Modeling Particulate Emissions

Med Colket

Technical Session 2C

Impact of Particulate Emissions from Gas Turbine Powered Aircraft

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14. ABSTRACT

Atmospheric levels of PM2.5 particulate matter near airports are increased by solid carbonaceous soot and condensable gaseous species emitted by military and commercial gas turbine aircraft engines. Carbonaceous materials are formed in the main combustor at elevated pressures and temperatures due to nucleation, surface growth, coalescence, aggregation and oxidation. Condensable materials nucleate in the engine exhaust plume at lower temperatures and at ambient pressures, followed by mass growth, and vaporization. Such gases may also condense onto existing soot emissions collocated in the plume. This presentation will review models developed to describe the formation of these two types of particulates and will compare and contrast the physics/chemistry associated with these processes and their interrelationships. Complicating the understanding the physics of formation for both the solid and volatile particles are sampling artifacts. A discussion of such issues will also be discussed briefly.

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MODELING OF PARTICULATE EMISSIONS

DR. MED COLKET
United Technologies Research Center
411 Silver Lane
East Hartford, CT 06108
(860) 610-7481
colketmb@utrc.utc.com

Atmospheric levels of $PM_{2.5}$ particulate matter near airports are increased by solid carbonaceous soot and condensable gaseous species emitted by military and commercial gas turbine aircraft engines. Carbonaceous materials are formed in the main combustor at elevated pressures and temperatures due to nucleation, surface growth, coalescence, aggregation, and oxidation. Condensable materials nucleate in the engine exhaust plume at lower temperatures and at ambient pressures, followed by mass growth, and vaporization. Such gases may also condense onto existing soot emissions collocated in the plume. This presentation will review models developed to describe the formation of these two types of particulates and will compare and contrast the physics/chemistry associated with these processes and their interrelationships. Complicating the understanding the physics of formation for both the solid and volatile particles are sampling artifacts. A discussion of such issues will also be discussed briefly.

Objectives and Outline

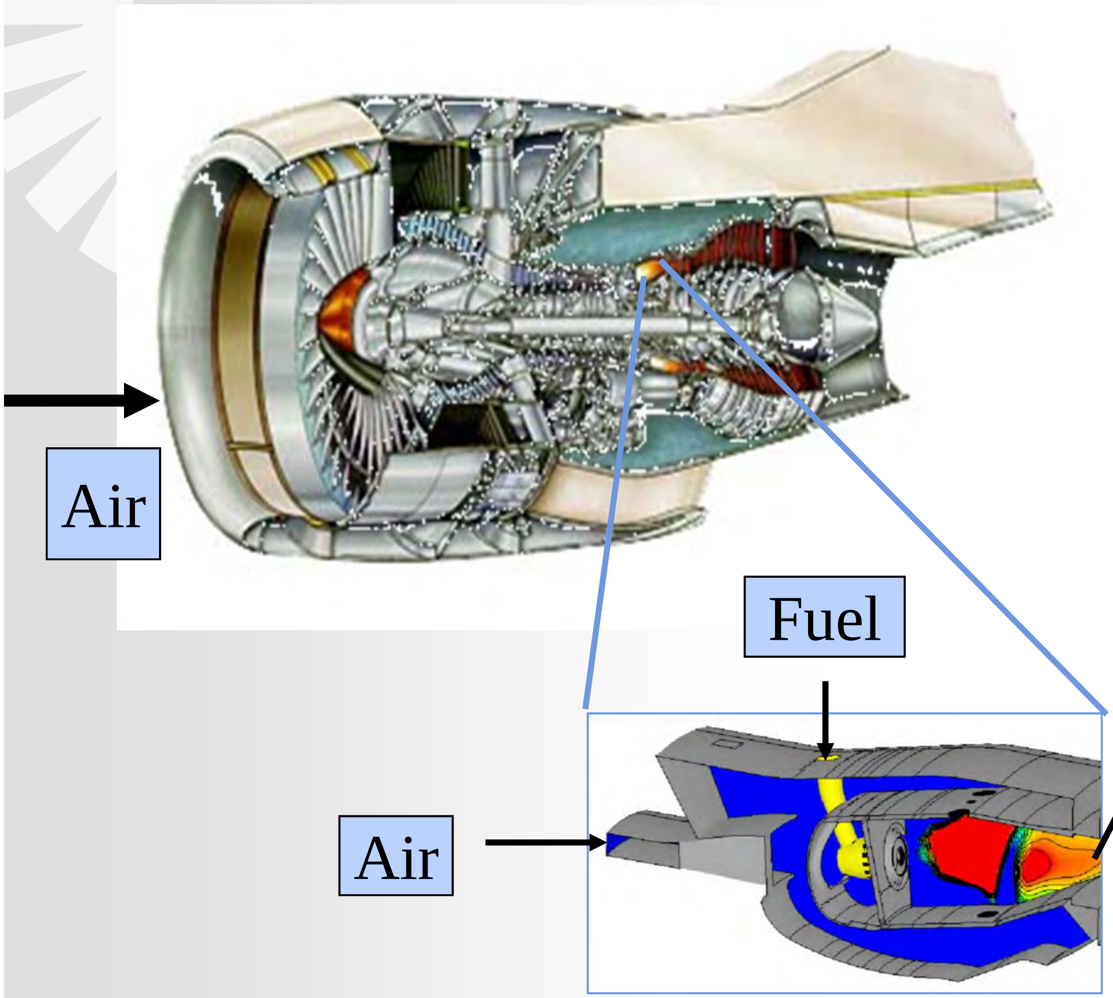
Objectives:

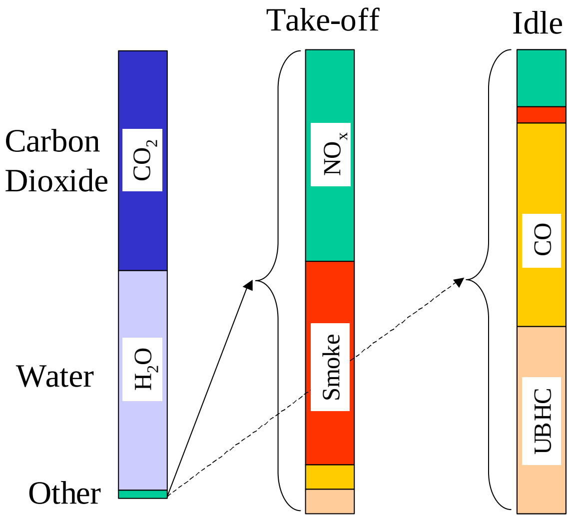
- Compare/contrast physical models/processes of gas turbine generated particulate emissions

Outline:

- Overview
- Contrast physical processes in particulate formation
- Soot Formation in combustors (non-volatile particulates)
  - Observations of soot formation in combustors
  - Physical/chemical models
  - Soot summary
- Volatile particulate formation
  - $H_2O + H_2SO_4/SO_3$
  - Hydrocarbons/oxygenates
- Extensions to volatile condensation on non-volatile particulates
- Summary

