Kinetic Parameters Estimation using Vehicle Data for Exhaust Aftertreatment Devices

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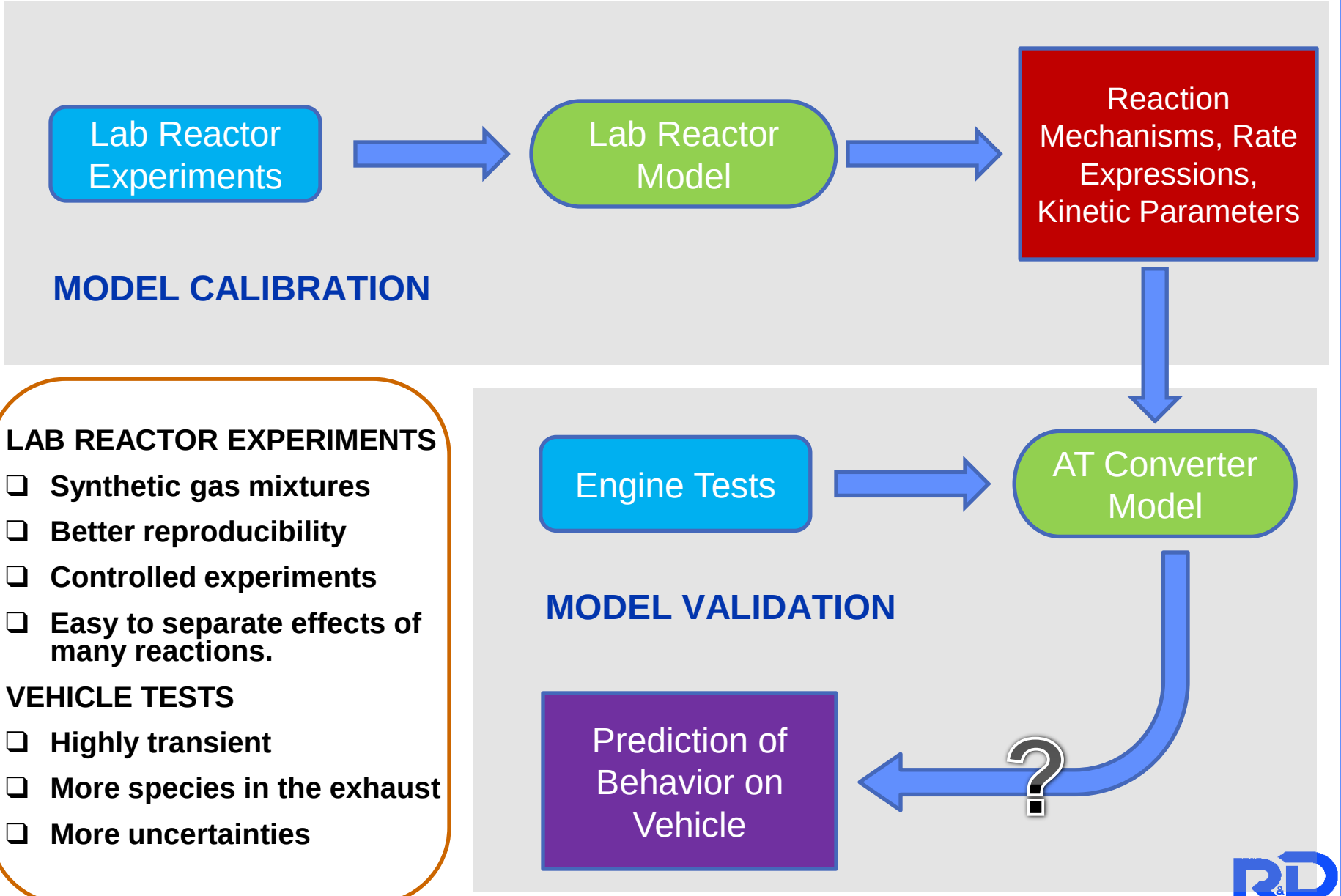
Kinetic modeling for exhaust AT system

- **Obtaining the right reaction mechanisms, rate expressions and rate constants.**
- **Necessary for improved predictability of the model.**
- **Kinetic Models**
  - Microkinetic models (fundamental)
    - Developed based on elementary surface reaction steps (e.g., adsorption, desorption, dissociation, surface reaction, etc)
    - Change in rate-controlling step captured automatically.
    - interaction among competing reactions/species accounted for “naturally”
    - Computationally intensive, takes a lot of time to develop, too many parameters
  - Global kinetics (semi-emprical)
    - “Semi-empirical” form of rate expressions (e.g., Langmuir-Hinshelwood) postulated based on mechanistic hypotheses
      - Takes into account inhibition by other species
      - Inhibition terms can be PGM-dependent i.e., Rh and Pt can have different inhibition terms.
    - Reasonable predictive capabilities
    - Helps in rapid design evaluations and control algorithms
    - Kinetic parameters estimated by fitting to experimental data

Kinetic model development and usage



LAB REACTOR EXPERIMENTS

- ❑ **Synthetic gas mixtures**
- ❑ **Better reproducibility**
- ❑ **Controlled experiments**
- ❑ **Easy to separate effects of many reactions.**

