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, H_2 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
    - Previously[1] used C_3H_6 as representative HC
        - **Conclusion** - Need more complex HC representation
    - ✓THC ≡ partially oxidized (**C_3H_6**) 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

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
  - C_3H_6: 1000, 300, 100, 30 ppm and 0ppm
  - O_2: 13 & 4%
  - H_2: 700, 200, 70 ppm
  - NO: 400, 100, 40, 10 ppm
  - Separate $NO+NO_2+O_2$ experiments to infer $NO-NO_2$ rate

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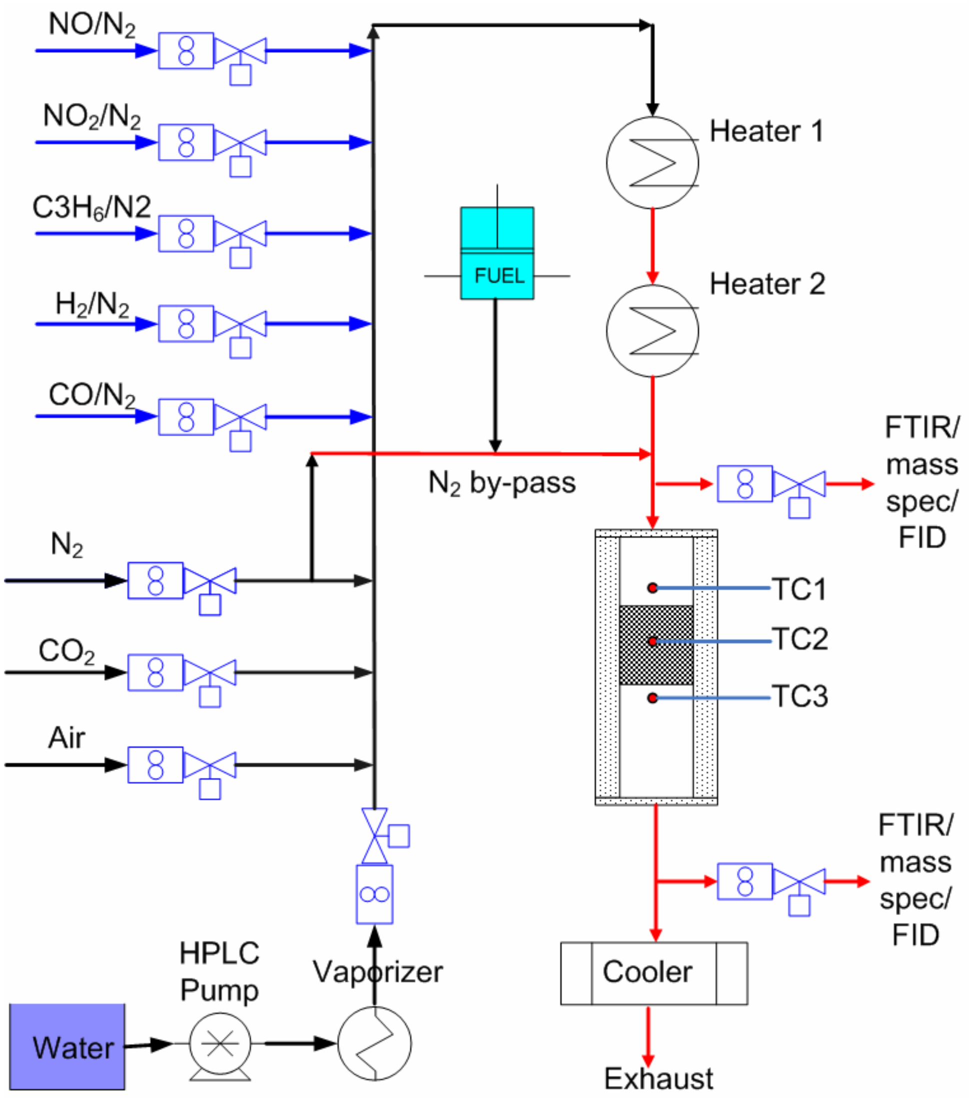
DOC catalyst

- 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_2O; 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
- 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)

$$\frac{w}{A}\frac{dx_{g,i}}{dz} = -k_{m,i}S\left(x_{g,i} - x_{s,i}\right) = \sum_{j=1}^{nrct} a_j s_{ij} r_j \qquad i = DF, C_3H_6, CO, H_2, NO, NO_2$$

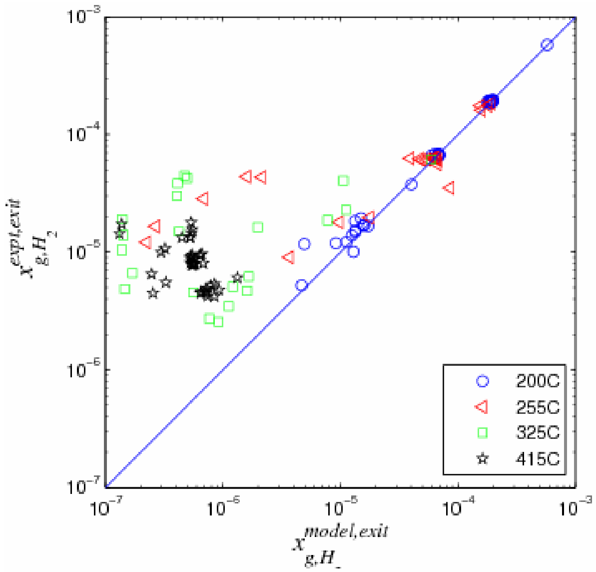
  - Solve for surface and gas concentrations with prescribed reaction rates (system of DAEs)
  - $T_g = T_s$
  - Temperature field inferred from experiments
- Estimated k_{DF} (mass transfer coeff) using experiments
  - Experimental conversions cannot exceed transport limited solution

