Modeling of Diesel Exhaust Systems:

A methodology to better simulate soot reactivity

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U.S. DEPARTMENT OF ENERGY

DEER 2011 DETROIT

Directions in Engine-efficiency and Emissions Research conference

Outline

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- Modeling Capability
- Application Example with Soot Regeneration Simulation
- Improving the Fidelity of Systems Simulation
  - Customizing Soot Models
- Conclusions and Path Forward

Modeling
Simulation Capability at BASF

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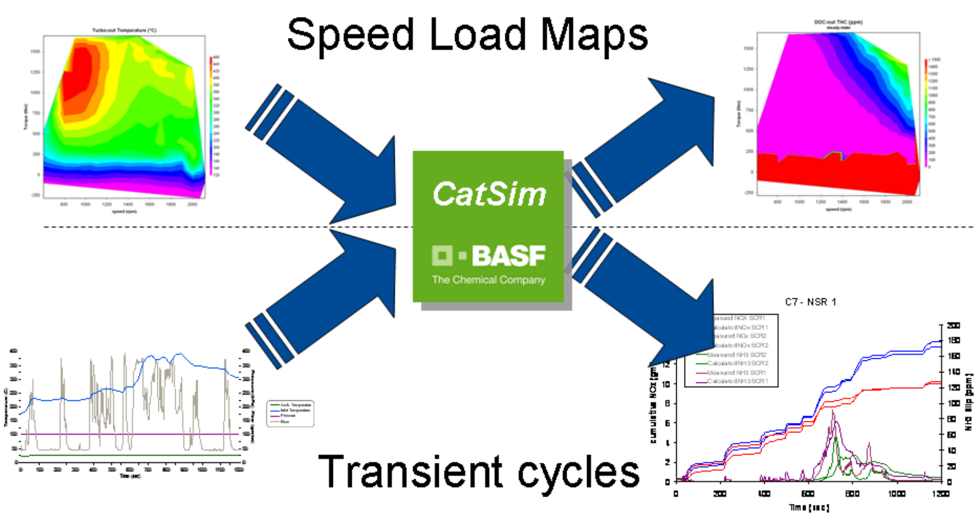
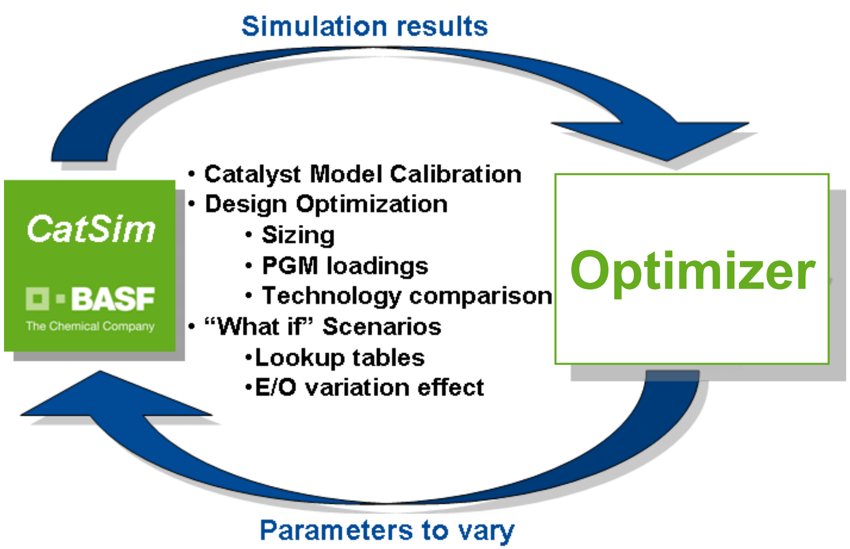
Philosophy of Modeling at BASF :
- Provide a theoretical foundation for catalyst submissions
- Reduce amount of experimental work needed
- Provide lookup tables to simplify customer calibration work
- Provide capability to simulate exhaust system response on future engines





CatSim Capabilities

- CatSim incorporates individual 0-D, 1-D and/or 1-D + 1-D models for:
  - Monolithic flow through catalysts (TWC, DOC, SCR, AMOX, LNT)
  - Monolithic based filters (CSF, SCRoF)
  - Pipes and cones
  - Injectors with feedback control via Matlab or Excel
  - Cold EGR
  - Junctions
- Each catalyst technology defined by washcoat properties and reaction kinetics
- Additional features include:
  - Homogeneous reactions
  - Multiprocessor capable

Filter Model: Processes Captured

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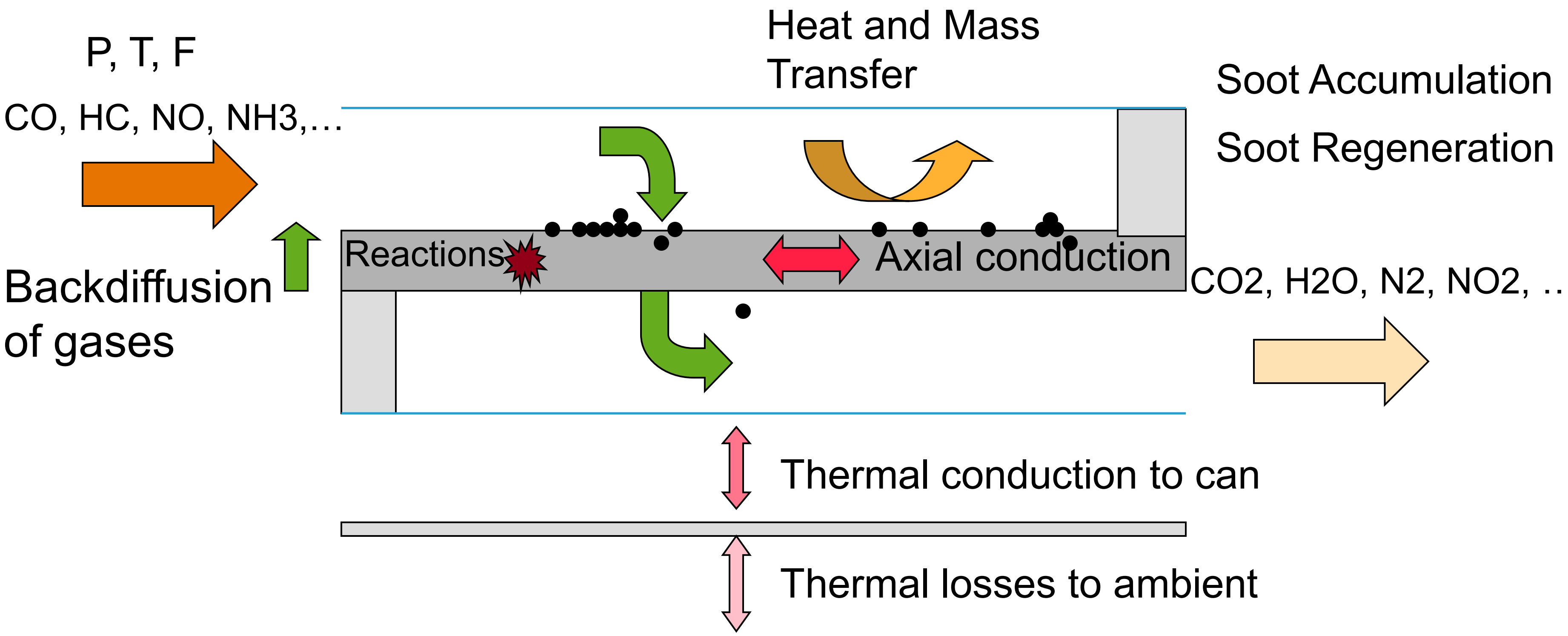

