Fundamental Three Dimensional Modeling and Parameter Estimation of a Diesel Oxidation Catalyst for Heavy Duty Trucks

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Outline

1. The fundamental model which was developed to incorporate a qualitative description of this process is presented

2. To quantitatively gain an accurate prediction of the exhaust gas composition kinetics steps of heterogeneous reactions over platinum are set up

3. A method to estimate and analyze the kinetic parameters of the mean field model by inverse modeling is proposed

    - Stochastic global optimization method, Evolution Strategy (ES)

    - Sensitivity analysis to assess the relative importance of each reaction in determining the conversions

Monolithic Converter Model

- The monolithic converter model was based on conservation equations for momentum, energy, mass along with constitutive relations for momentum, heat, and species fluxes
  - The incompressible Navier-Stokes equations govern the flow in the free channel sub domain

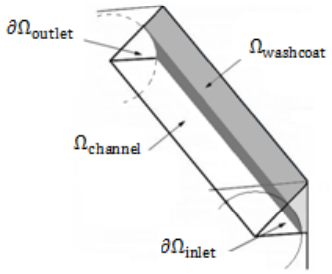
$$\rho\frac{\partial \mathbf{V}}{\partial t} = \nabla\cdot[-p\mathbf{I} + \mu(\nabla\mathbf{V} + (\nabla\mathbf{V})^T)] - \rho(\mathbf{V}\cdot\nabla)\mathbf{V}$$

$$\mathbf{V}\cdot\nabla = 0$$

  - The Brinkman equations govern the flow in the porous sub domain

$$\frac{\rho}{\varepsilon}\frac{\partial \mathbf{v}}{\partial t} = \nabla\cdot\left[-p\mathbf{I} + \frac{\mu}{\varepsilon}(\nabla\mathbf{v} + (\nabla\mathbf{v})^T)\right] - \frac{\mu}{\kappa}\mathbf{v}$$

$$\mathbf{v}\cdot\nabla = 0$$



  - The energy balance in the free channel sub domain

$$\rho\, C_p\frac{\partial T}{\partial t} = +\nabla\cdot(k\nabla T) - \rho\, C_p\mathbf{V}\cdot\nabla T$$

  - The energy balance in the porous sub domain

$$(\rho C_p)^s\frac{\partial T^s}{\partial t} = \nabla\cdot(k^s\nabla T^s) - \rho C_p\mathbf{v}\cdot\nabla T^s + (1-\varepsilon)A_s\sum_j^{N_j} r_j\left(-\Delta H_j\right)$$

Monolithic Converter Model

- The mass balance in the free channel sub domain

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i \nabla c_i - c_i \mathbf{V})$$

- The mass balance in the porous sub domain

$$\varepsilon \frac{\partial c_i^s}{\partial t} = \nabla \cdot (\varepsilon D_i^s \nabla c_i^s) - \nabla \cdot (c_i^s \mathbf{v}) + (1-\varepsilon) A_s \sum_j^{N_j} \upsilon_{ij} r_j$$

- One of the most common ways to describe the surface reactions and the adsorption/desorption is the mean-field approach
  - The reactions are average over the whole catalyst surface
  - The reactions rate equations are dependent on non-mobile surface fractional coverage θ_i

$$\Gamma_{cat} \frac{\partial \theta_i}{\partial t} = A_s \sum_j^{N_j} \upsilon_{ij} r_j$$

Micro Kinetic Model

- The mean-field kinetic model includes 7 reacting species and 17 heterogeneous reactions

  - Adsorption

$O_{2(g)} + 2* \xrightarrow{r_1} 2O*$ $\quad r_1 = A_1 \exp\left(-\frac{E_1}{RT}\right) c_{O_2(g)} \theta_*^2$

$NO_{(g)} + * \xrightarrow{r_3} NO*$ $\quad r_3 = A_3 \exp\left(-\frac{E_3}{RT}\right) c_{NO(g)} \theta_*$

$NO_{2(g)} + * \xrightarrow{r_5} NO_2*$ $\quad r_5 = A_5 \exp\left(-\frac{E_5}{RT}\right) c_{NO_2(g)} \theta_*$