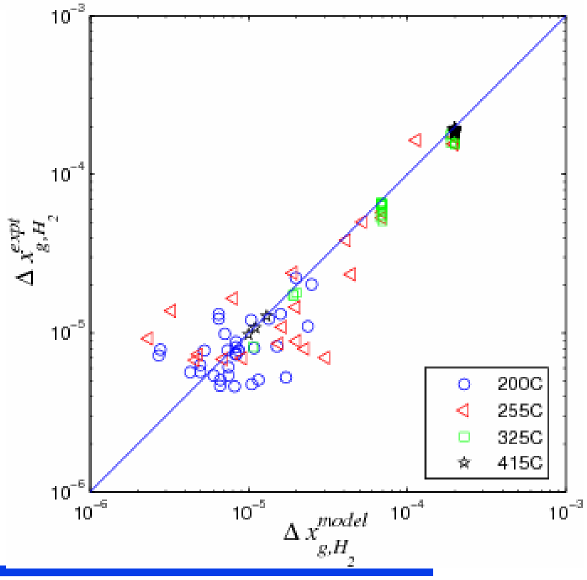
Outer problem

- Euclidean norm to compare model and experiments
- Objective function (norm)

$$norm = f\left(\left(\frac{x_{g,exit}^{model}}{x_{g,exit}^{expt}}\right)_{conv>50\%}, \left(\frac{\Delta x_g^{model}}{\Delta x_g^{expt}}\right)_{conv\le 50\%}\right)$$

- Scaled optimization parameters – O(1)





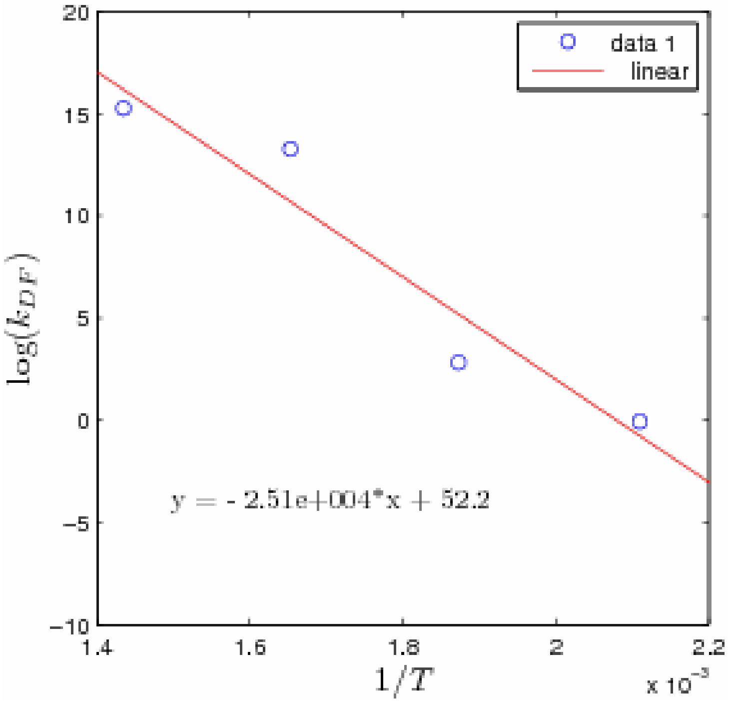
Initial rate form

- Initial rate – modified Voltz *et al.*[5]

$$-r_i = \frac{k_i \enclose{circle}{x_i} x_{O2}}{\cancel{T}\underset{\uparrow}{(}1+K_{C_3H_6}x_{C_3H_6}+K_{CO}x_{CO})^2\cancel{\left(1+K_2x_{C_3H_6}^2x_{CO}^2\right)}\left(1+K_{NO}x_{NO}^{\cancel{0.7}}\right)}$$

$$\Big\downarrow \quad i = DF, C_3H_6, CO, H_2$$

$$-r_i = \frac{k_i c_i c_{O_2}}{(1+K_{DF}c_{DF}+K_{C_3H_6}c_{C_3H_6}+K_{CO}c_{CO})^2(1+K_{NO}c_{NO})}$$



- Used results from individual temperatures to generate Arrhenius plots

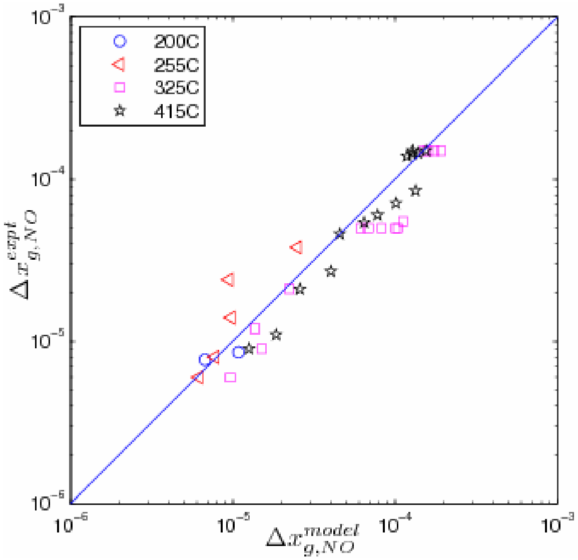
NO oxidation

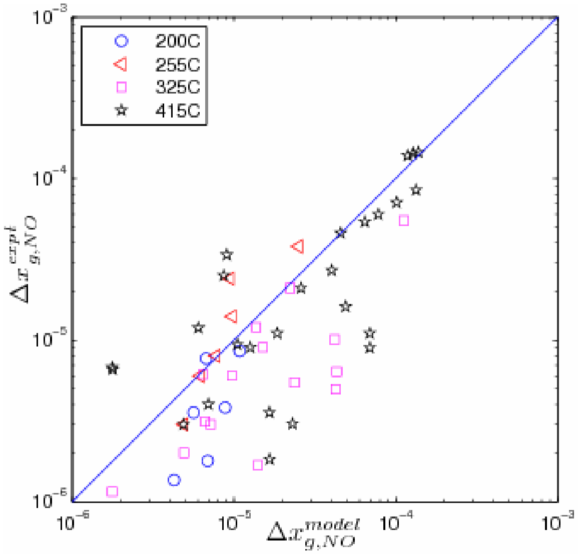
- Rate inferred from previous work[1]

$$r_{NO} = \frac{k_{NO} C_{NO} C_{O_2}^{0.5}}{(1+K_{NO}C_{NO})}\left(1-\frac{C_{NO_2}\sqrt{C_{ref}}}{K_e C_{NO} C_{O_2}^{0.5}}\right)$$