VEHICLE TESTS

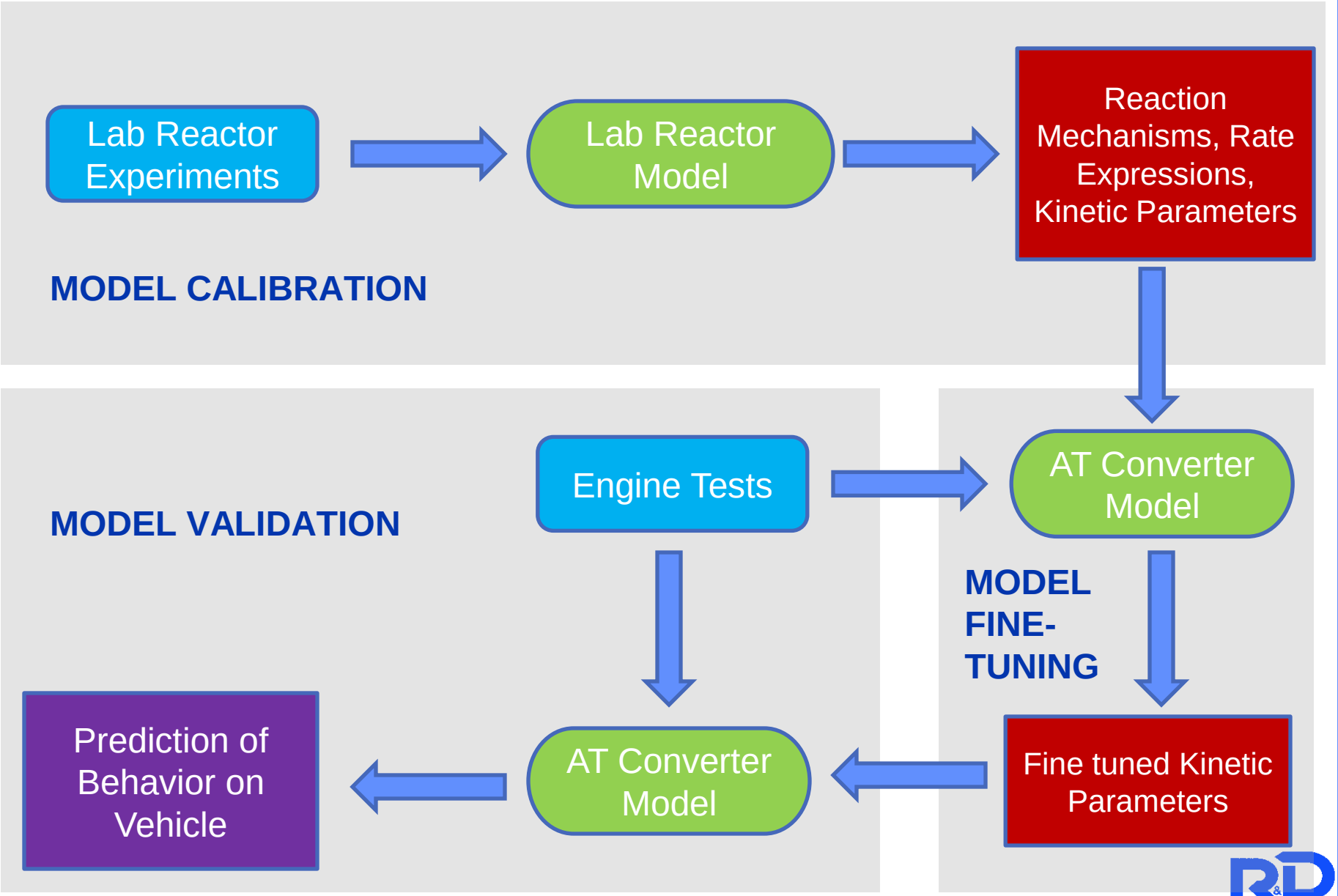
- ❑ **Highly transient**
- ❑ **More species in the exhaust**
- ❑ **More uncertainties**

Lack of portability of Kinetic models: Lab to Vehicle

- **Kinetic parameters are very sensitive to washcoat and catalyst formulations**
- **Kinetic parameters are very sensitive to catalyst aging**
  - Aging protocols (lab-scale, road-aged)
    - Difficult to get same levels of aging
  - Activity as a function of length
- **Reaction path could depend on species that are present in real exhaust but not present in synthetic exhaust**
  - Hydrocarbons (different C-numbers)
  - CO_2, H_2O (can play promoting and inhibiting roles)
- **Kinetic parameters are very sensitive to feed compositions/temperature**
  - Transient, engine type, load, speed, outdoor temperatures, drive-cycle, fuel type and additives.

- **Need to validate/tune the kinetic mechanism/parameters using vehicle data.**

Kinetic model development and usage



Kinetic Parameter Estimation from Vehicle Data

- **Illustration through Three-Way Catalyst as an example using 1D model**
- **Three-Way Catalyst Chemistry and Kinetics**
- **Reaction rates expressions**
  - **Turn-over numbers (mol/mol-site/sec)**
- **Oxidation, reduction, SR and WGS reactions**

$$R_j = \frac{k_j C_a C_b \exp\left(-\frac{E_j}{R_g T_s}\right)}{G}$$

$$G = \left(1 + K_1 C_{CO} + K_2 C_{C_3H_6}\right)^2 \left(1 + K_3 C_{CO}^2 C_{C_3H_6}^2\right)\left(1 + K_4 C_{NO}\right)$$

$$K_i = k_{i,G} \exp\left(-\frac{E_{i,G}}{T_s}\right) \qquad i = 1, \cdots, 4$$

- **Ceria Reactions:**

$$R_j = k_j \exp\left(-\frac{E_j}{R_g T_s}\right) C_a f(\theta)$$

- **Estimate pre-exponentials and activation energies**

S. No.	Reactions
Oxidation Reactions	
1	$CO + 0.5O_2 \rightarrow CO_2$
2	$C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O$
3	$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
4	$H_2 + 0.5O_2 \rightarrow H_2O$
NO Reduction Reactions	
5	$CO + NO \rightarrow CO_2 + 0.5\ N_2$
6	$C_3H_6 + 9NO \rightarrow 3CO_2 + 3H_2O + 4.5N_2$
7	$H_2 + NO \rightarrow H_2O + 0.5N_2$
Water-Gas and Steam Reforming Reaction	
8	$CO + H_2O \rightarrow CO_2 + H_2$
9	$C_3H_6 + 3H_2O \rightarrow 3CO + 6H_2$
Ceria Reactions (Oxygen Storage)	
10	$2Ce_2O_3 + O_2 \rightarrow 4CeO_2$
11	$Ce_2O_3 + NO \rightarrow 2CeO_2 + 0.5N_2$
12	$CO + 2CeO_2 \rightarrow Ce_2O_3 + CO_2$
13	$C_3H_6 + 12CeO_2 \rightarrow 6Ce_2O_3 + 3CO + 3H_2O$
14	$C_3H_8 + 14CeO_2 \rightarrow 7Ce_2O_3 + 3CO + 4H_2O$
15	$H_2 + 2CeO_2 \rightarrow Ce_2O_3 + H_2O$

