DEER 2005

Emission Control Technologies, Part 2

The State of the Science in Diesel Particulate Control

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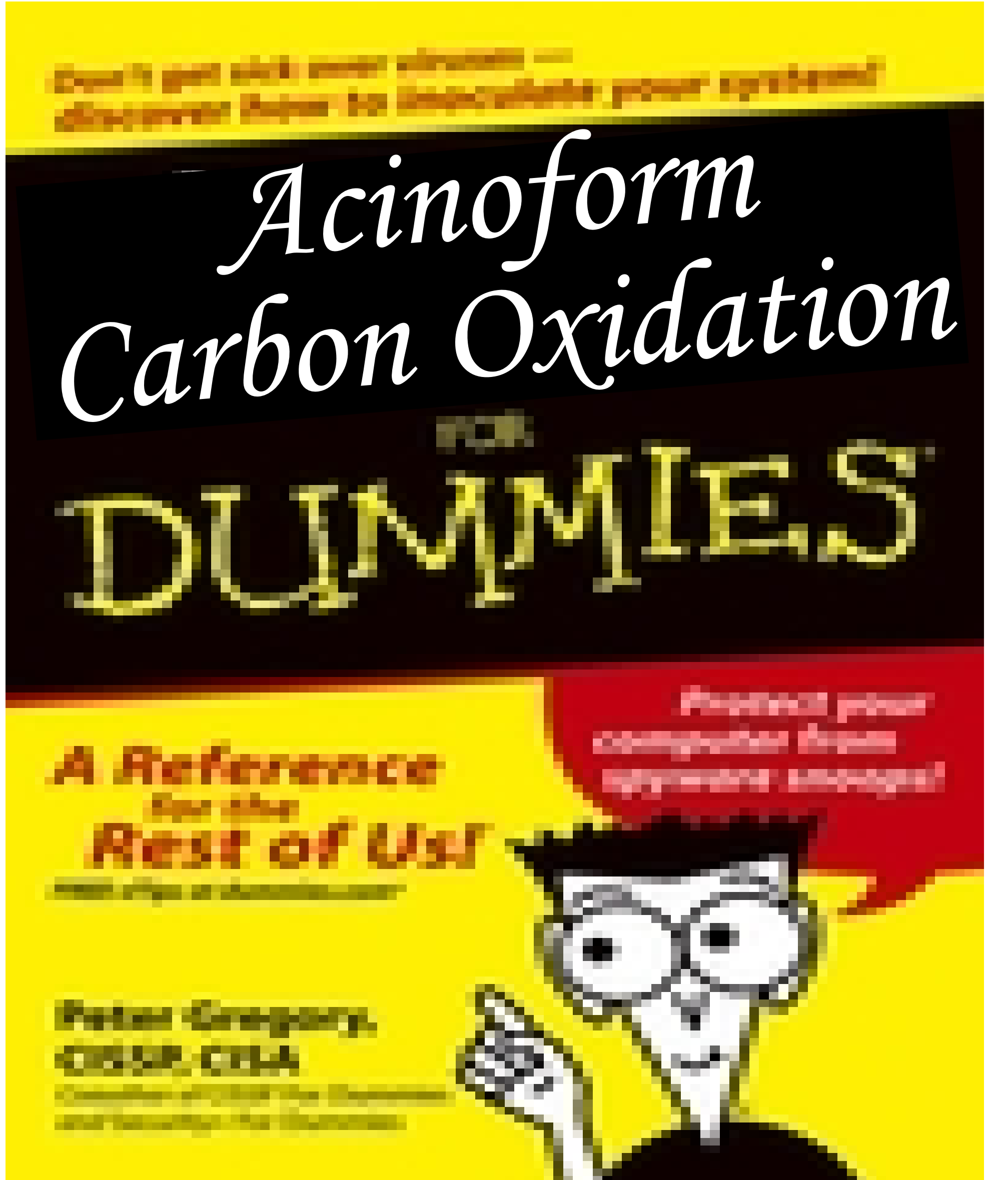
What about the state of "Engineering"?

Diesel Particulate Filtration

- Engineered solutions are expanding
  - Heavy duty retrofits
  - European light duty
- There WILL be engineered solutions to 2007 US Heavy Duty diesel
- Manufacturers are "polishing" their approaches

Engineers will always make do…

CONFIDENTIAL: Prototype 2007 HD truck – field test unit


Acinoform
Carbon Oxidation
FOR
DUMMIES
Protect your computer from spyware snoops!
A Reference for the Rest of Us!
Peter Gregory, CISSP, CISA

Diesel Particulates

- What do we know and what don't we know?
- We do know they are
  - Structurally homogenous (or perhaps comparable)
  - Chemically variable
  - Very dynamic
  - Sticky
- We don't know
  - Precisely how they oxidize
  - How to measure them in-situ
  - Precisely how they vary with operating conditions, design, aging
  - How to model DPFs from first principles