- 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

$$r_{NO} = \frac{k_{NO} C_{NO} C_{O_2}^{0.5}}{\underbrace{(1+K_{DF}c_{DF}+K_{C_3H_6}c_{C_3H_6}+K_{CO}c_{CO})^2}(1+K_{NO}C_{NO})}\left(1-\frac{C_{NO_2}\sqrt{C_{ref}}}{K_e C_{NO} C_{O_2}^{0.5}}\right)$$





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

Terms	Norm
All terms present	0.4529
$K_{DF}c_{DF}$	0.453 (removed)
$K_{C3H6}c_{C3H6}$	0.4529 (removed)
$K_{CO}c_{CO}$	1.1354 (removed)
$K_{NO}c_{NO}$	0.7853 (removed)
$K_{H2}c_{H2}$(added)	0.4527 (added)

→

Terms removed	Norm
$K_{DF}c_{DF}+K_{C3H6}c_{C3H6}$	0.453

Final rate forms

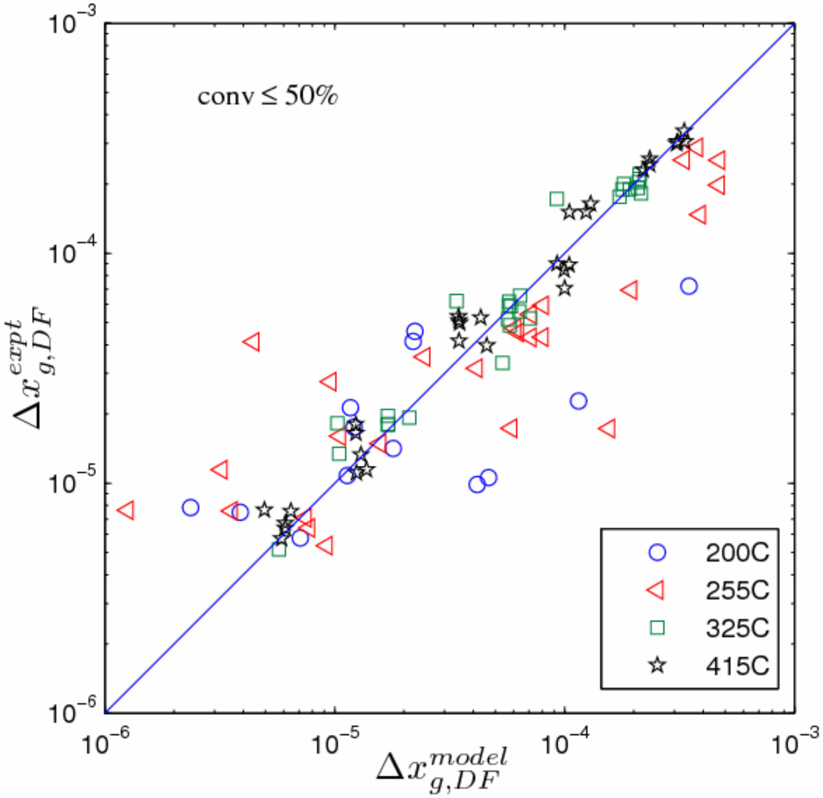
$$r_i = \frac{k_i c_i c_{O2}}{(1+K_{CO}c_{CO})^2(1+K_{NO}c_{NO})} \qquad i = DF, C_3H_6, CO, H_2$$

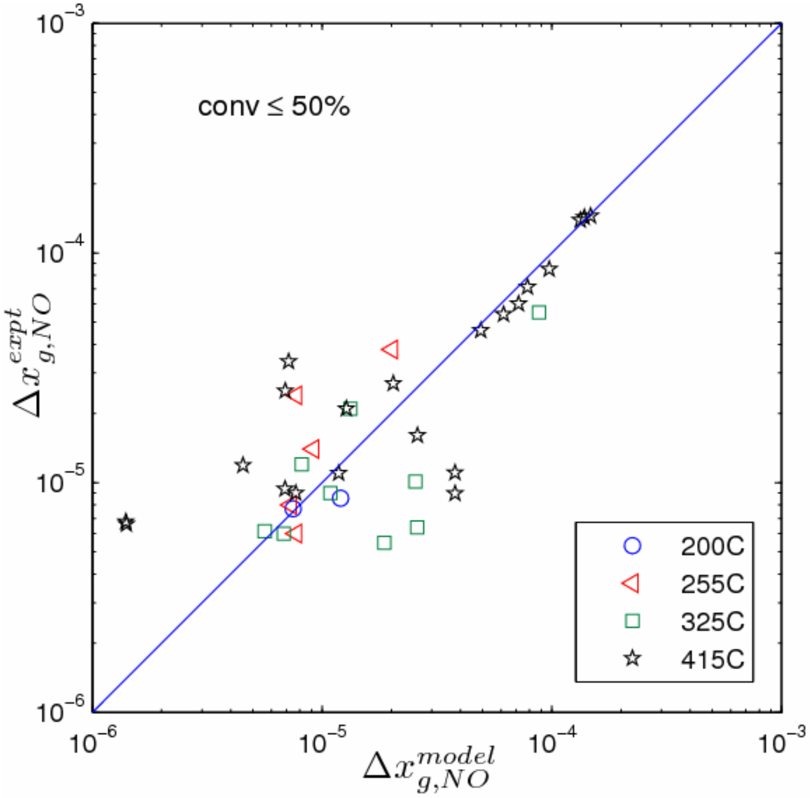
$$units = \frac{mol}{(mol.site)-s}$$

$$r_{NO} = \frac{k_{NO}c_{NO}c_{O_2}^{0.5}}{(1+K_{DF}c_{DF})^2(1+K_{NO}c_{NO})}\left(1-\frac{c_{NO_2}\sqrt{c_{ref}}}{K_e c_{NO} c_{O_2}^{0.5}}\right)$$