Vehicle data

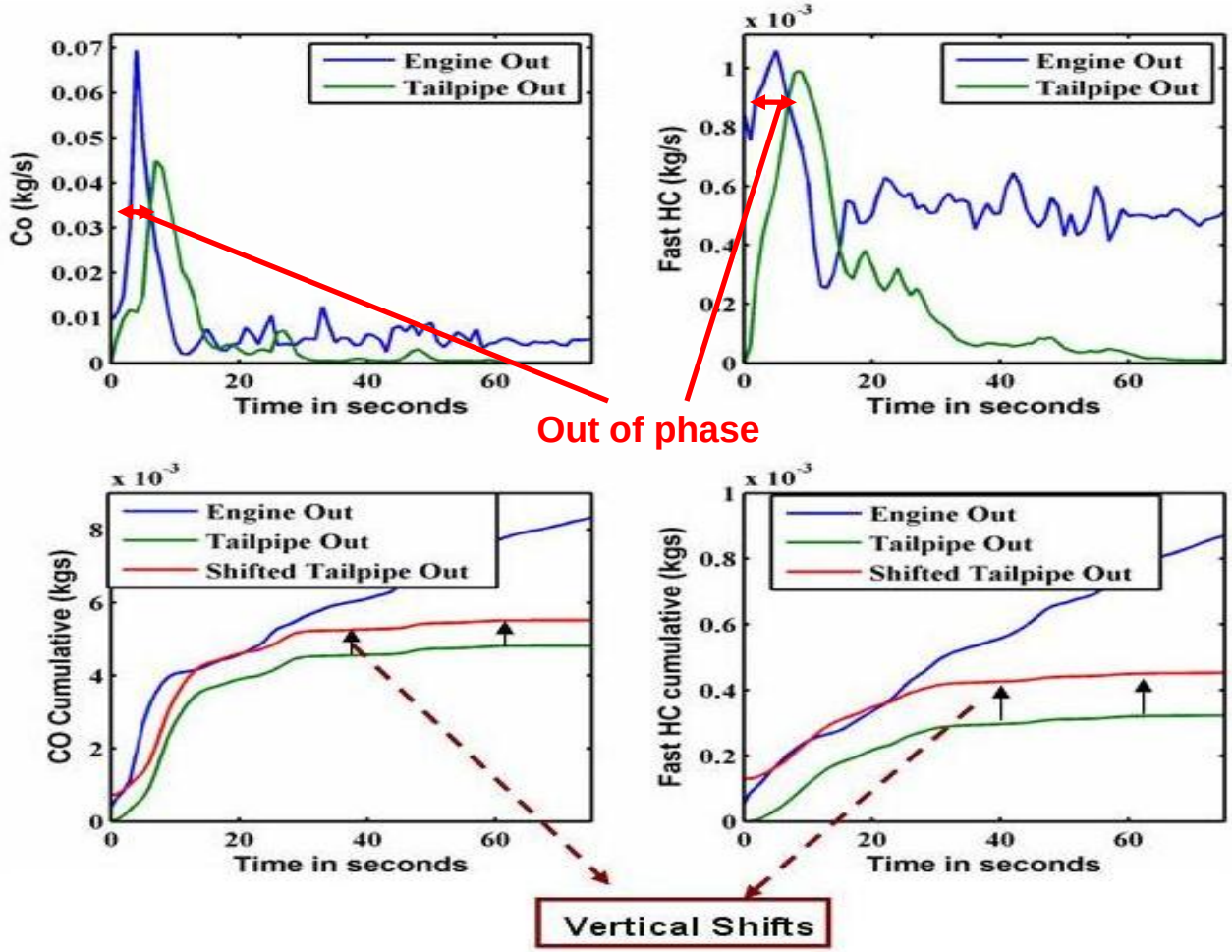
- **Six engine/vehicle experiments from GM powertrain**

Dataset detail, and Drive cycle	Abbreviation	Used for
Data set 1, FTP cycle	Set 1	Calibration
Data set 2, FTP cycle	Set 2	Calibration
Data set 3, FTP cycle	Set 3	Calibration
Data set 4, FTP cycle	Set 4	Calibration
Data set 5, FTP cycle	Set 5	Validation
Data set 6, NUDC cycle	Set 6	Validation

- All datasets trying to meet Bin5 emission standard or similar.
- 4 used for calibration and 2 for validation
- 5 of them on FTP cycle, 1 on NUDC
- All TWC were CC, 100k or more aged, very similar catalyst formulations (amount of PGM different)
- Active site density (mole-site/m^3) calculated from PGM loading and dispersion
- Different length, frontal area, CPSI, substrate thickness, PGM loading