Example of Application with Soot Regeneration Simulation

Filter Regeneration Simulation

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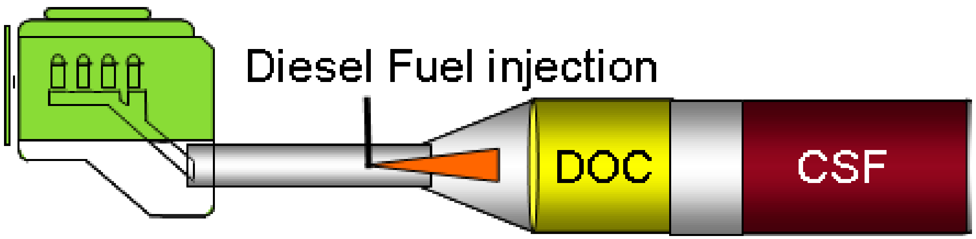

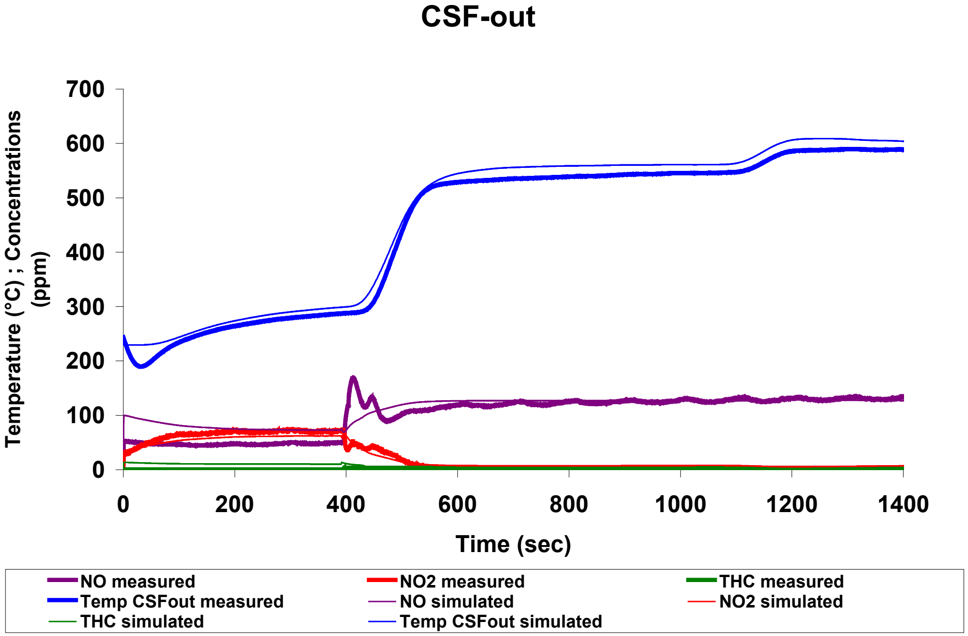

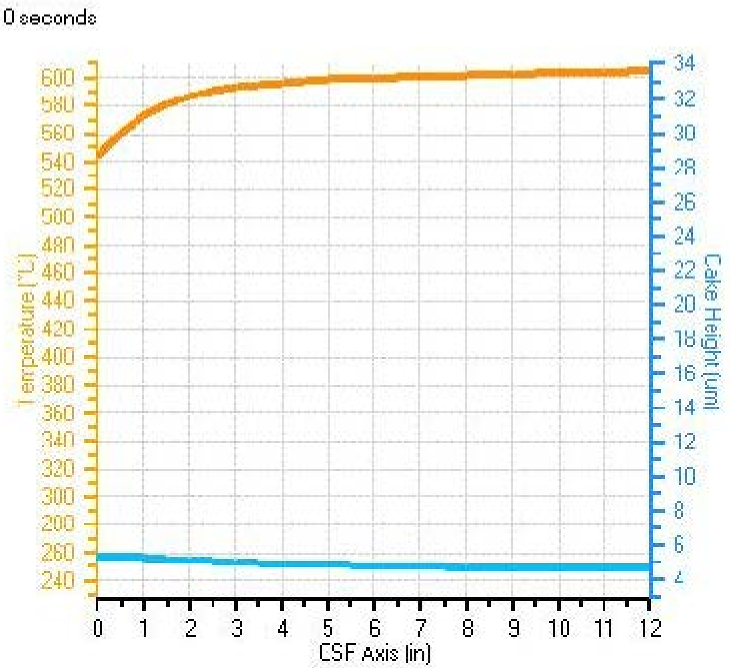

Filter Regeneration Simulation (2)

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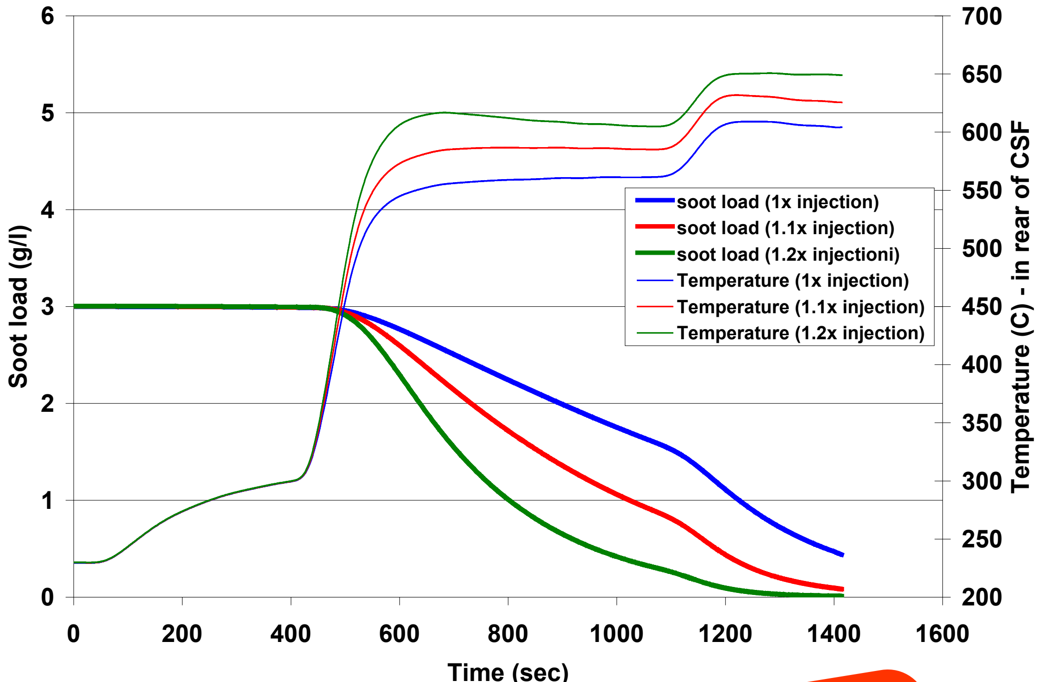

- *Soot properties are different from one engine to anot*
- *Soot properties are different f*
- *The regen* *kinetics of soot produced in BASF's lab. The soot g* *might have different physical properties leading to different reactivity.*

Can we improve that?