- 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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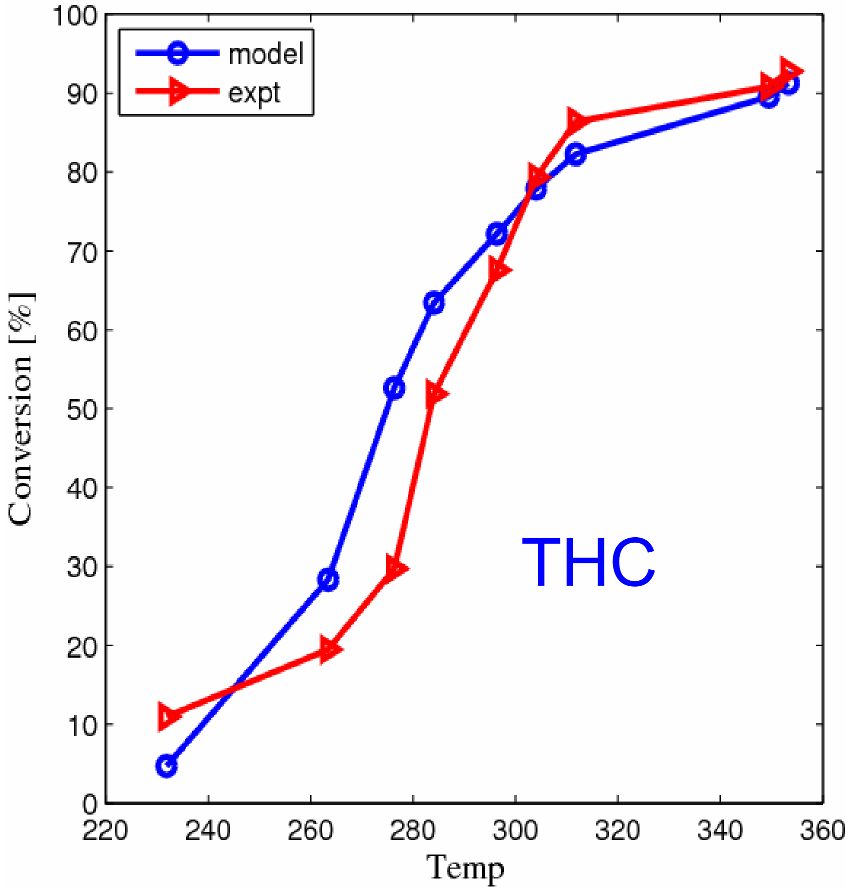
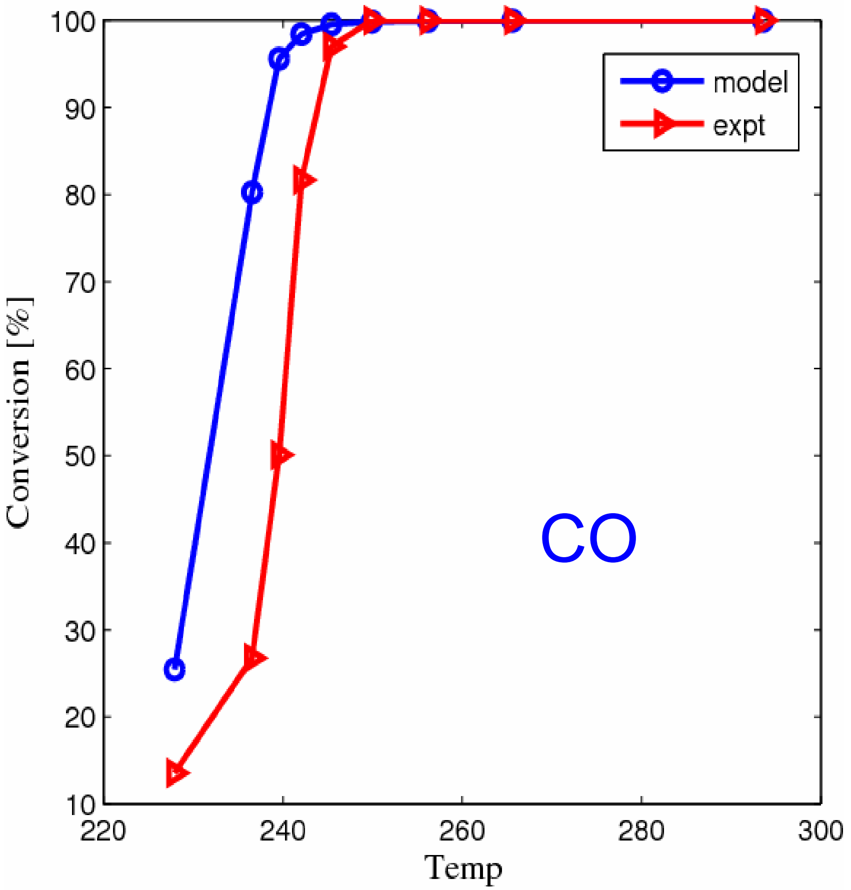
Engine validation