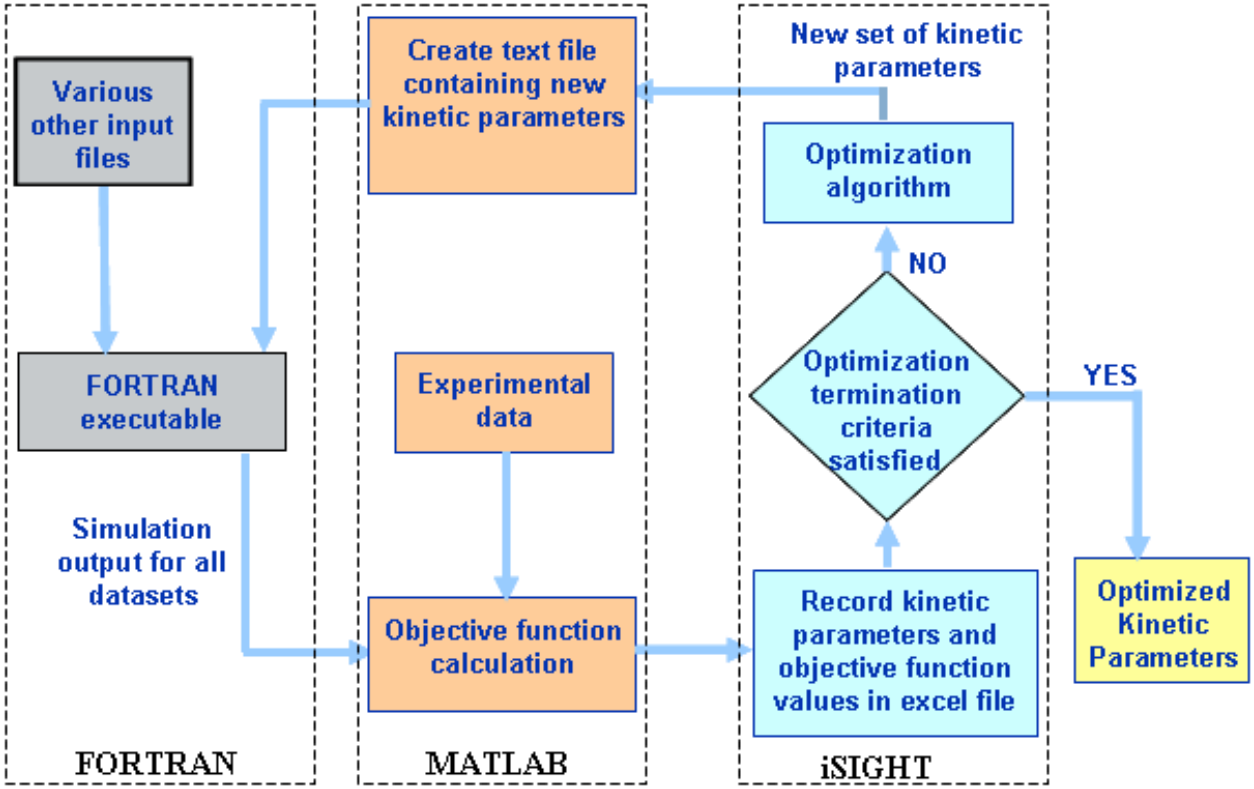
Vehicle Data Quality

- **Lack of synchronization between EO and TP data.**
  - Time alignment and absolute value measured



Kinetic Parameter Estimation methodology

- **Objective: Predict the first drive cycle (125s or so) using 1D model**
- **Estimate parameters through optimization to minimize error between measured and simulated data**
  - Combination of evolutionary/exploratory and local optimization methods. (iSIGHT) - Pointer Automatic Optimizer (PAO)

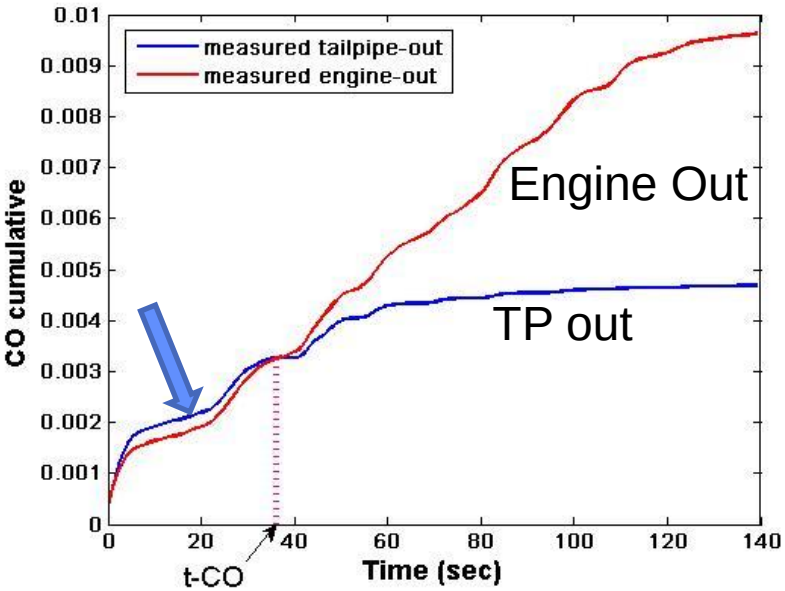


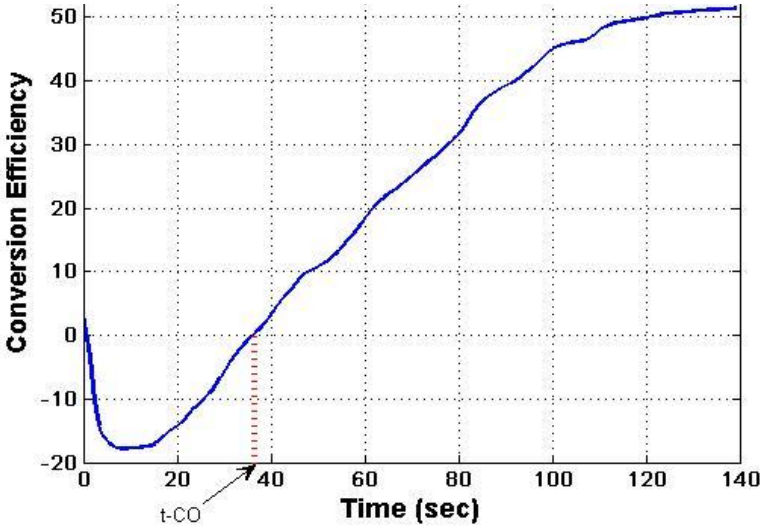
Choosing the data points for optimization

- **Key to any successful parameter estimation**
- **Only include data points that are sensitive to the parameters that are being estimated**
  - Trying to estimate kinetic parameters when the data is obtained at very slow or very fast kinetics would be ineffective.
- **Define conversion efficiency to automatically identify the data points for inclusion/exclusion**
- **Based on cumulative emissions**

$$\eta_j(t) = \left(1 - \frac{\left(\int_0^t x_{g,j} w M_j dt\right)_{outlet}}{\left(\int_0^t x_{g,j} w M_j dt\right)_{inlet}}\right) \times 100$$

- **Identify time instant after which conversion efficiency does not go below zero (or 10%).**





Choosing the objective function

- **Need to predict the entire time-dependent emission profile and NOT just the final value.**
- **Norm of the relative errors between cumulative predicted and measured TP out emissions**
  - Cumulative values show better sensitivity (than instantaneous values) to the kinetic parameters
    - Automatically has more weight to light-off, and avoids problems with 100% conversion

$$f_i = \sqrt{\frac{1}{n_{i,CO}} \sum_{t\_CO}^{t\_final} \left(\frac{m_{CO,meas} - m_{CO,sim}}{m_{CO,meas}} \right)^2 + \frac{1}{n_{i,HC}} \sum_{t\_HC}^{t\_final} \left(\frac{m_{HC,meas} - m_{HC,sim}}{m_{HC,meas}} \right)^2 + + \frac{1}{n_{i,NO}} \sum_{t\_NO}^{t\_final} \left(\frac{m_{NO,meas} - m_{NO,sim}}{m_{NO,meas}} \right)^2}$$

$$f = \sqrt{\sum_i f_i^2}$$

- **Individual objective functions for species**
  - Increased efficiency, helps in getting sensitivity information

$$f_{CO,i} = \sqrt{\frac{1}{n_{i,CO}} \sum_{t\_CO}^{t\_final} \left(\frac{m_{CO,meas} - m_{CO,sim}}{m_{CO,meas}} \right)^2} \quad f_{HC,i} = \sqrt{\frac{1}{n_{i,HC}} \sum_{t\_HC}^{t\_final} \left(\frac{m_{HC,meas} - m_{HC,sim}}{m_{HC,meas}} \right)^2} \quad f_{NO,i} = \sqrt{\frac{1}{n_{i,NO}} \sum_{t\_NO}^{t\_final} \left(\frac{m_{NO,meas} - m_{NO,sim}}{m_{NO,meas}} \right)^2}$$

