New Approach to Washcoat Diffusion Resistance

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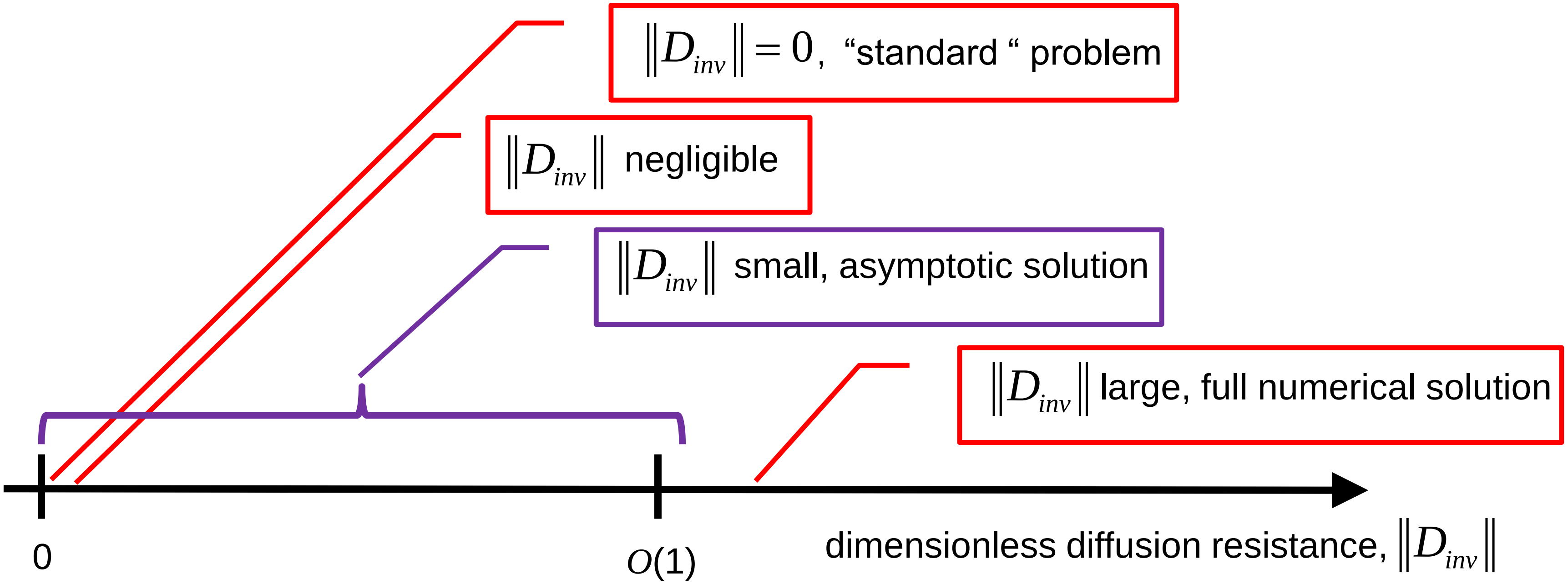
Gamma Technologies

Background and Overview



$\|D_{inv}\| = 0$, “standard “ problem

$\|D_{inv}\|$ negligible

$\|D_{inv}\|$ small, asymptotic solution

$\|D_{inv}\|$ large, full numerical solution

dimensionless diffusion resistance, $\|D_{inv}\|$

- $\|D_{inv}\|$ small: practical regime
  - tractable, fast

Outline

- Simplest case -- single layer, no coverages
  - Motivation – zeroth order, “standard” problem: no concentration gradients in washcoat
  - How asymptotic solution works
- Extensions -- coverages, dual layers
- Discussion, magnitude estimates, sample results
- Status

Dimensionless equations (including scalings)

- Generally
  - simpler
  - proper for asymptotics
  - computations
- Specifically
  - length of reactor
  - warm-up time
  - characteristic temperature
  - characteristic species mass fractions (and coverages)
- $O(1)$ variables and coefficients for major terms of “standard” problem
- Effective diffusivities, washcoat thickness ➔ D_{inv}

