Soot Formation and Oxidation at Elevated Pressures

Med Colket

Workshop on Techniques for High Pressure Combustion

Argonne National Laboratories, Chicago, Ill

August 29 – September 1, 2011

United Technologies Research Center

SERDP

DoD EPA DOE

Strategic Environmental Research and Development Program

Background

- Global Warming:
  - Studies suggesting that soot and related particulates contribute significantly to global warming
  - Changes in fuels has large 1st order effect on particulate emissions
- Health:
  - Increased understanding of health risks associated with ultrafine particles
- Regulation:
  - Enactment of EPA PM2.5 ambient standards (mass of particles below 2.5 microns)
  - Concern that local site implementation plans may limit commercial airline traffic or introduction of new engines/planes
- Durability:
  - Impact of soot radiation on combustor liners and related hardware
  - Soot deposition on surfaces
- Challenges:
  - Predicting or measuring time- and spatially-dependent soot fields (even at atmospheric pressure factor of two is best achievable)

Objectives and Outline

Objectives:

- Review challenges in modeling and measurements of soot at elevated pressures

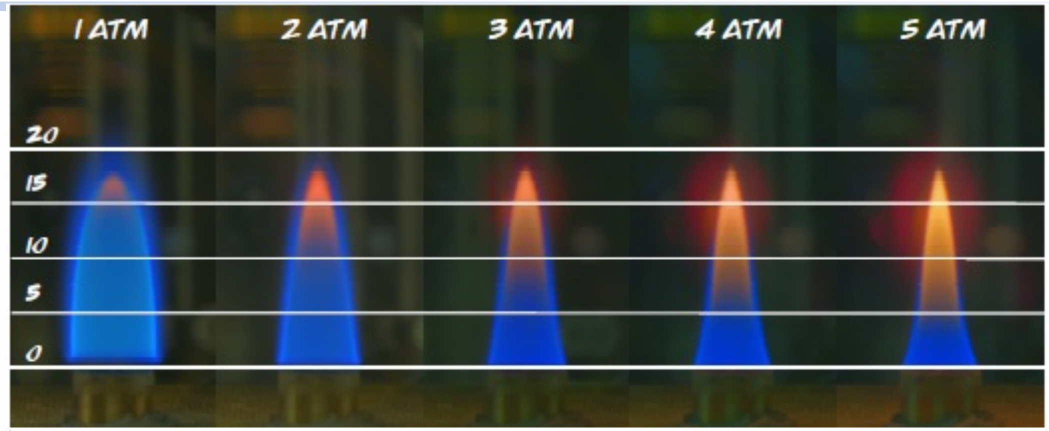
Outline:

- Observations of soot formation in combustors
  - Laboratory
  - Gas Turbine Combustor
  - Diesel spray
- Soot fundamentals
- Modeling
  - Approach
  - Simulation of pressure dependence
  - Simulation soot evolution in RQL combustor
- Conclusions/Recommendations

Images and LII Signals from Coflow Diffusion Flames

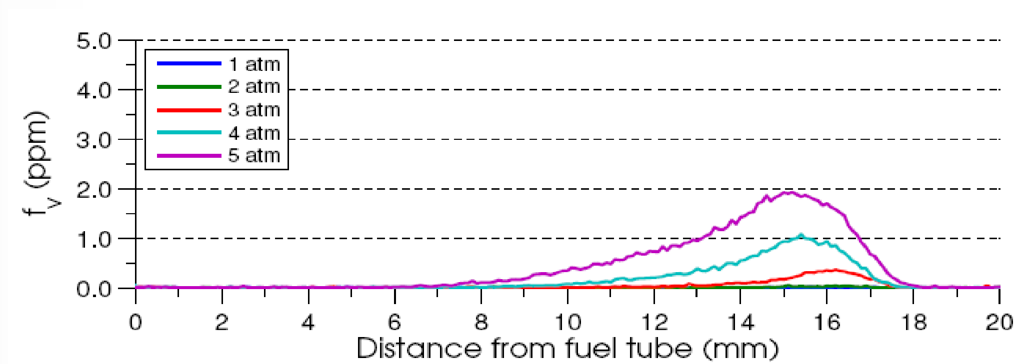
CoFlow C2H4 diluted flame
Courtesy of Bob Santoro, PSU

Photographs



Laser Induced Incandescence

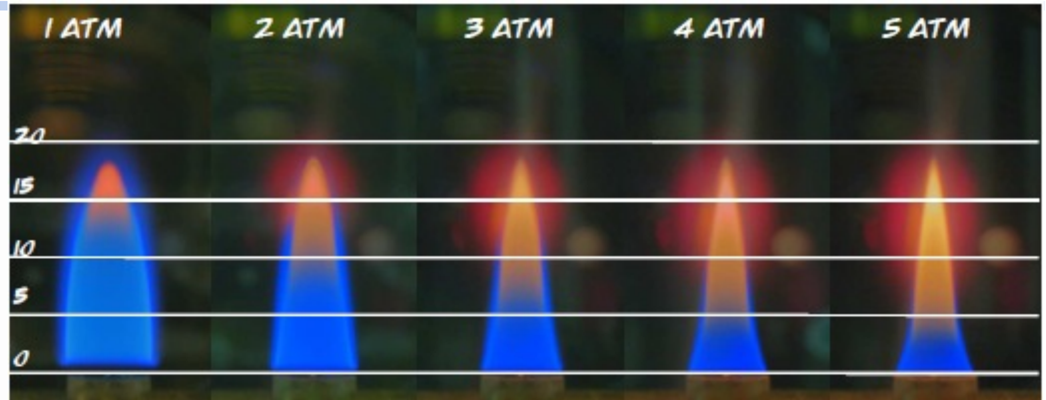
Computed soot volume fractions (f_v) with height



Images and LII Signals from Coflow Diffusion Flames

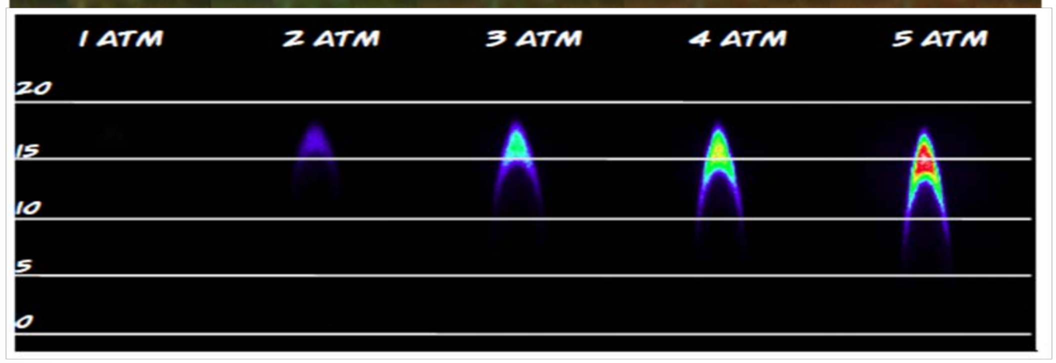
CoFlow C2H4 diluted flame
with 5% m-xylene
Courtesy of Bob Santoro, PSU

Photographs

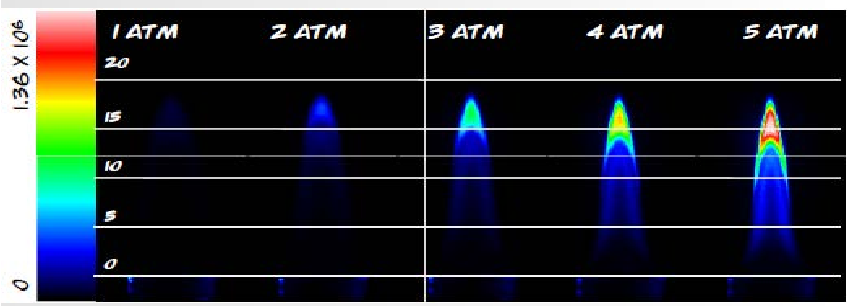


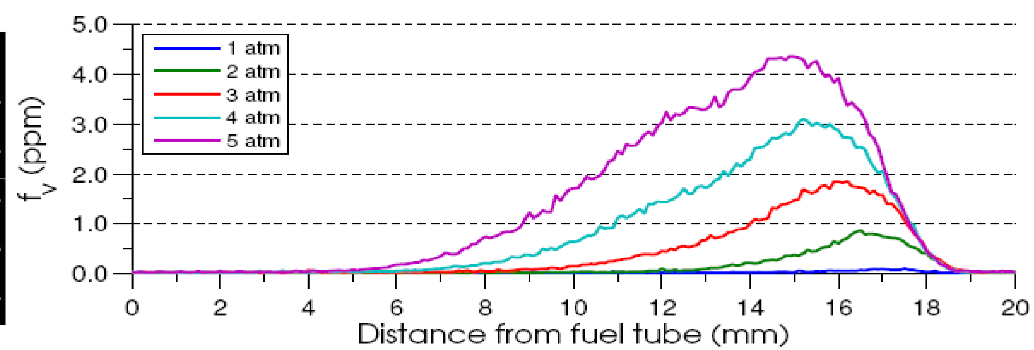
Temperature and OH
profiles also available