Improving the Fidelity of Systems Simulation

Customizing soot model

Soot Particulates

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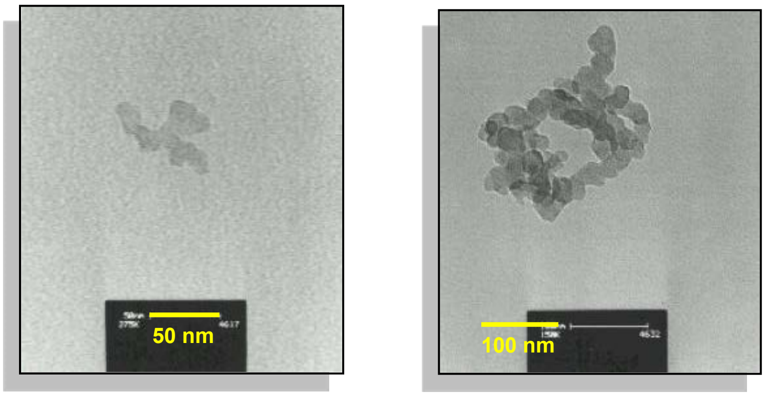
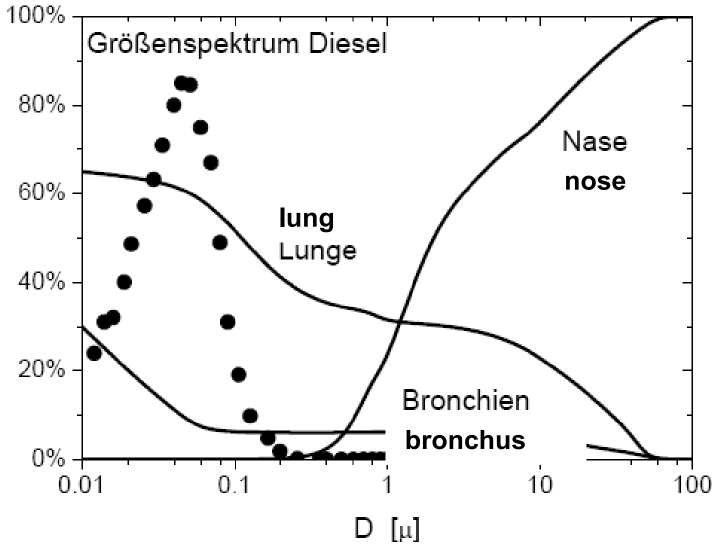
Transmission Electron Microscopy (TEM) of diesel soot particulates



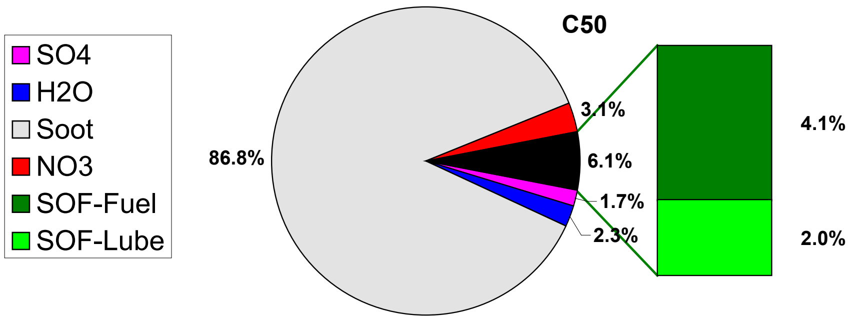
= Particle size distribution in diesel exhaust



LEONARDI, A.: *Feinste Schwebeteilchen aus Dieselmotoren.* , ETH Zürich, Diss. ETH Nr. 9515, 1991.

Particulate composition and morphology depend on the combustion process:
→Different engines will generate different soot
→Even different mode can generate different soot
→Composition and morphology will impact reactivity with O_2 and NO_2

Example of soot composition



See Also:

[1] K. Al-Qurashi et A. Boehman, "Impact of exhaust gas recirculation (EGR) on the oxidative reactivity of diesel engine soot ", Combustion and Flame, 155, 675-695 (2008).
[2] Juhun Song et al., "Impact of alternative fuels on soot properties and DPF regeneration", Combust. Sci. and Tech., 179, 1991-2037 (2007).
[3] R. Vander Wal et al., "HRTEM study of diesel soot collected from diesel particulate filters", Carbon, 45, 70-77 (2007)
[4] J. Rodriguez-Fernandez et al., "Characterization of the diesel soot oxidation process through optimized thermogravimetric method", Energy and Fuels, 25, 2039-2048 (2011)

Soot Reactivity and Surface Area (BET)

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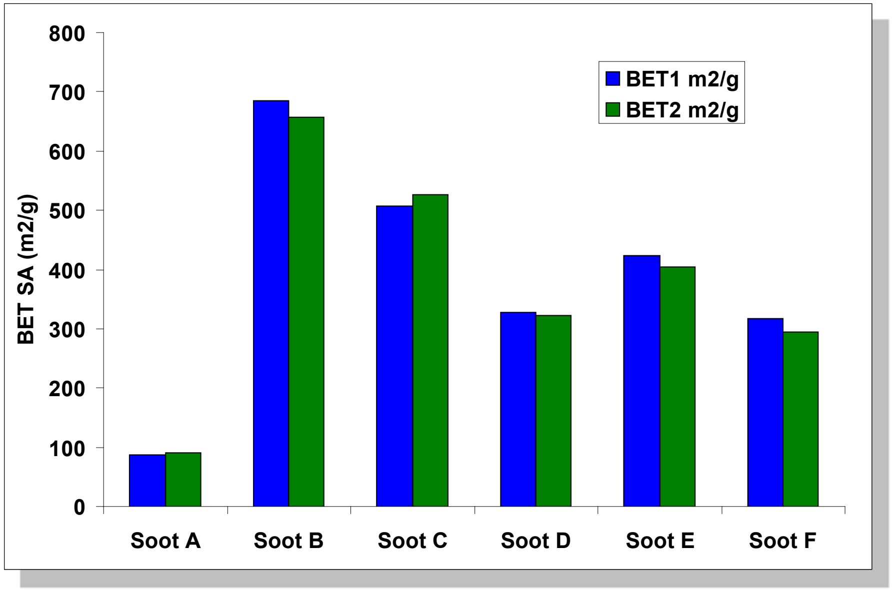
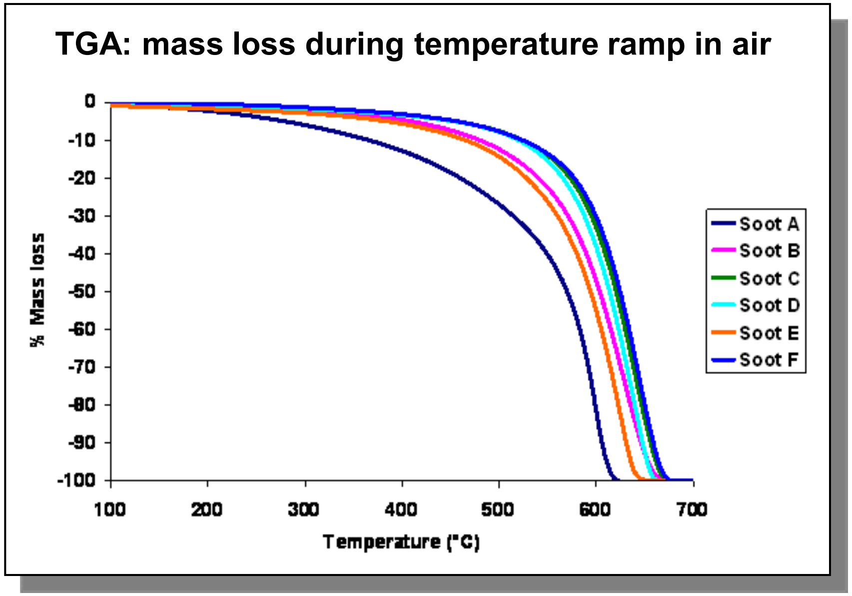
Soot A presents the lowest surface area but the highest reactivity





Soot Reactivity and Surface Oxygen (XPS)

