Development and Validation of A Model for 2-way DPF/SCR

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- Model Development for wall flow type SCR
- Validation of wall flow type SCR Model
- Application of Model –NH3 balance Monitor
- Review of test results –Effect of soot loading
- Model for soot loading effect on SCR
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Introduction

What is a 2-way DPF/SCR aftertreament device?

- Multifunctional device combining DPF and SCR
  a. Wall flow type DPF for soot trapping and oxidation
  b. SCR for NOx reduction
Issues

- DeNOx by SCR under wall flow type substrate
  - Model development for wall flow type SCR
  - Comparison study between flow channel type and wall flow type SCR

- Soot Filtration – DeNOx performance

- Soot Oxidation – DeNOx performance
  - NO₂ as a soot oxidizer and a reactant species in SCR
Model Structure

2-way DPF/SCR

DPF(Wall Flow Type)  SCR

Flow  Species Transport  Reaction Kinetics

Temperature

Soot Filtration

Soot Oxidation
Model Development for Wall Flow Type SCR
Species Transport Equation (S.T.E) - General

\[ \frac{\partial C_i}{\partial t} = -\nabla \cdot N_i + R_{v,i} \]

where

\[ N_i = C_i v + J_i \]

\[ J_i = -D_i \nabla C_i \]

To solve this equation directly
1. needs a lot of computer resources or solving time
2. is not an appropriate way for system simulation
# Scaling Analysis

<table>
<thead>
<tr>
<th>Transport by</th>
<th>Time scale</th>
<th>Order of Value (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet channel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Convection along channel</td>
<td>$L/U_{in}$</td>
<td>~1E-2</td>
</tr>
<tr>
<td>Diffusion along channel</td>
<td>$L^2/D$</td>
<td>~1E+2</td>
</tr>
<tr>
<td>Diffusion to filter wall</td>
<td>$a/k$</td>
<td>~1E-2</td>
</tr>
<tr>
<td>Filter wall</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Convection</td>
<td>$w/u_w$</td>
<td>~1E-2</td>
</tr>
<tr>
<td>Diffusion along wall thickness</td>
<td>$w^2/D_w$</td>
<td>~1E-3</td>
</tr>
<tr>
<td>Diffusion to catalyst surface</td>
<td>$d_p/k_w$</td>
<td>~1E-3</td>
</tr>
<tr>
<td>Time scale for external perturbation (Boundary Condition variation)</td>
<td></td>
<td>1~10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Definition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pe_{ch}$</td>
<td>$L \cdot U_{in}/D$</td>
<td>~1E+4</td>
</tr>
<tr>
<td>$Pe_w$</td>
<td>$w \cdot u_w/D_w$</td>
<td>~10</td>
</tr>
</tbody>
</table>
Scaling Analysis
Species Transport Equation (S.T.E.) - Simplified

\[
\frac{\partial C_i}{\partial t} = -\nabla \cdot N_i + R_{v,i}
\]

where

\[
N_i = C_i v + J_i
\]

\[
J_i = -D_i \nabla C_i
\]

Quasi steady assumption at each time step even in transient problem
Final Form of S.T.E.

Gas Phase

I. \( \frac{\partial}{\partial x} (uC_{b,i}) + \frac{4}{a} (u_w C_{b,i}) + \frac{4k_c}{a} (C_{b,i} - C_{wf,i}|_{y=0}) = 0 \)

B.C. \( x = 0, \quad C_{b,i} = C_{b,i,inlet} \)

II. \( \frac{\partial}{\partial y} (u_w C_{wf,i}) - D_w \frac{\partial^2 C_{wf,i}}{\partial y^2} + k_w S(C_{wf,i} - C_{ws,i}) = 0 \)

B.C. \( y = 0, \quad C_{wf,i} = C_{wf,i}|_{y=0} \quad y = w, \quad \frac{\partial C_{wf,i}}{\partial y} = 0 \)