Aircraft Emissions - Produced by Combustion of Fuel and Air





Combustion Products

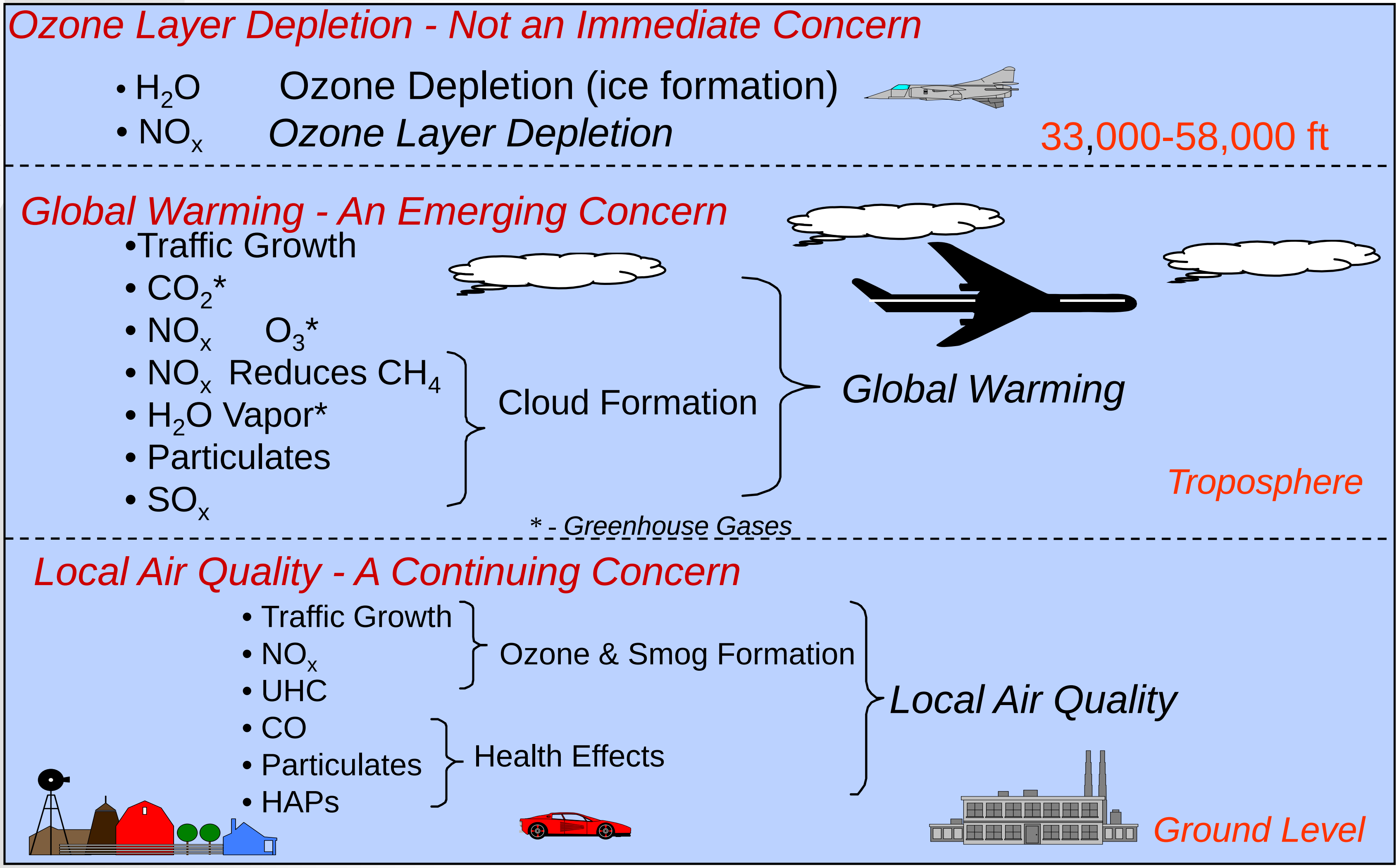
Carbon Dioxide - CO2
Water Vapor - H2O

Nitrogen Oxides - NOx
Carbon Monoxide - CO
Unburned Hydrocarbons - UBHC
Smoke

Particulates
Hazardous Air Pollutants- HAPs

Impact Of Aircraft Emissions is Altitude Dependent

More than a local concern



Ozone Layer Depletion - Not an Immediate Concern

- H_2O Ozone Depletion (ice formation)
- NO_x *Ozone Layer Depletion*

33,000-58,000 ft

Global Warming - An Emerging Concern

- Traffic Growth
- CO_2*
- NO_x O_3*
- NO_x Reduces CH_4
- H_2O Vapor*
- Particulates
- SO_x

Cloud Formation

Global Warming

Troposphere

** - Greenhouse Gases*

Local Air Quality - A Continuing Concern

- Traffic Growth
- NO_x
- UHC
- CO
- Particulates
- HAPs

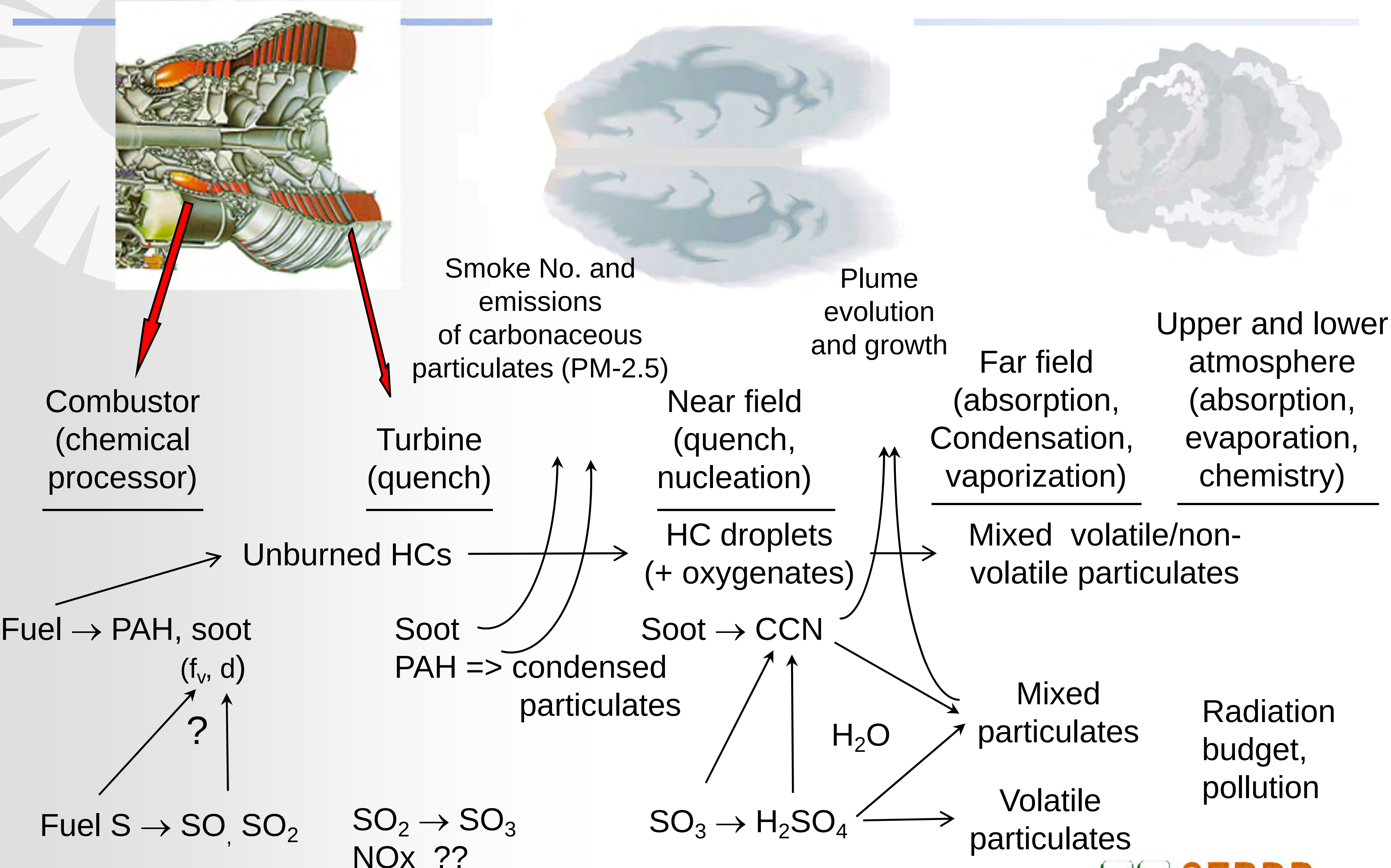
Ozone & Smog Formation

Health Effects

Local Air Quality

Ground Level

Complexities of Particulate Evolution



Smoke No. and emissions of carbonaceous particulates (PM-2.5)

Plume evolution and growth

Combustor (chemical processor)

Turbine (quench)

Near field (quench, nucleation)

Far field (absorption, Condensation, vaporization)

Upper and lower atmosphere (absorption, evaporation, chemistry)

Unburned HCs

HC droplets (+ oxygenates)

Mixed volatile/non-volatile particulates

Fuel → PAH, soot (f_v, d)

?