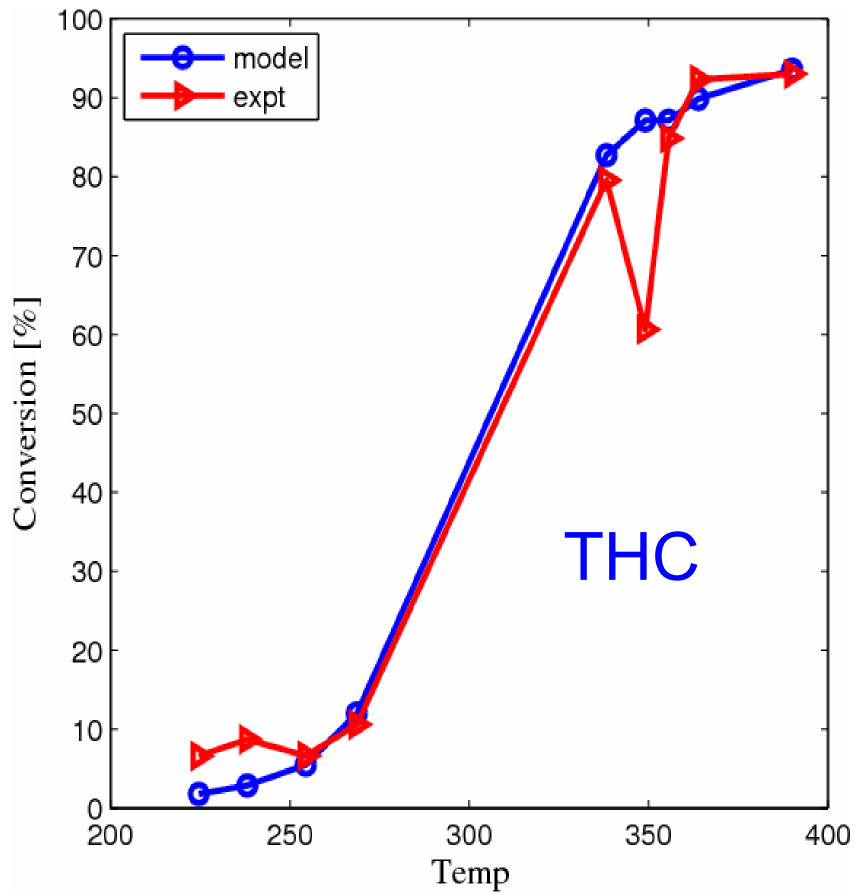
- 1.7L isuzu diesel engine
- Run conventional and PCI combustion modes with same catalyst
  - 2300 rpm; conventional and PCI combustion modes
  - Low/medium loads (~ 2.5 bar bmep)
- Other properties – Knafl [2]

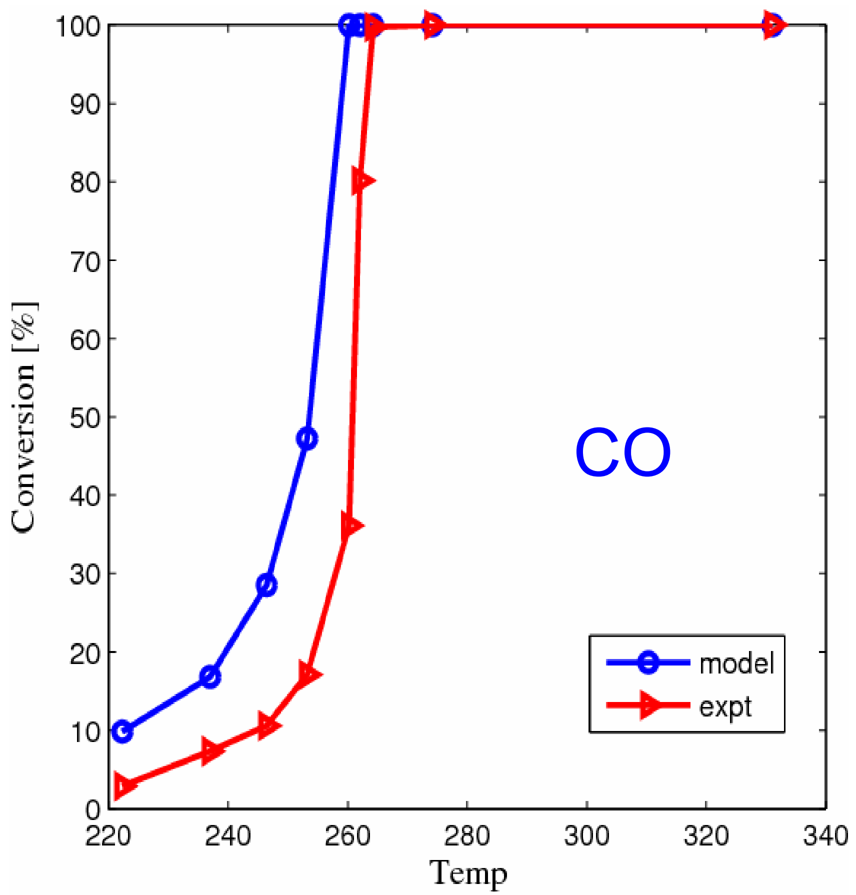
Engine validation – 2300 rpm conventional combustion





Engine validation – 2300 rpm PCI combustion





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[3]
- ✓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

Acknowledgements

- Prof. Dennis Assanis – University of Michigan
- Dr. Se H. Oh – GM
- Dr. Richard J. Blint – GM
- Dr. Alexander Knafl – University of Michigan/ GM
- Calvin Koch, Terry Talsma, Mike Rogers - GM

References

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4. “A new method for prediction of binary gas phase diffusion coeffficients”, Fuller, E. N., Schettler, P. D., Giddings, C. J., *Ind. Eng. Chem. Res*, 1966, 58(5), 19.
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Questions?

Back-up slides

Fuel properties

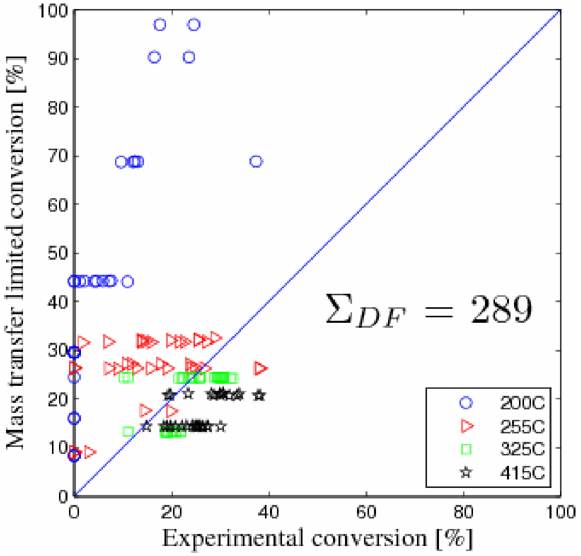
Properties	Swedish low sulfur diesel fuel	US Diesel # 2
Cetane no.	51.6	49.6
Sulfur content	12 ppm (wt)	500 ppm (wt)
LHV	43.5 MJ/kg	42.9 MJ/kg
Stoic AFR	14.74	14.46
Density	810 (kg/m^3)	840 (kg/m^3)
C:H:O	$C_1H_{1.966}O_0$	$C_1H_{1.77}O_0$