III. \( k_w S(C_{wf,i} - C_{ws,i}) = a_s \sum_k RR(k) \)

IV. \( c_b u_w + k_c (C_{b,i} - C_{wf,i}|_{y=0}) = C_{wf,i}|_{y=0} \cdot u_w - D_w \frac{\partial C_{wf,i}}{\partial y}|_{y=0} \)

Adsorption phase (NH₃ only)

\[ \frac{d\theta}{dt} = RR(1) - RR(2) - 2RR(3) - 4RR(5) - 2RR(6) - 4RR(7) - 2RR(8) \]

= net adsorption – ammonia oxidation – SCR reaction
Final Form of S.T.E.

\[
\frac{\partial}{\partial x} \left( u^o C_{b,i}^o \right) + \frac{4}{a} \left( u_w C_{wf,i} \bigg|_{y=w} \right) = 0
\]

\[
C_{b,out} = \frac{1}{a \cdot u_{out}} \int 4 \left( u_w C_{wf,i} \bigg|_{y=w} \right) dx
\]

- Diffusion through boundary layer can be ignored (wall injection)

- Convective flux only \(\rightarrow\) Channel outlet concentration can be found by simple mass balance

Depsick et. al., Journal of Engineering for Gas Turbines and Power 2008 vol.130
Solver Development

- Total $4n+1$ coupled equations and $4n+1$ unknowns of $C_{b,i}$, $C_{wf,i}$, $C_{ws,i}$, $C_{wf,i}(y=0)$ and $\theta$
  - 2n equations of differential equations
  - 2n equations of algebraic equations
  - One equation of differential equation ($d\theta/dt$)

- 2n differential equations are converted to algebraic equation by FVM (Finite Volume Method).
## SCR Reaction and its Rate Expression

<table>
<thead>
<tr>
<th>Description</th>
<th>Reaction Rate</th>
<th>Rate Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia adsorption</td>
<td>RR(1)</td>
<td>( RR(1) = A_1 C_{NH_3} (1 - \theta) )</td>
</tr>
<tr>
<td>ammonia desorption</td>
<td>RR(2)</td>
<td>( RR(2) = A_2 \exp \left( \frac{-E_{A_2}}{R_u T} \right) \theta )</td>
</tr>
<tr>
<td>ammonia oxidation</td>
<td>RR(3)</td>
<td>( RR(3) = A_3 \exp \left( \frac{-E_{A_3}}{R_u T} \right) C_{O_2} \cdot \theta )</td>
</tr>
<tr>
<td>NO oxidation</td>
<td>RR(4)</td>
<td>( RR(4) = A_4 \exp \left( \frac{-E_{A_4}}{R_u T} \right) C_{NO} \sqrt{C_{O_2}} \cdot \theta - k_{4,b} C_{NO_2} ) where ( k_{4,b} = A_4 \exp \left( \frac{-E_{A_4}}{R_u T} \right) / K_{eq} ) and ( K_{eq} = \exp \left( \frac{-\Delta S}{R_u} \right) \exp \left( \frac{-\Delta H}{R_u T} \right) )</td>
</tr>
<tr>
<td>Standard NH(_3) SCR</td>
<td>RR(5)</td>
<td>( RR(5) = A_5 \exp \left( \frac{-E_{A_5}}{R_u T} \right) C_{NO} \cdot \theta )</td>
</tr>
<tr>
<td>Rapid NH(_3) SCR</td>
<td>RR(6)</td>
<td>( RR(6) = A_6 \exp \left( \frac{-E_{A_6}}{R_u T} \right) C_{NO} C_{NO_2} \cdot \theta )</td>
</tr>
<tr>
<td>NH(_3) SCR with NO(_2)</td>
<td>RR(7)</td>
<td>( RR(7) = A_7 \exp \left( \frac{-E_{A_7}}{R_u T} \right) C_{NO_2} \cdot \theta )</td>
</tr>
<tr>
<td>N(_2)O formation by SCR</td>
<td>RR(8)</td>
<td>( RR(8) = A_8 \exp \left( \frac{-E_{A_8}}{R_u T} \right) C_{NO_2} \cdot \theta )</td>
</tr>
</tbody>
</table>