Equations for trace species vectors

channel: $$W\frac{\partial \omega_g}{\partial z} = K(\omega_s - \omega_g)$$ axial, $0 < z \le 1$

washcoat at each z: $$\frac{\partial^2 \omega}{\partial x^2} = -D_{inv} R$$ washcoat, $0 < x \le 1$

boundary conditions: $\left(\omega_s = \omega(x = 0)\right)$

$$\frac{\partial \omega}{\partial x} = D_{inv} K(\omega_s - \omega_g)$$ $x = 0$, channel interface

$$\frac{\partial \omega}{\partial x} = 0$$ $x = 1$, substrate interface

- Integration + b.c. ➔ $K(\omega_s - \omega_g) = \bar{R} \equiv \int_0^1 R\,dx$, independent of $\left\| D_{inv} \right\|$
- Motivation: $D_{inv} \to 0$ ➔ “standard” problem

Asymptotic solution

- Extend zeroth order ($\left\|D_{inv}\right\| = 0$) solution to first order.
- Advantage – 2nd order terms ($O(\left\|D_{inv}\right\|^2)$) neglected
- Fortunately tractable

Key points that enable asymptotic solution

- Species: $\omega(x) = \omega_{con} + D_{inv}\omega_{var}(x) + O(\|D_{inv}\|^2)$

- Species rates: $R(\omega(x)) = R(\omega_{con}) + \cancel{\left.\frac{\partial R}{\partial \omega}\right|_{\omega_{con}} \left(\omega(x) - \omega_{con}\right)} + O(\|D_{inv}\|^2)$

  - In particular, point-wise: $R(\omega(x)) = R(\omega_{con}) + O(\|D_{inv}\|)$

    Use in $\boxed{\frac{\partial^2 \omega}{\partial x^2} = -D_{inv} R}$ to obtain $\omega_{var}(x)$

  - If $\omega_{con} = \bar{\omega}$, $\overline{R(\omega)} = R(\bar{\omega}) + O(\|D_{inv}\|^2)$

    Use in $\boxed{K(\omega_s - \omega_g) = \overline{R(\omega)} = R(\bar{\omega}) + O(\|D_{inv}\|^2)}$ to obtain $\omega_{con} = \bar{\omega}$

- Reaction-diffusion solution: $\omega(x) = \bar{\omega} + D_{inv} R(\bar{\omega}) \left[\frac{1}{6} - \frac{1}{2}(1-x)^2 \right] + O(\|D_{inv}\|^2)$

  - In particular $\omega_s(\bar{\omega}) = \bar{\omega} - D_{inv} R(\bar{\omega})/3 + O(\|D_{inv}\|^2)$

Extensions

- Coverages
  - Assume any initial x-variations are $O(\|D_{inv}\|)$
  - Species rate argument generalizes to reaction rates and coverages:

$$r(\omega,\theta) = r(\overline{\omega},\overline{\theta}) + \left.\frac{\partial r}{\partial \omega}\right|_{\overline{\omega},\overline{\theta}} (\omega - \overline{\omega}) + \left.\frac{\partial r}{\partial \theta}\right|_{\overline{\omega},\overline{\theta}} (\theta - \overline{\theta}) + O(\|D_{inv}\|^2)$$

  - θ drops out in favor of $\overline{\theta}$

- Dual washcoat layers
  - Each layer has own reactions, species $\left(\overline{\omega}^{(1)}, \overline{\omega}^{(2)}\right)$, coverages $\left(\overline{\theta}^{(1)}, \overline{\theta}^{(2)}\right)$, etc.
  - Overall rate balance

$$K(\omega_s - \omega_g) = R^{(1)}(\overline{\omega}^{(1)}, \overline{\theta}^{(1)}) + R^{(2)}(\overline{\omega}^{(2)}, \overline{\theta}^{(2)})$$

  - Reaction-diffusion equations remain analytically solvable
  - Additional (nonlinear) equations ($\overline{\omega}^{(2)}$) from continuity at interface between layers

Limitations

- Asymptotics not designed for scaled ω_i small, ~ $O(\|D_{inv}\|)$ x-variations
  - Normally below ppm detection limit or below absolute error tolerance of numerics
- Large diffusion resistance regime
  - too thick washcoat or too small D_{eff}
  - Asymptotics often surprisingly good.