Particulate Life Cycle - A Natural Example

Formation

Source

Destruction

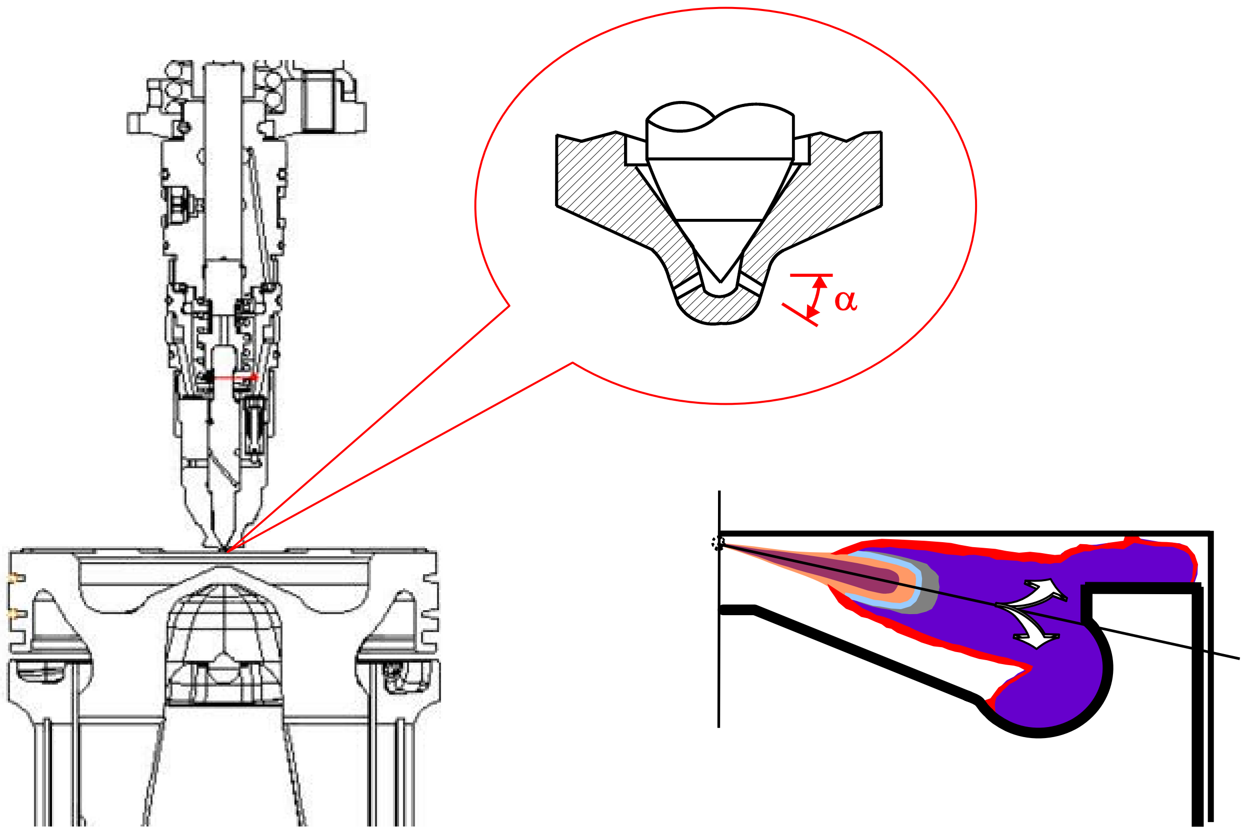
Deposition

Transport/
Evolution

SOURCE

Today's Diesel Engine:

4 stroke, electronic DI, Turbocharged with VG or WG, Intercooled, 4 valve, central vertical injector, low swirl, high EGR...



2010 Diesel Engine:

?

What will the particulates from this engine look like

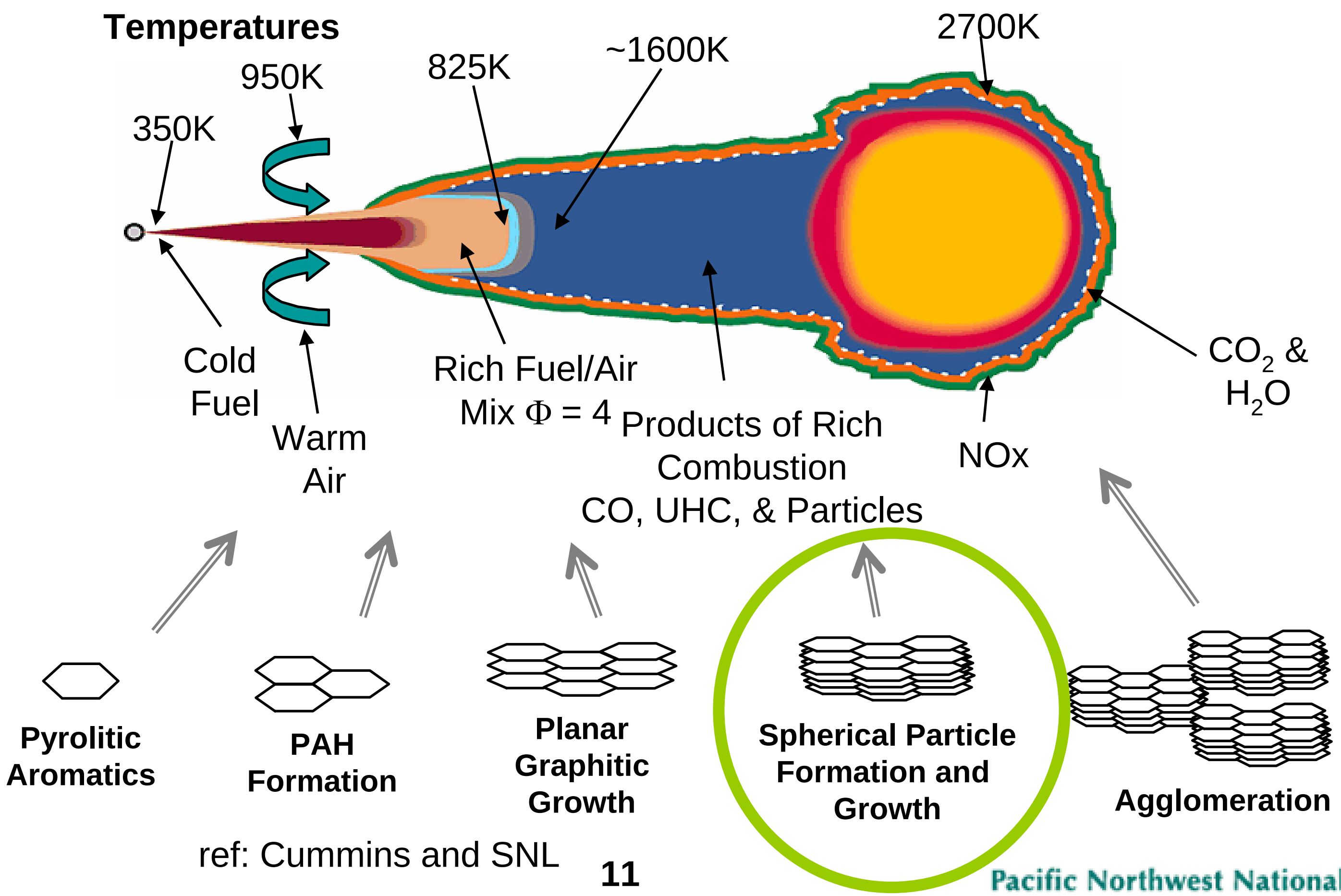
?