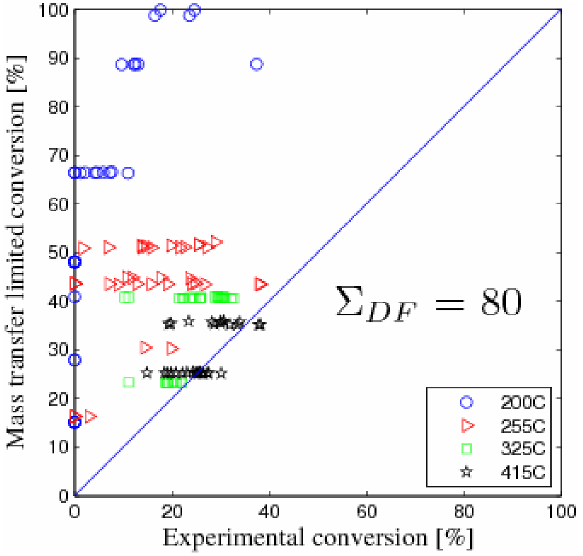
Diffusion coefficient for diesel fuel

- Experimental conversions should not exceed transport limited solution
- Binary diffusion coefficients – Fuller *et al.*[4]
  - f(T, P, mol.wt, Σ_i)
  - Mol.wt of diesel = 200 = $C_{14.6}H_{24.8}$ (Heywood[5])

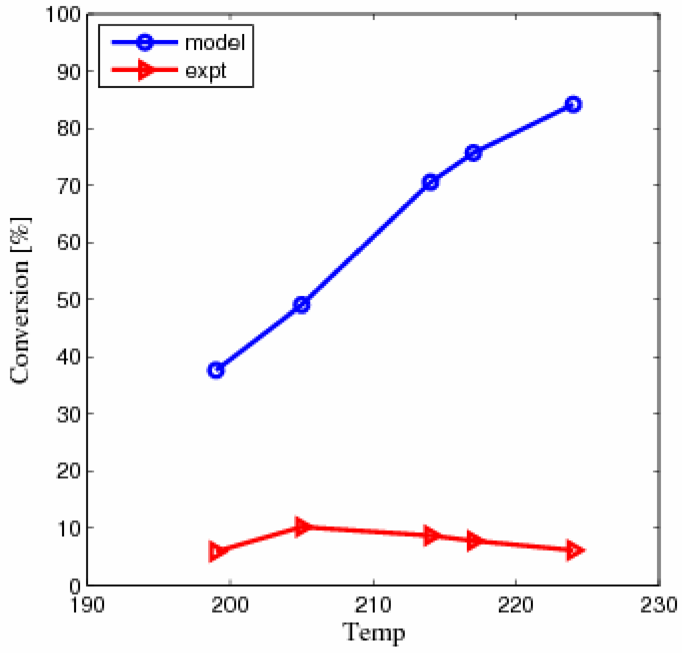
$$\Sigma_{C_xH_y} = 15.9x + 2.31y$$

(Poling, Prausnitz and O'Connell[6])