Estimate $\left\| D_{inv} \right\|$

$$D_{inv} = \begin{bmatrix} D_r / D_{eff,1} & & & 0 \\ & D_r / D_{eff,2} & & \\ & & \cdot & \\ 0 & & & D_r / D_{eff,2} \end{bmatrix}$$

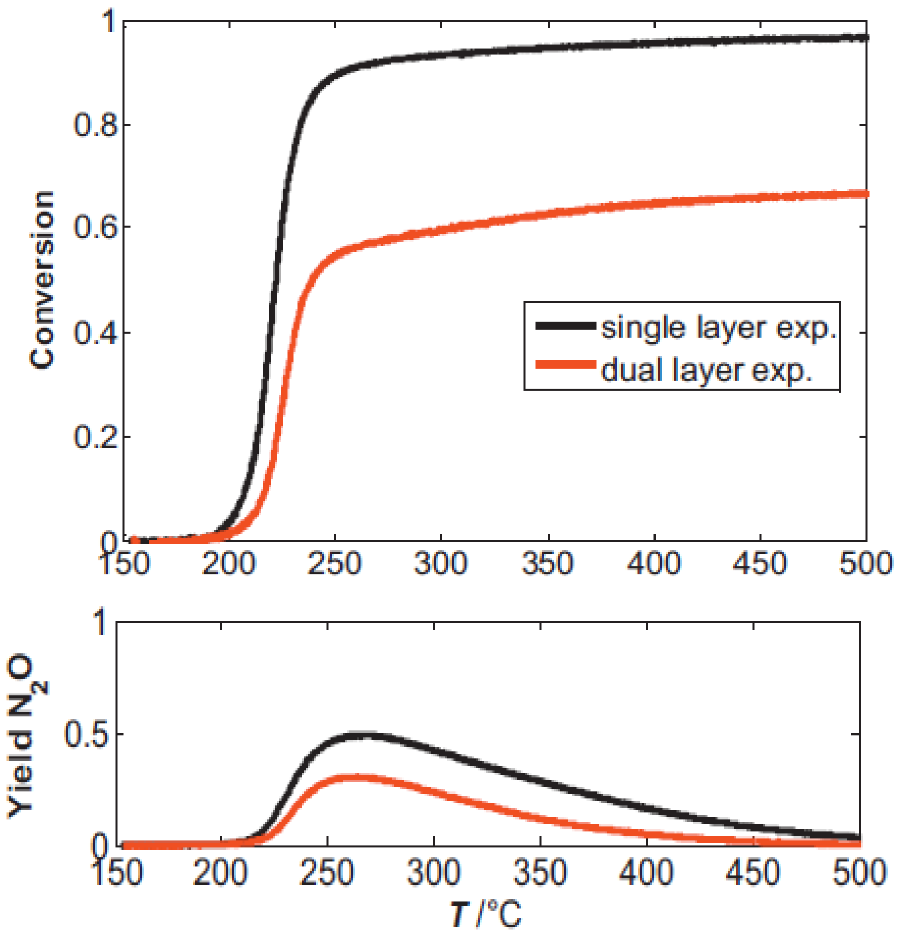
$D_{eff,i}$: effective diffusivity
$(SV)_{ref}$: reference space velocity
δ : effective washcoat thickness
f_{wc} : washcoat solid fraction
D_h : hydraulic diameter

- Reference effective diffusivity, $D_r = (SV)_{ref}\,\delta^2 / f_{wc}$ [m²/s]
  - $\delta^2 / f_{wc} \approx D_h \delta / 4 \approx 7.5 \times 10^{-9}$ [m²] (square channels, D_h = 1mm , δ = 30 μm)
  - $(SV)_{ref}$: consistency with other equations. Should approximate actual $SV \approx 15 s^{-1}$
  - $D_r \approx 1.1 \times 10^{-7}$
- Commonly measured range, $D_{eff} = O(10^{-6})$ [m²/s] :