Diluted combustion (eg HCCI) attempts to end the story at this point **{numerous OFCVT supported projects – see Advanced Combustion Technologies sessions}**

FORMATION

Working Definition

NOTE: Much of this understanding evolved from DOE OFCVT funded research at SNL and LLNL



ref: Cummins and SNL

The Spherule (ref: Glassman, 1977)

- ~ 1% by weight hydrogen (or C_8H)
- most commonly 10-50nm in diameter
- ~10^4 crystallites (from XRD)
- crystallite is 5-10 sheets of carbon (electron diffraction)
- individual sheets are like ideal graphite
- each contain about 100 carbon atoms
- each are approx 2-3nm on a side
- sheets are randomly stacked (i.e. turbostratic)
- interlayer spacing is 0.344nm (vs. 0.335 for graphite)
- average spherule contains about 10^5 to 10^6 carbon atoms

Spherules Are All The Same But Different

R.L. Vander Wal, A.J. Tomasek / Combustion and Flame 134 (2003) 1–9 5

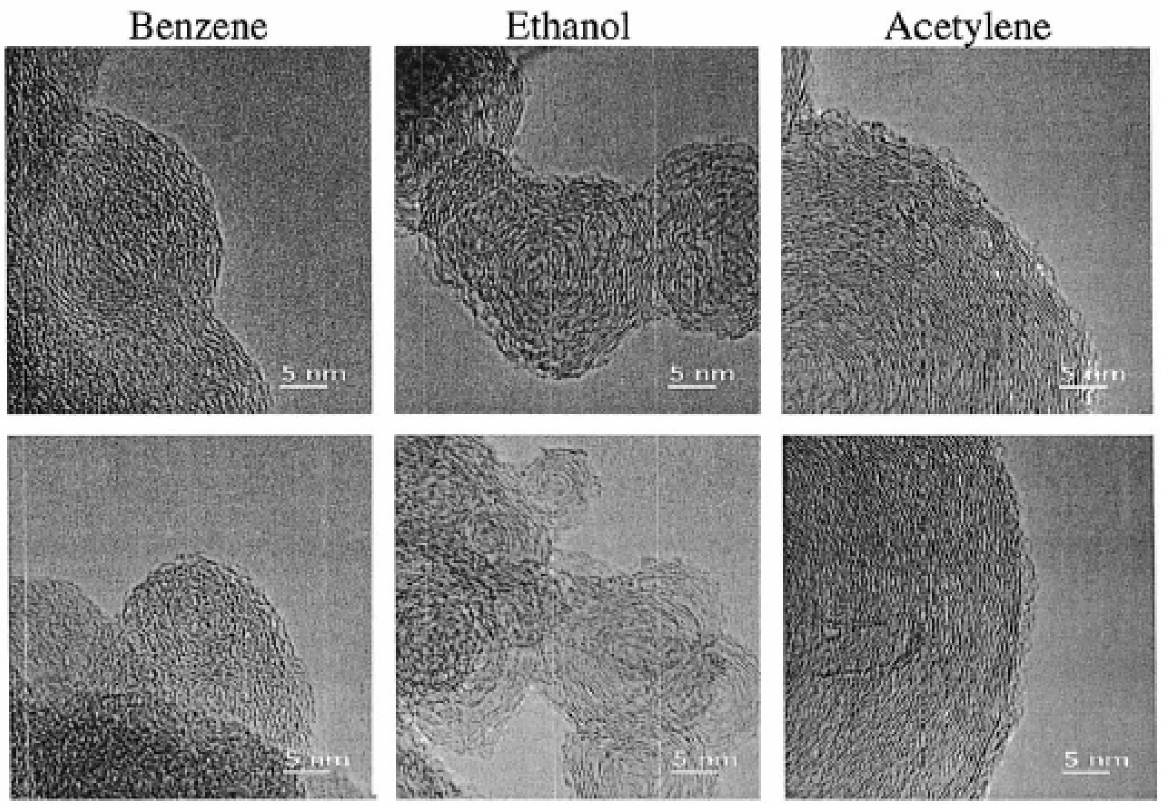


Fig. 3. HRTEM images of the soots derived from pyrolysis of a) benzene; b) ethanol; and, c) acetylene. The images are of the nascent soot, before oxidation.