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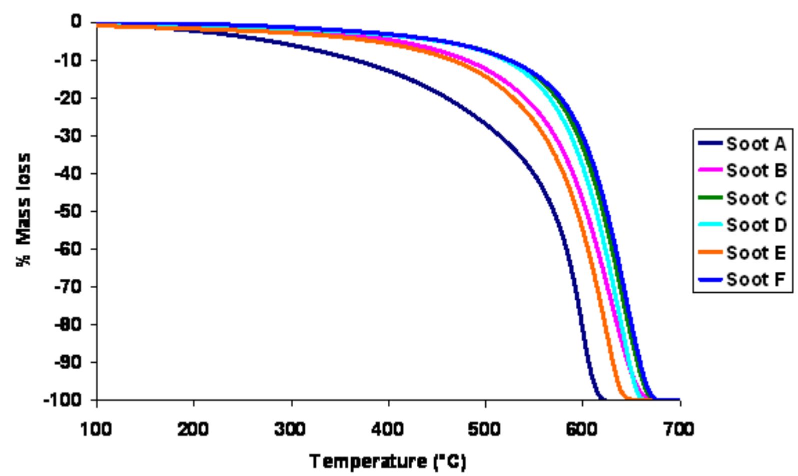
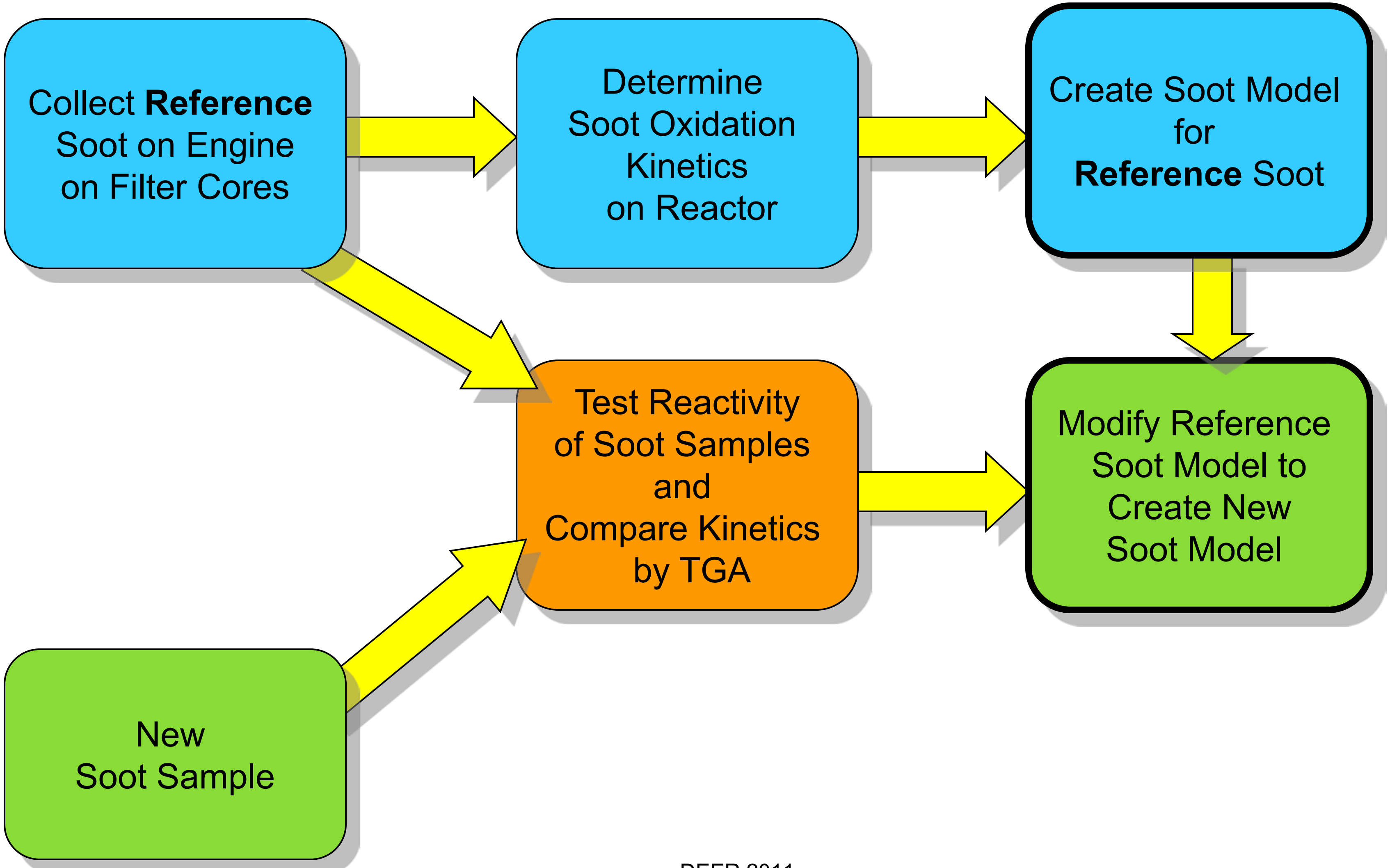
Soot A presents more surface oxygen than other samples, which could be the cause of highest reactivity

Oxygen 1s Overlay
Soot A Soot C Soot E

TGA : mass loss during temperature ramp in air



Customizing Soot Model Process



Collection of Soot on Filter Cores

Collect Reference Soot on Engine On Filter Cores

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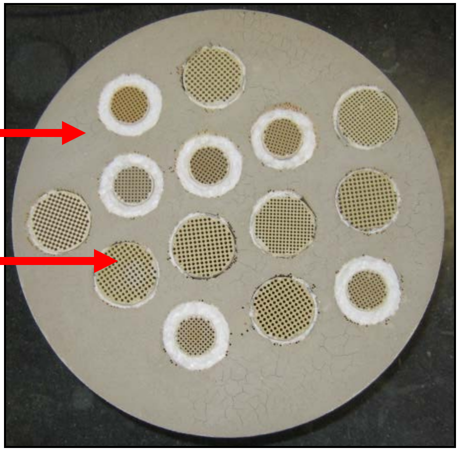
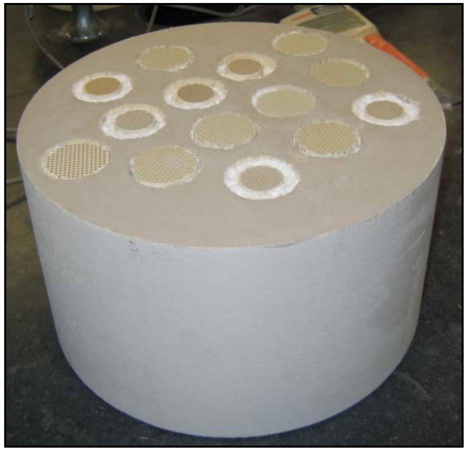
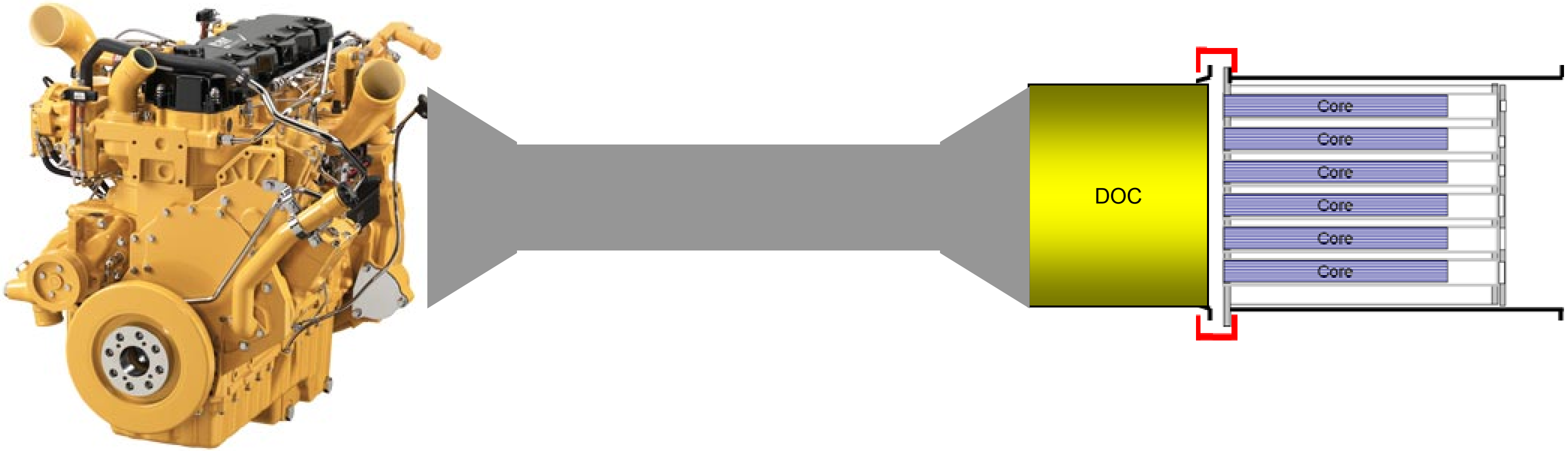
Monolith with plugged cells