$CO_{(g)} + * \xrightarrow{r_7} CO*$ $\quad r_7 = A_7 \exp\left(-\frac{E_7}{RT}\right) c_{CO(g)} \theta_*$

$CO_{2(g)} + * \xrightarrow{r_9} CO_2*$ $\quad r_9 = A_9 \exp\left(-\frac{E_9}{RT}\right) c_{CO_2(g)} \theta_*$

$H_2O_{(g)} + * \xrightarrow{r_{11}} H_2O*$ $\quad r_{11} = A_{11} \exp\left(-\frac{E_{11}}{RT}\right) c_{H_2O(g)} \theta_*$

  - Desorption

$2O* \xrightarrow{r_2} O_{2(g)} + 2*$ $\quad r_2 = A_2 \exp\left(-\frac{E_2(1-\alpha_2\theta_O)}{RT}\right) \theta_O^2$

$NO* \xrightarrow{r_4} + NO_{(g)} + *$ $\quad r_4 = A_4 \exp\left(-\frac{E_4 - \alpha_4\theta_O}{RT}\right) \theta_{NO}$

$NO_2* \xrightarrow{r_6} + NO_{2(g)} + *$ $\quad r_6 = A_6 \exp\left(-\frac{E_6(1-\alpha_6\theta_O)}{RT}\right) \theta_{NO_2}$

$CO* \xrightarrow{r_8} CO_{(g)} + *$ $\quad r_8 = A_8 \exp\left(-\frac{E_8 - \alpha_8\theta_{CO}}{RT}\right) \theta_{CO}$

$CO_2* \xrightarrow{r_{10}} CO_{2(g)} + *$ $\quad r_{10} = A_{10} \exp\left(-\frac{E_{10}}{RT}\right) \theta_{CO_2}$

$H_2O* \xrightarrow{r_{12}} H_2O_{(g)} + *$ $\quad r_{12} = A_{12} \exp\left(-\frac{E_{12}}{RT}\right) \theta_{H_2O}$

  Surface reactions

$NO_{(g)} + O* \xrightarrow{r_{13}} NO_2*$ $\quad r_{13} = A_{13} \exp\left(-\frac{E_{13} - \alpha_{13}\theta_O}{RT}\right) c_{NO(g)} \theta_O$

$NO_2* \xrightarrow{r_{14}} NO_{(g)} + O*$ $\quad r_{14} = A_{14} \exp\left(-\frac{E_{14}}{RT}\right) \theta_{NO_2}$

$CO* + O* \xrightarrow{r_{15}} CO_2* + *$ $\quad r_{15} = A_{15} \exp\left(-\frac{E_{15} - \alpha_{15}\theta_{CO}}{RT}\right) \theta_{CO}\theta_O$

$CO_2* + * \xrightarrow{r_{16}} CO* + O*$ $\quad r_{16} = A_{16} \exp\left(-\frac{E_{16} + \alpha_{16}\theta_O}{RT}\right) \theta_{CO_2}\theta_*$

$\frac{1}{3}C_3H_{6(g)} + 3O* \xrightarrow{r_{17}} CO_{2(g)} + H_2O_{(g)}$ $\quad r_{17} = A_{17} \exp\left(-\frac{E_{17} - \alpha_{17}\theta_O}{RT}\right) c_{CH_2}\theta_O$

Formulation of the Inverse Optimization Problem

- The inverse parameter estimation is formulated here as a nonlinear optimization problem
  - The mean field model´s kinetic parameters are calibrated by minimizing a suitable objective function based on the deviations between observed and predicted system response
- The formulation of the objective function (or misfit function) from the maximum likelihood theory leads to a weighted least squares problem

$$Q(\boldsymbol{x}) = \sum_{j=1}^{n} \sum_{i=1}^{m} W_{i,j} \left\{ \left[y_{pred}(\boldsymbol{x}, i) - y_{obs}(i) \right]_j \right\}^2$$

- The optimization problem is stated as the minimization of a weighted distance measure:

$$Q_{\min} = \min_{LB \leq xUB} \left(Q(\boldsymbol{x}) \right)$$

  - Because of the nonlinear, non-differentiable and constrained nature of the system dynamics, the problem is multimodal (non convex)