Soot

PAH => condensed particulates

Soot → CCN

Mixed particulates

Radiation budget, pollution

H_2O

Fuel S → SO, SO_2

$SO_2 \rightarrow SO_3$

NOx ??

$SO_3 \rightarrow H_2SO_4$

Volatile particulates

Formation Processes for Various Particulates

Arise from Multiple Chemicals, Locations and Conditions

	Soot
Classification	**Non-volatile**
Formed	Main burner
Chemical precursors	Polycyclic hydrocarbons
‘Nucleation’	‘Inception’
Condensation	Polycyclic hydrocarbons
Surface Growth	C_2H_2
Coalescence	Young soots
Agglomeration	.
Vaporization	>2000K
Oxidation	In burner

Formation Processes for Various Particulates

Arise from Multiple Chemicals, Locations and Conditions

	Soot	**H_2SO_4/H_2O**	**Hydrocarbons**
Classification	**Non-volatile**	**Volatile**	**Volatile**
Formed	Main burner	Plume	Plume (idle)
Chemical precursors	Polycyclic hydrocarbons	SO_2 => SO_3 => H_2SO_4	Partially oxidized fuel
'Nucleation'	'Inception'	Nucleation	Nucleation
Condensation	Polycyclic hydrocarbons	H_2O/H_2SO_4 (+ oxygenates)	Partially oxidized fuel, Lube oil
Surface Growth	C_2H_2	N/A	N/A
Coalescence	Young soots	.	.
Agglomeration	.	N/A	N/A
Vaporization	>2000K	.	.
Oxidation	In burner	N/A	N/A

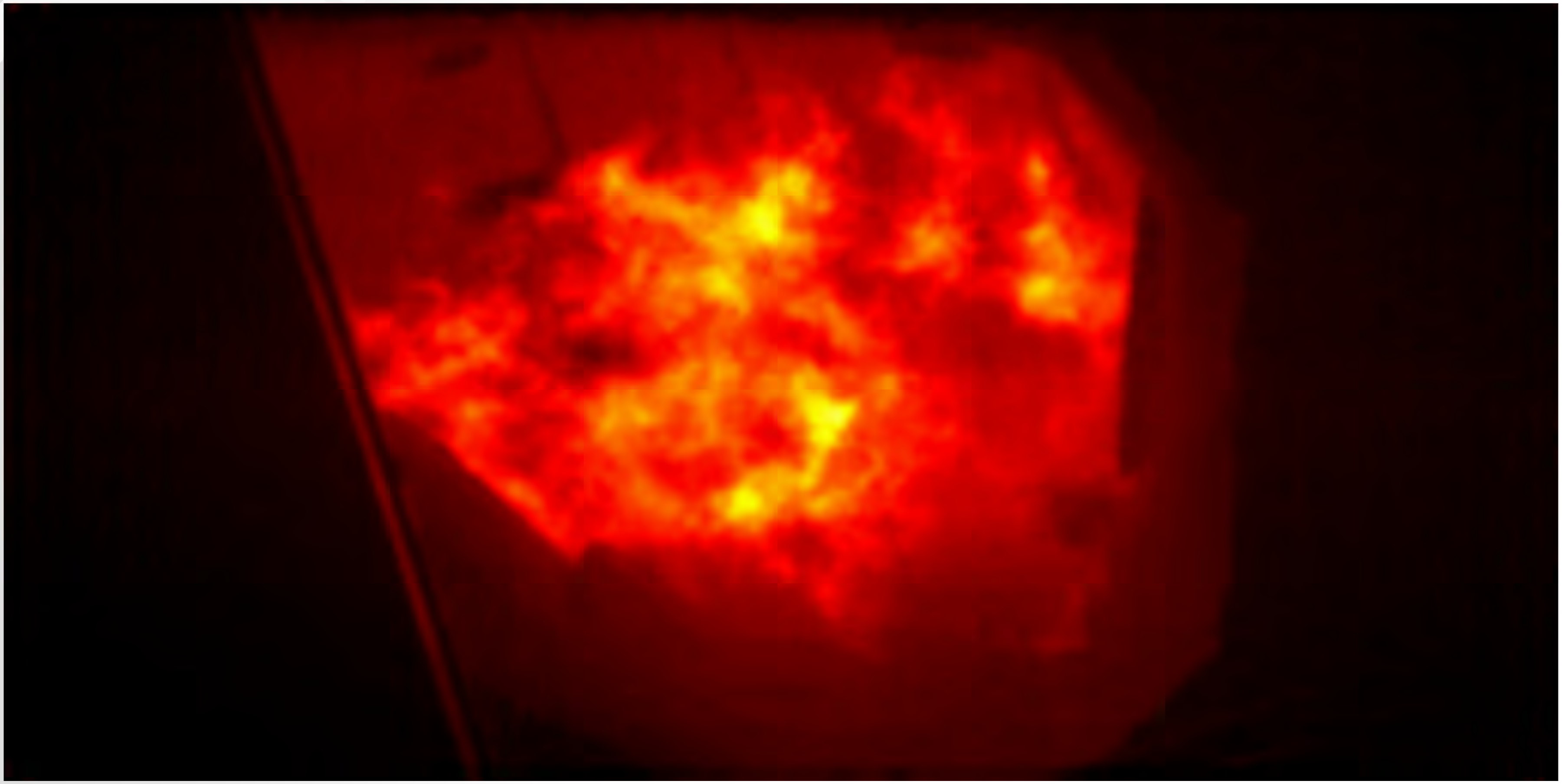
Formation Processes for Various Particulates

Arise from Multiple Chemicals, Locations and Conditions

	Soot	**H_2SO_4/H_2O**	**Hydrocarbons**	**$Soot/H_2SO_4/H_2O$**	**Soot/hydrocarbons**
Classification	**Non-volatile**	**Volatile**	**Volatile**	**NV/V**	**NV/V**
Formed	Main burner	Plume	Plume (idle)	Plume	Plume (idle)
Chemical precursors	Polycyclic hydrocarbons	$SO_2 \Rightarrow SO_3 \Rightarrow H_2SO_4$	Partially oxidized fuel	H_2O/H_2SO_4 (+ oxygenates)	Partially oxidized fuel
'Nucleation'	'Inception'	Nucleation	Nucleation	N/A	N/A
Condensation	Polycyclic hydrocarbons	H_2O/H_2SO_4 (+ oxygenates)	Partially oxidized fuel, Lube oil	H_2O/H_2SO_4 (+ oxygenates)	Partially oxidized fuel
Surface Growth	C_2H_2	N/A	N/A	N/A	N/A
Coalescence	Young soots	.	.	.	.
Agglomeration	.	N/A	N/A	?	?
Vaporization	>2000K	.	.	.	.
Oxidation	In burner	N/A	N/A	N/A	N/A