Laser Induced
Incandescence



PLIF images of large PAH

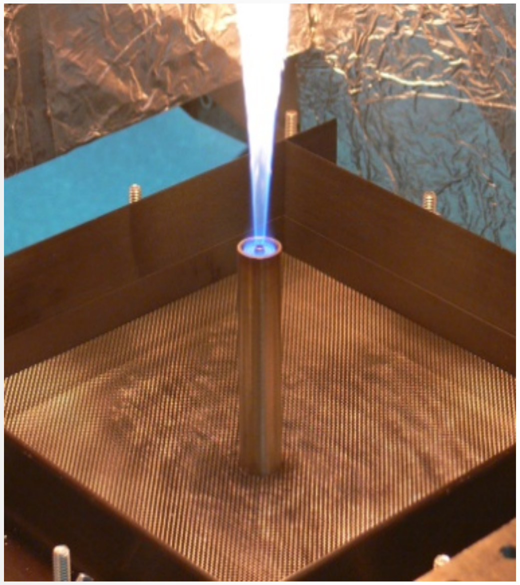


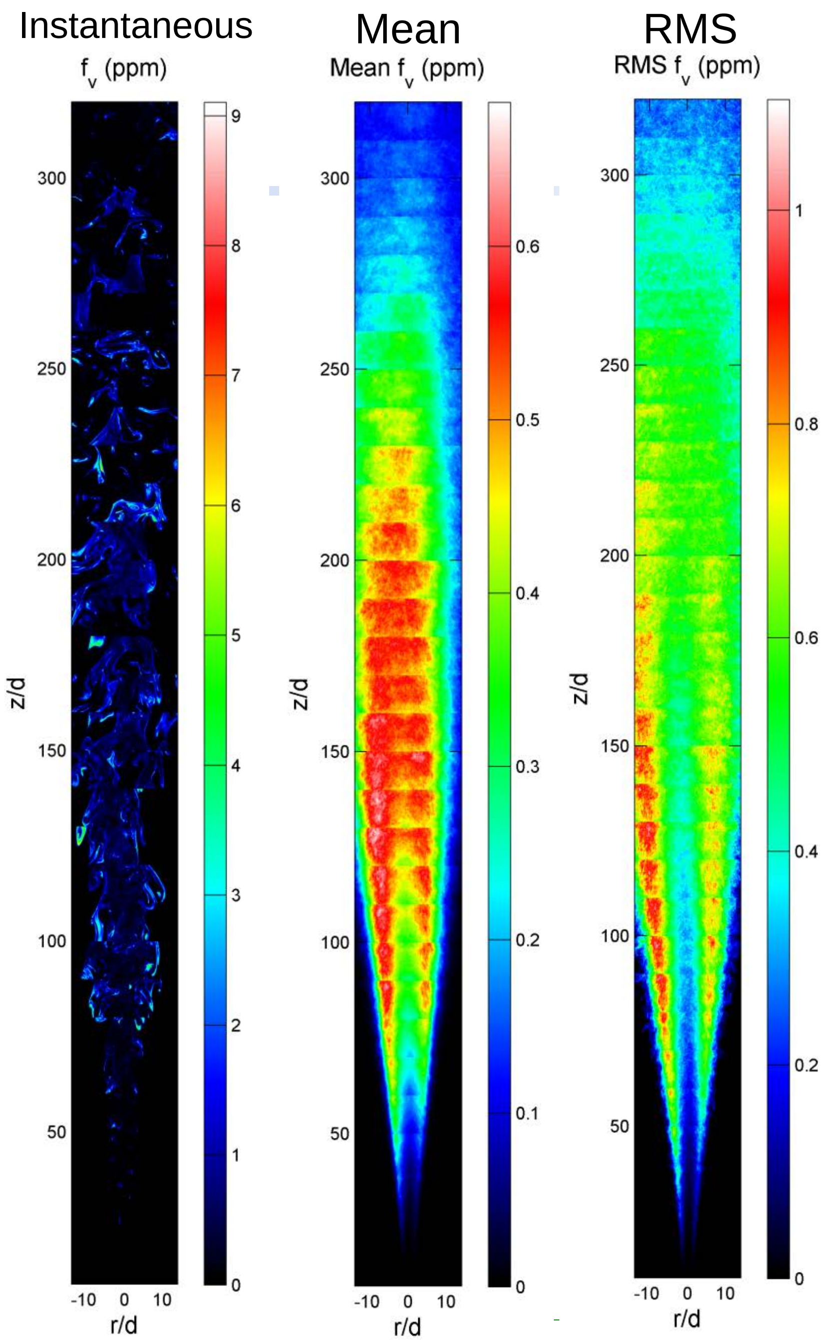


Soot in Turbulent Surrogate JP-8 Jet Flame (1 atm)

Courtesy of Shaddix and Pickett, Sandia
Re no. ~ 20,000

Photograph of flame base

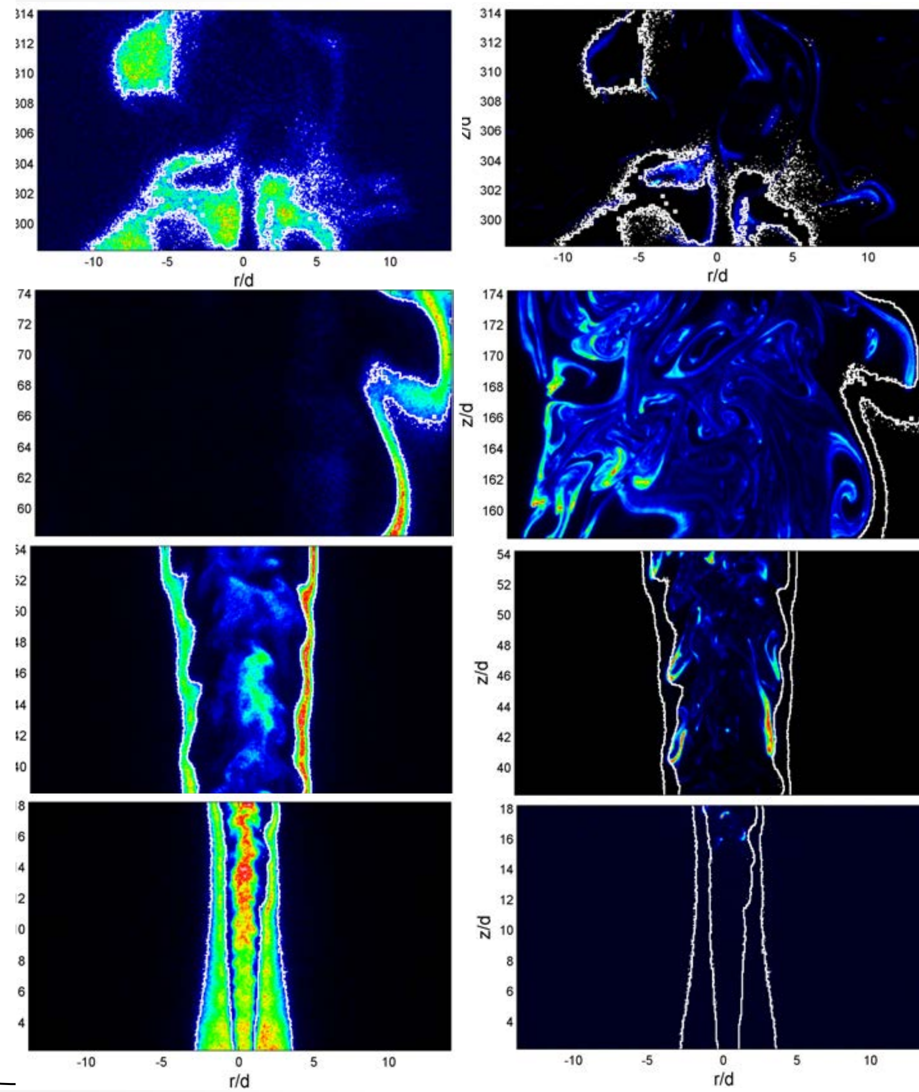




Instantaneous, mean, and rms soot volume fractions (f_v) measured by LII imaging. The mean and rms statistics are computed from 1000 instantaneous images taken at each height.

Soot, OH, PAH in turbulent 'JP-8' jet (Re ~ 20,000)

Courtesy of Chris Shaddix and Lyle Pickett, Sandia



LIF from OH• and PAH (in interior regions, particularly low in flame)

1 atm

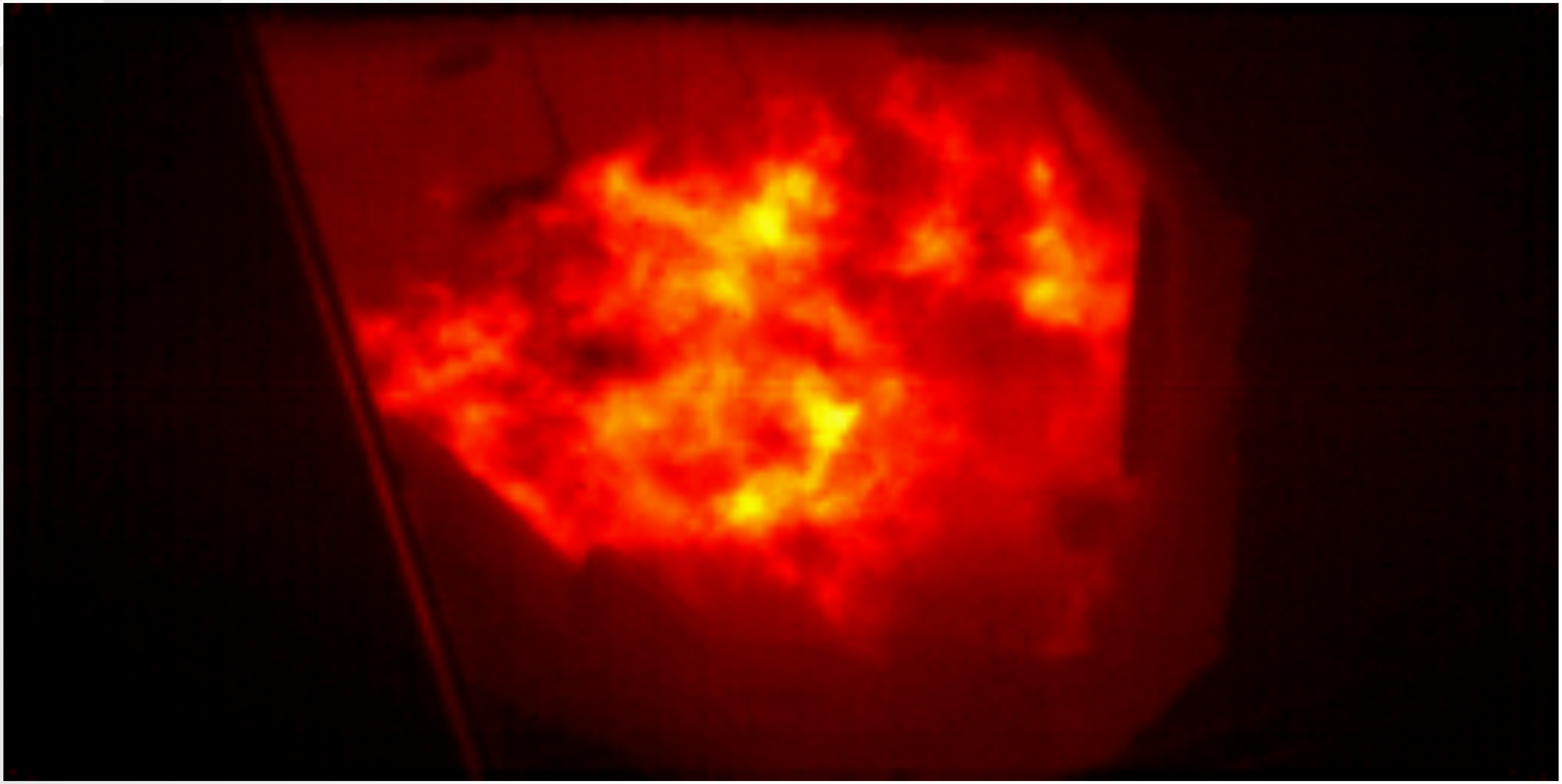
Soot LII, with boundaries of OH• in white

High speed video of Soot Formation (1 atm) - lean

Gas Turbine combustion
(Courtesy of M. Roquemore, AFRL)

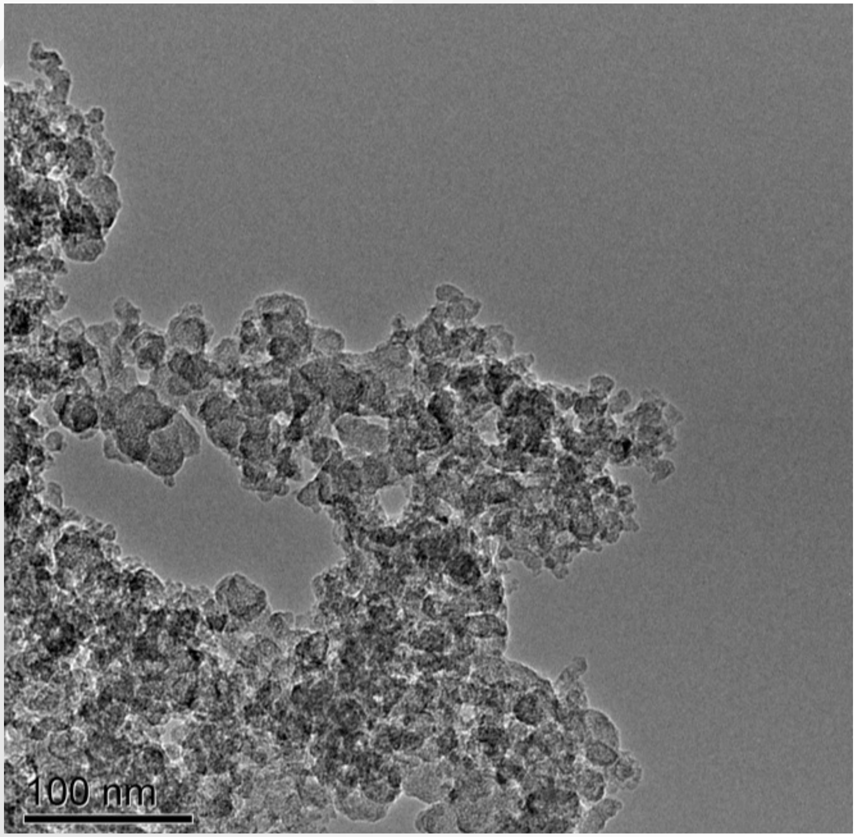
Video of soot formation at 10 atmospheres – less lean

