Diesel Aftertreatment System Analyses with DOC and SCR Models

Santhoji Katare
Chemical Engineering Department
Ford Research & Advanced Engineering
Dearborn, MI

10th CLEERS workshop, May 1-3, 2007
Dearborn, MI
# Acknowledgements

## Diesel aftertreatment modeling
- Jeong Kim
- Paul Laing
- Joseph Patterson

## Diesel catalysis
- Giovanni Cavataio
- Douglas Dobson
- Christine Lambert
- Cliff Montreuil

## Advanced Diesel program
- Michael Goebelbecker
- Kevin Murphy
- Peter Nelson

---

Ford Research & Advanced Engineering
Recent progress & key challenges

C. Lambert et al., DOE funded project, 2001 – 2005

- Typical AT system for lean NOx control: DOC + SCR + CDPF
- Several challenges but good progress
- Models facilitated progress
- Current modeling efforts to support vehicle programs

DOC: Oxidize HC & CO; Generate NO₂
SCR: Reduce NOx (using NH₃ + NO₂)
CDPF: Control PM

CDPF: Catalyzed Diesel Particulate Filter
Outline

**Diesel Oxidation Catalyst (DOC) model**
- Model calibration
- Prediction of post-DOC NO$_2$ on a vehicle

**Selective Catalytic Reduction (SCR) model**
- Model calibration
- Effect of stored NH$_3$ on SCR performance
- Prediction of tailpipe NOx and NH$_3$ slip in a vehicle

**DOC+SCR system applications**
- Importance of post-DOC NO$_2$ on SCR performance
- Optimization of urea injection strategy
Uniform Flow (1-D)

First principles energy balance & heat transfer coupled with empirical chemistry.

Conduction along substrate

Heat Transfer to Atmosphere

$O_2$, $HC$, $CO$, PM, $NO$, $NO_2$ m, $T_{gas}$

$hA(T_{wall} - T_{amb})$

Surface reaction rate, $R$
(from empirical map)

$hA[T_{gas} - T_{wall}]$

$kA([ ]_{gas} - [ ]_{wall})$

Computationally non-intensive semi-empirical modeling approach
DOC model – Hybrid approach to leverage data

HC storage/release (PDEs)

Thermal balances (PDEs)

Rate inhibition (Correlations)

Conversion map (Data)

"Information hooks"

Monolith channel

Predict vehicle data

Optimizer (Agent-based)

DOC Model

Katare & Laing, SAE 2006-01-0689
Typical pulsator map

Inlet Temperature [°C]

Conversion [-]

Key input to the DOC model

SV: 35k 1/h
Degreened DOC

CO
HC
NO → NO₂
At the bulk-solid interface
\[ \frac{dC_s}{dt} = k_c S (C_f - C_s) - k_a (1 - \theta) C_s N + k_d \theta N = 0 \]

In the zeolite phase
\[ \frac{d\theta}{dt} = k_a (1 - \theta) C_s - k_d \theta \]

\[ k_d = k_{do} \exp(-E_d / RT) \]
\[ k_a, N, \theta_o \]

2 nonlinear equations & 5 parameters
Model can predict HC adsorption, desorption and light-off

Parameter estimation using in-house “stochastic optimizer” *

$k_a = 1.06 \times 10^4$ m$^3$/mol/s

$k_{do} = 3.7 \times 10^2$ 1/s

$E_d = 9.26$ kcal/mol

$N = 1.4$ mol/kg

$\theta_0 = 0.32$ --

Total amount of the trap material (N) could be optimized

* Katare & West, *Complexity, 11, 4, 2006*
Predicting engine dynamometer CO and HC emissions

Model predictions reasonable

Post DOC  Model  Data

Euro test time (s)

2.2 L Puma engine

HC  Engine out

Euro test time (s)

Euro test time (s)

Cumulative CO emissions (g)

Cumulative HC emissions (g)
DOC oxidizes NO to NO$_2$ – critical for SCR operation

NO oxidation chemistry is complex
Predicting post DOC NO\textsubscript{2} on a Ford developmental vehicle

Model can predict DOC-out NO\textsubscript{2}: Useful information for the downstream SCR

Engine exhaust flow and T

Map

Pulsator map

CO

HC

NO \rightarrow NO\textsubscript{2}

FG NO\textsubscript{x}

NO\textsubscript{2} vehicle data

NO\textsubscript{2} model

Normalized NO\textsubscript{x} and NO\textsubscript{2}

DOC inlet T [C]

Inlet T [C]

120k miles aged DOC

T DOC in

DOC inlet T [C]

FTP time [s]
Outline

**Diesel Oxidation Catalyst (DOC) model**
- Model calibration
- Prediction of post-DOC NO$_2$ on a vehicle

**Selective Catalytic Reduction (SCR) model**
- Model calibration
- Effect of stored NH$_3$ on SCR performance
- Prediction of tailpipe NOx and NH$_3$ slip in a vehicle

**DOC+SCR system applications**
- Importance of post-DOC NO$_2$ on SCR performance
- Optimization of urea injection strategy
Introduction to Selective Catalytic Reduction (SCR)