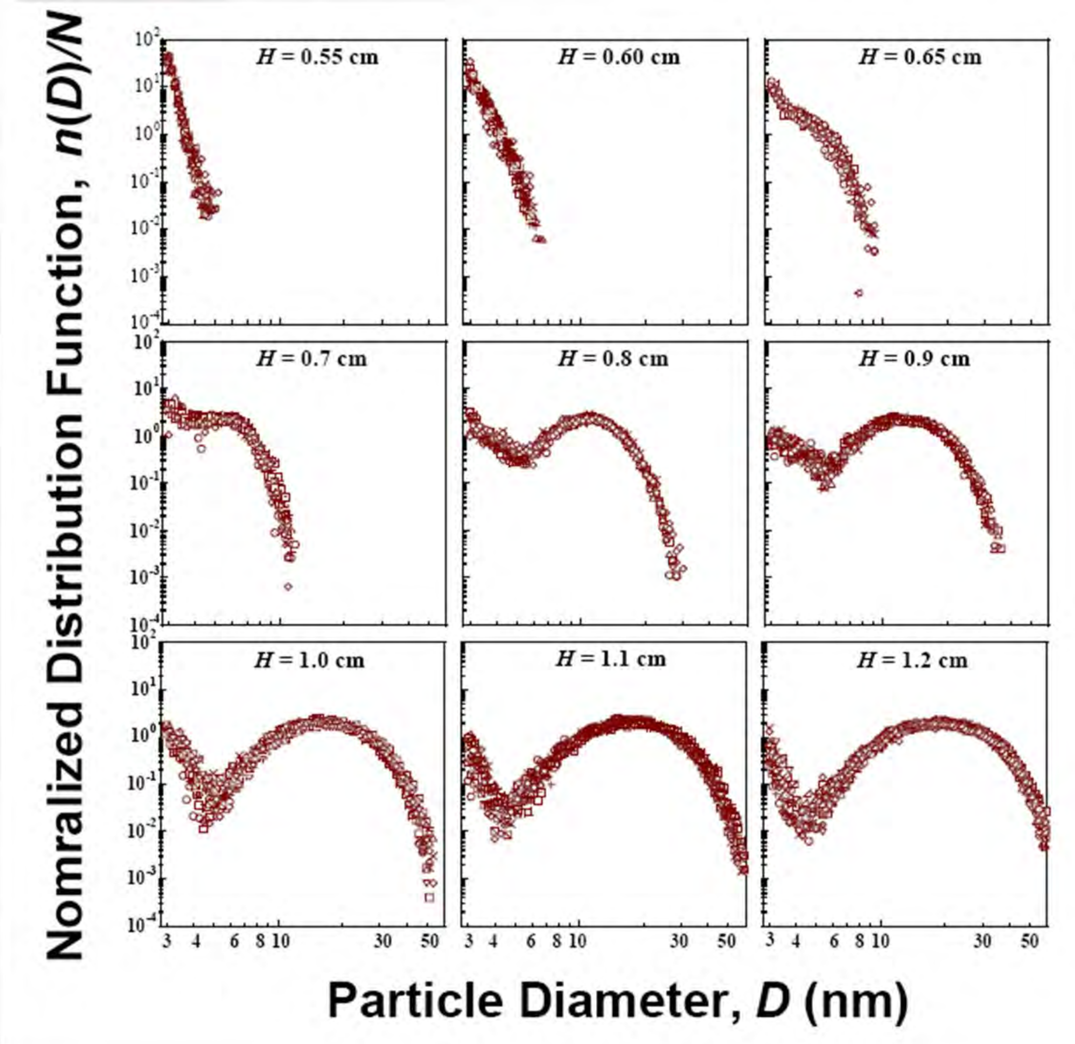
Video of soot formation at 10 atmospheres

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



Soot Particle Evolution in Laminar Premixed Flame

Transition from nucleation mode to coagulation/growth – ***The Beginning***



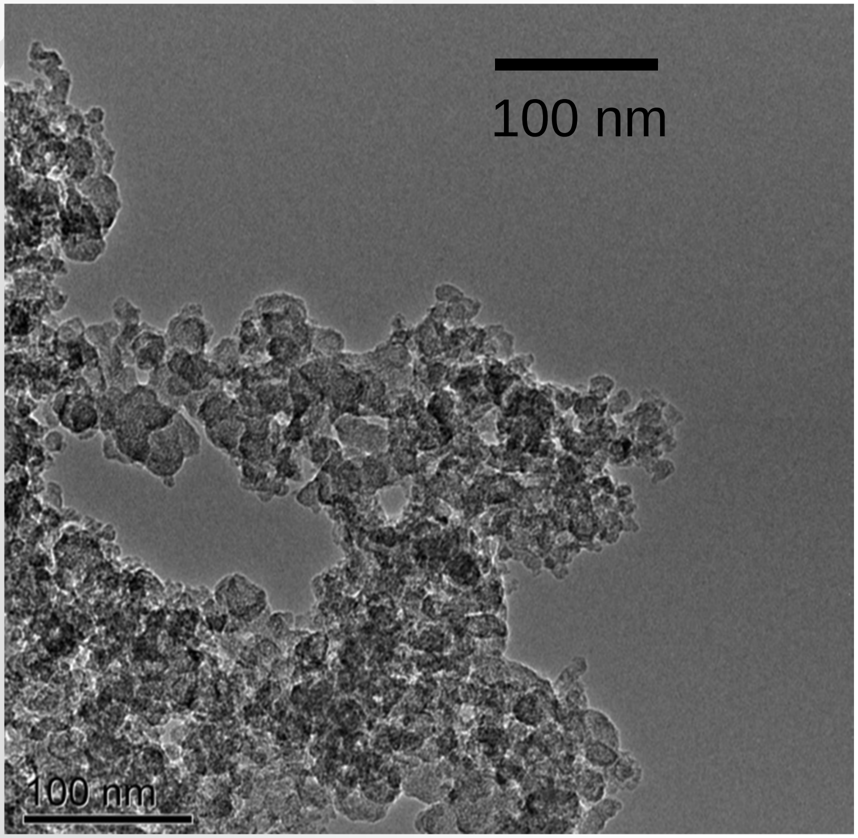
Particle Size distributions in Laminar, premixed flame using Dilution probe and mobility particle sizer, with corrections for probe perturbations in modeling

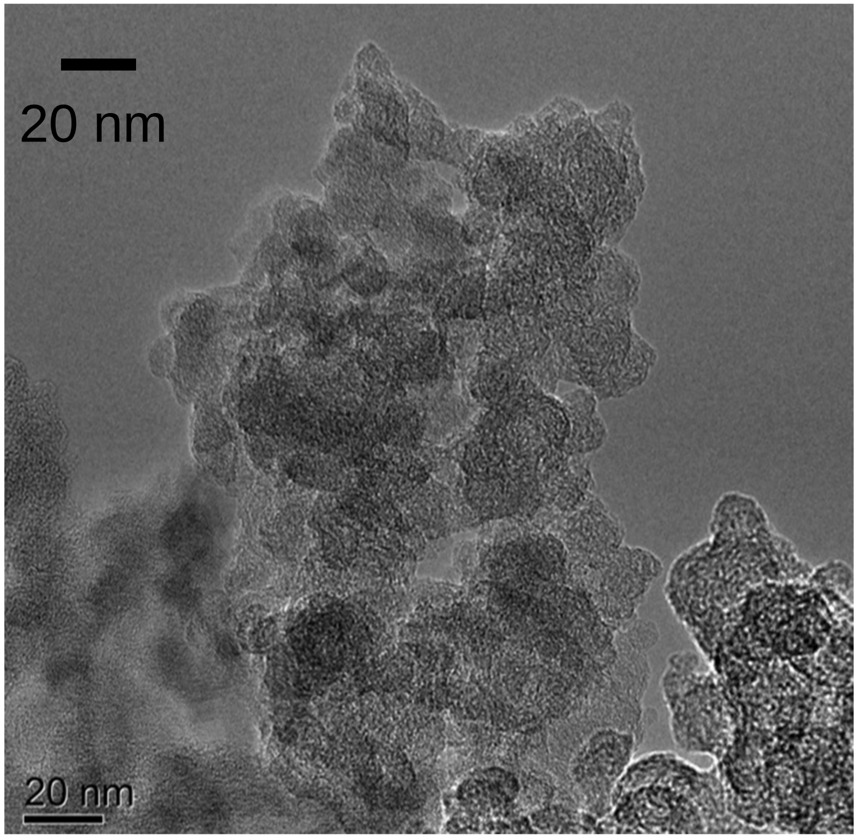
Courtesy of H. Wang and co-workers

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

Exhaust Particulates – The End

Gas Turbine combustor
Courtesy of Randy Vander Wal, PSU)





