Global kinetics for a commercial diesel oxidation catalyst with two exhaust hydrocarbons

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DEER 2007
Diesel Aftertreatment

• Perennial soot-NOx trade-off
• Combination of in-cylinder combustion strategies and complex aftertreatment systems
• High hydrocarbons and CO from advanced combustion modes (Premixed compression ignition - PCI)
• Stoichiometric NO-NO$_2$ ratio for SCR
• Exotherms for DPF regeneration
• Solution – Diesel oxidation catalyst (DOC)
DOC Kinetics Development

• Scope
  - Global oxidation – HCs, CO, H₂ and NO
  - No post injection; Lean exhaust (Conventional + PCI)

• Global kinetics
  - FTP data – Undesired complexity
  - Light-off curves – Narrow temperature window
  ✓ Bench scale reactor data – Realistic domain

• HC speciation
  - Previously¹ used C₃H₆ as representative HC
    - Conclusion - Need more complex HC representation
  ✓ THC ≡ partially oxidized (C₃H₆) and un-burnt fuel (DF)
  ✓ Un-burnt fuel = Swedish low sulfur diesel fuel
Overview

Define experimental parameter range

Test matrix

Lab reactor experiments

Inlet & outlet concentrations at discrete temperatures

Generate global kinetic rates

Rate expressions with known constants

Validation

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Engine Systems Research
Concentration and temperature domain

- 2006 CIDI FTP, US06 and 2010 PCI cal – upper bounds for concentrations
- Lower bounds for concentrations – factors of 3 – represents axial gradients in the reactor
- Impose realistic constraints (e.g. CO/3 < THC etc.)
- Four discrete temperature levels
- Random sampling in concentration domain for each temperature
  - 135 total test points
Test Matrix

• Temperatures
  - 200, 255, 325 and 415°C
  - Equal spacing in 1/T
  - > 415°C, mass transport limited

• Concentrations
  - CO: 3000, 900, 300, 100, & 30 ppm
  - DF: 1000, 600, 200, 60 & 20 ppm
  - C₃H₆: 1000, 300, 100, 30 ppm and 0 ppm
  - O₂: 13 & 4%
  - H₂: 700, 200, 70 ppm
  - NO: 400, 100, 40, 10 ppm
  - Separate NO+NO₂+O₂ experiments to infer NO-NO₂ rate
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DOC catalyst

• Commercial DOC catalyst intended for 2010 standards
• Composition and loading proprietary, but CO chemisorption results adequate (site-density)
  - Chemisorption = 0.331 mol-site/m$^3$
• Hydro-thermally aged in furnace
  - 16 hrs at 650°C
  - 10% H$_2$O; 2.2Lpm flow
Reactor set-up

- High space velocity integral reactor – up to 2 million h\(^{-1}\)
- All experiments at 1.6 atm
- Low/moderate conversions
- \(\text{H}_2\) analyzed with mass spectrometer
- THC analyzed with hot FID
- All other species analyzed with FTIR
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Global Rate Generation

- Inner problem – Calculates exit concentrations
  - Needs a prescribed rate and transport properties
- Outer problem – optimization – minimizes objective fn
  - Generates set of $A_i$ and $E_i$ for a given rate form
- Complex optimization problem – used local methods
  - Scaling
- Simplifying assumptions to generate proper initial guesses
- Relax assumptions successively for full problem
- Remove inhibition terms and re-optimize
  - Analyze using objective function if goodness of fits could be maintained with reduced degrees of freedom
**Inner problem**

- Calculates exit concentrations based on inlet concentrations, mass transport and reaction rates

- Simplified reactor code (Matlab)

\[
\frac{w}{A} \frac{dx_{g,i}}{dz} = -k_{m,i} S (x_{g,i} - x_{s,i}) = \sum_{j=1}^{nrct} a_{j} s_{ij} r_{j} \quad i = DF, C_3H_6, CO, H_2, NO, NO_2
\]

- Solve for surface and gas concentrations with prescribed reaction rates (system of DAEs)

- \( T_g = T_s \)

- Temperature field inferred from experiments

- Estimated \( k_{DF} \) (mass transfer coeff) using experiments

- Experimental conversions cannot exceed transport limited solution
Outer problem