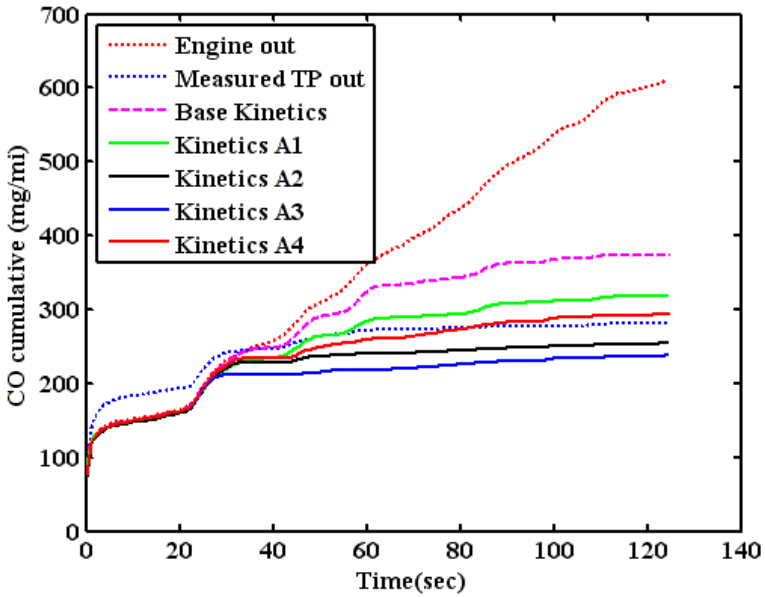
- **Objective functions are scaled for number of data points for each species and normalized for each species [each and every value contributed to the objective function is of O(1)]**

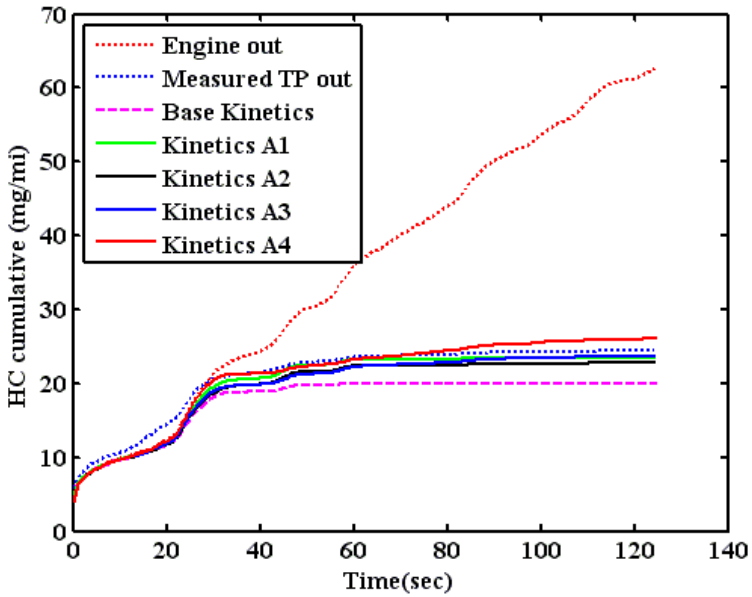
Evolution of estimated kinetic parameters

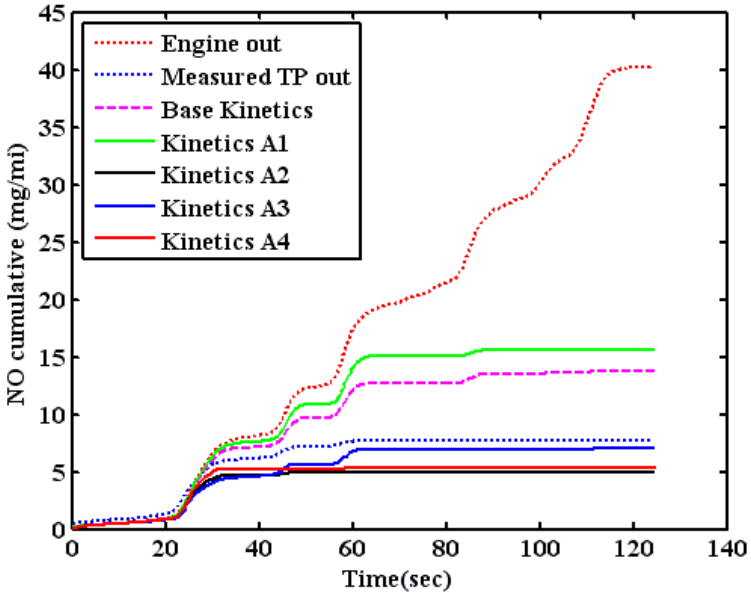
- **Predicting light-off: WGS and SR not included in optimization**
- **Base kinetics from controlled laboratory experiments and literature**
  - Estimating only the pre-exponentials
- **Slowly increasing the complexity of the optimization**
  - Only CO and HC in objective functions
  - Assuming values for certain parameters (relaxed later)
  - Including inhibition terms
  - Expanding the lower and upper bounds as necessary