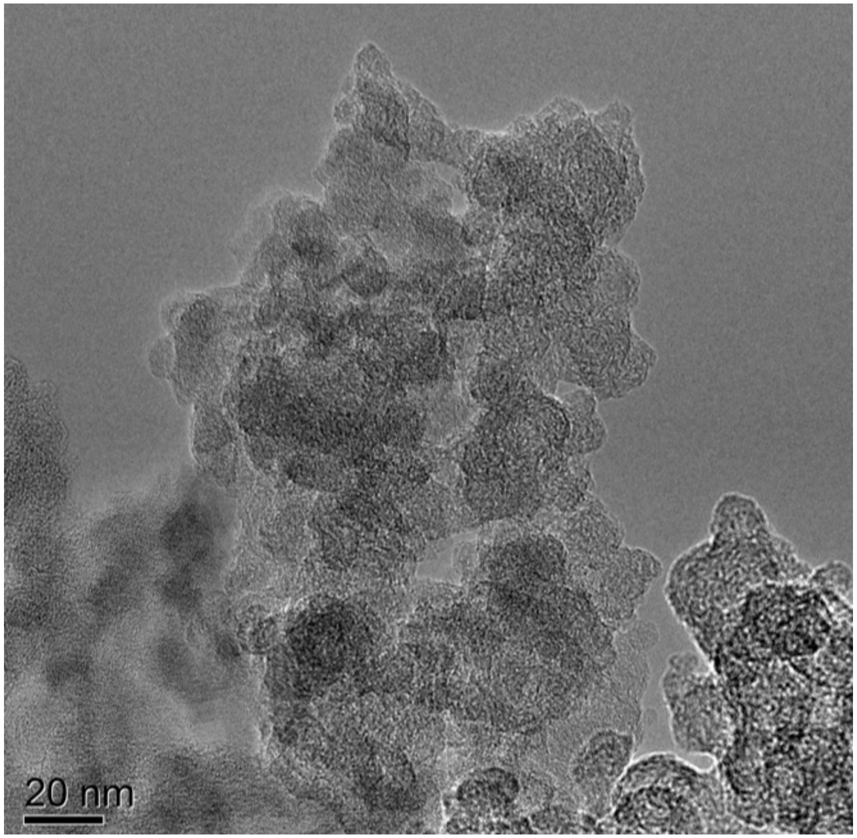
Gas Turbine combustor
Courtesy of M. Roquemore, AFRL – 20,000 FPS)



TEM photographs of soot from gas turbine (80% power)

Gas Turbine combustor
Courtesy of Randy Vander Wal, PSU)





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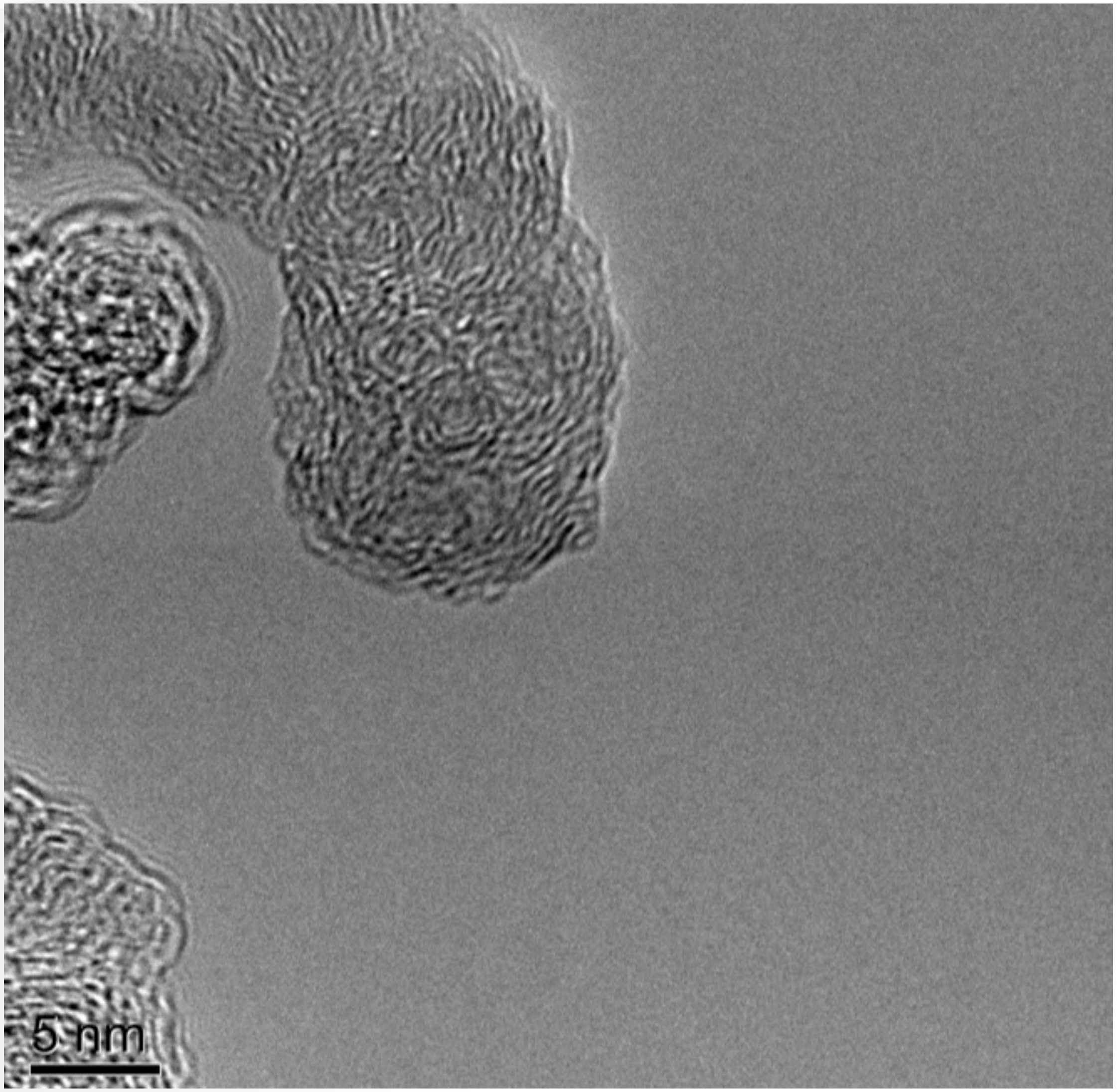
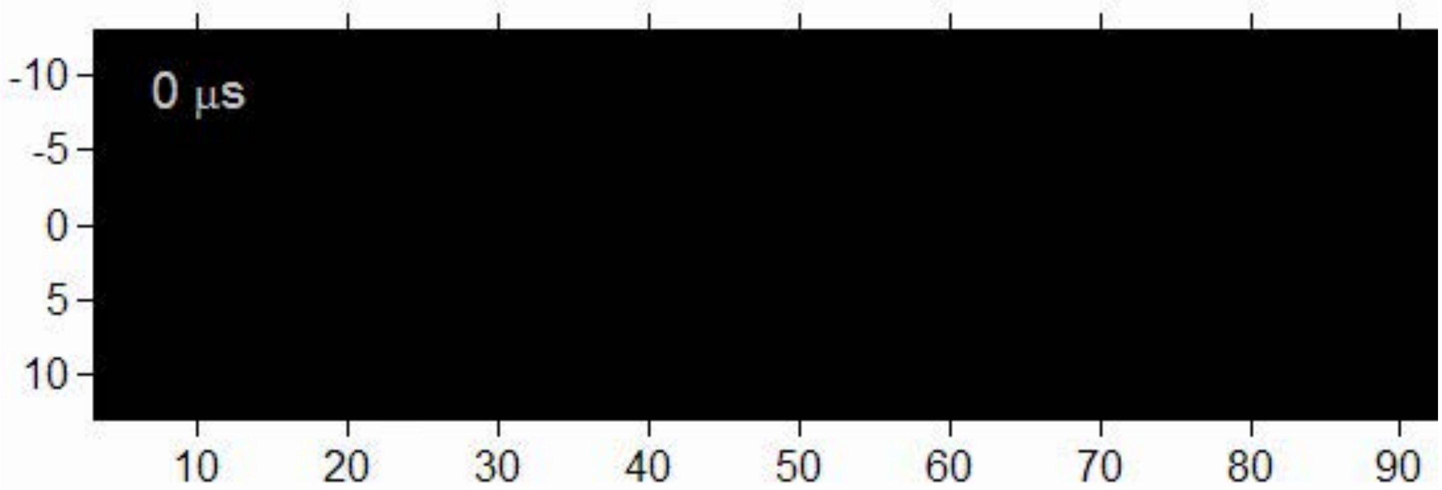
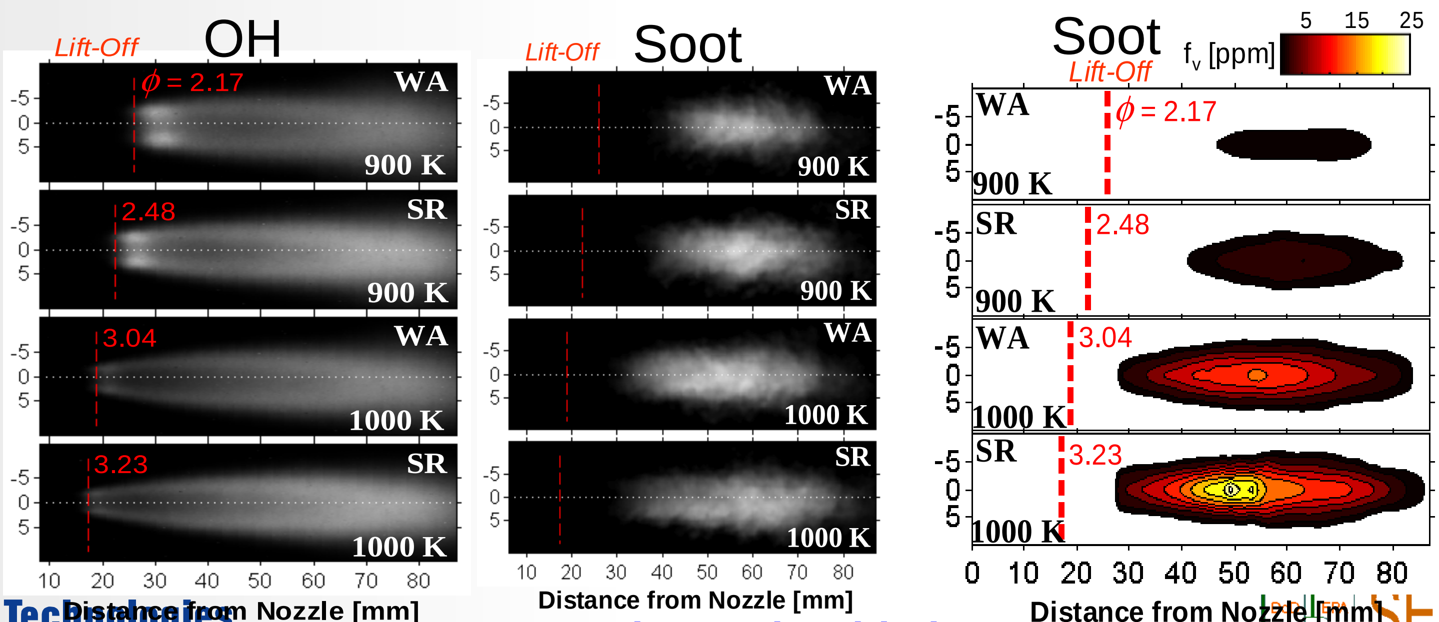


Soot Formation Following Ignition (at 40 atmospheres)



Ignition and soot formation in diesel fuel spray (JP-8) Courtesy of Lyle Pickett and Chris Shaddix (Sandia)