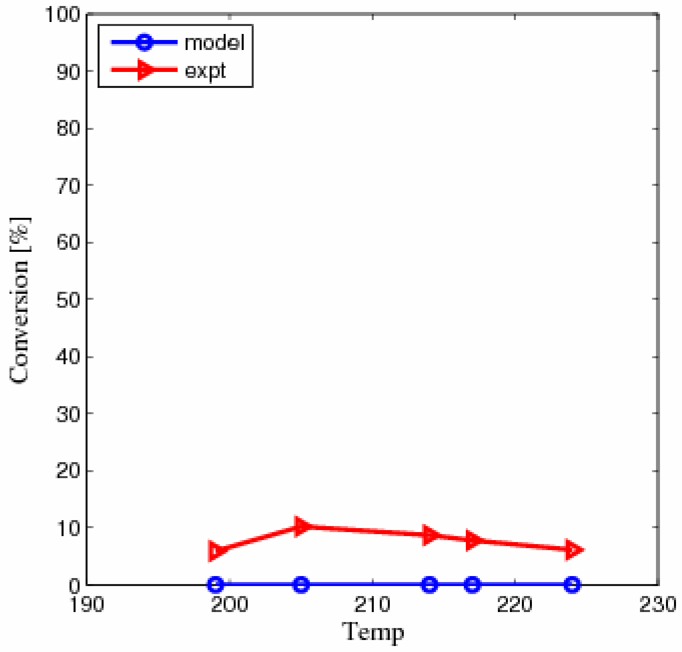




NO reaction rate



$K_{CO}c_{CO}$ inhibition



$K_{DF}c_{DF}$ inhibition

Scaling of optimization parameters

$$\hat{E} = \frac{E_i}{RT_r}$$

Scaling for activation energy

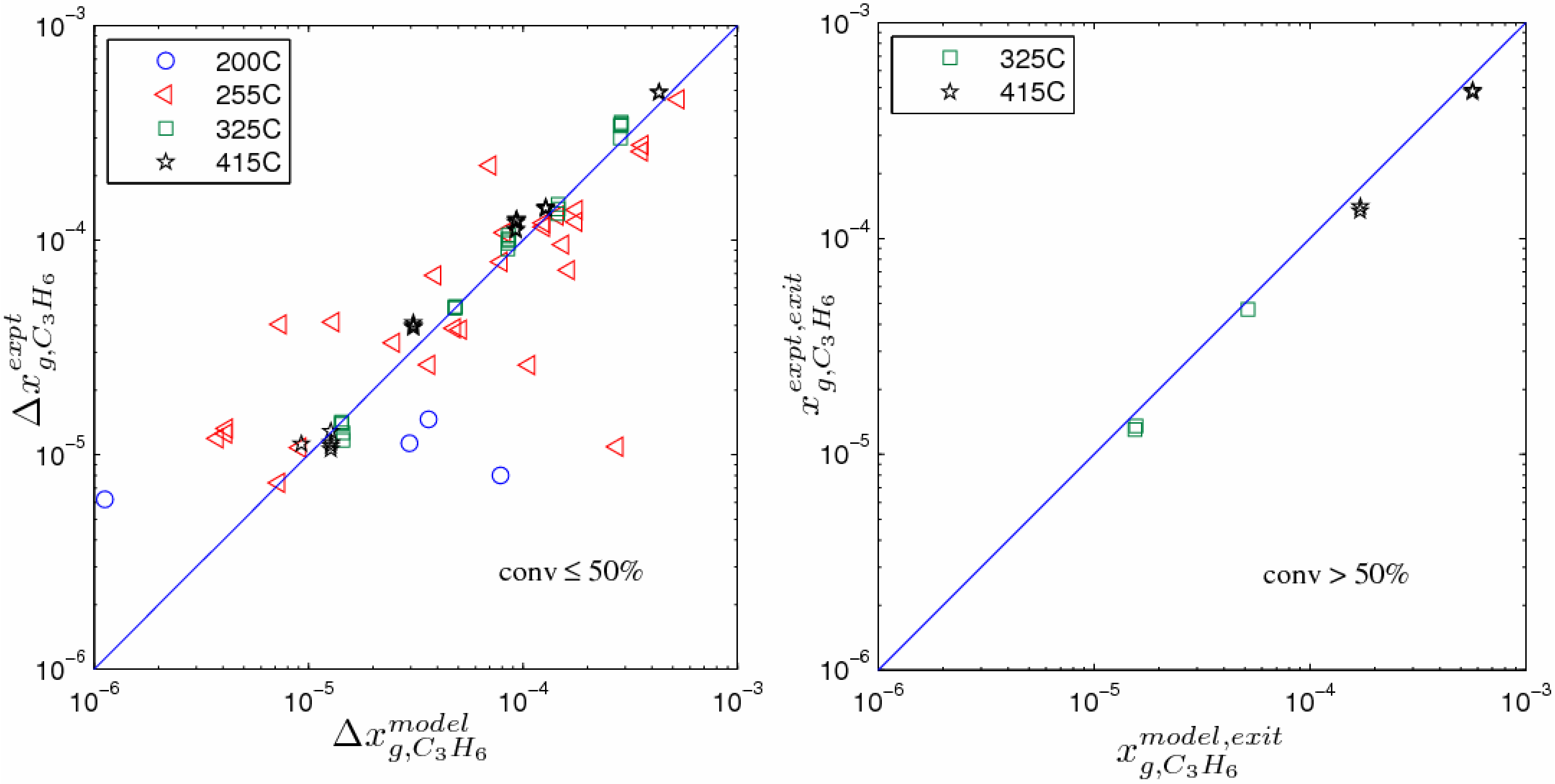
$$\hat{A}a_i = Aa_i e^{-\hat{E}a_i} c_r x_{r,i}$$

Scaling for inhibition term pre-exponential

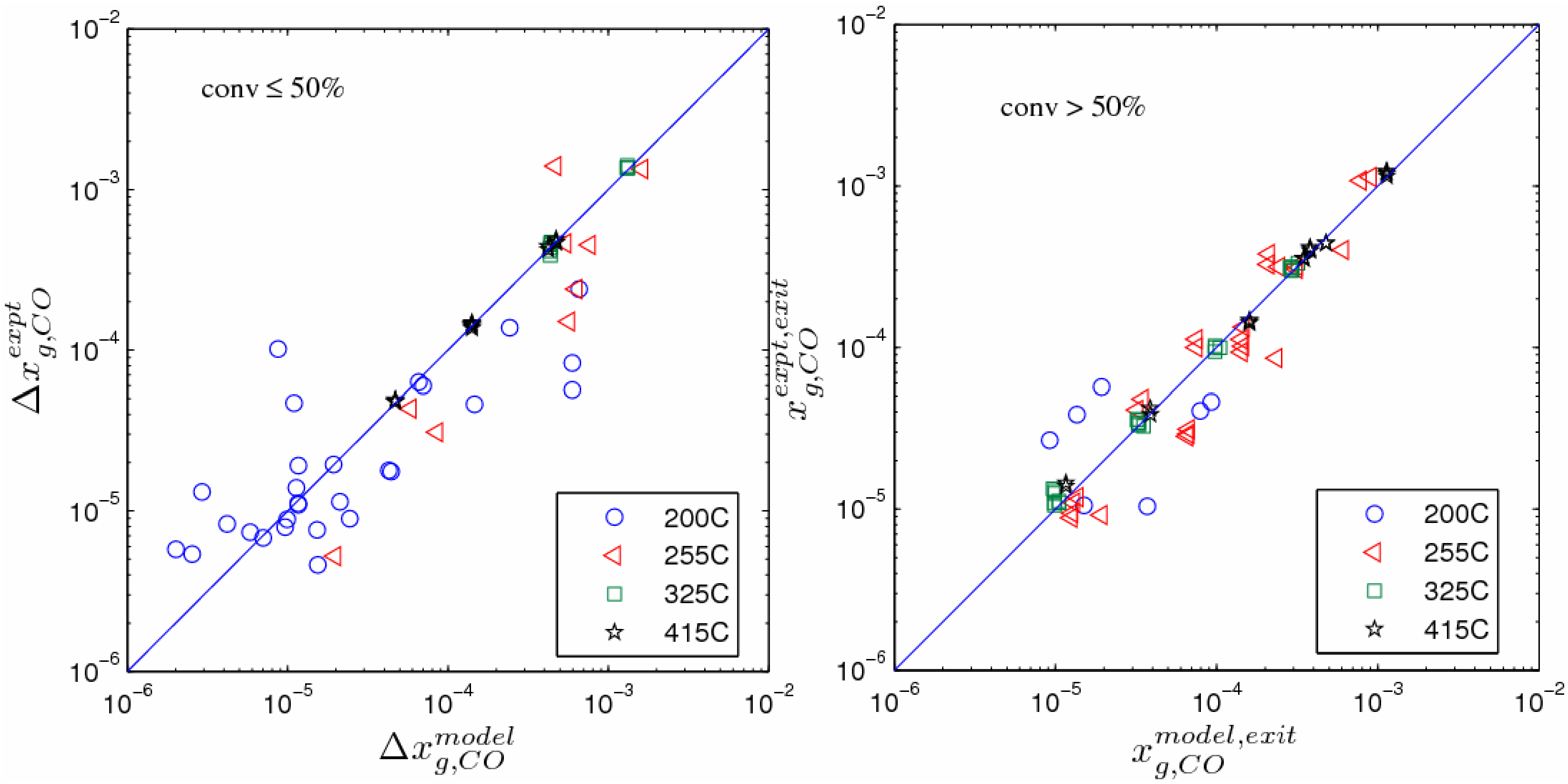
$$\hat{A}_i = \frac{Va_i}{w_r} A_i e^{-\hat{E}_i} c_r^2 x_{r,i} x_{O_2}$$