Reaction kinetics	**A1**	**A2**	**A3**	**A4**
Optimization Algorithm	Pointer Automatic Optimizer	Same as A1	Same as A1	Manual tuning
Optimization Parameters	11 pre-exponential factors: $k_1, k_2, k_3, k_4, k_5, k_6, k_7, k_{10}, k_{11}, k_{12}, k_{13}, k_{15}$ and $k_4 = 10k_1$ $k_{14} = k_{13}$	Same as A1	Total: 17 13 pre-exponential factors (11 as in A1, k_4, k_{14}) + $k_{1G}, k_{2G}, k_{3G}, k_{4G}$	--
Initial values	'Base' kinetics	A1	A2	A3
Objective function include	CO and HC (Single objective function)	CO, HC, and NO (Single objective function)	CO,HC and NO (Three different objective functions, one each for CO, HC and NO)	--
Datasets used	Set 1, 2, 3, 4	Same as A1	Same as A1	Set 1
Comments	Good match for CO and HC. NO predictions are off	Improvements in NO predictions but low sensitivity for CO and HC oxidation reactions.	Improved predictions for HC and NO but more sensitivity towards Ceria reactions	Right sensitivities with good match for CO, HC and NO

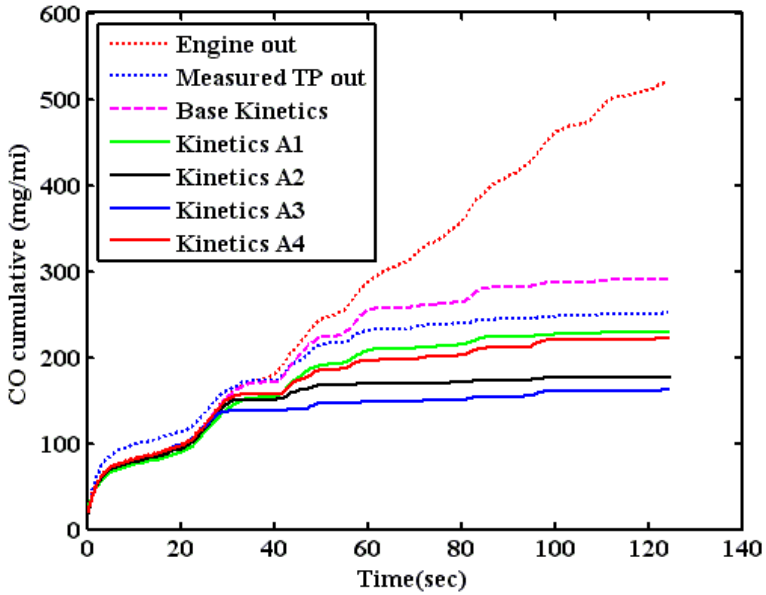
Model Calibration Results (Dataset-2)

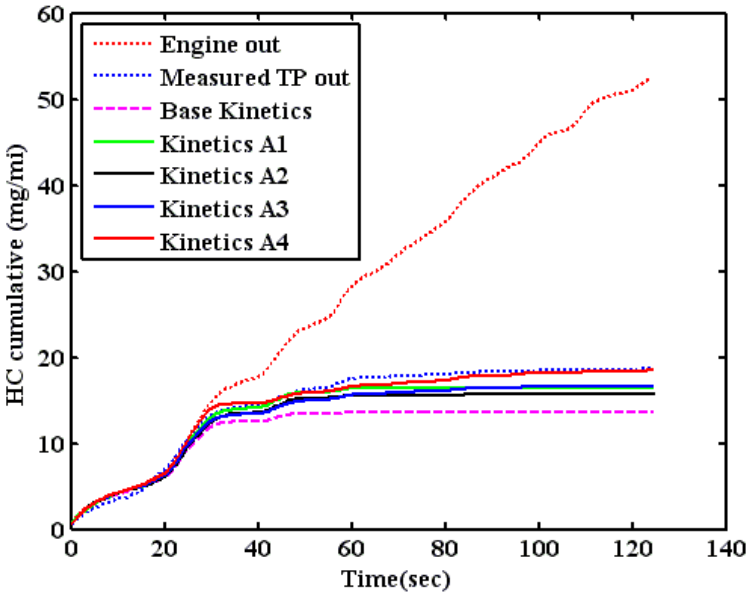


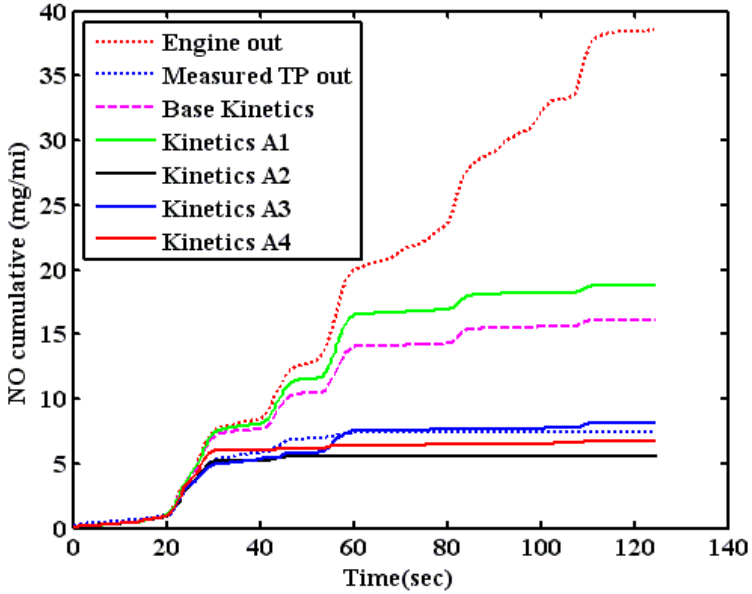




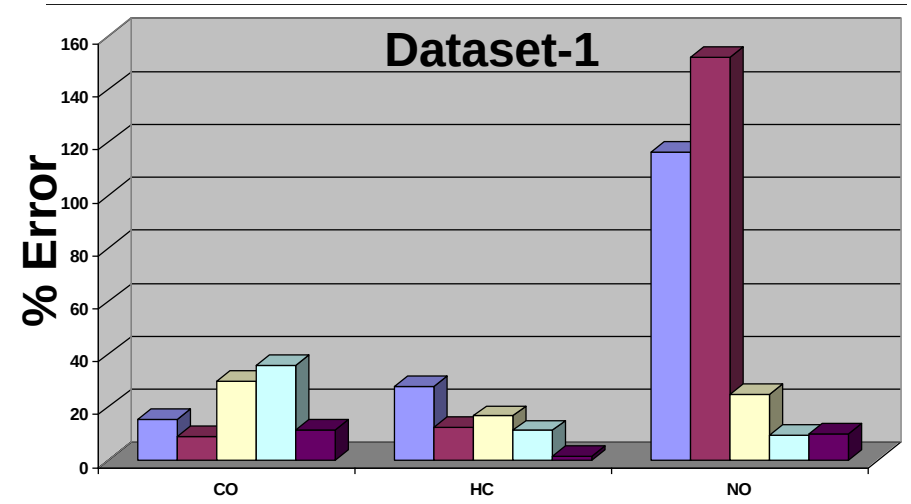
Model Calibration Results (Dataset-1)