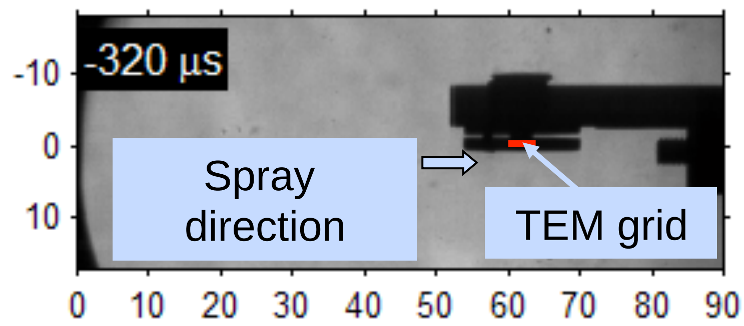


Soot Formation and Oxidation

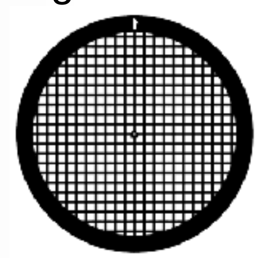
Soot sampling from sprays within high-temperature, high-pressure combustion vessel

From Kook and Pickett, PROCI, 33, 2011

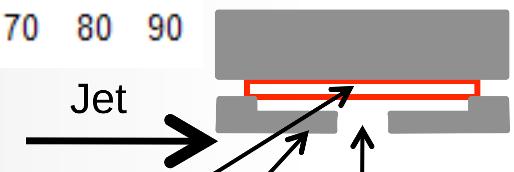
TEM probe within the combustion vessel



3 mm diameter TEM grid:



copper mesh covered by an amorphous carbon film

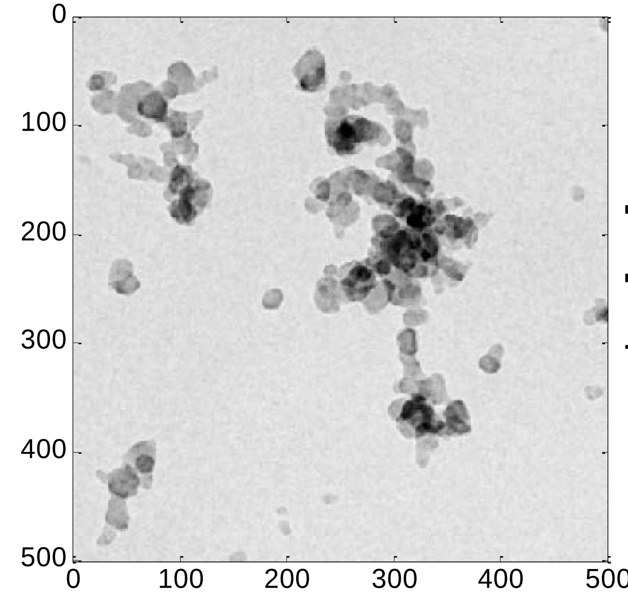


TEM grid held within the probe to protect it from excessive heating

Restrictive passage quenches reaction and protects the TEM grid.

Soot-laden gas skims past the probe, enters through a 1-mm diameter hole, and deposits on the TEM grid.

TEM image of soot particles



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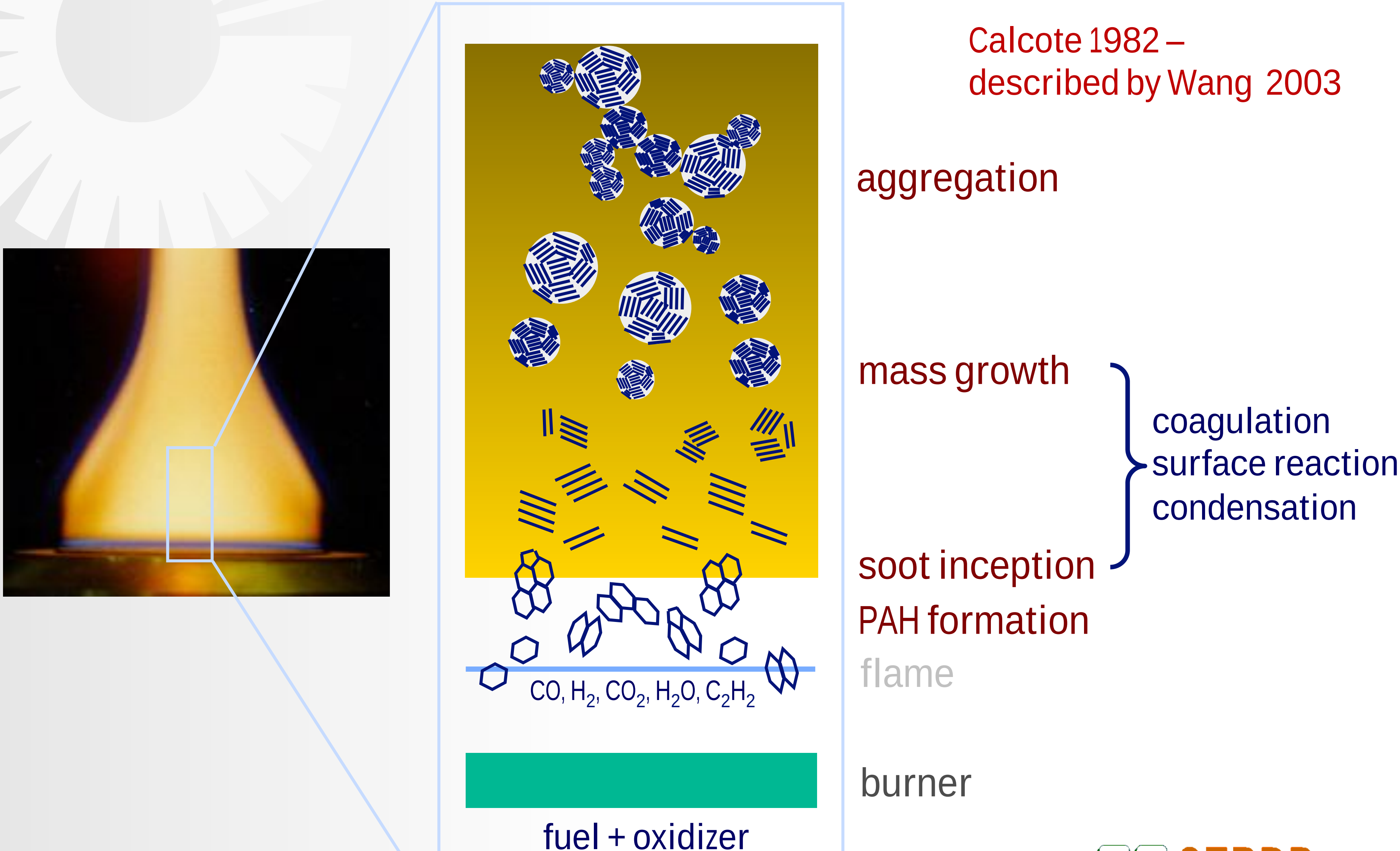
‘Sooting’ PSR Based upon established particle physics

Processes all occur simultaneously in well-mixed systems (stirred reactor)

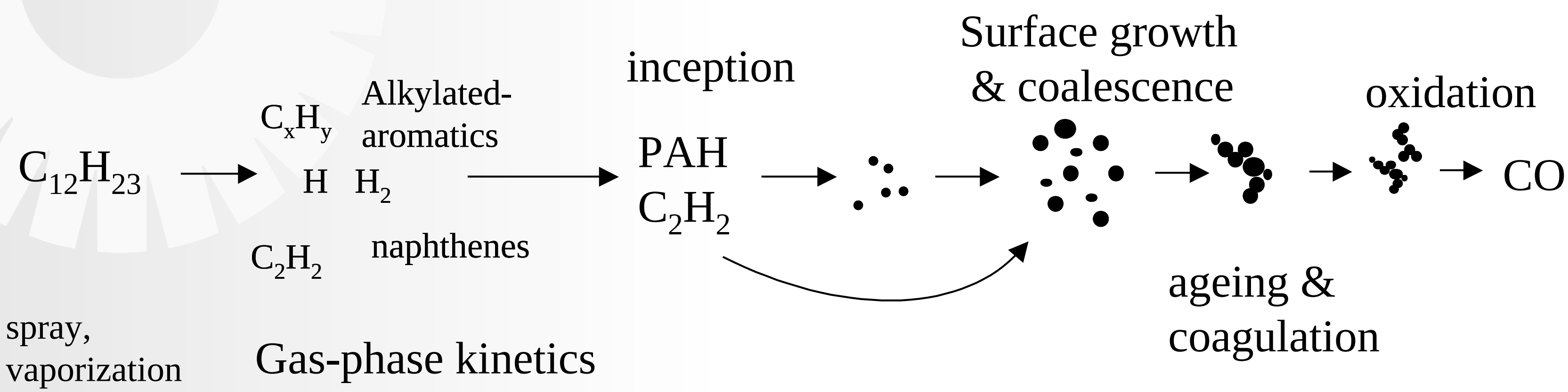
Calcote 1982 –
described by Wang 2003



Soot Formation and Oxidation

Physics for Treatment of Soot/Particle Emissions

Physical Processes in Soot Formation



Sooting NETPSR code includes detailed treatment of particle inception, surface growth, surface oxidation, aerosol particle dynamics (sectional) to predict particle size distribution through reactor network (simulated combustor)

Gas-Phase Kinetics

Combustor*

- Detailed reaction mechanism from Babushok and Tsang (2004) – heptane
- Includes PAH fomation, truncated above 202 amu
- Total mechanism: ~240 species and ~1500 reactions

Soot Kinetics

Inception and Growth based upon prior work

Inception: Dimerization of pyrene (and other 202 amu species), after Appel, et al, 2000.

$$dS_1/dt = k[C_{16}H_{10}]^2$$

Surface Growth: Mass growth onto any particle is assumed be proportional to particle surface area, after Colket and Hall, 1994 (MODFW)

$$H + C(s) \Leftrightarrow \dot{C}(s) + H2$$
$$H + \dot{C}(s) \Leftrightarrow C(s)$$
$$\dot{C}(s) \Leftrightarrow C2H2 + products$$
$$C2H2 + \dot{C}(s) \Leftrightarrow C(s)CH\dot{C}H$$
$$C(s)CH\dot{C}H \Leftrightarrow C'(s) + H$$

Soot Kinetics

Based on OH, O_2 and available particle surface area

Oxidation by OH – 13% collision efficiency after Neoh, Howard and Sarofim (1981).

$$R_{OH} = (0.13)\, N_{OH} \sqrt{\frac{R_{gas} T}{2\pi W_{OH}}}\ \frac{12}{N_A}\ \text{gm/sec/cm}^2$$