Global Optimization

- One approach to surmount the non convexity of the optimization problems is to use global optimization methods which ensure better efficiency and robustness
- Global optimization methods can be roughly classified as deterministic and stochastic strategies
- Stochastic methods for global optimization ultimately rely on probabilistic approaches
  - Given that random elements are involved, these methods only have weak theoretical guarantees of convergence to the global solution
  - These methods do not require transformation of the original problem, which can be treated as a black box

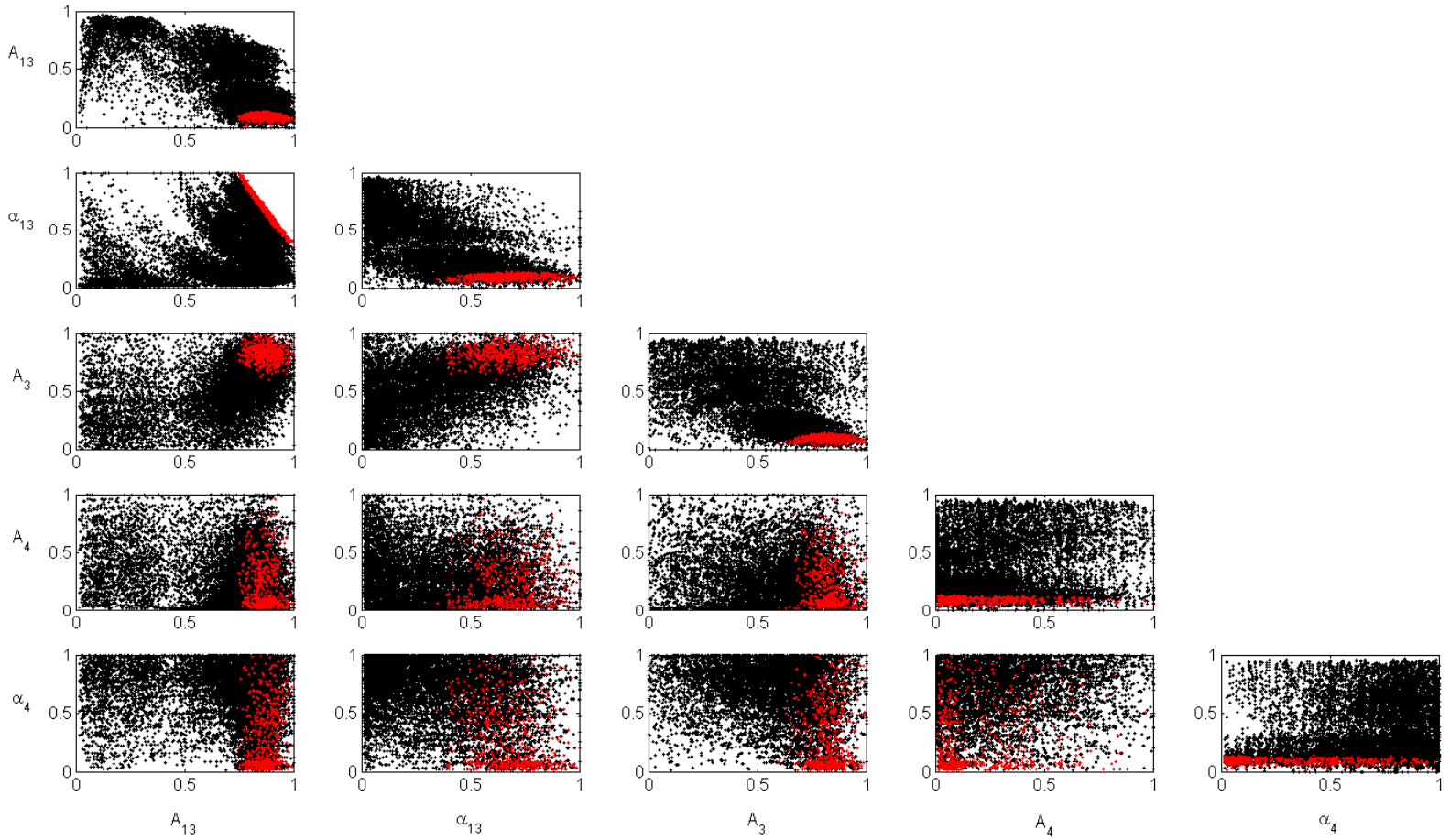
Solution Methodology

- The ability to interface with programming languages like MATLAB, enables a COMSOL-generating M-file to be converted into a function that can be executed by an optimization routine
    - Running this M-file in MATLAB, the FEM structure is created in MATLAB's workspace
    - The objective function requires the forward model-predicted average gas channel composition at the outlet