NOTE: DOE OFCVT funded research currently proposed

Spherule Aggregation Yields Particulate a.k.a. acinoform carbon

A.A. Onischuk et al. / Aerosol Science 34 (2003) 383–403 399

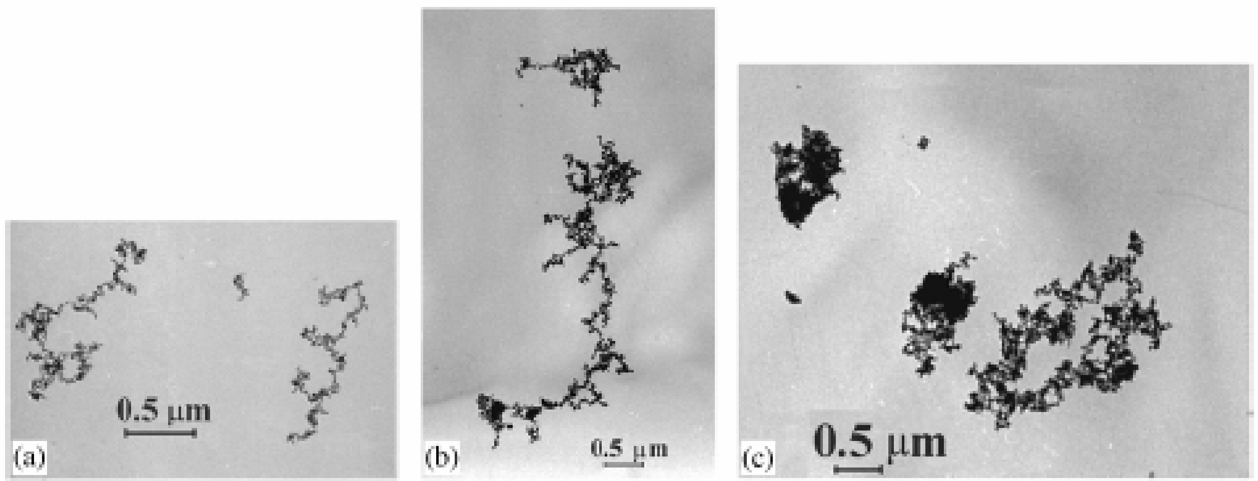
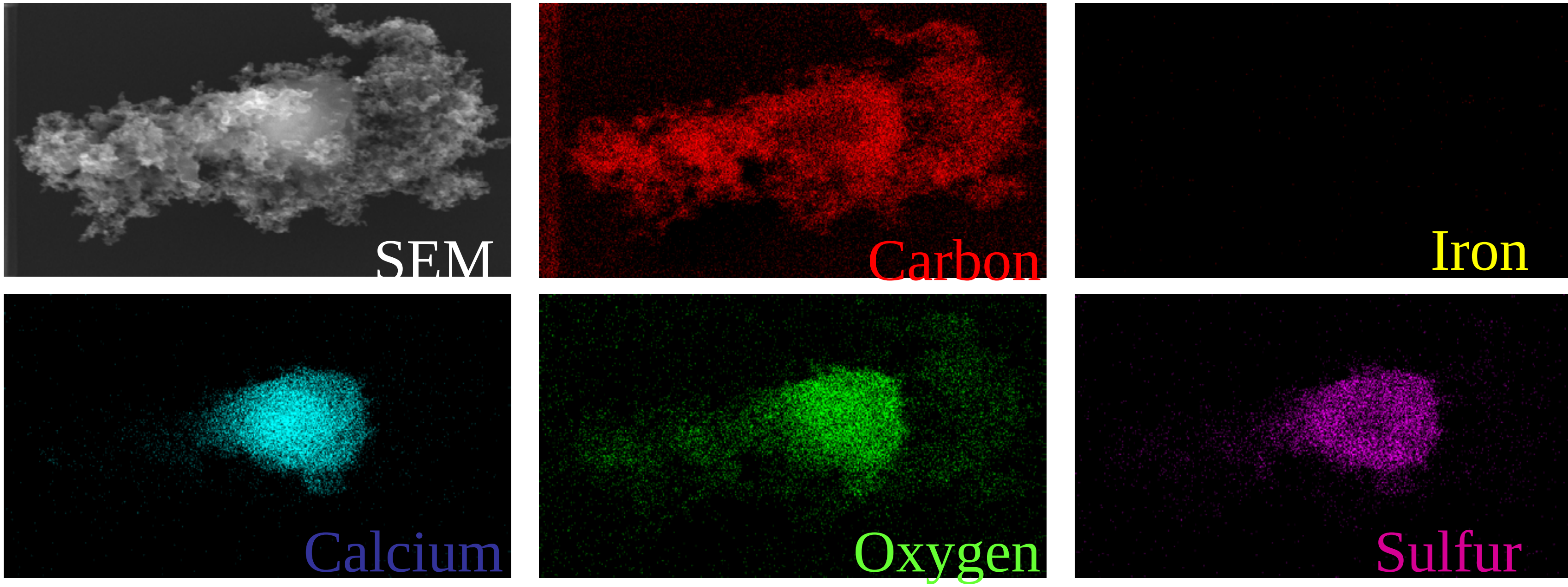


Fig. 20. TEM micrograms of soot aggregates formed at different times of coagulation t in the afterflame zone. (a) $t = 10$ s, chain-like aggregates; (b) $t = 140$ s, chain-like aggregates, and (c) $t = 1000$ s, compact aggregates. Initial time $t = 0$ s corresponds to the moment of sucking at the height above burner of 30 cm (see Fig. 1).

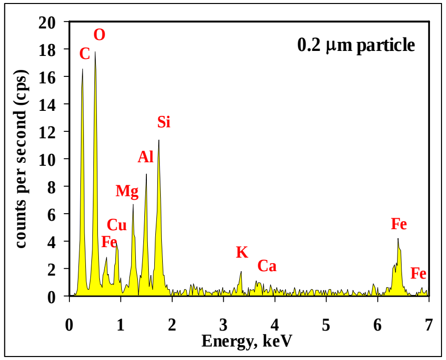
Reality - Soot Bouillabaisse



EDX elemental mapping of internally mixed diesel soot particle of ~2 μm size.