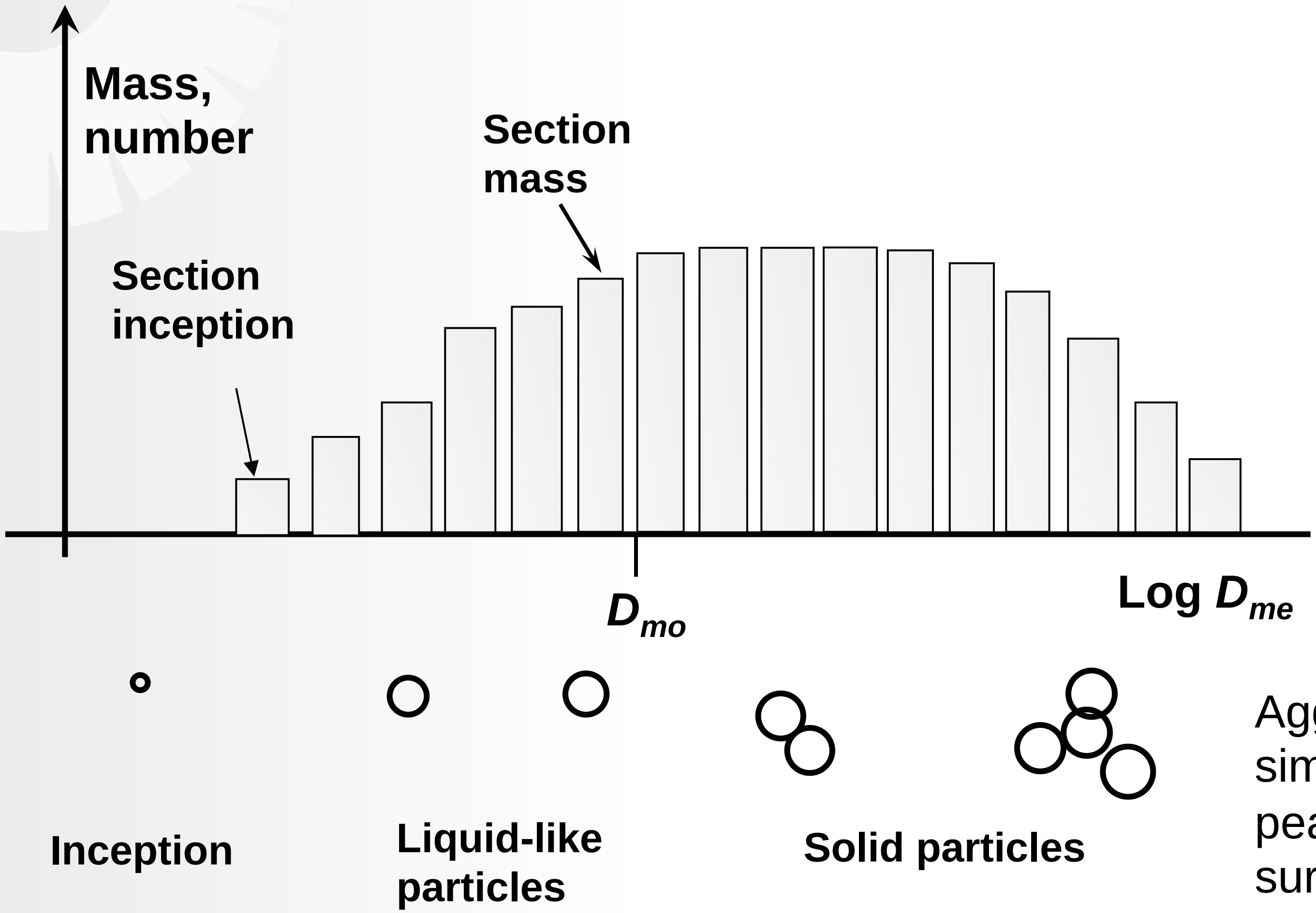
Oxidation by O2 – Nagle and Strickland-Constable (1963)

$$R_{O_2} = 12\left(\frac{K_a P_{O_2} \chi'}{\left(1 + K_z P_{O_2}\right)} + K_b P_{O_2}\left(1 - \chi'\right) \right) \text{gm/sec/cm}^2$$

Sectional Modeling of Soot Growth in PSR Code

Discrete particle size (logarithmic scale)

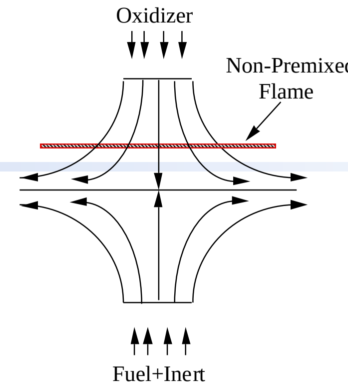
Surface growth and coalescence – based on free molecular form (Kn > 1)*



Agglomeration simulated with peak size for surface growth

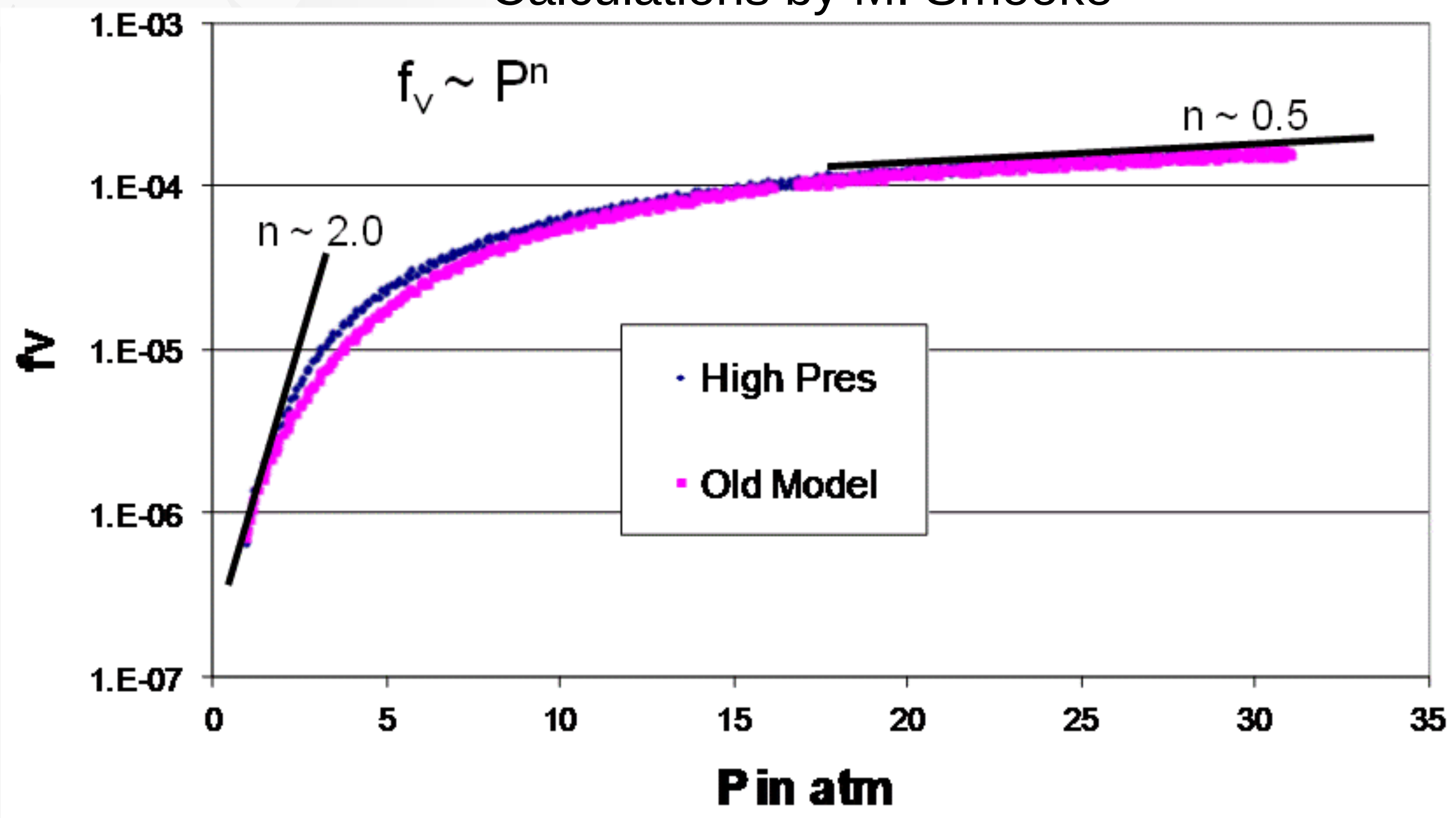
* Follows development by Gelbard and coworkers (see Hall, et al, 1997)

Simulation of Pressure Dependence



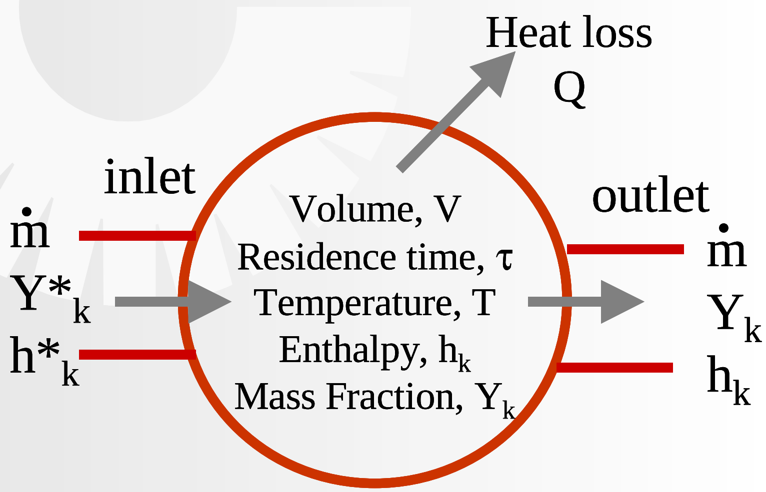
Pressure dependence decreases rapidly for counter-flow diffusion flames

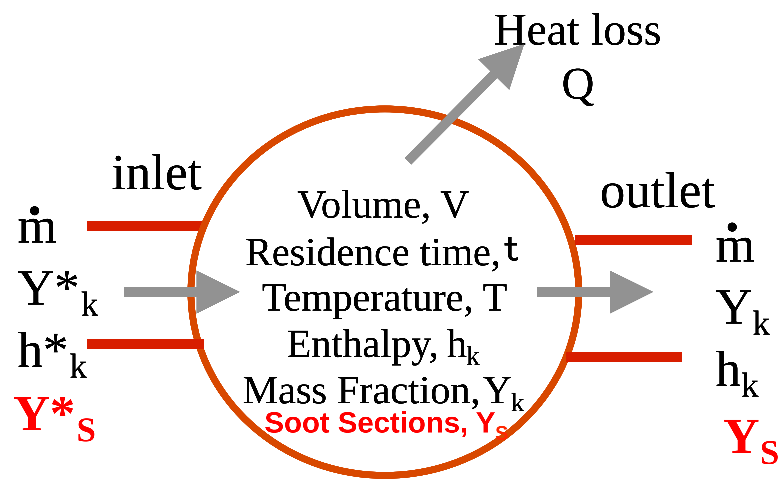
Calculations by M. Smooke



Modeling Approach (single Perfectly Stirred Reactor)

Modify Sandia PSR (CHEMKIN) model by adding sectional soot equations





Conservation equations modified to add sectional equations* to model soot particles, with source terms in species equations to account for scrubbing

Species

$$\dot m(Y_k - Y_k^*) - \omega_k^g W_k V = 0, \quad k = 1,2,\ldots K$$

$$\dot m(Y_k - Y_k^*) - \left(\omega_k^g + \omega_k^s\right) W_k V = 0, \quad k = 1, 2, \ldots K$$

