NO_2
    \]
  - NO oxidation and adsorption on Ba:
    \[
    2NO + \frac{3}{2}O_2 + BaCO_3 = Ba(NO_3)_2 + CO_2
    \]
  - NO\textsubscript{2} adsorption on Ba near a Pt site:
    \[
    3NO\textsubscript{2} + BaCO_3 = Ba(NO_3)_2 + NO + CO_2
    \]
  - NO\textsubscript{2} adsorption on Ba far from a Pt site:
    \[
    3NO\textsubscript{2} + BaCO_3 = Ba(NO_3)_2 + NO + CO_2
    \]

# TWO DIFFERENT KINETIC SCHEMES TESTED

<table>
<thead>
<tr>
<th>First scheme</th>
<th>Second scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>$NO + \frac{1}{2}O_2 \leftrightarrow NO_2$</td>
<td>$NO + \frac{1}{2}O_2 \leftrightarrow NO_2$</td>
</tr>
<tr>
<td>$2NO + \frac{3}{2}O_2 + BaCO_3 = Ba(NO_3)_2 + CO_2$</td>
<td>$2NO + \frac{3}{2}O_2 + BaCO_3 = Ba(NO_3)_2 + CO_2$</td>
</tr>
<tr>
<td>$3NO_2 + BaCO_3 = Ba(NO_3)_2 + NO + CO_2$</td>
<td>$\begin{cases} 3NO_2 + BaCO_3 = Ba(NO_3)_2 + NO + CO_2 \end{cases}$</td>
</tr>
<tr>
<td>$3NO_2 + BaCO_3 = Ba(NO_3)_2 + NO + CO_2$</td>
<td>$Ba(NO_3)_2 = 2NO_2 + BaO + O_2$</td>
</tr>
<tr>
<td>$Ba(NO_3)_2 = 2NO_2 + BaO + O_2$</td>
<td></td>
</tr>
</tbody>
</table>
REACTION RATES COMMON TO BOTH SCHEMES

- **Reversible NO oxidation:**
  
  \[ r_{oxNO} = k_{oxNO} \exp\left( -\frac{Ea_{oxNO}}{RT}\right)[NO][O_2]^{0.5} \]

- **NO adsorption:**
  
  \[ r_{redNO_2} = \left( k_{oxNO} / K_{eq} \right) \exp\left( -\frac{(Ea_{oxNO} + Ea_{eq})}{RT_{sol}}\right)[NO_2] \]

- **NO adsorption:**
  
  \[ r_{adsNO} = k_{adsNO} \exp\left( -\frac{Ea_{adsNO}}{RT}\right)[NO][BaCO_3][O_2]^{1.5} \]

- **Thermal NO\(_2\) desorption:**
  
  \[ r_{desNO_2} = k_{desNO_2} \exp\left( -\frac{Ea_{desNO_2}}{RT}\right)[Ba(NO_3)_2] \]
DIFFERENCES ON THE ADSORPTION RATE

- **Scheme 1:**

\[
r_{ads\,1\,NO_2} = k_{ads\,1\,NO_2} \exp\left(-\frac{Ea_{ads\,1\,NO_2}}{RT}\right)[NO_2][BaCO_3]
\]

\[
r_{ads\,2\,NO_2} = k_{ads\,2\,NO_2} \exp\left(-\frac{Ea_{ads\,2\,NO_2}}{RT}\right)[NO_2][BaCO_3]
\]

- **Scheme 2:**

\[
r_{adsNO_2}^* = \frac{k_{adsNO_2} \exp\left(-\frac{Ea_{adsNO}}{RT}\right)[NO_2][BaCO_3]}{1 + k_{inibNO_2} \exp\left(-\frac{Ea_{inibNO_2}}{RT}\right)[Ba(NO_3)_2][L]}
\]

With [L] number of all the adsorption sites
04

MODEL CALIBRATION
To calibrate the parameters of the model:

- Sample catalyst on Synthetic Gas Test Bench (~0,2L)
- Catalyst used: Commercial Pt/Rh/Pd catalyst on Ba/Al₂O₃ support
- Gas in (Diesel like synthetic gas):
  - Gas analyzer: after the catalyst with NOₓ measurement first and NO in a 2nd test
  - Isothermal adsorption tests with variation of total gas flow, temperature, NO/NOₓ ratio, concentrations of HC, CO and NOₓ

To validate the calibration:

- Real condition test with Engine Test Bench
- Same impregnation and ageing than the sample catalyst (2,2L)
- New European Driving Cycle (NEDC)
- Gas analyzers: before and after the catalyst with NO and NOₓ measurement
Construction of a Matlab function:

```matlab
function y = optim(x)
```

\[ y: \text{difference between model and test} \]

\[ x: \text{calibration parameters} \]

- Comparison between instantaneous values
- Comparison between cumulative values

Use of an optimization tool on the `optim` function: `lsqnonlin`
EXEMPLE OF PARAMETER VARIATION

- Parameters variation for a largest area of optimization:
  - All the “Ea” are fixed before the optimization
  - The optimization method make variations on the 5 “k” in the same time
  - The best solution is kept for the previous “Ea”
  - “Ea” values are modified
  - The 10 parameters cannot be negative

```matlab
i=0;
for Ea1=50000:10000:100000
    for Ea2=0:200:1000
        for Ea3=0:200:1000
            for Ea4=0:200:1000
                for Ea5=50000:10000:100000
                    x0=[1e5;0.5e-3;3e-2;0.6e-2;80];
                    lb=[0;0;0;0;0];
                    ub=[ ];
                    k=lsqnonlin(@optimf02,x0,lb,ub);
                    i=i+1;
                    resultat(i).constantes=[k(1) k(2) k(3) k(4) k(5);Ea1 Ea2 Ea3 Ea4 Ea5];
                end
            end
        end
    end
end
```
RESULTS
SCHEME 1 : CALIBRATION ON CUMULATED VALUES

- Instant values (filtered) Error = 9.9685%
- Cumulative values Error = 1.6534%
- Computer software: sim, xp

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15/09/2009
MODEGAT 2009
SCHEME 1: VALIDATION ON CUMULATED VALUES

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MODEGAT 2009
## RESULTS SUMMARY

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>SCHEME 1</th>
<th>SCHEME 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calib Instant</td>
<td>Calib Cum</td>
</tr>
<tr>
<td></td>
<td>Inst</td>
<td>Cum</td>
</tr>
<tr>
<td>TOTAL</td>
<td>9,9%</td>
<td>2,9%</td>
</tr>
<tr>
<td>NO(_X)</td>
<td>9,0%</td>
<td>2,7%</td>
</tr>
<tr>
<td>NO</td>
<td>10,6%</td>
<td>2,9%</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>10,2%</td>
<td>3,2%</td>
</tr>
<tr>
<td>TOTAL</td>
<td>7,4%</td>
<td>8,4%</td>
</tr>
<tr>
<td>NO(_X)</td>
<td>6,5%</td>
<td>8,9%</td>
</tr>
<tr>
<td>NO</td>
<td>7,1%</td>
<td>9,4%</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>8,7%</td>
<td>6,8%</td>
</tr>
</tbody>
</table>
CONCLUSIONS AND PROSPECTS
**Conclusions:**

- Different schemes of NO/NO\(_2\) adsorption on Lean NO\(_X\)- Trap have been tested
- An automatic calibration method has been developed and tested
- A predictive model has been developed for NO/NO\(_2\) differentiation
- A calibration has been made with sample catalyst, and the same calibration seems to be predictive on real condition tests

**Prospects:**

- To validate the calibration method with other real condition tests
- To make this type of study for other post-treatment models (DOC, SCR, DPF,…)
- To improve the calibration method in order to reduce the calibration time
- To improve the optimization target to better fit curves at low / high temperatures
- To do specific sample tests on commercial catalyst in order to understand and improve the tested schemes
END

THANK YOU FOR YOUR ATTENTION