Filter Cores







Test Protocol

Determine Soot Oxidation Kinetics on Reactor

Create Soot Model for Reference Soot

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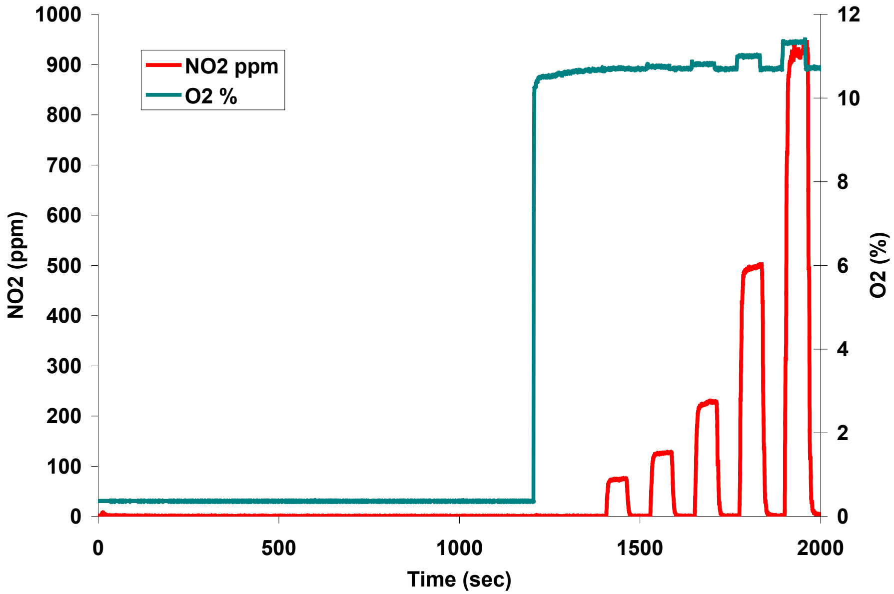
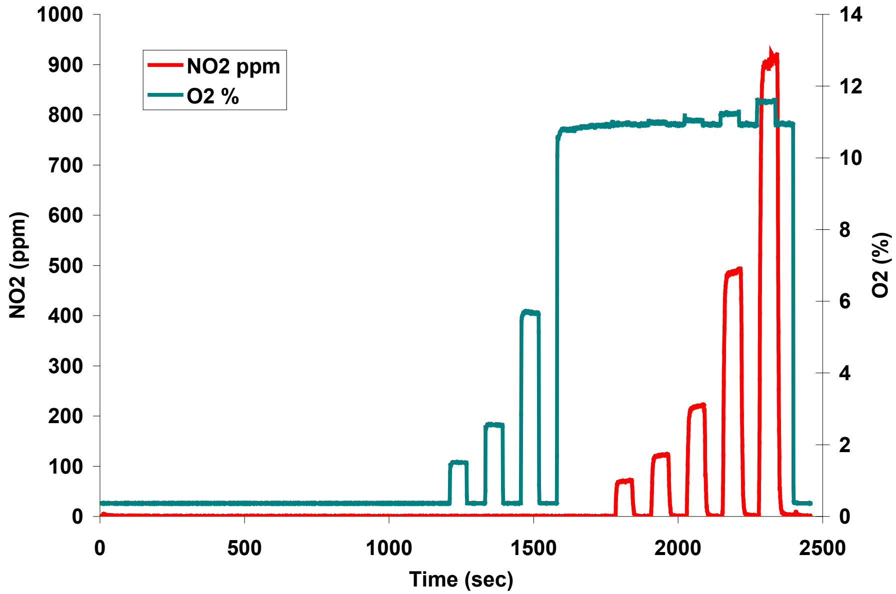
Temperatures (C): {200, 250, 300, 350, 400, 450}



Temperatures (C): {500, 550, 600, 650}



Soot loading of the filter was determined by C balance (CO and CO_2 produced)

Reactor Results Used for Calibration of the Soot Model

Determine Soot Oxidation Kinetics on Reactor

Create Soot Model for Reference Soot

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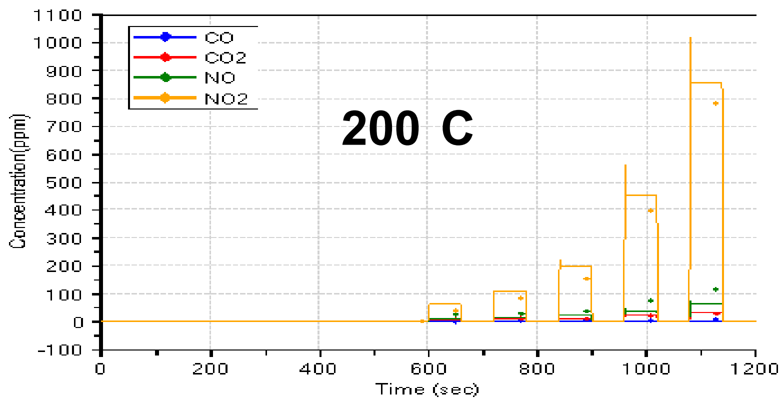