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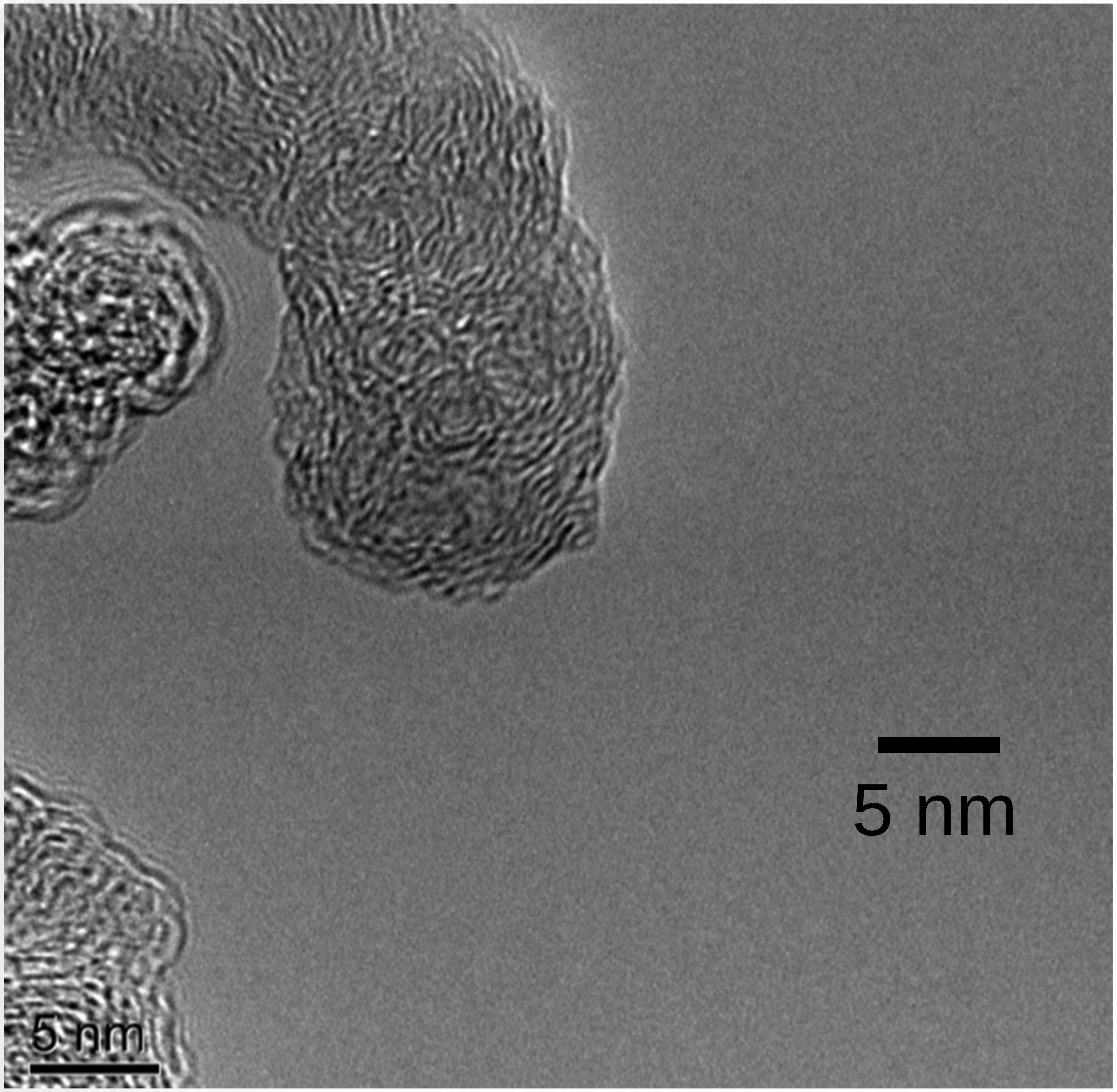
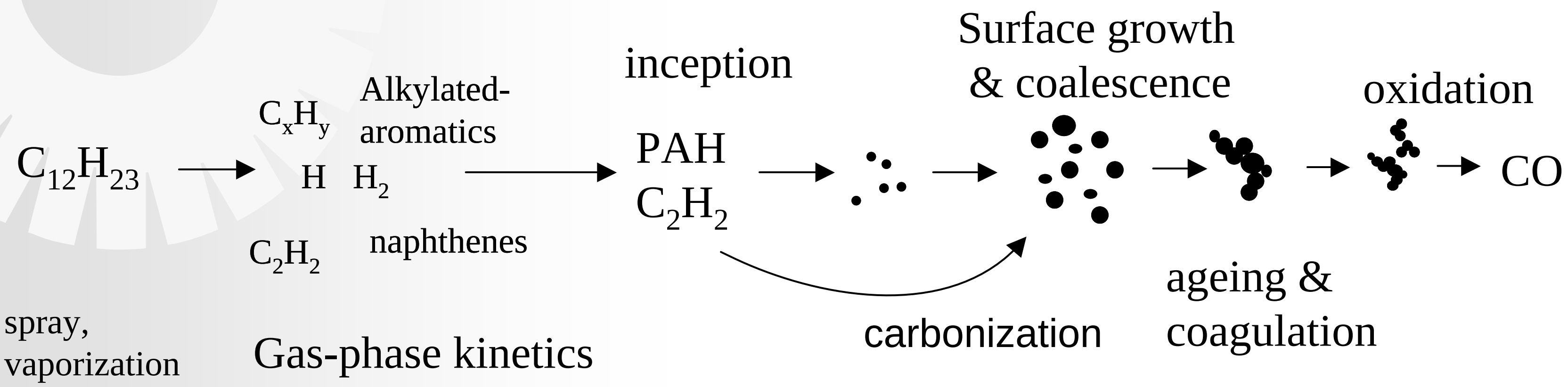


Physics for Treatment of Soot/Particle Emissions

Physical Processes in Soot Formation



$C_{12}H_{23}$ → C_xH_y Alkylated-aromatics H H_2 C_2H_2 naphthenes → inception PAH C_2H_2 → → Surface growth & coalescence → ageing & coagulation → oxidation → CO

carbonization

spray, vaporization

Gas-phase kinetics

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)

Soot Formation Kinetics

Inception: Dimerization of pyrene (and other 202 amu species), after Appel, et al, 2000. (Full detailed kinetics required!)

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

Condensation:

Mass growth due to collision with PAH, followed by dehydrogenation

$C_{16}H_{10} + C(s) \Rightarrow C(s)\text{-}C_{16}H_{10}$
$C(s)\text{-}C_{16}H_{10} \Rightarrow C'(s) + 5H_2$

Surface Growth:

Mass growth (via acetylene addition) assumed proportional to particle surface area