$$\langle c_i \rangle|_{\partial\Omega_{\text{outlet}}} = \frac{1}{A}\int_{\Omega} c_i(t, \boldsymbol{X}) dA$$

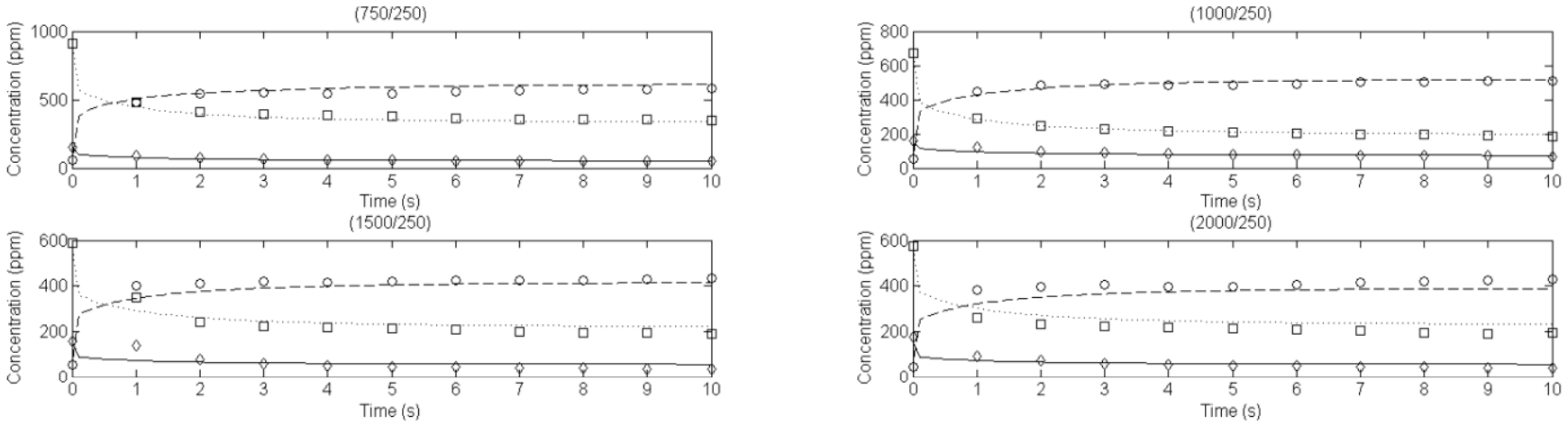
- One function evaluation is performed for every calibration variable set
    - The outcome of the Evolution Strategy is much dependent on the size of the population

Results and Discussion



Results and Discussion

- The model predicted temporal conversion of the species NO, NO_2 and C_3H_6 were calibrated with transient experimental data set
- The results from the model calibration confirmed the validity of the inverse modeling methodology but provided no information about the quality of the forward model itself



Comparison between the experimental observed and the model predicted outlet concentrations. Observed [NO_2] (○); [NO] (□); [C_3H_6] (◊). Predicted [NO_2] (---); [NO] (···); [C_3H_6] (—).

Conclusions

- A methodology for catalytic converter parameter estimation has been presented
  - The PDE-based forward model was implemented in COMSOL Multiphysics, which provides a seamless interface into MATLAB
- The applied Evolutionary Strategy was able to successfully solve the inverse problem associated with the mean field model
  - A possible drawback of ES methods, in spite of these good results, is computational effort required
  - Stochastic methods lend themselves to parallelization very easily
- A graphic method for confirming that the optimum has been reached was presented
  - The sensitivity of the calibration parameters could easily be studied as well as the parameter intercorrelation

This methodology has proven powerful when studying chemical pathways, but can easily be applied for solving a wide variety of PDE-based inverse problems