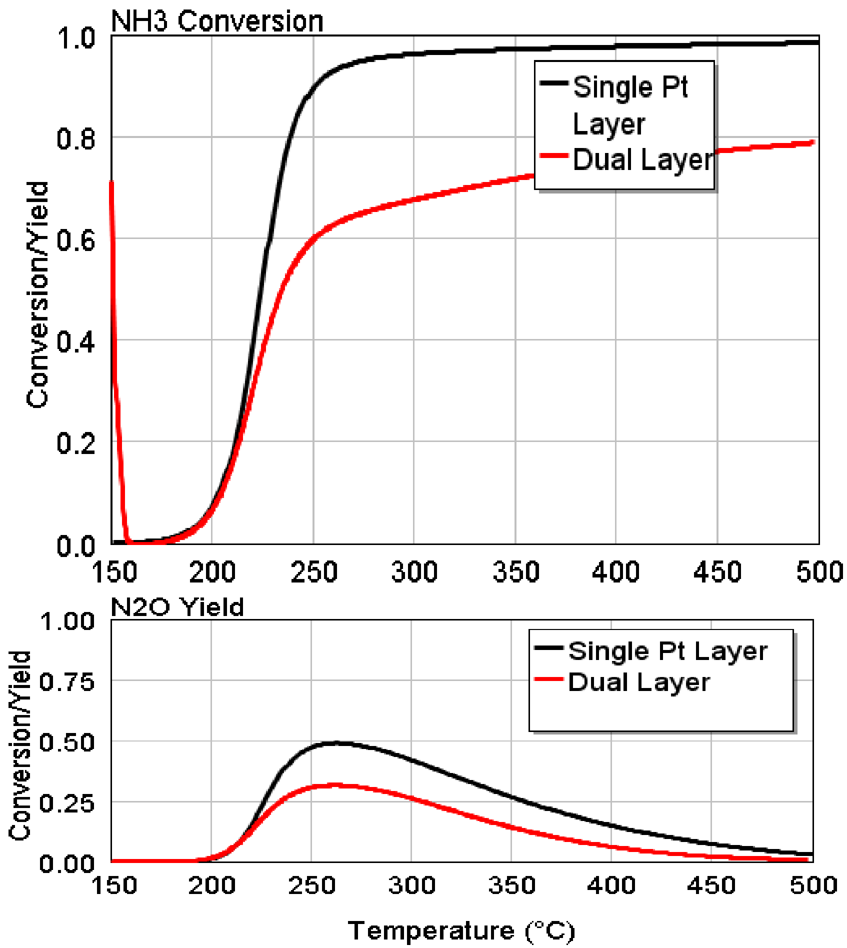
  "sweet spot" – $\left\| D_{inv} \right\|$ small, but not negligible.