Scaling for rate constant pre-exponential

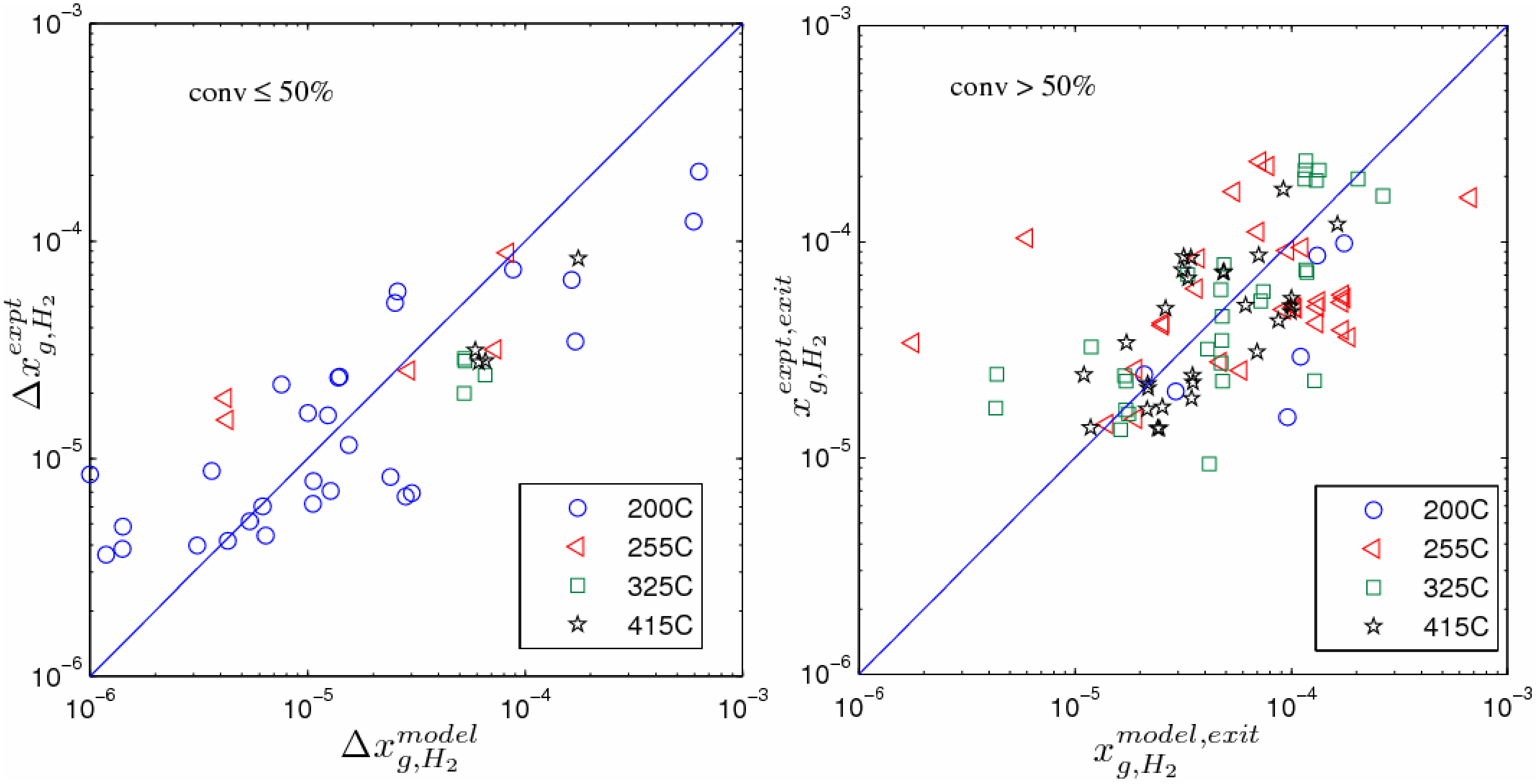
Optimization results – C_3H_6



Optimization results - CO



Optimization results – H_2



Diesel Oxidation Catalyst (DOC)

- Major reactions – HC, CO, H_2 and NO oxidation

Example:

$$r_{CO} = \frac{k_{CO} c_{CO} c_{O2}}{(1 + K_{CO} c_{CO})^2 (1 + K_{NO} c_{NO})}$$

$$k_{CO} = A_i \exp\left(\frac{-E_i}{RT}\right)$$

$$K_{CO} = Aa_i \exp\left(\frac{-Ea_i}{RT}\right)$$

Scope

- Global oxidation rates for HC species, CO, H_2, NO
- No post injection
- No HC storage
- Lean - Conventional and PCI