Sectional

$$\dot m(Y_k - Y_k^*) - Q_k V = 0, \quad k = K+1, K+2, \ldots K+M$$

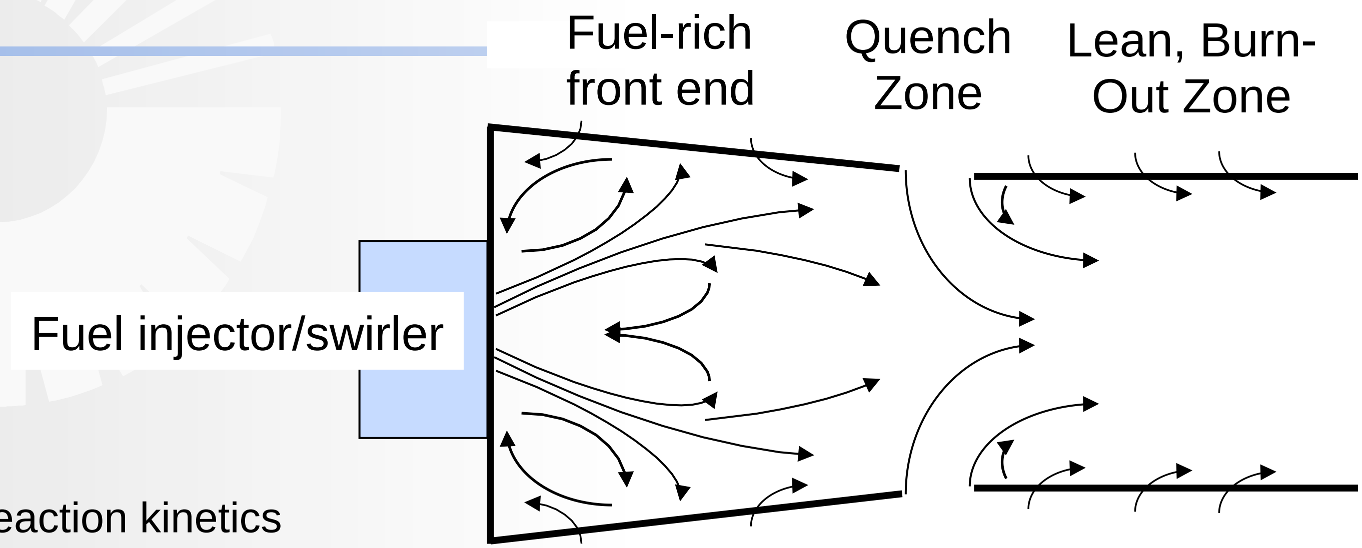
Energy

$$\dot m \sum_{k=1}^{K} (Y_k h_k - Y_k^* h_k^*) + Q = 0$$

$$\dot m \sum_{k=1}^{M} (Y_k h_k - Y_k^* h_k^*) + Q = 0$$

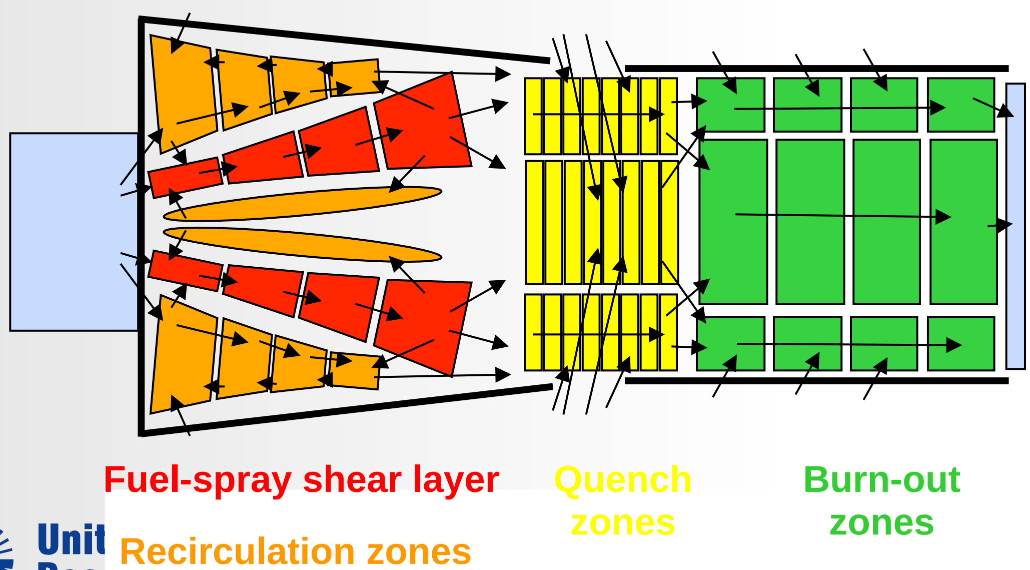
* Sectional equations allow predictions of particle size distributions. Size classes divided by logarithmic scale.

Idealized Rich-Quench-Lean (RQL) Combustor



Full set of reaction kinetics and soot equations solved for each reactor volume

Network Reactor Simulation



Reactor flux, volumes, back-mixing, etc. determined by geometry, flow splits, and empirical tuning to NOx, CO emissions

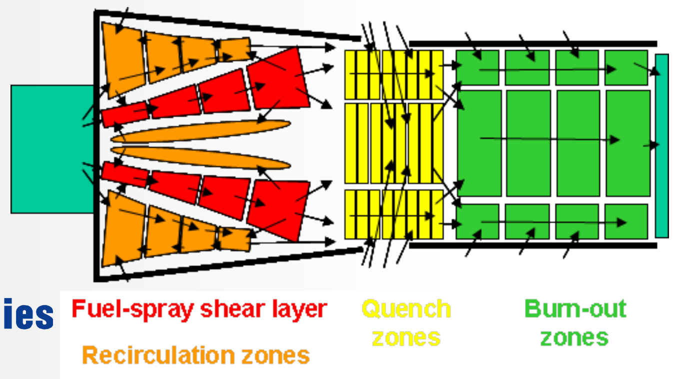
Simulation Results

General characteristics of soot formation, growth and oxidation

- Plotted as function of local equivalence ratio (phi)

Computations of typical particle size distribution and its evolution through combustor

- Fuel-shear layer
- Outer recirculation zone
- Quench zone
- Burn-out zone



Burner conditions:

- Rig simulated Take-off
- T3 = 811K (1000F)
- P3: 16.3 atm

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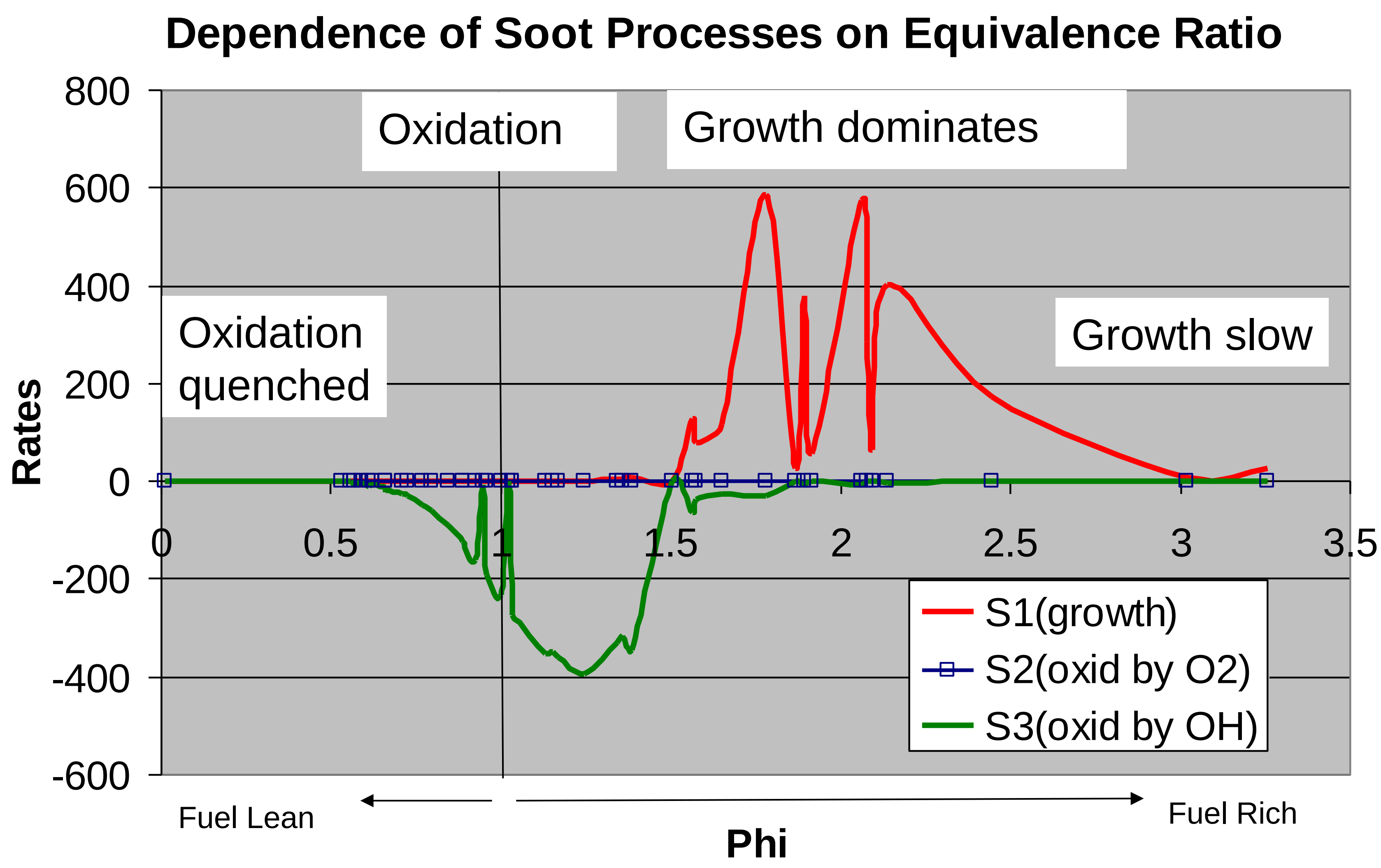
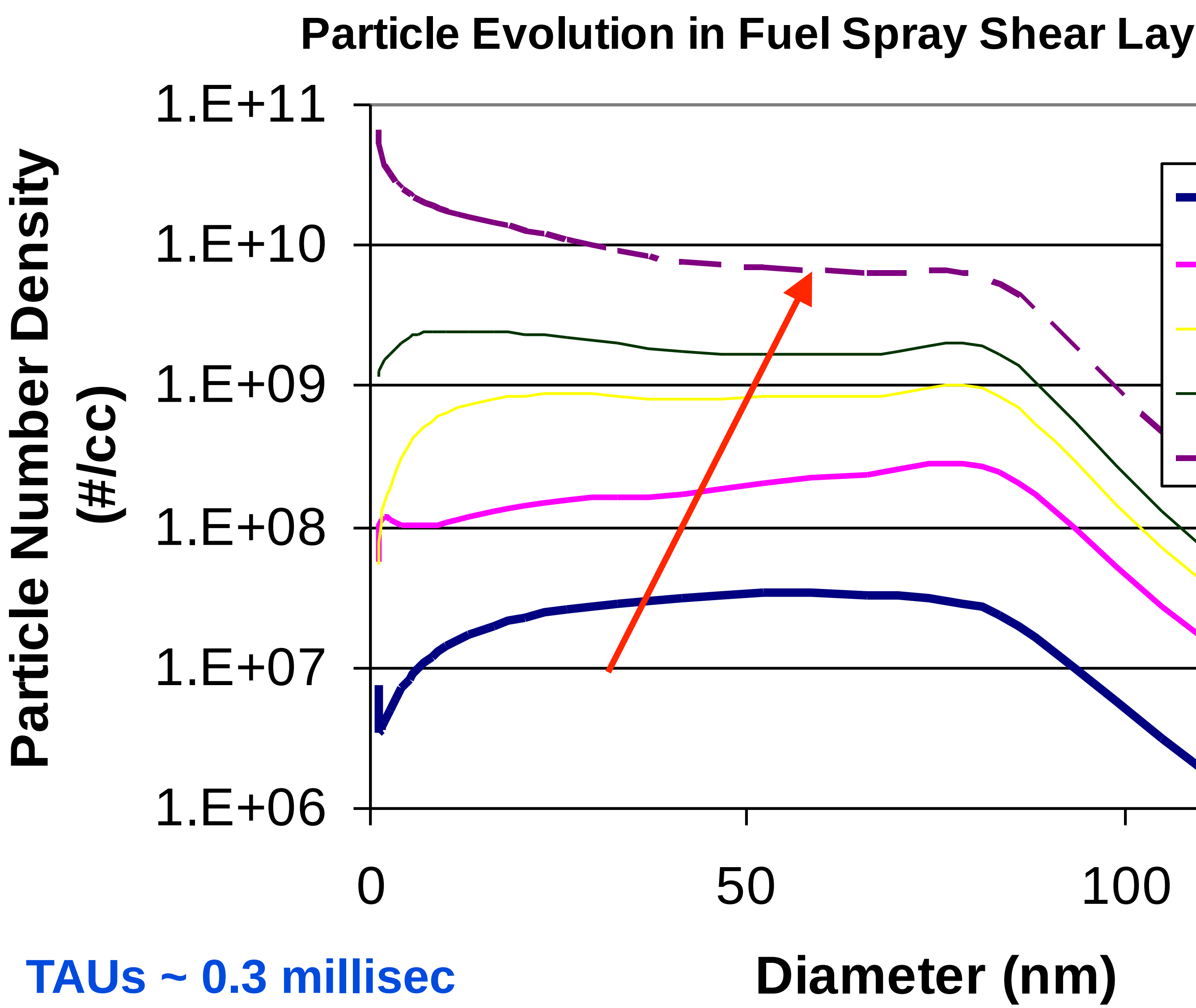
General Formation Characteristics