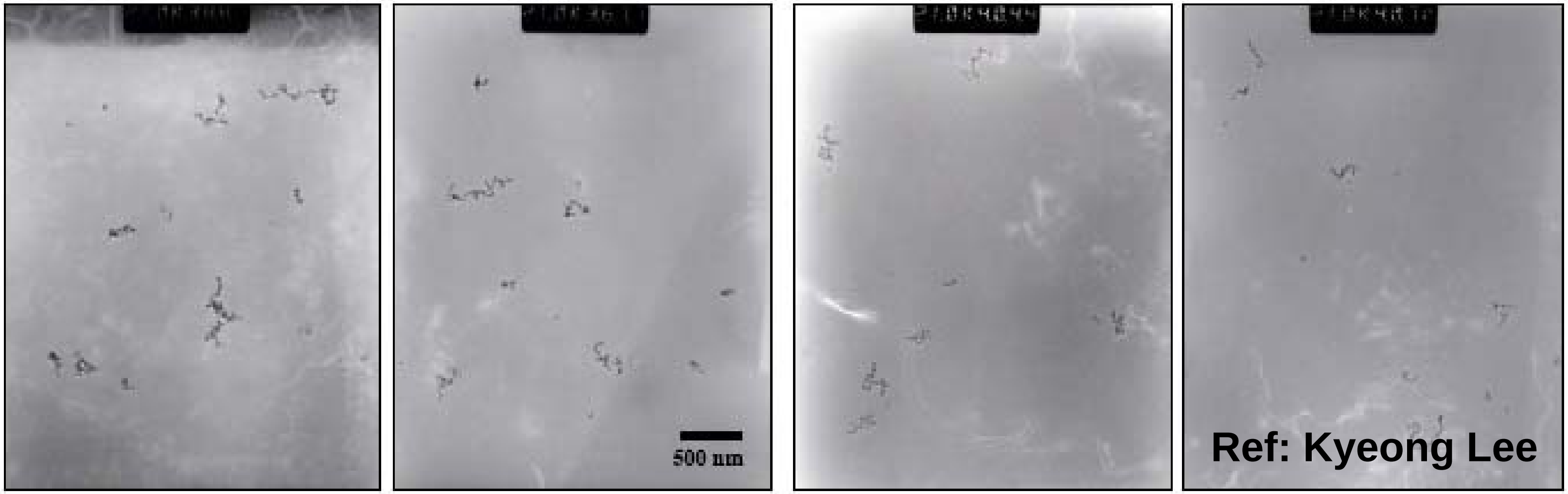
ref: PNNL data, ESEM/EDX analysis

NOTE: DOE funded research at PNNL

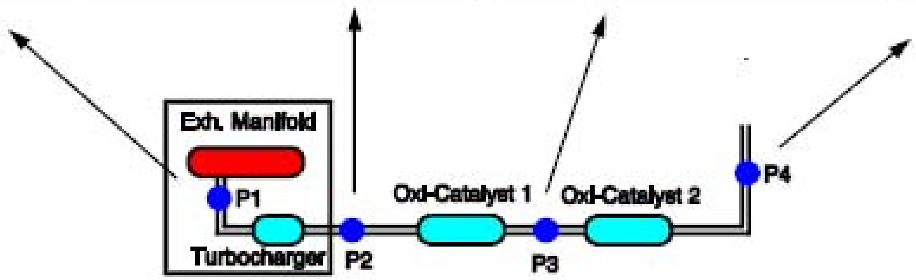


TRANSPORT/EVOLUTION

Particulate Evolution Effects



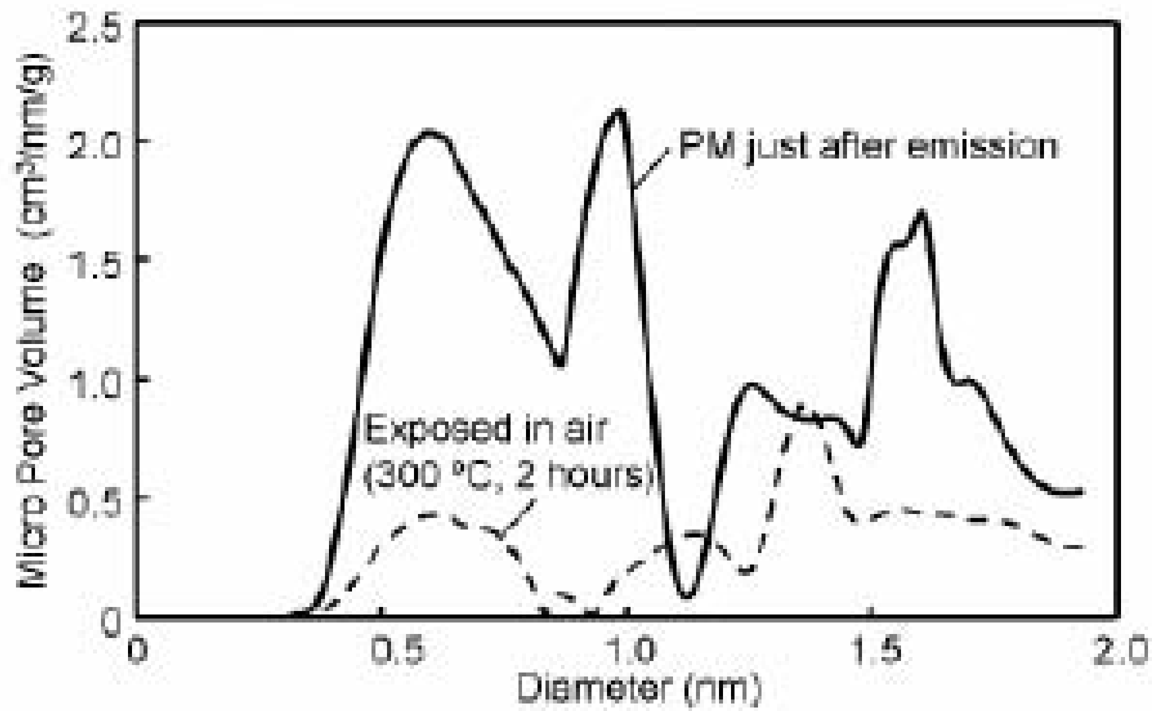
2500 rpm
25 % load



Particle size
& concentration

NOTE: DOE OFCVT funded research at ANL

Diesel Particulates Age



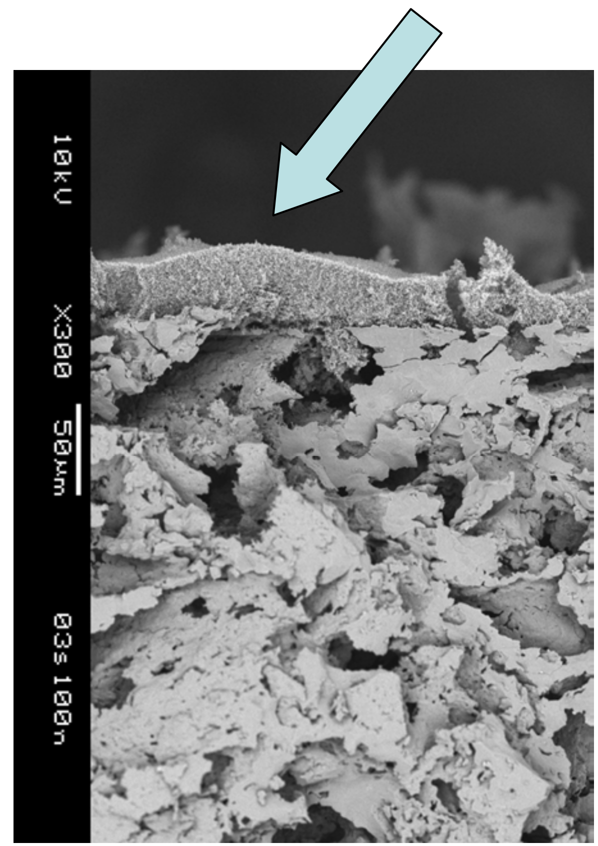
Fresh soot has more micropores and higher activity than older soot

Ref: Toyota

DEPOSITION

Soot Filter Devices

- Extremely effective
- Captures most forms of PM
- Many physical designs
- Many material choices
- Majority rely on…
  - Cake filtration, or
  - Depth filtration, or
  - Both
- They plug up