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

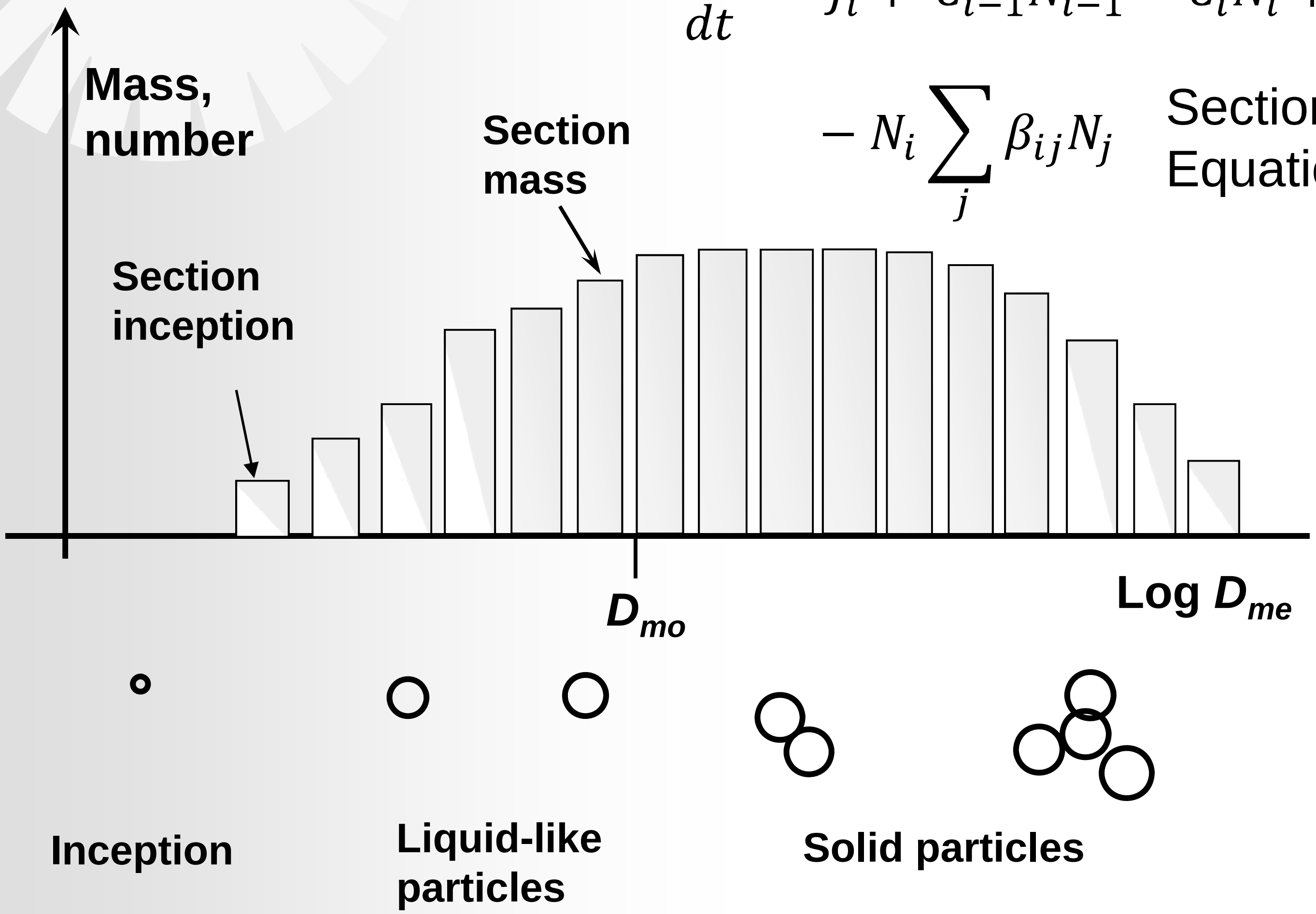
Sectional Modeling of Soot Growth

Discrete particle size (logarithmic scale)

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

$$\frac{dN_i}{dt} = J_i + C_{i-1}N_{i-1} - C_iN_i + {}^{1}/_{2} \sum_{j+k=i} \beta_{jk}N_kN_j - N_i \sum_{j} \beta_{ij}N_j$$

Sectional Conservation Equation



Agglomeration simulated with peak size for surface growth

Soot Kinetics

Based on OH, O_2 and available particle surface area

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

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

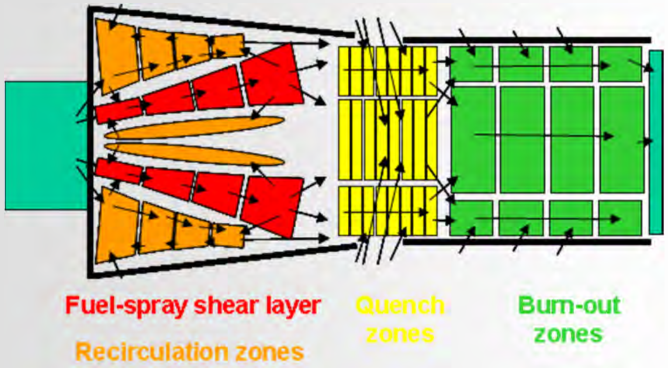
Oxidation by OH dominates!!

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

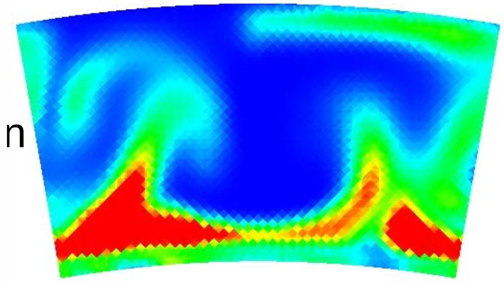
$$R_{O_2} = 12\left(\frac{K_a P_{O_2} \chi'}{\left(1 + K_z P_{O_2}\right)} + K_b P_{O_2}\left(1 - \chi'\right)\right) \text{gm/sec/cm}^2$$

Soot Modeling - Summary Comments

- Formation occurs at phi>1.5, and oxidizes at 0.7<phi<1.5
- 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 quenched below phi of 0.7

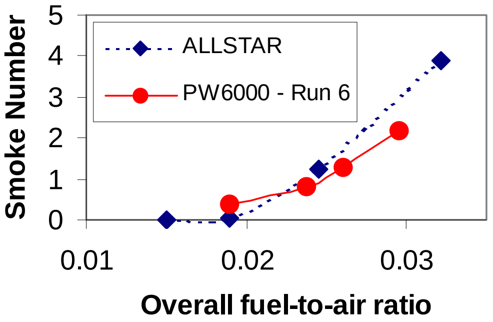


Exit plane distributions



Predicting trends

Predicted vs. Measured SN



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Effects of Different Levels of Fuel Sulfur

U. Schumann, et al (1995)

Rolls-Royce/SNECMA M45H MK501 turbofan engines. Bypass 3:1 and 32.4 KN takeoff thrust

% thrust	SN
7	2.7
30	10.9
85	46.3

Increased sulfur causes sooner onset of contrail formation and a 25-50% increase in number of particulates.

Formation of Aqueous (Volatile) Particulates

H_2SO_4 /SO_3 is key to plume formation

From Brown, et al, 1996

Source of sulfur –

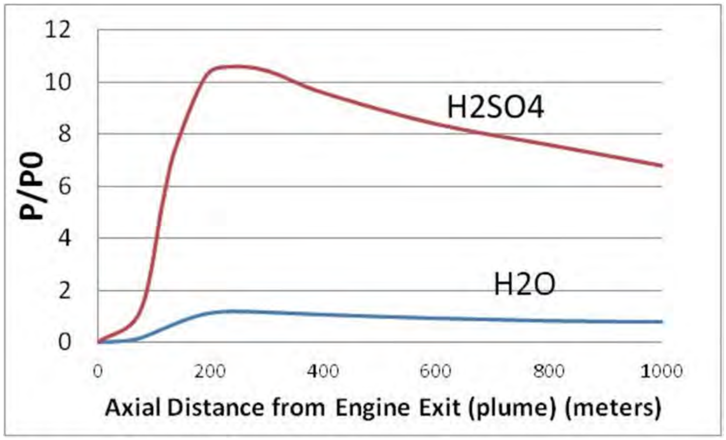
Fuel sulfur => SO_2 (~1 g/kg fuel at exit of burner) =>
SO_3 (few percent of SO_2)=> H_2SO_4

Nucleation rates

J ~ exp (-ΔG*/RT), where ΔG* is critical energy to form embryo

$\Delta G^* = \text{fn}((\mu_{liquid} - \mu_{gas}), \text{surface tension})$

Surface tension for water is very high….hard to form small (pure water) droplets!