Soot Formed at phi > 1.5, oxidized 0.7<phi<1.5 (by OH)

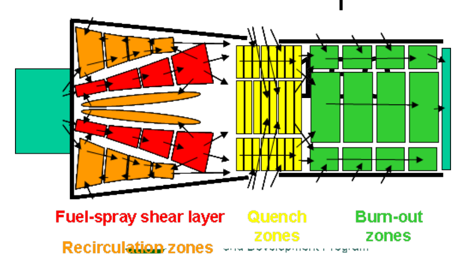


Particle Formation in Fuel Spray Shear Layer

Number density increase dramatically with position

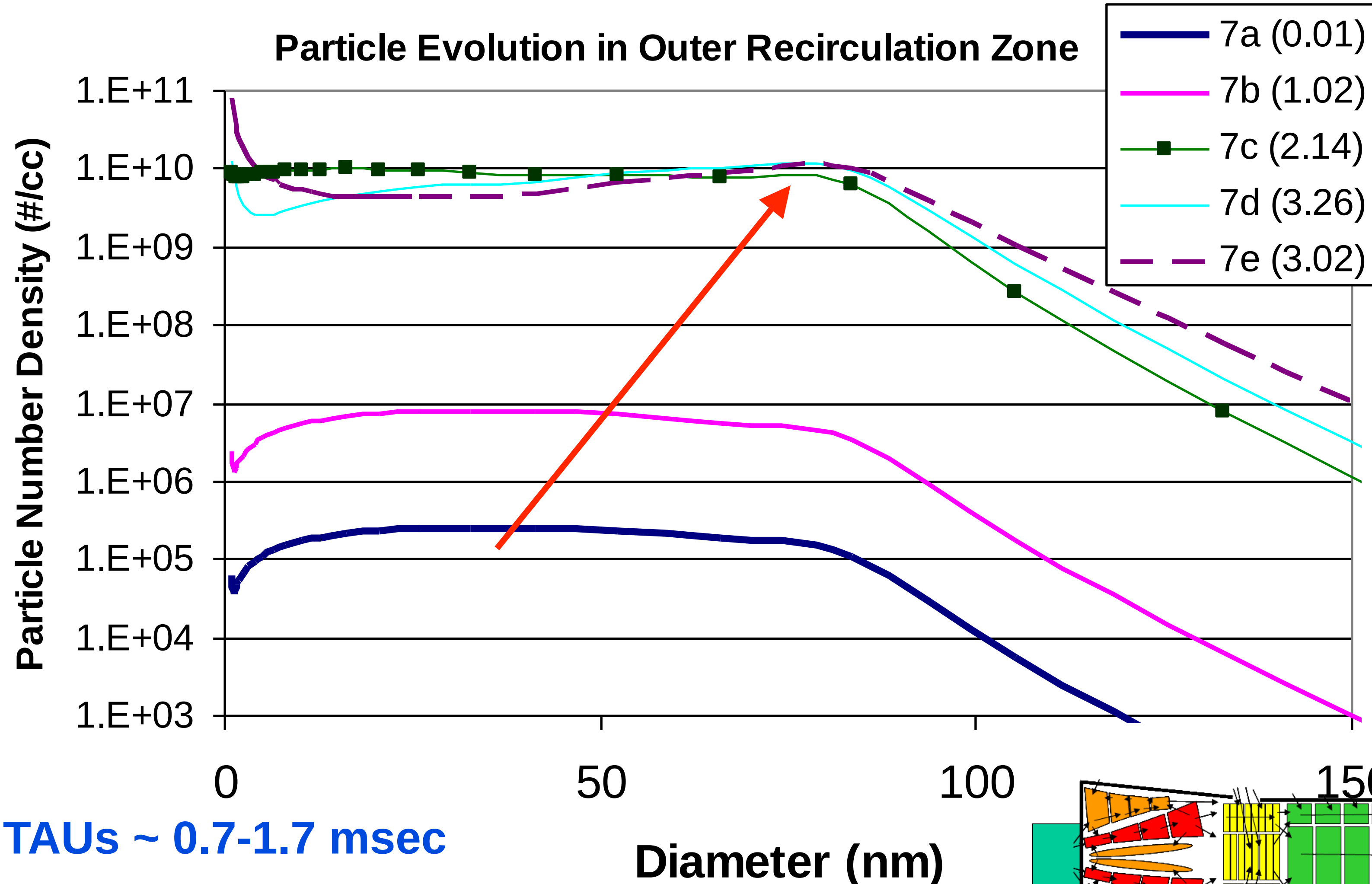


TAUs ~ 0.3 millisec

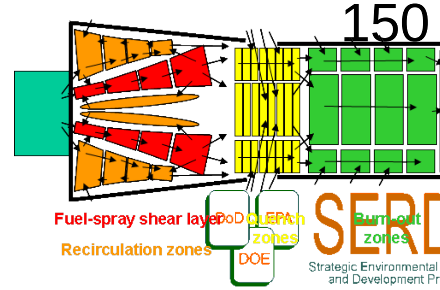


Particle Formation in Outer Recirculation Zone

Number density saturates due to long residence times

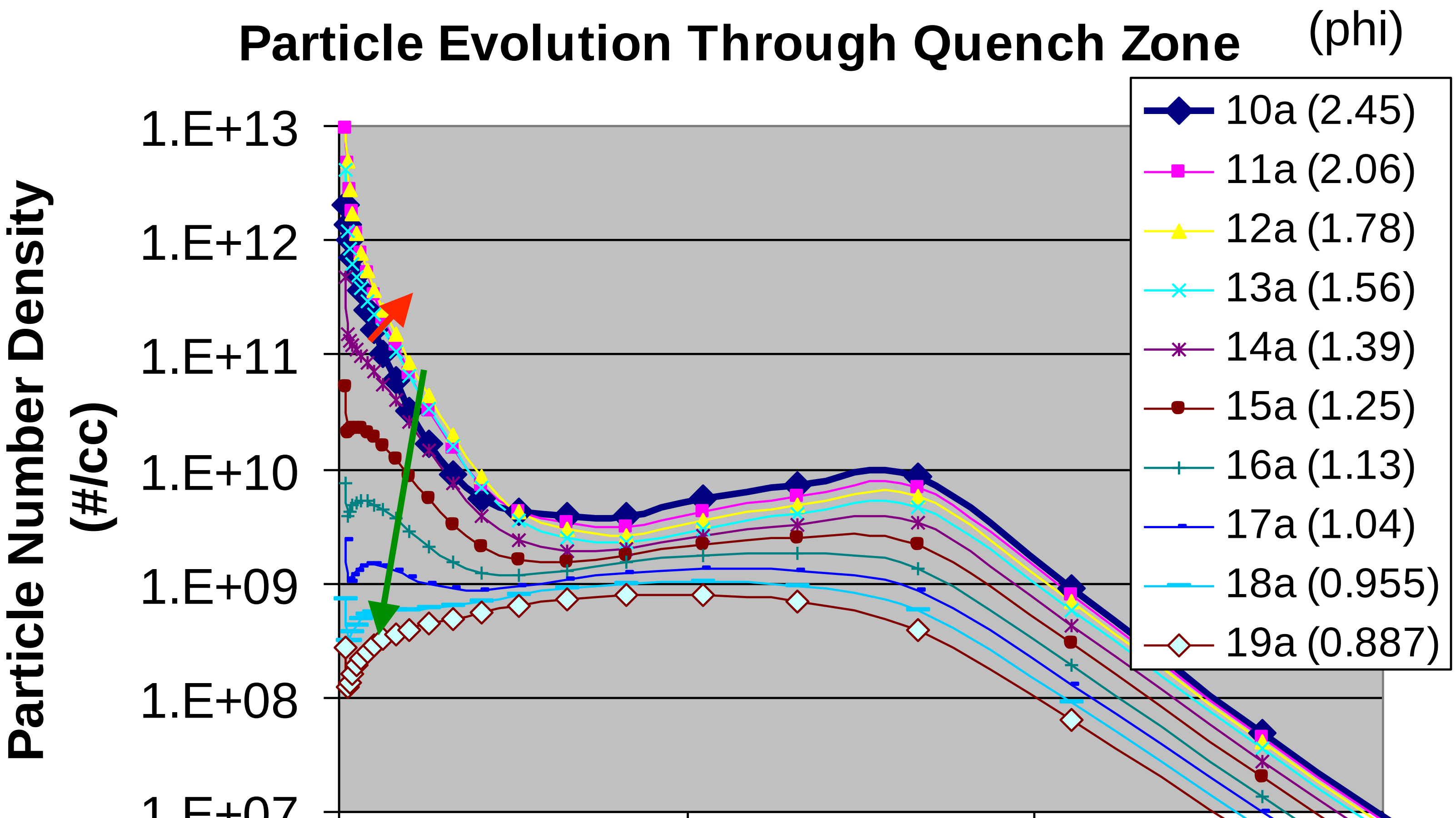


TAUs ~ 0.7-1.7 msec

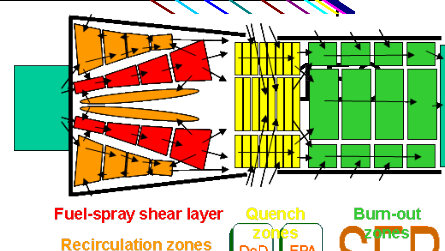


Particle Evolution Through Quench Zone

Particles first increase and then decrease: fastest changes in small particles



TAUs ~ 0.02-0.05 msec



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Soot Formation and Oxidation

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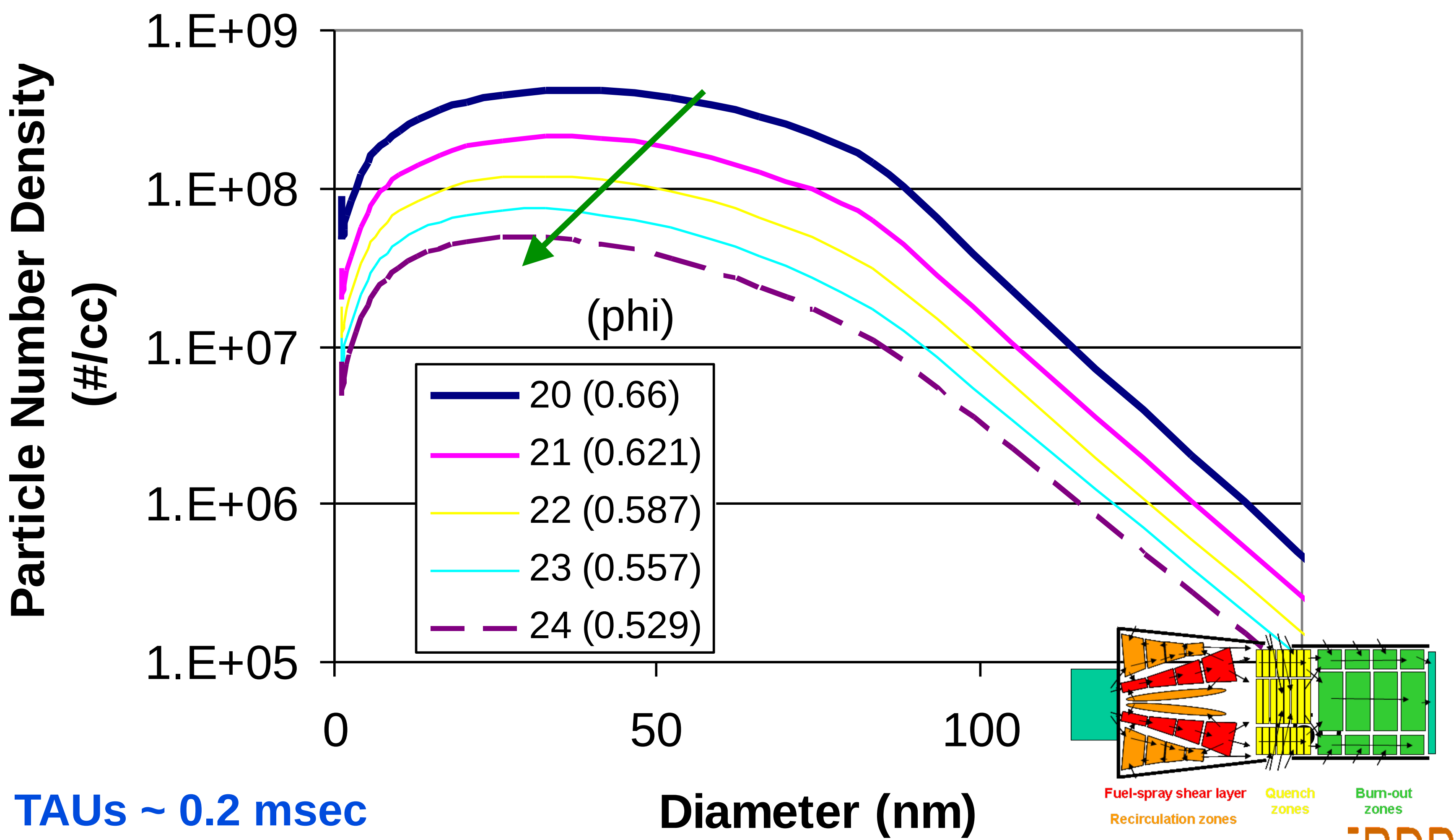
Particle Oxidation in Burn-Out Zone