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- **Modeling Ea**
- **Non-Linear**
Activation Energy for Desorption

Dependence of activation energy on surface coverage
1. Linear form

\[ E_{a,\text{des}} = E_{a,\text{des}0}(1 - \alpha \theta) \]

2. Exponential form

\[ E_{a,\text{des}} = E_{a,\text{des}1} \exp(-\beta \theta) + E_{a,\text{des}2} \]
Validation of Model - TPD

Initial Temp. : 200degC

Initial Temp. : 250degC

Initial Temp. : 300degC

Initial Temp. : 350degC
TPD-NH$_3$ Concentration Distribution
Model Validation – DeNOx (Steady State)

1. Model is calibrated under no soot loading and $\alpha=0.9$ condition.

2. Reaction constants for adsorption and desorption are carried over from TPD results.

3. Reaction constants for RR(3) to RR(8) are calibrated to match the simulation results to experiment’s
# Model Validation – DeNOx (Steady State)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>195 ppm</td>
</tr>
<tr>
<td>NO₂</td>
<td>5 ppm</td>
</tr>
<tr>
<td>NH₃</td>
<td>180 ppm</td>
</tr>
<tr>
<td>S.V.</td>
<td>23000 (1/hr)</td>
</tr>
</tbody>
</table>

**NOx conversion**

**NO₂ concentration**

**NH₃ conversion**
DeNOx-Species Spatial Distribution

Concentration distribution along the channel axial position

Concentration distribution through catalytic filter wall
Vel., Flux, and Surface coverage

- **Wall flow vel.**
- **Channel flow vel.**
- **Total convective flux**

**Velocity field**

**Mass flux to catalytic filter wall**

**Surface Coverage**
Monitoring Ammonia Balance

Manipulating the S.T.E for ammonia

\[ \dot{N}_{in,NH3} = \dot{N}_{out,NH3} + \int a_s \frac{d\theta}{dt} dV + \int a_s \cdot 2RR(3) dV + \int a_s (4RR(5) + 2RR(6) + 4RR(7) + 2RR(8)) dV \]

A: rate of ammonia slip
B: net ammonia adsorption rate
C: rate of ammonia oxidation
D: SCR reaction rate
Test condition—NH₃ Balance

Test Condition
1. No adsorbed ammonia initially
2. Constant rate of ammonia injection
3. Step temperature increasing at certain points

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Velocity</td>
<td>23000(1/hr)</td>
</tr>
<tr>
<td>NO</td>
<td>200 ppm</td>
</tr>
<tr>
<td>NO₂</td>
<td>0 ppm</td>
</tr>
<tr>
<td>NH₃</td>
<td>180 ppm</td>
</tr>
</tbody>
</table>

Inlet condition
Results – NH₃ Balance

Outlet concentration

Ammonia Balance

NH₃-in

SCR rate

NH₃-out

NH₃-oxidation

Net Adsorption
Effect of Soot Deposit (Filtered Soot) on SCR Reaction
Review – Experiment (I)

Observation (I)
1. Regeneration starts at lower temperature comparing non catalyzed DPF
2. Soot oxidation rate decreases as temperature increases from 400 to 500 degC

Conclusion (I)
1. Catalytic oxidation at the temperature of 200 to 400 degC → soot inside the filter wall
2. Thermal oxidation (above 400 deg) → soot on the filter wall
Review – Experiment (II)

Observation (II)
1. Deterioration of NOx reduction performance
   1) Only occurs at 200 and 300 degC
   2) Can be recovered if soot is burned out.