Comparison with Data

- Single-layer Pt NH_3-oxidation catalyst. Then add Fe-zeolite SCR



Published Experimental Results *



GTI Prediction

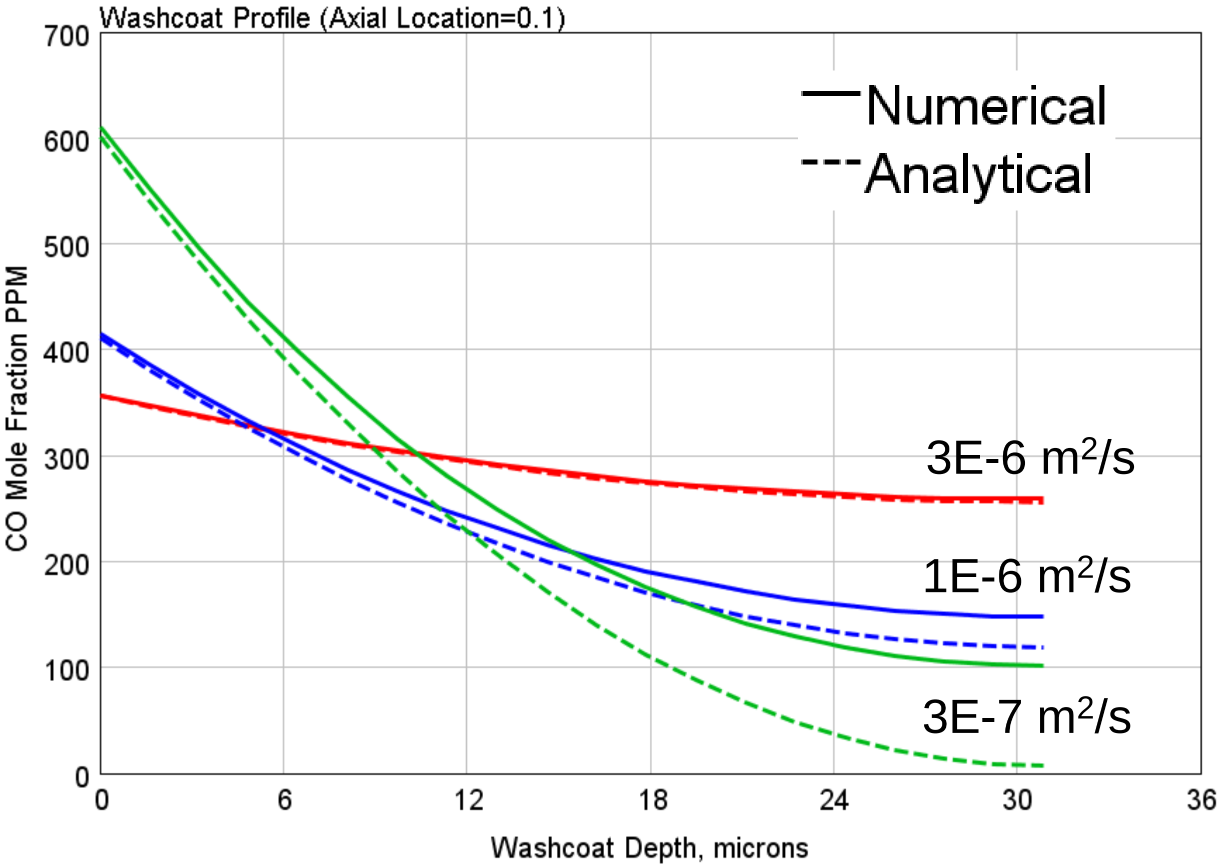
* Scheuer, etal. App Cat B: Environmental, 111-112 (2012) pp. 445-455 (Figure 5)

Comparison with 1+1D

- CO oxidation

$$R_{CO}\left(\frac{mol}{m^3_{reactor}\,s}\right)=\frac{3.55E10\exp\left(\frac{-9782}{T}\right)C_{CO}C_{O_2}}{\left(1+248\exp\left(\frac{-615}{T}\right)C_{CO}\right)^2}$$

- 3.2 liter reactor
- 400 cpsi
- 27000 1/hr SV
- 1000 ppm CO
- 10% O_2
- 500 K Inlet Temp.



Summary

- Fast
  - Similar to “standard” problem
- Respects reaction scheme
  - approximation only exploits diffusion resistance
- Can be structured close to “standard” problem, especially single layer
- Solid mathematics – not *ad hoc*
- Not for large diffusion resistance -- large catalyst underutilization
- No boundary, asymptotics degrades gradually
- Captures dominant effects from small-to-moderate diffusion resistance

Status

- Publication ASAP
  - Manuscript: finishing touches
  - Full disclosure – you should be able to implement
    - Single layer especially not difficult
- Single layer with coverages in GT-Power last fall (version 7.4)
- Dual layer
  - Full functionality next fall (full release)
  - “Beta”

Backups

Qualitative Comparison to Literature

- Scheuer et. al. (2012) compares ammonia oxidation between a catalyst with a single platinum layer and one with Fe-zeolite SCR layer over a platinum layer
- GTI has already calibrated an AOC mechanism (single platinum layer) to this paper's data
  - Mechanism and comparison available in ASC_GTI_2013.gtm example
- GTI used its two-site SCR mechanism (also available as example) for the top layer in this study
- Knowns:
  - Inlet conditions, 10 micron Pt washcoat thickness, 71 micron SCR washcoat thickness, 300,000 1/hr SV
- Assumptions:
  - Both washcoats use tortuosity = 3, washcoat porosity = 40%, 5 micron pore diameter

Washcoat Profiles