Action is at the Deposition Scale

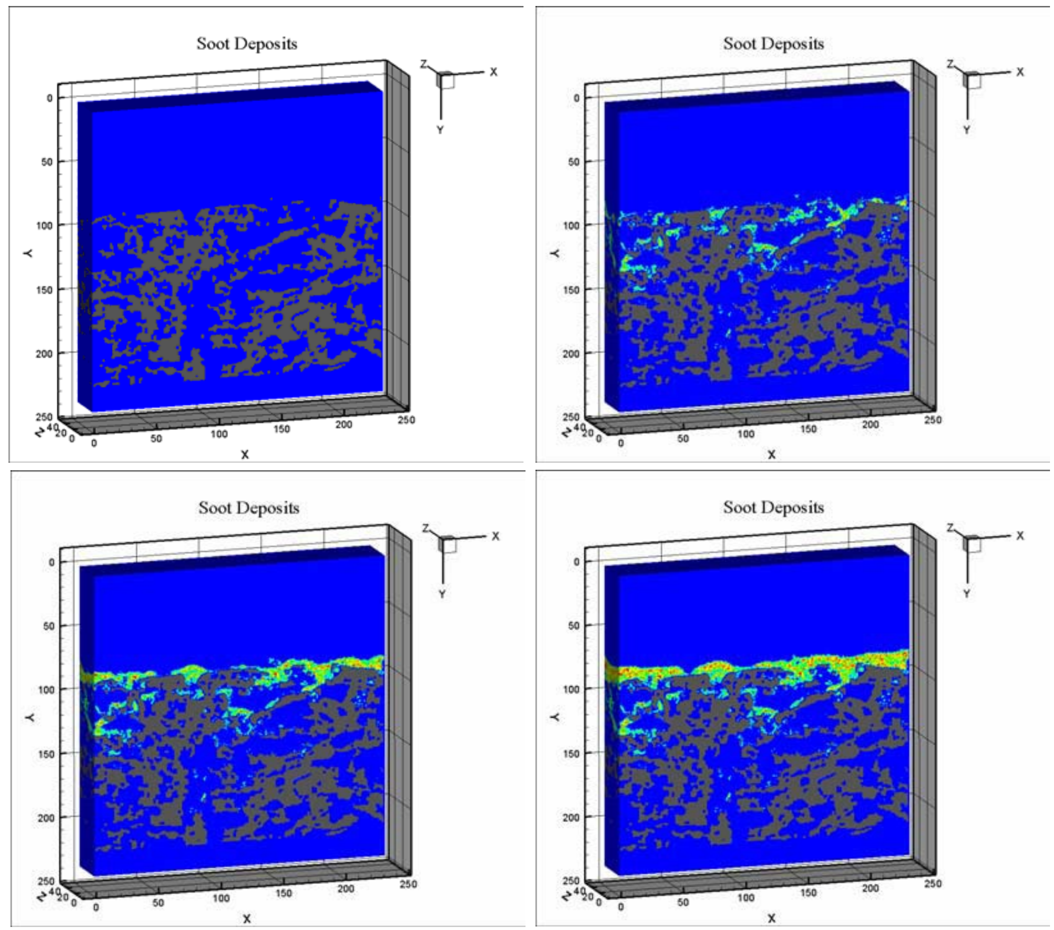
- filter plugging
- thermal failures
- filtration performance
- size and cost
  - efficient regen.

Cake Layer

- only ~15-50 microns thick
- involves heat & mass transfers, aerosol deposition, surface chemistry, catalysis...

Model Results – Deposit Formation
ref: CLEERS DPF

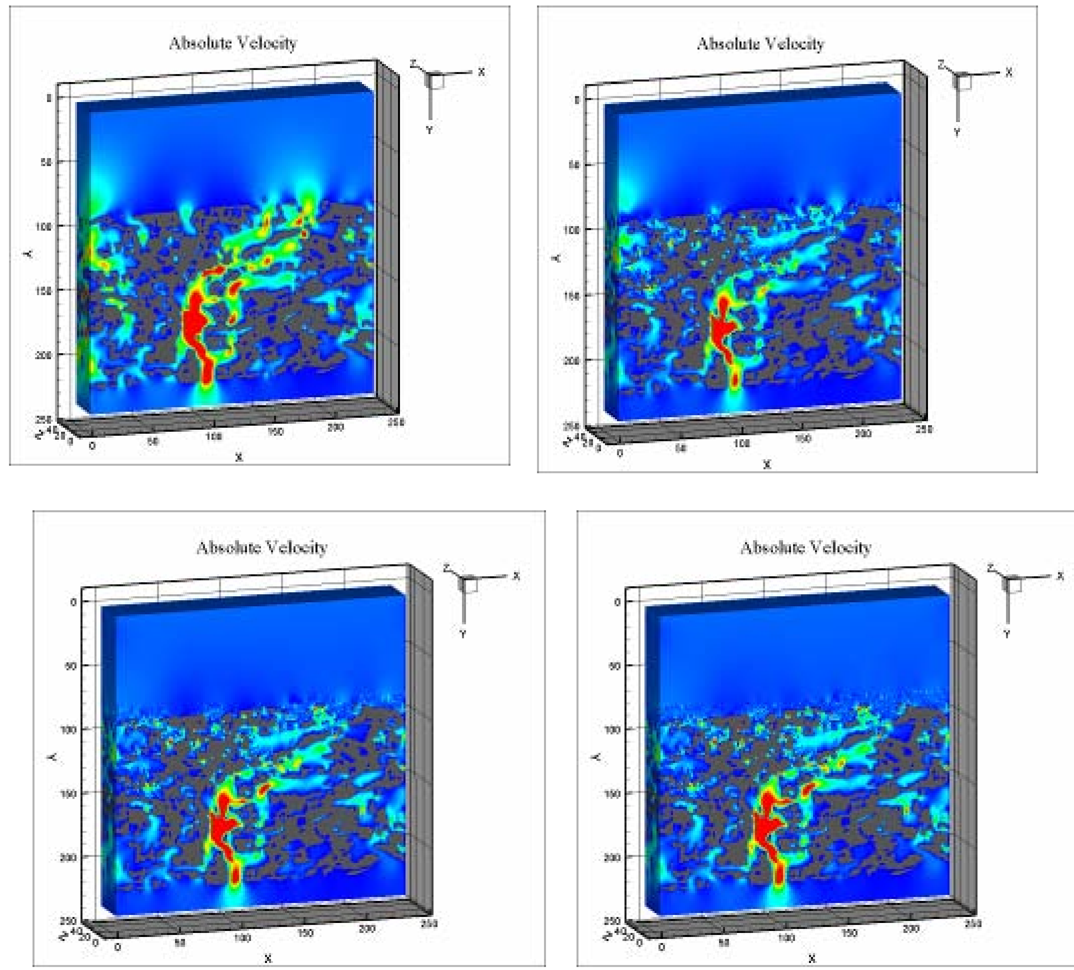
- Substrate shown in dark grey
- Deposit density indicated by color
- Initial deep bed filtration
- Transition to cake filtration