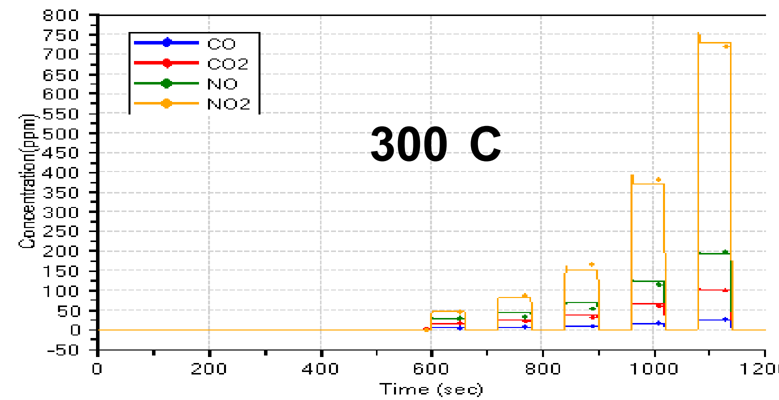

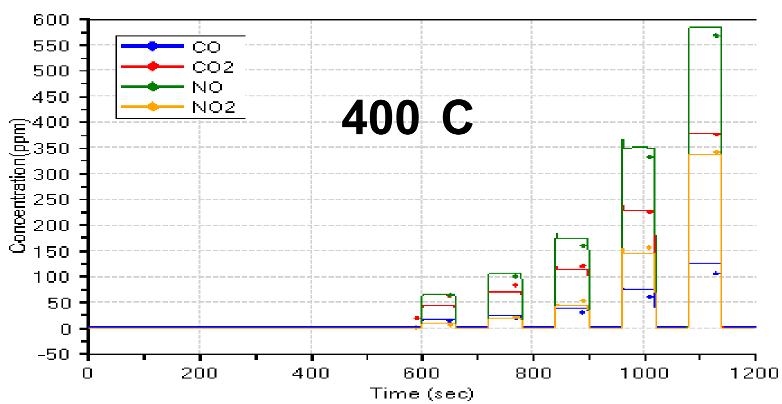

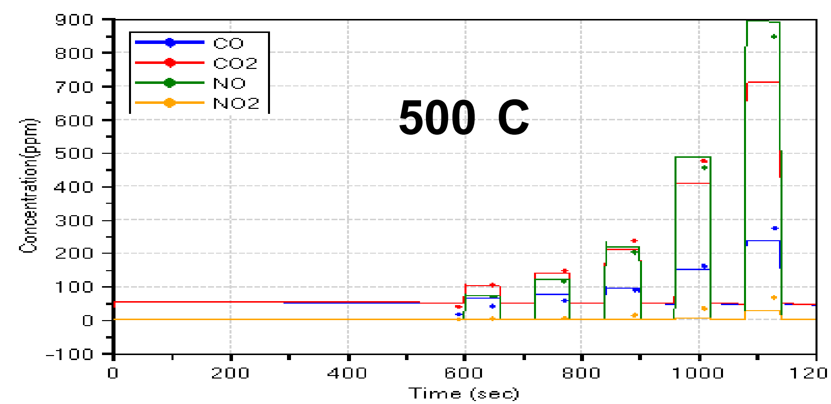

Parity Plots

Measured Vs. Calculated Concentrations

Create Soot Model for Reference Soot

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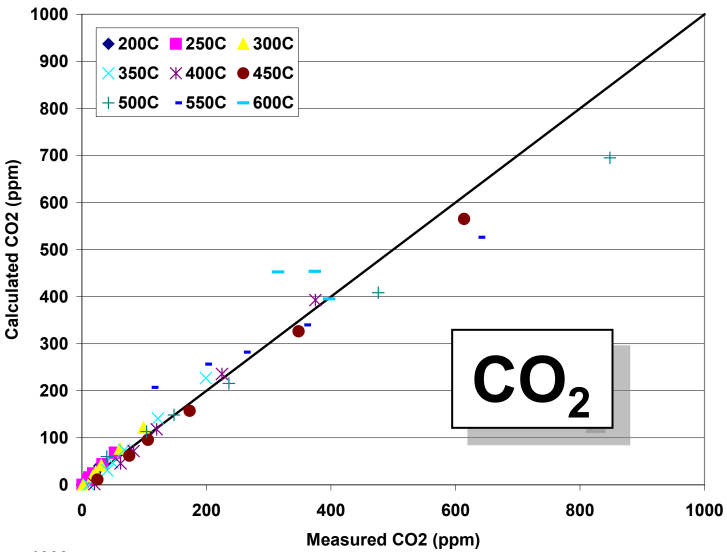

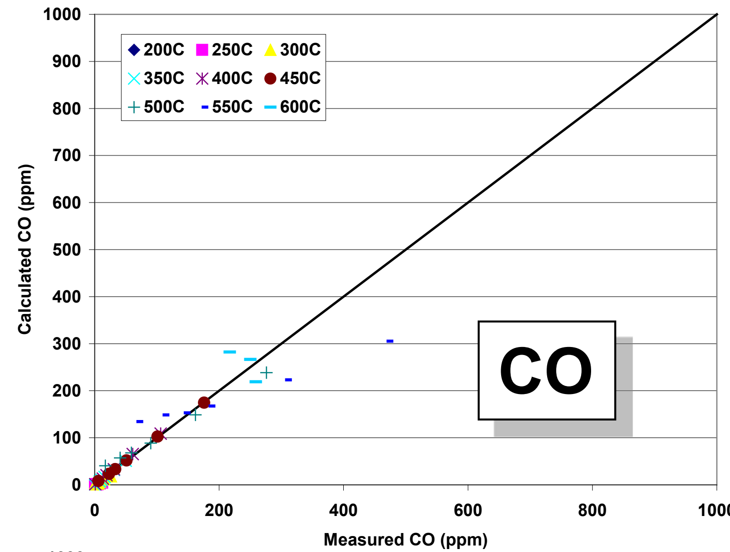

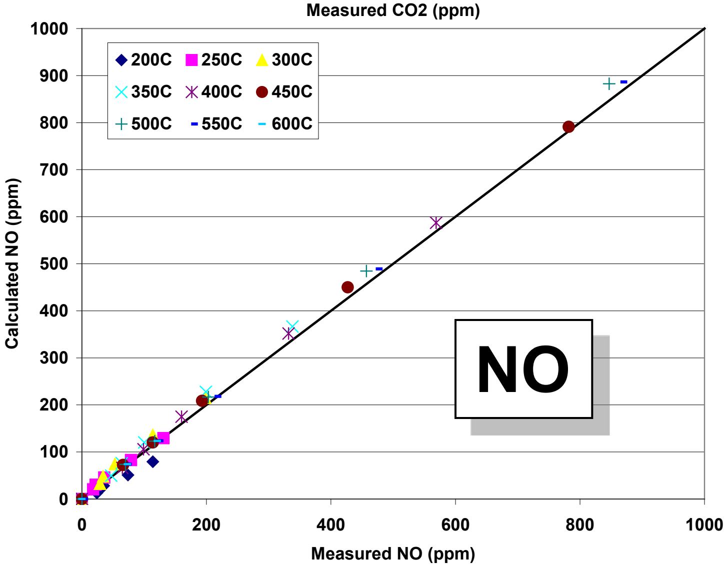

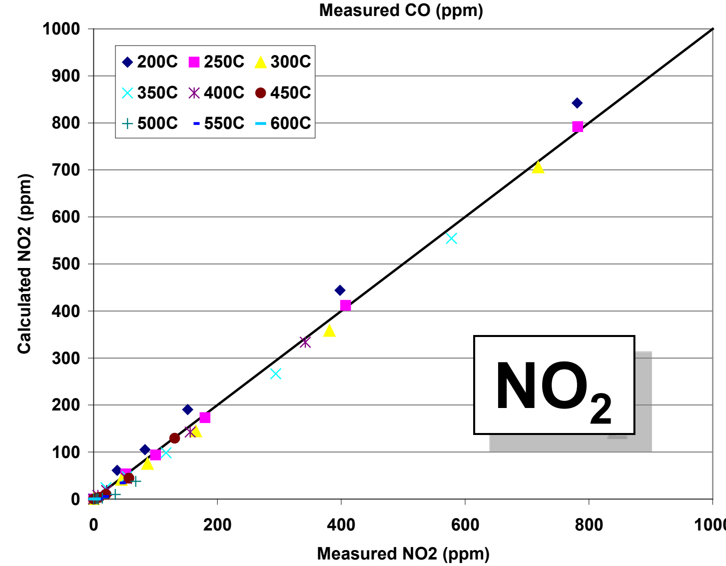

Soot Model

Create Soot Model for Reference Soot

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- $C + O_2 \rightarrow CO_2$
- $C + ½ O_2 \rightarrow CO$
- $C + 2 NO_2 \rightarrow CO_2 + 2 NO$
- $C + NO_2 \rightarrow CO + NO$
- $C + NO_2 + ½ O_2 \rightarrow CO_2 + NO$

Model Vs. Engine Data

The soot model correctly simulates soot regeneration, NO_2 consumption and CO formation