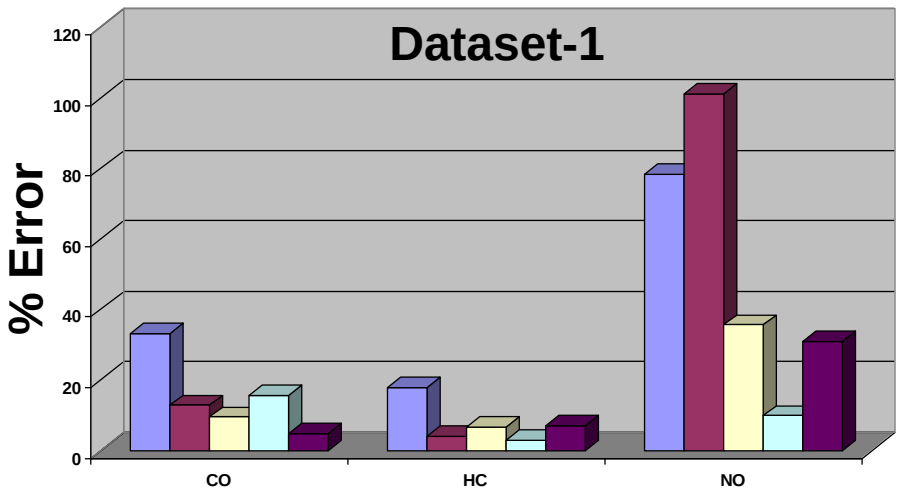


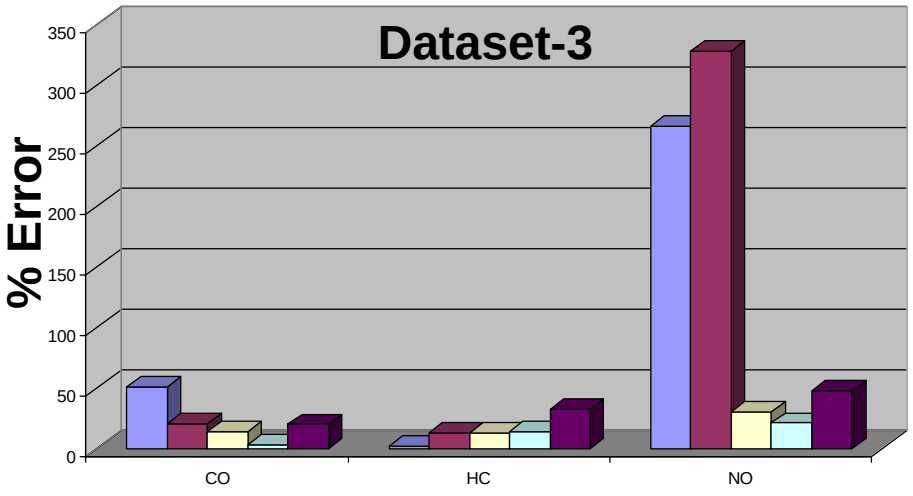


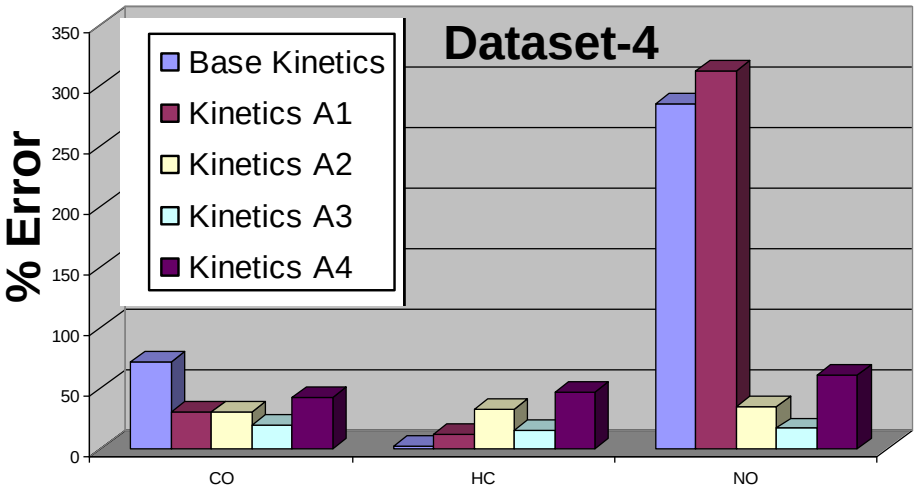


Model Calibration (%) Error at 125s

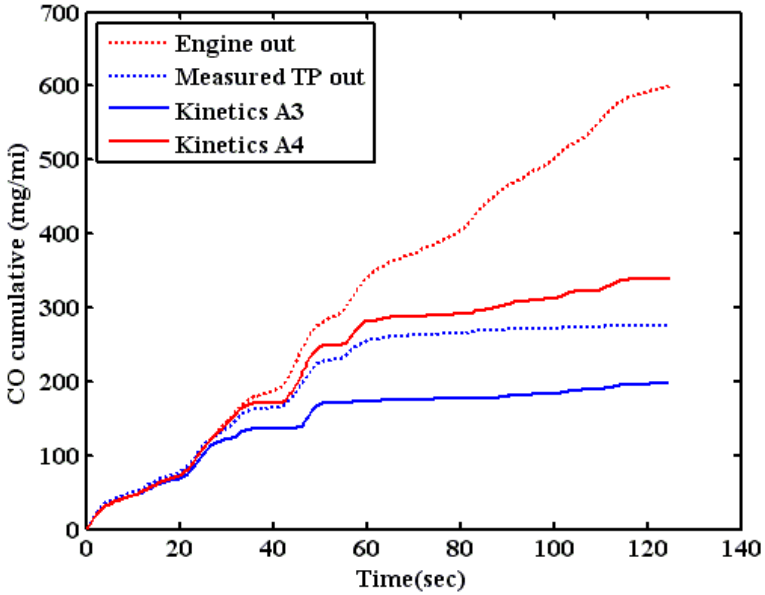


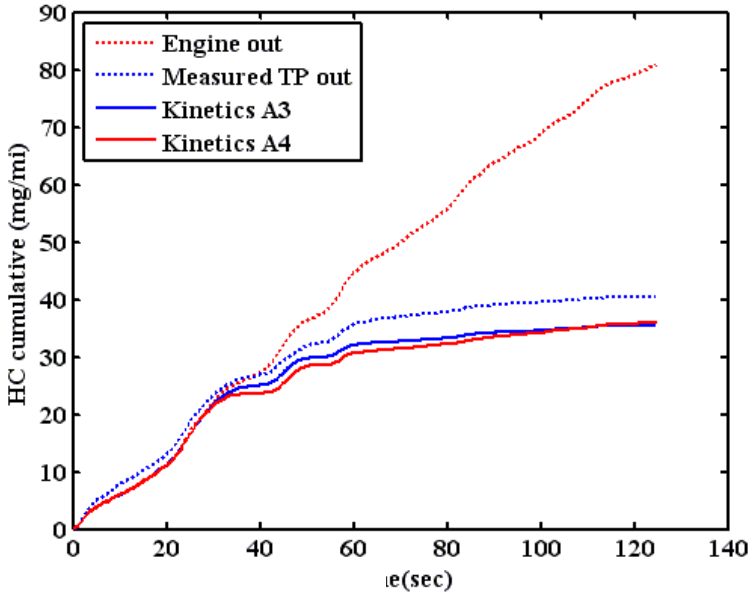


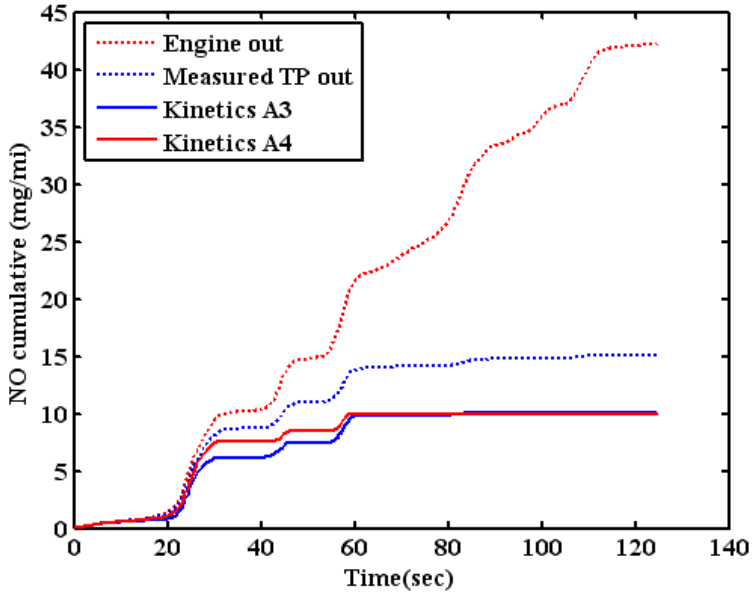




Model Prediction (Dataset-5)







Summary

- **Kinetics obtained from laboratory experiments do not translate directly for predicting vehicle data.**
- **Kinetic modeling at the vehicle level needed to predict vehicle data**
- **Prediction of time-dependent cumulative emissions (rather than emissions at a given time instant) is critical**
- **Choice of data points, objective functions, parameters, methods of optimization crucial for successful optimization (/ parameter estimation)**
- **Calibrated model able to predict light-off for TWC applications reasonably well.**
- **Model was further fine-tuned for lean-gasoline applications**
- **Model calibration for SULEV emission standards more challenging**
  - Quality of experimental data becomes very critical.
- **Model is only as good as the experimental data.**

Key Points – 1

- **Choice of parameters**
  - Choose all the unknown parameters.
  - Estimated parameters are only as good as uncertain (known) parameters.
  - Chosen parameters should have good sensitivity to the measured outputs.
- **Choice of Experiments and Model**
  - Right experiments: Transient/Steady-State
  - Parameters to be estimated should have a good sensitivity on the measured outputs
  - Model should describe the experimental condition well.
    - Choice of 1D, 2D, 3D
    - Inclusion/Exclusion of heat loss, flow effects

Key Points – 2

- **Choice of Objective function**
  - Log-based (log of simulated/measured), sum of squares of the difference (simulated-measured)
  - Important to pick a objective function that shows sufficient sensitivity to the parameters that are being estimated.