NOTE: DOE OFCVT funded research at PNNL

Model Results – Flow Field

- Soot has little impact on flow field deep within substrate (*most of the time*)
- Bulk of flow passes through a few major flow routes
- Flow near surface is redistributed by dense deposits

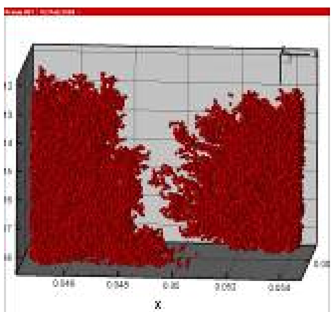


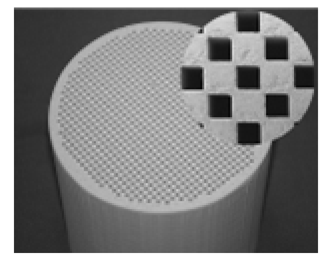
The State of the Science

The Multi-scale Dilemma

How do you experimentally validate the fine scale models?

How do you best add value to device scale models using the fine scale models?





Particle **Pore** **Channel** **Device** **System**

10^{-9} (nm) **10^{-8}** **10^{-7}** **10^{-6}** (µm) **10^{-5}** **10^{-4}** **10^{-3}** (mm) **10^{-2}** **10^{-1}** **10^{0}** (m)

meters

NOTE: DOE OFCVT funded research at PNNL/ORNL

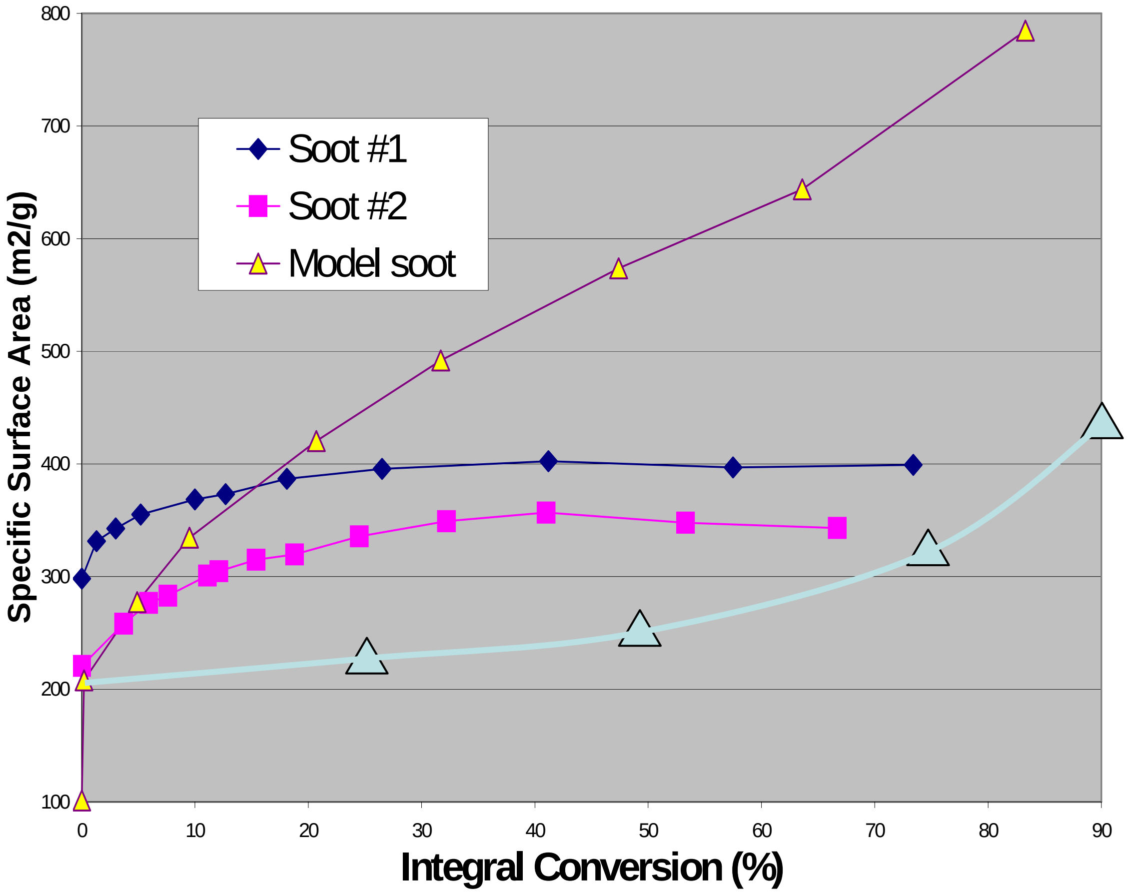
Destruction

Destruction

- Combustion Triangle
  - Fuel
    - How does each part of the particle burn?
  - Oxidizer
    - What is delivering the oxygen to the carbon and how?
  - Heat
    - What are the local heat and mass transfer conditions?