Oxidation reduces number density and size (and mass)

Particle Oxidation in Burn-Out Zone



TAUs ~ 0.2 msec

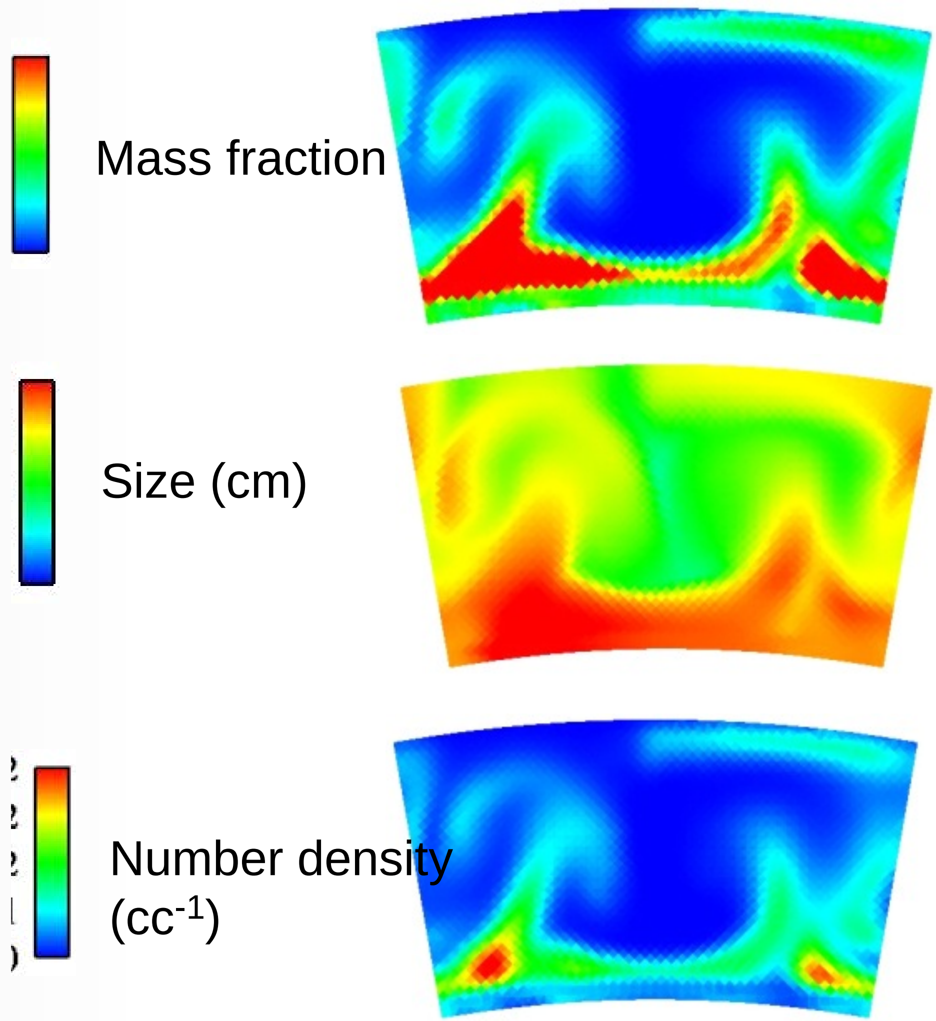
Simulations of Soot at Combustor Exit Plane

Peak soot mass fractions decreases by 4 orders of magnitude from front end (of RQL burner) to exit plane.

Number density decreases by two orders of magnitude

Numbers in agreement with experimental data (~30% mass and size)

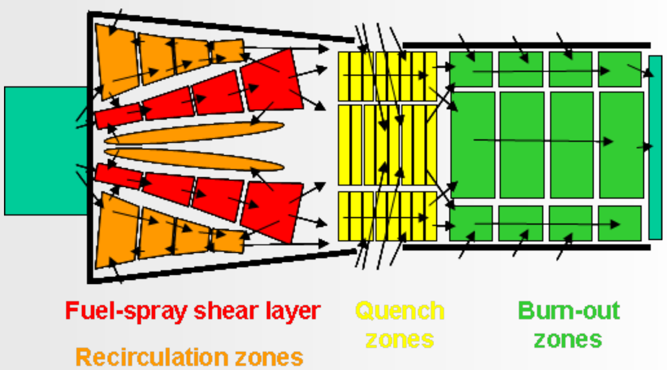
Reduced-order soot model employed

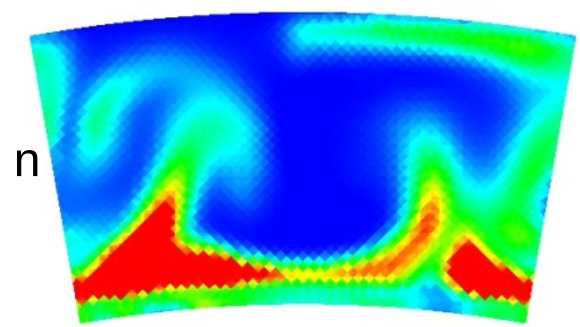


Courtesy of PW

Summary/Conclusions

- Formation occurs at phi>1.5, and oxidizes at 0.7<phi<1.5
- Particle evolution depicts rapid growth in #/cc, size and mass in fuel-rich front end
- Particle formation saturates in long residence time, fuel-rich recirculation zones
- Formation continues into leading edge of quench zone
- Particle oxidation limited by quenching to below phi of 0.7



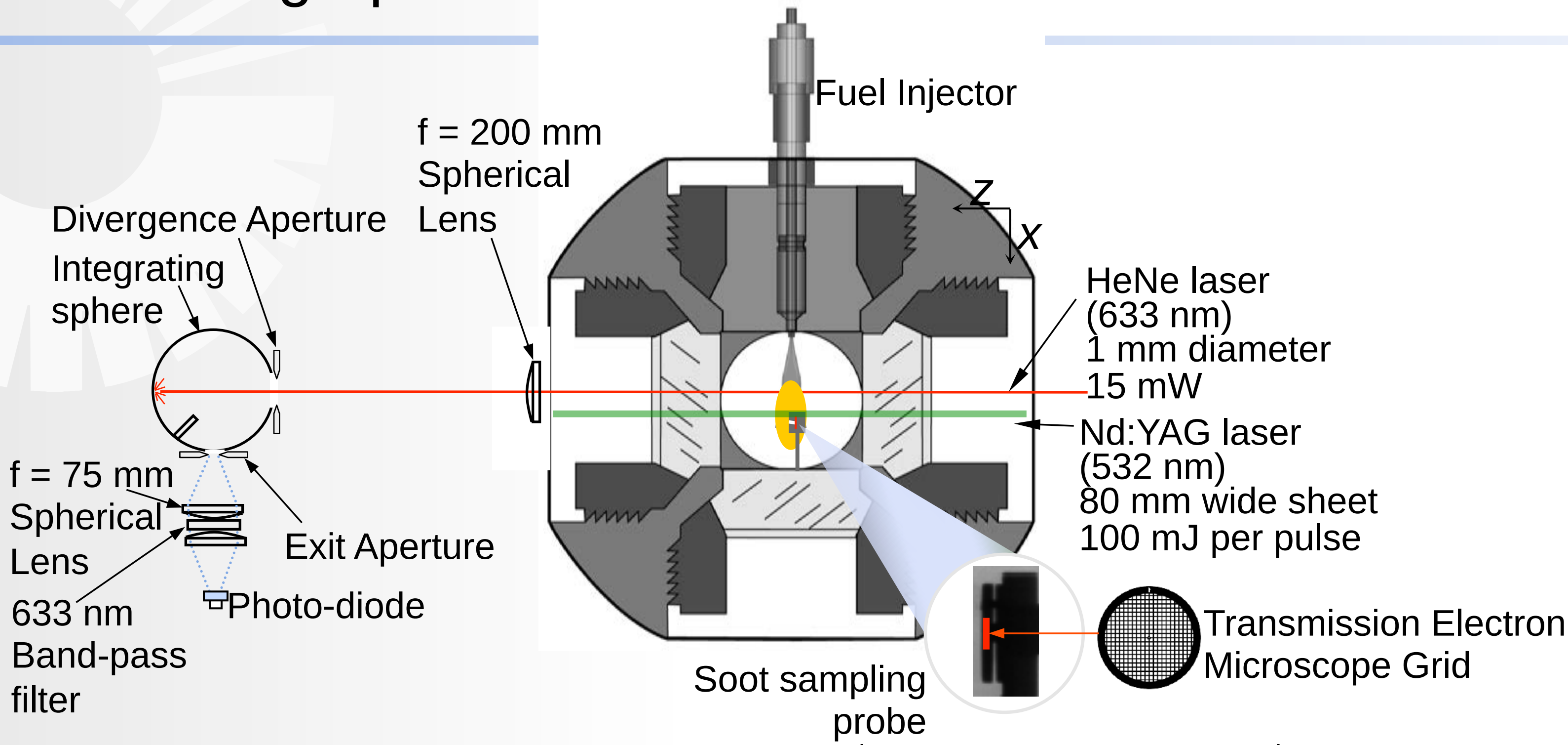


Recommendations: Research Needs

- Spray and fuel distribution is critical
- Validated detailed reaction models for fuels of interest
  - Particularly for fuel-rich chemistry, PAH formation
- Reduced chemistry with soot precursor modeling
- Simultaneous information on T, [OH], f/a, soot mass and diameters (ideally PSD) – in heavy soot laden flows
- Optical thickness
- CFD models that can incorporate detailed reaction chemistry, including PAH, soot equations, mass scrubbing, PSD, oxidation, and radiation effects
- Probe sampling effects (loss of small particles to walls)
- Soot physics: inception (liquid-like particles), agglomeration, PSD
- Fuel effects

THANK YOU!

Experiments were performed in an optically-accessible high-temperature/high-pressure combustion vessel.



	Operating Conditions
Ambient Gas O_2	15%
Ambient Gas Temperature	1000 K
Ambient Gas Density	22.8 kg/m^3
Ambient Gas Pressure	6.7 MPa
Injection Pressure	150 MPa
Injection Duration	7 ms
Fuels tested	WA, SR