- Euclidean norm to compare model and experiments

- Objective function (norm)

\[
\text{norm} = f \left( \left( \frac{x_{g,\text{exit}}^{\text{model}}}{x_{g,\text{exit}}^{\text{exp}}} \right)_{\text{conv}>50\%}, \left( \frac{\Delta x_{g}^{\text{model}}}{\Delta x_{g}^{\text{exp}}} \right)_{\text{conv}\leq50\%} \right)
\]

- Scaled optimization parameters – O(1)
Initial rate form

- Initial rate – modified Voltz *et al*.\(^5\)

\[
-i \frac{dx}{dT} = \frac{k(x) x_{O_2}}{T(1 + K_{C_3H_6} x_{C_3H_6} + K_{CO} x_{CO})^2[1 + K_{H_2} x_{H_2} x_{C_3H_6}^2 x_{CO}^2]^{1 + K_{NO} x_{NO}}}
\]

\[
i = DF, C_3H_6, CO, H_2
\]

\[
-i \frac{dx_i}{dt} = \frac{k_i c_i c_{O_2}}{(1 + K_{DF} c_{DF} + K_{C_3H_6} c_{C_3H_6} + K_{CO} c_{CO})^2(1 + K_{NO} c_{NO})}
\]

- Used results from individual temperatures to generate Arrhenius plots
NO oxidation

- Rate inferred from previous work\(^1\)
  
  \[ r_{NO} = \frac{k_{NO} C_{NO} C_{O_2}^{0.5}}{(1 + K_{NO} C_{NO})} \left( 1 - \frac{C_{NO_2} \sqrt{C_{ref}}}{K_e C_{NO} C_{O_2}^{0.5}} \right) \]

- Rate over predicts for cases with reductants

- Need to modify the rate to incorporate the effect of reductants

- Same form for NO inhibition term as other rates

\[ r_{NO} = \frac{k_{NO} C_{NO} C_{O_2}^{0.5}}{(1 + K_{DF} C_{DF} + K_{C_2H_6} C_{C_2H_6} + K_{CO} C_{CO})^2 (1 + K_{NO} C_{NO})} \left( 1 - \frac{C_{NO_2} \sqrt{C_{ref}}}{K_e C_{NO} C_{O_2}^{0.5}} \right) \]
Optimization of full problem

• All reactions optimized over entire domain

• Successively removed terms in the inhibition to reduce degrees of freedom
  - Keep the term if there is significant deterioration in norm
  - Remove the term if norm is unaffected

• Re-optimize at the end of every iteration

<table>
<thead>
<tr>
<th>Terms</th>
<th>Norm</th>
</tr>
</thead>
<tbody>
<tr>
<td>All terms present</td>
<td>0.4529</td>
</tr>
<tr>
<td>$K_{DF}c_{DF}$</td>
<td>0.453 (removed)</td>
</tr>
<tr>
<td>$K_{C3H6}c_{C3H6}$</td>
<td>0.4529 (removed)</td>
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<tr>
<td>$K_{CO}c_{CO}$</td>
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<td>$K_{NO}c_{NO}$</td>
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<td>$K_{H2}c_{H2}$(added)</td>
<td>0.4527 (added)</td>
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</table>

<table>
<thead>
<tr>
<th>Terms removed</th>
<th>Norm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{DF}c_{DF}+K_{C3H6}c_{C3H6}$</td>
<td>0.453</td>
</tr>
</tbody>
</table>
Final rate forms

\[ r_i = \frac{k_i c_i c_{O2}}{(1 + K_{CO} c_{CO})^2(1 + K_{NO} c_{NO})} \quad i = DF, C_3H_6, CO, H_2 \]

\[ r_{NO} = \frac{k_{NO} c_{NO} c_{O2}^{0.5}}{(1 + K_{DF} c_{DF})^2(1 + K_{NO} c_{NO})} \left(1 - \frac{c_{NO2} \sqrt{c_{ref}}}{K_e c_{NO} c_{O2}^{0.5}}\right) \]

units = \frac{mol}{(mol/site) - s}

- Inhibition from hydrocarbons or enhancement due to \( H_2 \) was not required to capture the behavior over wide concentration and temperature domain
- Need DF inhibition to correctly capture NO behavior
Optimization results – DF & NO