Condensation rates

$dm/dt \sim (P_i - P_i^{saturation})$

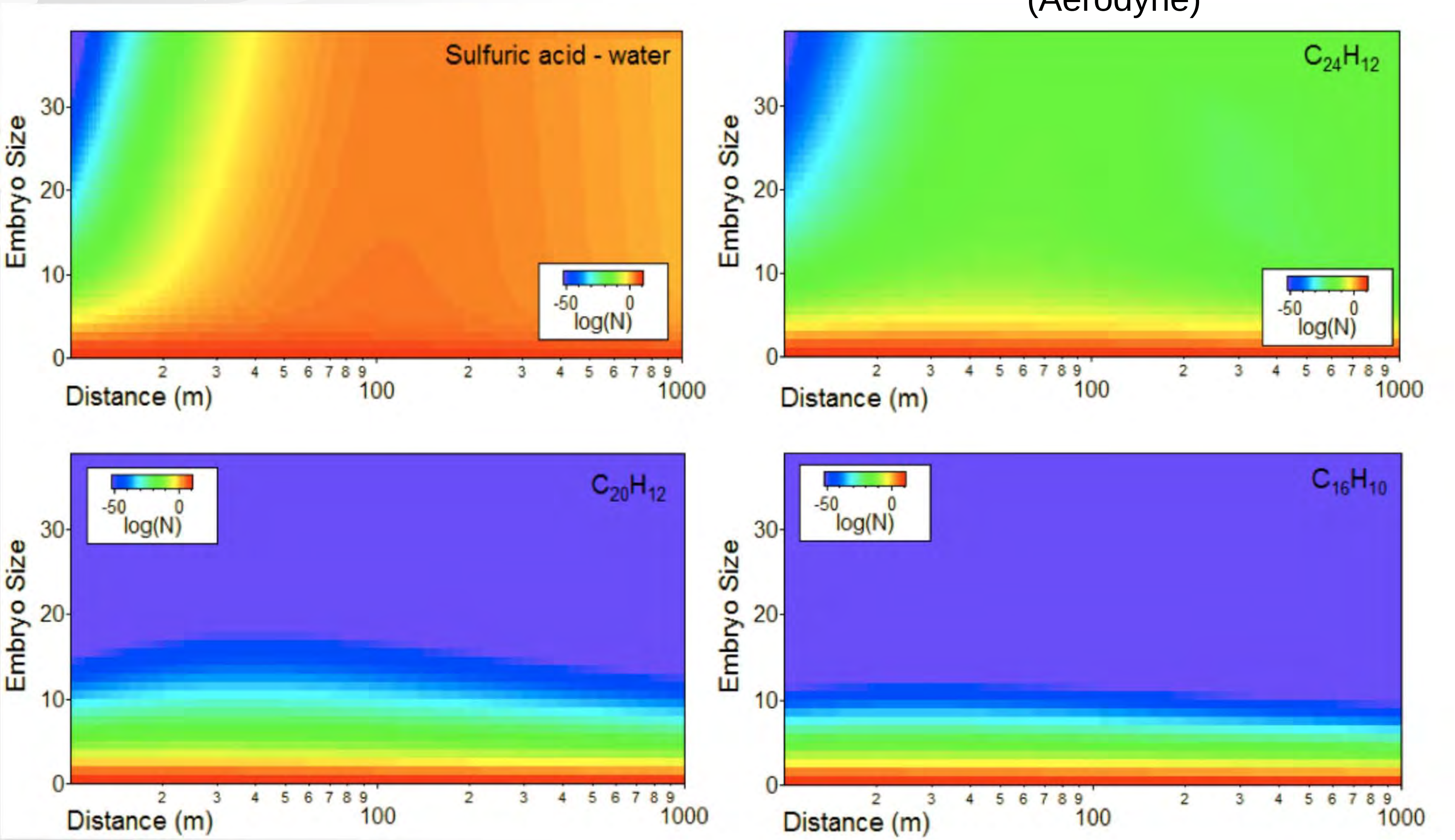
Sulfur affinity for water

1 ppm nucleates water at 50% RH
(Roth, et al, 1994)

Calculations of Homogeneous Nucleation

Dominated by H_2SO_4/H_2O clusters

Calculations by Hsi-Wu Wong (Aerodyne)



Sulfuric acid-water and hydrocarbon embryo concentration from binary sulfuric acid-water nucleation and (pure) hydrocarbon nucleation, respectively

Non-Volatile – Volatile Interactions

Changing Fate of Carbonaceous Particulates (soot):

Combustor Exit	Engine Exit	Exhaust Plume
100% hydrophobic	99% hydrophobic 1% hydrophilic	~70% hydrophobic ~ 30% hydrophilic

Hydrophobic particle + hydrocarbon (or oxygenate) = Non-aqueous HC coat on soot particle

Activation

+ H_2SO_4 = Hydrophilic particle + H_2O/H_2SO_4 = Aqueous coat on soot particle

+ oxygenate = Hydrophilic particle + H_2O/H_2SO_4 = Aqueous coat on soot particle

Non-Volatile – Volatile Interactions

Changing Fate of Carbonaceous Particulates (soot):

Combustor Exit	Engine Exit	E[illegible]t Plume
100% hydrophobic	99% hydrophobic	[illegible]% hydrophobic
	1% hydrophilic	30% hydrophilic

Hydrophobic particle + hydrocarb[illegible] oxygenate) = HC coat on soot particle (non-aqueous)

Activation

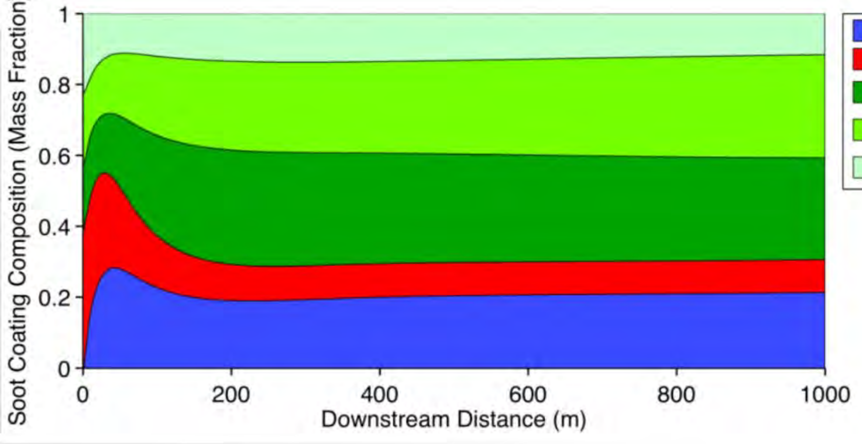
+ H_2SO_4 = Hydr[illegible]c particle + H_2O/H_2SO_4 = Aqueous coat on soot particle

+ oxyg[illegible] = Hydrophilic particle + H_2O/H_2SO_4 = Aqueous coat on soot particle

Example Predictions for Sample Case

Water/sulfuric acid and Unburned HCs contribute to both soot coating and volatile aerosols

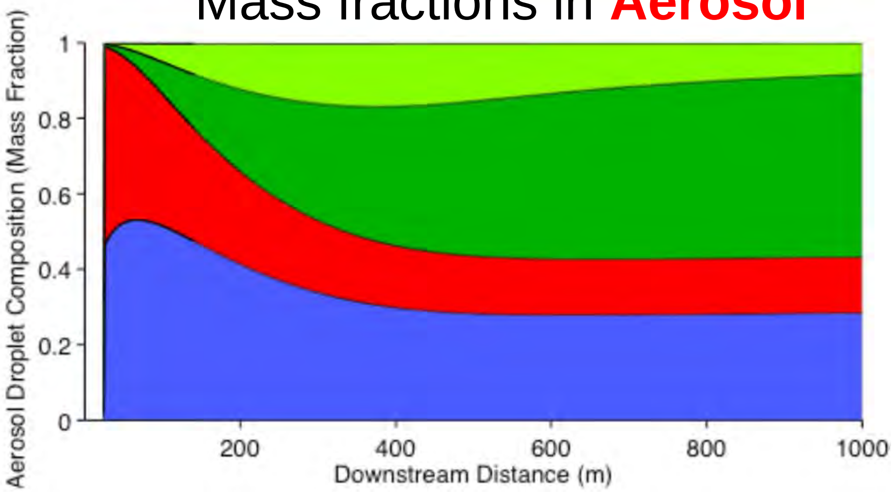
Mass fractions on **Soot**



🟦 Water
🟥 Sulfuric Acid
🟩 $C_{24}H_{12}$
🟩 $C_{20}H_{12}$
🟩 $C_{16}H_{10}$

Aerosol model allows for co-condensation of aqueous and non-aqueous materials

Mass fractions in **Aerosol**



Total condensed (volatile material) is continuing increasing

Calculations by Hsi-Wu Wong (Aerodyne)