<u>Assumption:</u> E/O soot rate was constant during the tests

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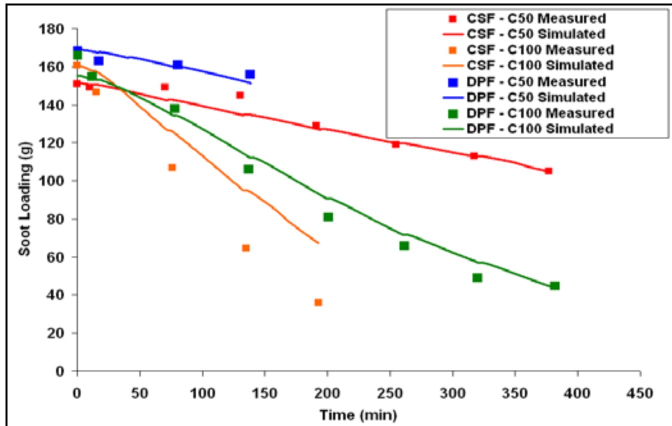
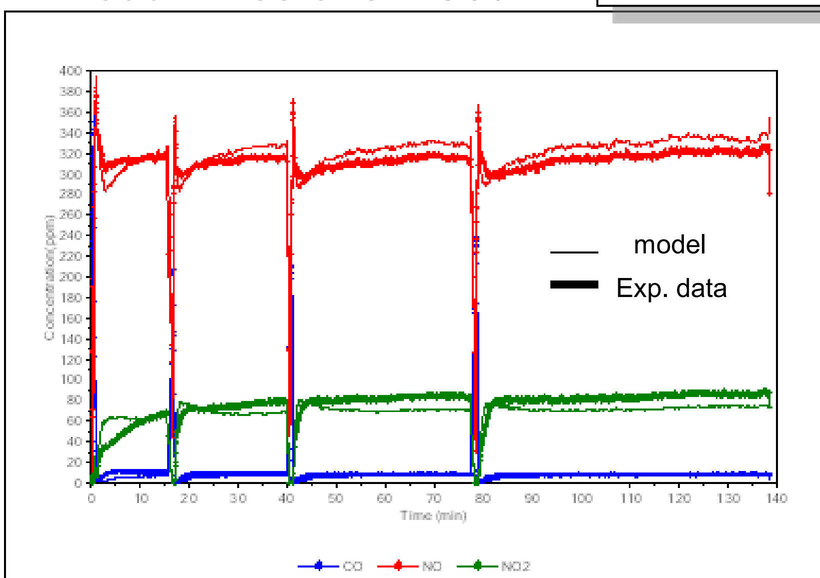
C50
Temperature: 320 C
Flow rate: 970 kg/h
NO_x: ~405 ppm

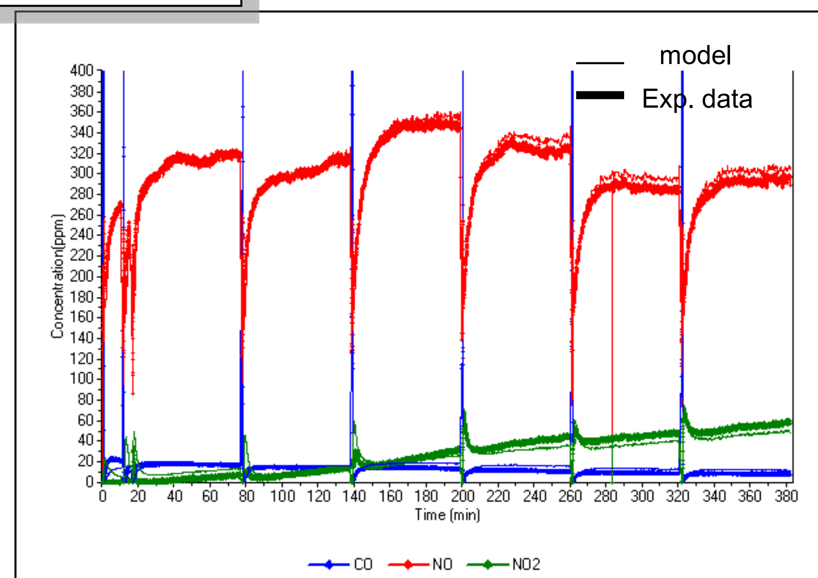


C100
Temperature: 434 C
Flow rate: 940 kg/h
NO_x: ~ 370 ppm

DPF-out Emissions – C50



DPF-out Emissions – C100

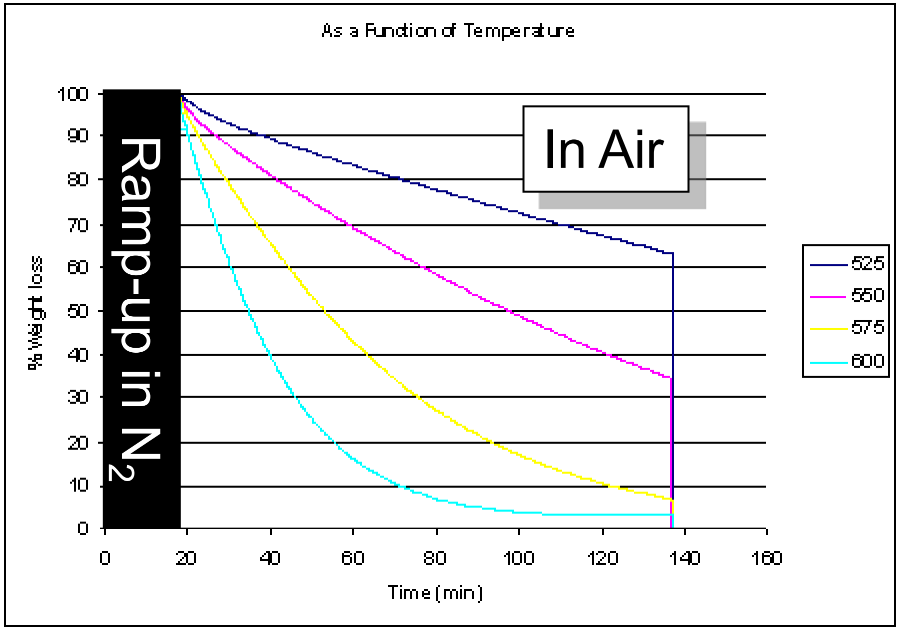


Thermo-Gravimetric Analysis (TGA)

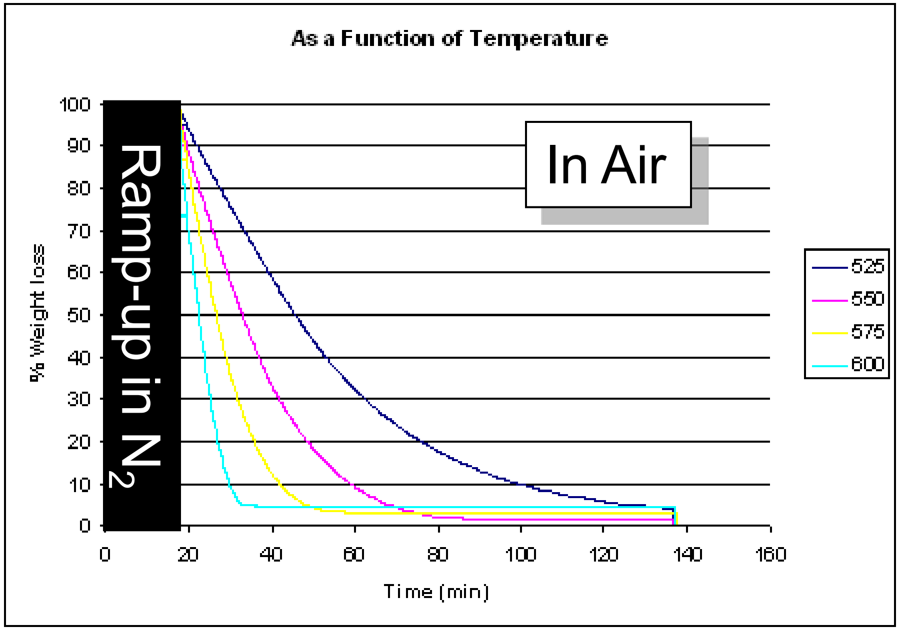
Weight Loss Due to O_2 Oxidation

Test Reactivity of Soot samples and Compare Kinetics by TGA

New Soot



Reference Soot



Thermo-Gravimetric Analysis (TGA)