Conclusion (II)
1. At 400 degC or above, there is no soot inside the filter wall because of catalytic oxidation of soot.
2. Soot deposit inside the filter wall disrupts mass transfer from fluid side to catalytic site. → reason for poor NOx conversion efficiency at 200 and 300 degC when soot exists.
Model for soot deposit effect on SCR

Idea of Thiele Modulus and Effectiveness Factor can be extended to soot loading case

$$\eta = \frac{\text{actual reaction rate inside the washcoat}}{\text{ideal reaction rate}}$$
Diffusion-Reaction Equation for soot deposited case

For catalyst washcoat

\[ 0 \leq \bar{\xi} \leq \delta_w \quad \frac{\partial^2 \bar{C}}{\partial \bar{\xi}^2} - \Phi^2 \bar{C} = 0 \]

at \( \bar{\xi} = 0, \quad \frac{\partial \bar{C}}{\partial \bar{\xi}} = 0 \) at \( \bar{\xi} = 1, \quad \bar{C} = 1 \)

For soot deposit layer

\[ \delta_w < \bar{\xi} \leq \delta_s \quad \frac{\partial^2 \bar{C}}{\partial \bar{\xi}^2} = 0 \]

at \( \bar{\xi} = 1, \quad \bar{C} = 1 \)

at \( \bar{\xi} = \frac{\delta_w}{\delta_s}, \quad \bar{C} = \frac{C_{ws}}{C_i} \)

where \( \bar{C} = C/C_i \), \( \bar{\xi} = \xi/\delta_w \) and \( \Phi = \sqrt{\frac{k_v \delta_w^2}{D_{eff,w}}} \) Thiele Modulus
Solution & Effectiveness Factor

Solution

\[
\bar{\xi}(\bar{\xi}) = \frac{\sinh(\Phi_w \bar{\xi})}{\sinh(\Phi_w)} \quad \text{for } 0 \leq \bar{\xi} \leq \delta_w
\]

\[
\bar{\xi}(\bar{\xi}) = \frac{\delta_c(C_{ws} - C_1)}{C_1(\delta_z - \delta_w)} \bar{\xi} + \frac{C_1 \delta_z - C_{ws} \delta_w}{C_1(\delta_z - \delta_w)} \quad \text{for } \delta_w < \bar{\xi} \leq \delta_z
\]

where

\[
C_1 = \frac{D_{eff,s}}{(\delta_z - \delta_w)} C_{ws}
\]

\[
\sqrt{D_{eff,w}} k_v \tanh(\Phi_w) + \frac{D_{eff,s}}{(\delta_z - \delta_w)}
\]

Effectiveness Factor

\[
\eta_s = \frac{D_{eff,s}}{k_v \delta_w} \left( \frac{\sqrt{D_{eff,w}} k_v \tanh(\Phi_w)}{(\delta_z - \delta_w) \sqrt{D_{eff,w}} k_v \tanh(\Phi_w) + D_{eff,s}} \right)
\]

\[
\lim_{\delta_z \rightarrow \delta_w} \eta_s = \frac{\sqrt{D_{eff,w}} k_v \tanh(\Phi_w)}{k_v \delta_w} = \frac{\tanh(\Phi_w)}{\Phi_w} = \eta_c
\]

\[
k_{app,s} = \eta_s k_v
\]
Implementation of Effectiveness Factor

Comparison of clean and soot deposit case: Simulation
Simulation and Experimental Results

![Graph showing NOx conversion efficiency vs. temperature (degree C)].

- **clean (exp.)**
- **soot deposited (exp.)**
- **clean (sim.)**
- **soot deposited (sim.)**
Concentration of soot deposit inside the filter wall

Concentration of soot deposit : only inside the filter wall
Conclusion

1. Introduction of model development for wall flow type SCR
2. Model was validated over TPD, steady NOx reduction test case.
3. The results are investigated in space and they gives the insight for the utilization of catalyst.
4. Ammonia balance monitor → can be applied to control model
5. Soot deposit inside the filter wall → Resistance to mass transfer for catalytic reaction → Decreasing overall SCR performance
6. Extended Thiele modulus and effectiveness factor → For effect of soot loading on SCR performance
Acknowledgement

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Experimental Work: Steven Schmieg

Thank You!