- Ultimately: $C_{(s)} + O_2 \rightarrow CO_2$

Shrinking Core Model



Ref: PNNL & Cummins

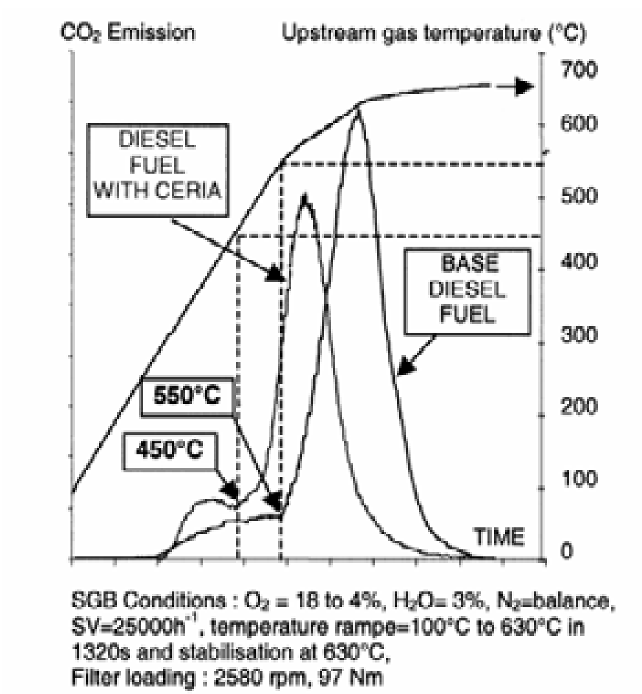
Reaction Kinetics

- General form
  - R(eaction Rate) = N_t * k(T) * $f(p_{o_2}, p_{H_20},\ldots)$
  - Where k(T) = temperature dependence
- Simplest assumption
  - k(T) = k_0 * exp(-E_a/RT) “Arrhenius equation”
  - E_a = activation energy
  - Other formulations envisioned, e.g. modified Arrhenius
- Activation Energy
  - Wide range reported in literature
    - 36 kJ/mol to 170 kJ/mol (ref: Yezerets, et al 2002-01-1684)
  - Highly dependant on methodology, H_2O, soot…

The State of the Science

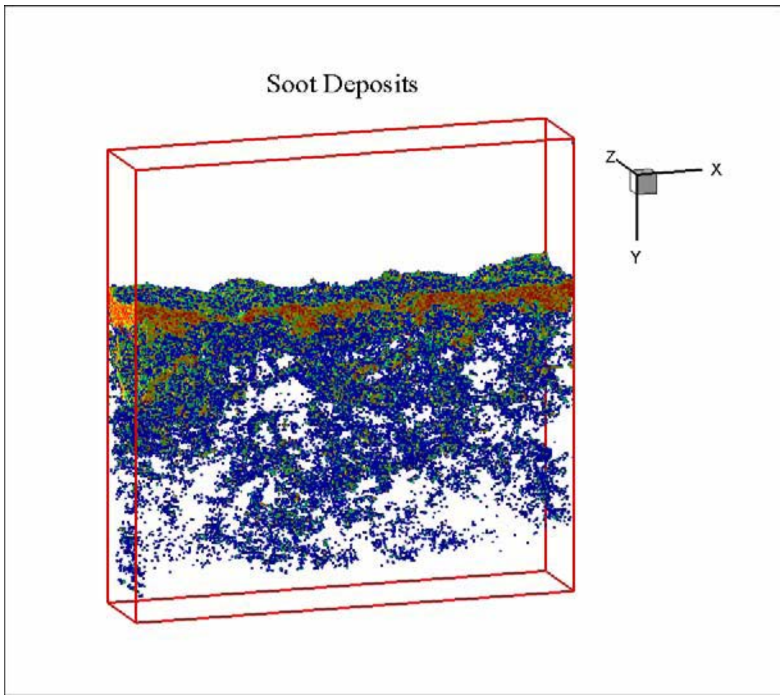
The Multi-scale Dilemma (again)

Model Results:
Chemistry, Mass, and Heat Transfer Intimately Coupled



SGB Conditions : O_2 = 18 to 4%, H_2O= 3%, N_2=balance, SV=25000h^{-1}, temperature rampe=100°C to 630°C in 1320s and stabilisation at 630°C,
Filter loading : 2580 rpm, 97 Nm

Figure 3. Thermal Gravimetric comparison between Ceria additized and non additized particulate



Ref: Peugeot DPF SAE paper

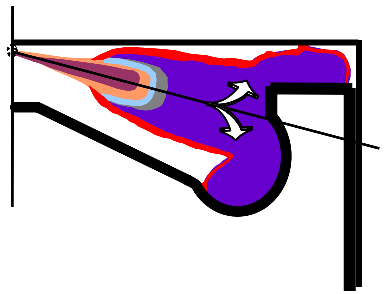
Future Activities
ref: CLEERS DPF

OXIDATION

- Incorporate “clean” data into models
  - TGA derived reaction rates
  - also, reaction orders in carbon and oxygen
- Translate “clean” data into appropriate global parameters for device models
  - global rates are different than local rates
  - ignition, flames, and propagation are confounding effects

NOTE: DOE OFCVT funded research at PNNL (CLEERS)

In conclusion - Much still to be done



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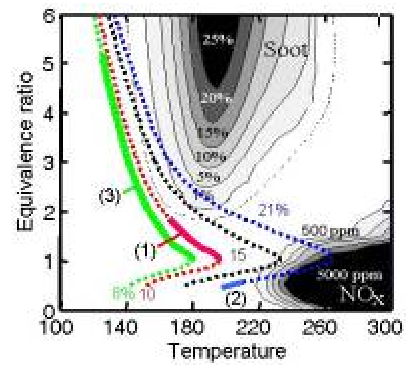
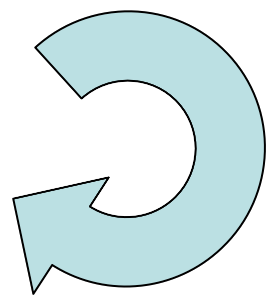
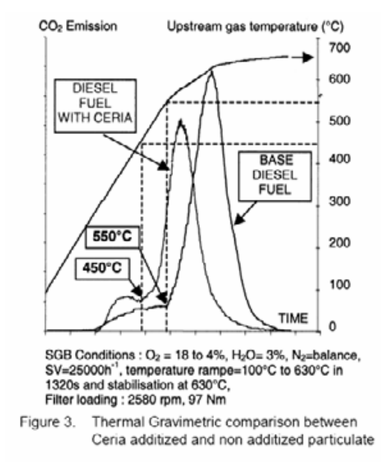


Formation



Deposition



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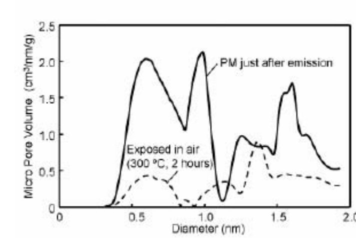
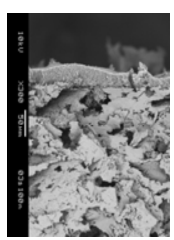
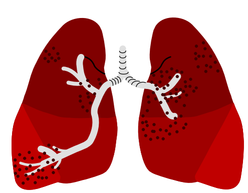
Destruction



Fresh soot has more micropores and higher activity than older soot





Transport/
Evolution