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Engine validation

- 1.7L isuzu diesel engine
- Run conventional and PCI combustion modes with same catalyst
  - 2300 rpm; conventional and PCI combustion modes
  - Low/medium loads (~ 2.5 bar bmep)
- Other properties – Knafl $^2$
Engine validation – 2300 rpm conventional combustion

THC

CO

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Engine validation – 2300 rpm PCI combustion

THC

CO
Conclusions

- Global oxidation reaction rates for DF, $C_3H_6$, CO, $H_2$ and NO in the presence of excess $O_2$ developed over wide concentration and temperature domain representing diesel exhaust from both conventional and PCI combustion.

- Developed methodology for generating global reaction rates.

- Total hydrocarbons in diesel exhaust categorized as $C_3H_6$ (partially oxidized), DF (un-burnt fuel).

- Kinetic models capture full-scale converter light-off well for variety of engine testing conditions.
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• Calvin Koch, Terry Talsma, Mike Rogers - GM
References

1. “Global kinetics for platinum diesel oxidation catalysts” – Chaitanya S. Sampara, Edward J. Bissett and Matthew Chmielewski, Accepted for publication in *Ind. Eng. Chem. Res*


Questions?
Back-up slides
## Fuel properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Swedish low sulfur diesel fuel</th>
<th>US Diesel # 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane no.</td>
<td>51.6</td>
<td>49.6</td>
</tr>
<tr>
<td>Sulfur content</td>
<td>12 ppm (wt)</td>
<td>500 ppm (wt)</td>
</tr>
<tr>
<td>LHV</td>
<td>43.5 MJ/kg</td>
<td>42.9 MJ/kg</td>
</tr>
<tr>
<td>Stoic AFR</td>
<td>14.74</td>
<td>14.46</td>
</tr>
<tr>
<td>Density</td>
<td>810 (kg/m³)</td>
<td>840 (kg/m³)</td>
</tr>
<tr>
<td>C:H:O</td>
<td>C(<em>{1})H(</em>{1.966})O(_{0})</td>
<td>C(<em>{1})H(</em>{1.77})O(_{0})</td>
</tr>
</tbody>
</table>
Diffusion coefficient for diesel fuel

- Experimental conversions should not exceed transport limited solution

- Binary diffusion coefficients – Fuller et al.\(^4\)

\[ f(T, P, \text{mol.wt}, \Sigma_i) \]

- Mol.wt of diesel = 200 = \( \text{C}_{14.6}\text{H}_{24.8} \) (Heywood\(^5\))

\[ \Sigma_{C_xH_y} = 15.9x + 2.31y \]

(Poling, Prausnitz and O’Connell\(^6\))
NO reaction rate

$K_{CO}c_{CO}$ inhibition

$K_{DF}c_{DF}$ inhibition
Scaling of optimization parameters

\[ \hat{E} = \frac{E_i}{RT_r} \]

Scaling for activation energy

\[ \hat{A}a_i = Aa_i e^{-\hat{E}a_i} c_r x_{r,i} \]

Scaling for inhibition term pre-exponential

\[ \hat{A}_i = \frac{V a_i}{w_r} A_i e^{-\hat{E}_i} c_r^2 x_{r,i} x_{O_2} \]

Scaling for rate constant pre-exponential
Optimization results – C\textsubscript{3}H\textsubscript{6}
Optimization results - CO
Optimization results – $H_2$

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Diesel Oxidation Catalyst (DOC)

• Major reactions – HC, CO, H₂ and NO oxidation

Scope

• Global oxidation rates for HC species, CO, H₂, NO
• No post injection
• No HC storage
• Lean - Conventional and PCI

Example:

\[
\begin{align*}
n_{CO} &= \frac{k_{CO}c_{CO}c_{O2}}{(1 + K_{CO}c_{CO})^2(1 + K_{NO}c_{NO})} \\
k_{CO} &= A_i \exp\left(-\frac{E_i}{RT}\right) \\
K_{CO} &= Aa_i \exp\left(-\frac{Ea_i}{RT}\right)
\end{align*}
\]