  - Separate objective functions – can help in sensitivity analysis
  - Weighting the objective function
    - More weight to reliable data points
  - Scaling the objective function
    - Important to get all the outputs scaled to same order of magnitude (concentrations, temperature)
    - With number of data-points
  - Exclusion of inappropriate data that are insensitive to the parameters and exclusion of inaccurate experimental data.

Key Points – 3

- **Choice of Optimization methods/algorithm**
  - Exploratory and/or local optimization methods
  - Pointer Automatic Optimizer (iSIGHT)
- **Parameter Estimation Process**
  - Initial guess crucial for local methods
  - Physical bound and constraints for the parameters
    - Smaller the space (narrow bounds), less the time for optimization
    - Flexible to relax the bounds
  - Scale the parameters – O(1)
  - Estimating the right parameters from the right data
  - Increase the complexity systematically
    - Start with fewer parameter (most dominant ones)
    - Local sensitivity analysis can help determine the dominant parameters.

Key Points – 4

- **Runtime, Analysis and other factors**
  - When using iSIGHT, start with all unknown (and uncertain) parameters
    - Helps in creating a database, which can be later used for analysis.
  - Computational time for each simulation (and objective function calculation) and the time available for optimization process can help in deciding the optimization method (local or exploratory or mix of the two)
  - Failures in the numerical code – Penalty for failure runs
  - Split the available data into two buckets – one for calibration and one for validation
  - Analyze the optimization results
    - Sensitivity to certain parameters
    - Relaxing the bounds (some parameters hitting the bounds)
  - Use values from previous optimization runs as initial guesses.