- Base metals such as Cu and Fe on honeycombs
- Selectively reduce NOx to N₂
- Aqueous urea sprayed onto the catalyst
- Urea → thermal decomposition + hydrolysis to NH₃ on the catalyst

\[
4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O
\]
Standard SCR

\[
4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O
\]
Fast SCR

When feed NO = NO₂ SCR reaction is faster
SCR NOx performance increases with NO\textsubscript{2} in the feed

NO\textsubscript{2} information from DOC model is key for simulating SCR performance
Temperature programmed desorption of NH$_3$

**Model**
- Initial T: 150°C
- 120k miles aged SCR

**Data**
- Temkin isotherm captures NH$_3$ ads/des data reasonably
- Model calibrated at 150°C and verified at other T and C$_{NH3}$

**Parameters**
- $k_a = 0.61$ m$^3$ / mol s
- $k_{do} = 2 \times 10^5$ 1/s
- $E_{do} = 20$ kcal/mol
- $\alpha = 0.45$
- $\Omega = 0.23$ mol NH$_3$ / kg wc
Calibrated model over predicted vehicle NOx conversion

Thermal balances (PDEs)

Optimizer (Agent-based)

Over predicted vehicle NOx conversion

Catalyst Temperature (ºC)

Gross NOx conversion (%)

Model showed the right trends but had to assume
(1) low urea to NH₃ conversion or
(2) very high HC deactivation to explain vehicle data
NOx performance increases with increasing NH$_3$ storage

Currently a standard protocol for screening catalysts
Model predicts vehicle Tail Pipe (TP) NOx

120k miles aged SCR
NH₃ slip prediction

120k miles aged SCR

Model – experiment closure: Model → Experiment → Data → More accurate model
Outline

Diesel Oxidation Catalyst (DOC) model
• Model calibration
• Prediction of post-DOC NO₂ on a vehicle

Selective Catalytic Reduction (SCR) model
• Model calibration
• Effect of stored NH₃ on SCR performance
• Prediction of tailpipe NOx and NH₃ slip in a vehicle

DOC+SCR system applications
• Importance of post-DOC NO₂ on SCR performance
• Optimization of urea injection strategy
System: DOC + SCR Models

DOC Model

- HC storage/release (PDEs)
- Thermal balances (PDEs)
- Rate inhibition (Correlations)
- Optimizer (Agent-based)
- Conversion map (Data)

SCR Model

- Thermal balances (PDEs)
- Conversion map (Data)

Predict $X_{NOx}$ & $NH_3$ slip

Temperature $T$ & $NO_2/NOx$
Optimum DOC for an efficient SCR?

Very little NO$_2$ produced by current DOC formulations

Ideal DOC
NO = NO$_2$

Increasing DOC volume increases NO$_2$
But SCR performance also requires
- DOC with low thermal inertia
- Rapid warm up
(tradeoff - HC v.s. DOC NO$_2$ v.s. SCR X$_{NOx}$)

Model provided insight into system design issues

Urea injection strategy as a function of vehicle speed over an FTP test

Region 1
Very low urea injection

Region 2
Optimum!

Region 3
Limited by SV & T

Assuming 100% NH$_3$ to NOx conversion over DPF

Each point corresponds to a simulated urea injection strategy that max $[X_{NOx}/NH_3$ slip$]$.

Possible to use models to come up with effective urea injection strategies
Summary

Math models enable effective analysis and afford insight into diesel AT systems.

Models leverage laboratory data to predict vehicle experiments.

Optimization & statistical tools enhance model development process.

DOC model
  Predicted post DOC NO₂ on a vehicle
  Extrapolated fresh catalyst information to predict aged catalyst performance

SCR model
  Motivated the need for analyzing SCR performance = f (NH₃ storage)
  Predicted vehicle NOₓ conversion and NH₃ slip

DOC+SCR system analysis
  Highlighted importance of NO₂/NOₓ from DOC for SCR performance
  Optimization of the urea injection strategy
  (trade-off between NOₓ conversion & NH₃ slip)
Experiments and models drive each other leading to insight
Model calibration with NH₃ storage information required

NH₃ storage decreases with increasing temperature

Increasing T reduces NH₃ storage ability

Catalyst as a storage cup

More accurate picture of the catalyst

Research & Advanced Engineering
Stochastic algorithms for parameter estimation & optimization

AT models are nonlinear and multi-dimensional
Local optimizers may not be efficient

- Do not get trapped in local optima – more robust and efficient than a local optimizer
- Examples: Genetic algorithms, Particle swarm optimization, Differential evolution

**In-house built optimizer – can be customized**
Practical utility of the model: Case study

Burn soot off DPF by down stream injection of fuel (HC)

Performance: \( \frac{T_{\text{out}} - T_{\text{in}}}{\text{HC slip}} \) v.s. \((T_{\text{in}}, SV)\)

Aged DOC inlet T for exotherm generation given fresh DOC data?
Calibrating model to fresh DOC data using pulsator map

Model calibrated with “fresh” DOC data
Predict “aged” DOC performance
Extrapolating model to predict performance of aged DOC

Aged catalyst can not generate exotherm when $T_{in} < 300 \, ^\circ C$

Model established limits to exotherm generation strategy