Weight Loss Due to NO_2 Oxidation

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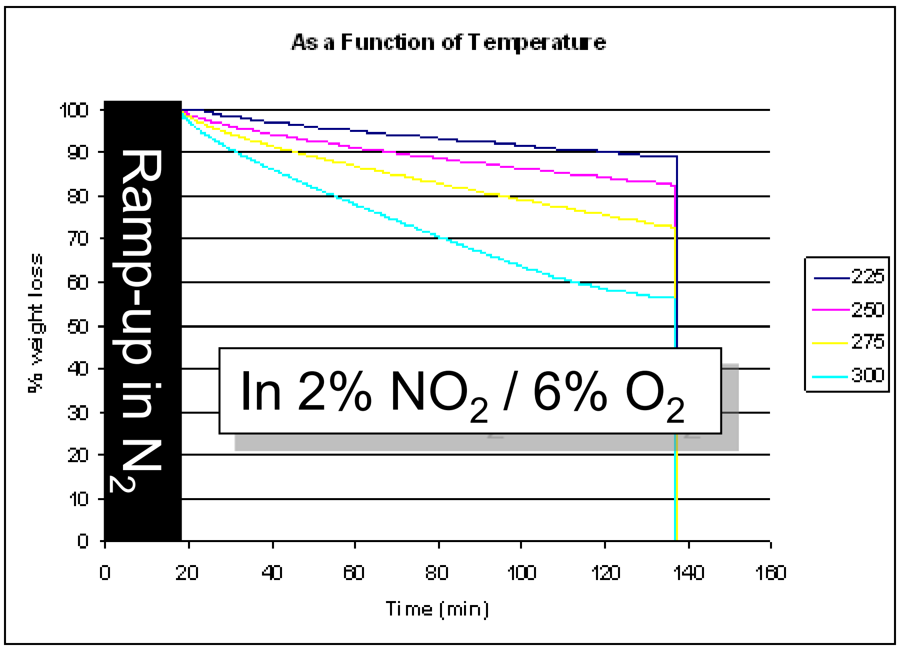
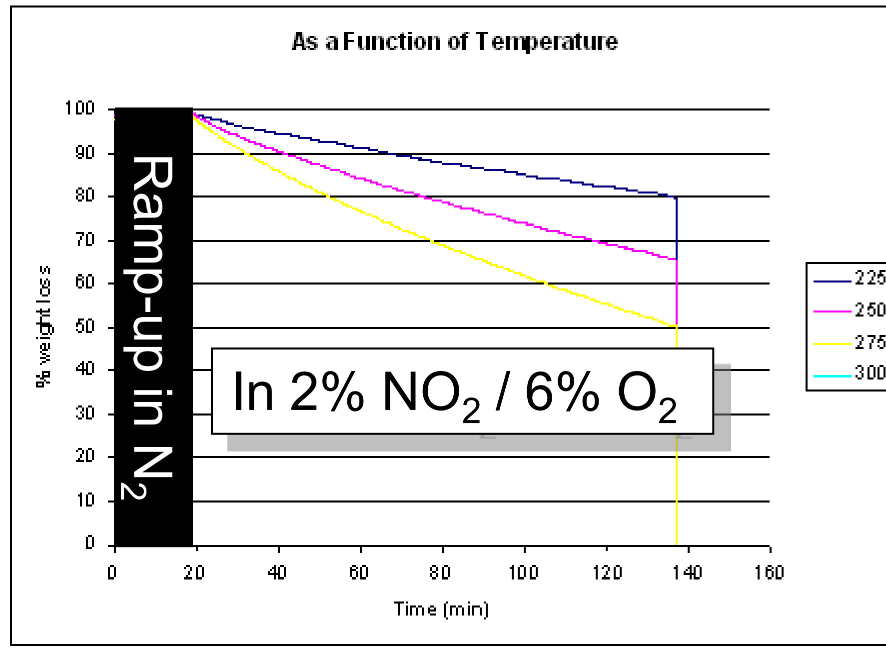
Test Reactivity of Soot samples and Compare Kinetics by TGA

New Soot



Reference Soot



Thermo-Gravimetric Analysis
Kinetic Constants Comparison

Modify Reference Soot Model to Create Customer's Soot Model

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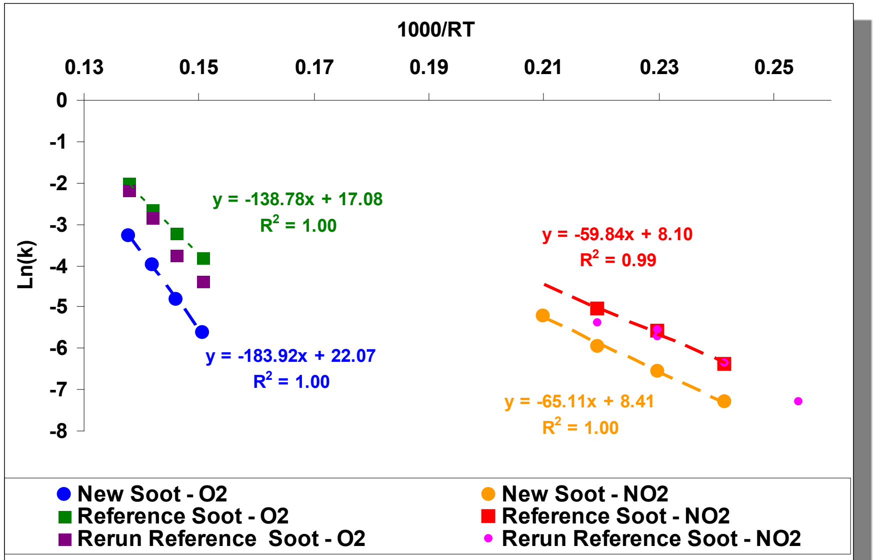
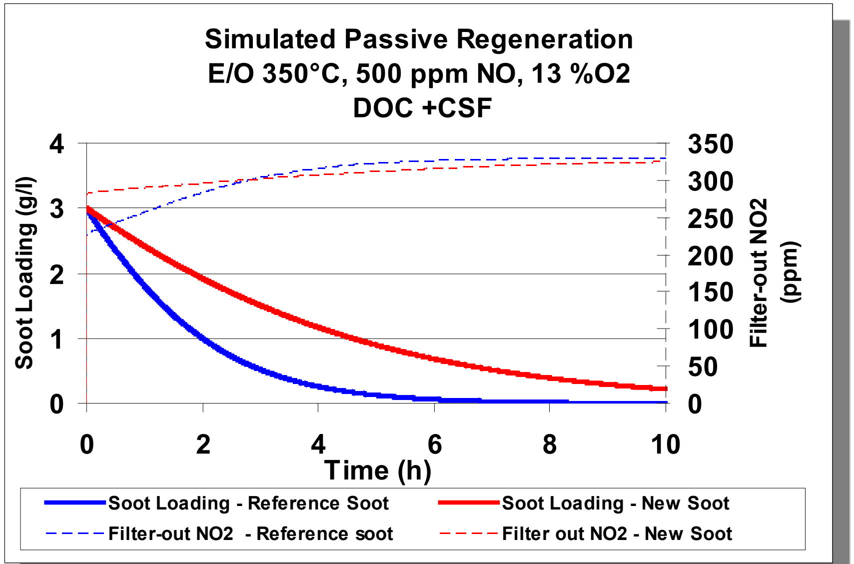
•Kinetics information obtained by TGA is used to **modify the reference soot model** (the relative difference in pre-exponential coefficients is the information used to modify the reference soot model and create a model for the "new soot").

•This allows a better estimation of regeneration durations depending on the conditions (temperature, flow, NO_2…) and interaction with deNOx system (ex: NO_2 at SCR-in).





Conclusions / Path Forward

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- Conclusions
  - A soot model was developed for soot oxidation on reactor and used as a reference.
    - This model allowed a good prediction of engine data
  - A methodology to simulate soot from different origins was proposed.
    - use a different soot sample from another origin (different engine) and compare its reactivity to the reference soot sample by solely using thermo-gravimetric analysis. The relative difference of reactivity was used to create a model of this “new soot” sample.
- Path Forward
  - Final validation: compare predictions from this soot model generated with this methodology to engine data.

Thank You
For your attention