Summary

- Very similar processes controlling volatile/non-volatile particulates – but different species and conditions govern rates
- Soot inception/nucleation is poorly defined
- Hydrocarbon nucleation/condensation negligible, except perhaps for idle conditions and in the case of lube oil emissions
- Volatile/non-volatile particulate interactions remains active area of research
  - Activation processes/rates

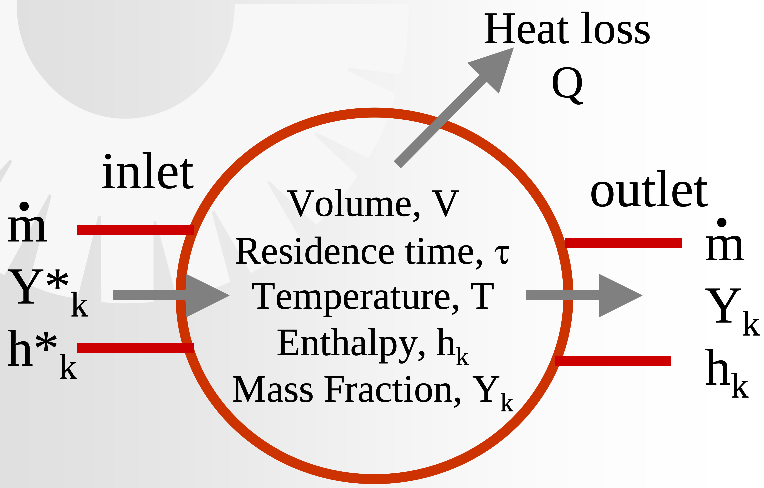
THANK YOU!

- Dave Liscinsky (UTRC)
- Bob Hall (UTRC, retired)
- Heidi Hollick (UTRC)
- Rick Miake-Lye (Aerodyne)
- Hsi-Wu Wong (Aerodyne)
- Mel Roquemore (AFRL)

SERDP: WP1577, WP1625

Modeling Approach (single Perfectly Stirred Reactor)

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



Heat loss

Q

inlet

$\dot{m}$

Y^*_k

h^*_k

Volume, V

Residence time, τ

Temperature, T

Enthalpy, h_k

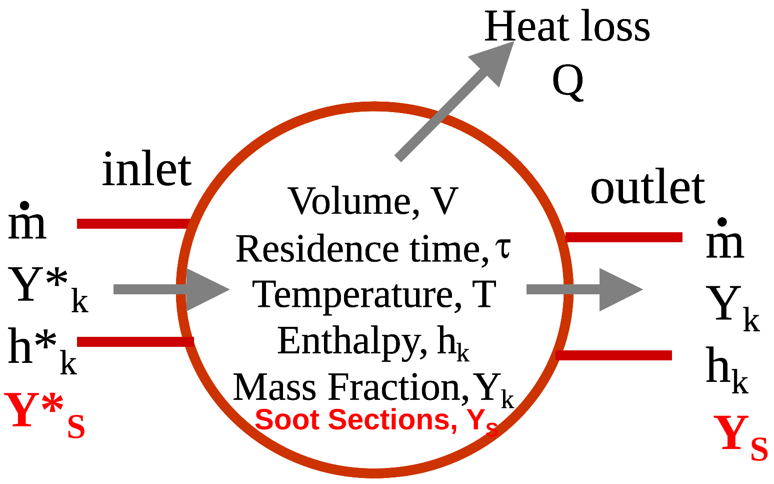
Mass Fraction, Y_k

outlet

$\dot{m}$

Y_k

h_k



Heat loss

Q

inlet

$\dot{m}$

Y^*_k

h^*_k

Y^*_S

Volume, V

Residence time, τ

Temperature, T

Enthalpy, h_k

Mass Fraction, Y_k

Soot Sections, Y_S

outlet

$\dot{m}$

Y_k

h_k

Y_S

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

$$\dot{m}(Y_k - Y_k^*) - \dot{\omega}_k^g W_k V = 0, \quad k = 1,2,....K$$

Species

$$\dot{m}(Y_k - Y_k^*) - \left(\dot{\omega}_k^g + \dot{\boldsymbol{\omega}}_{\mathbf{k}}^{\mathbf{s}}\right) W_k V = 0, \quad k = 1, 2, ...K$$

Sectional

$$\dot{\mathbf{m}}(\mathbf{Y}_\mathbf{k} - \mathbf{Y}_\mathbf{k}^*) - \dot{\mathbf{Q}}_\mathbf{k}\mathbf{V} = \mathbf{0}, \quad \mathbf{k} = \mathbf{K}+\mathbf{1},\mathbf{K}+\mathbf{2},...\mathbf{K}+\mathbf{M}$$

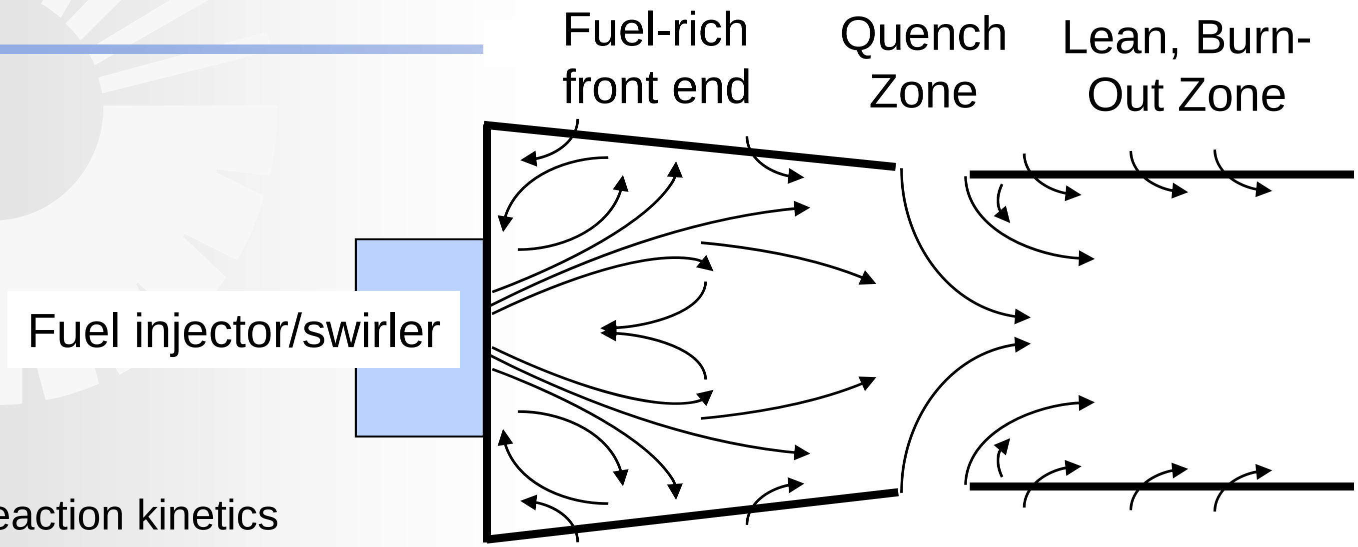
Energy

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

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

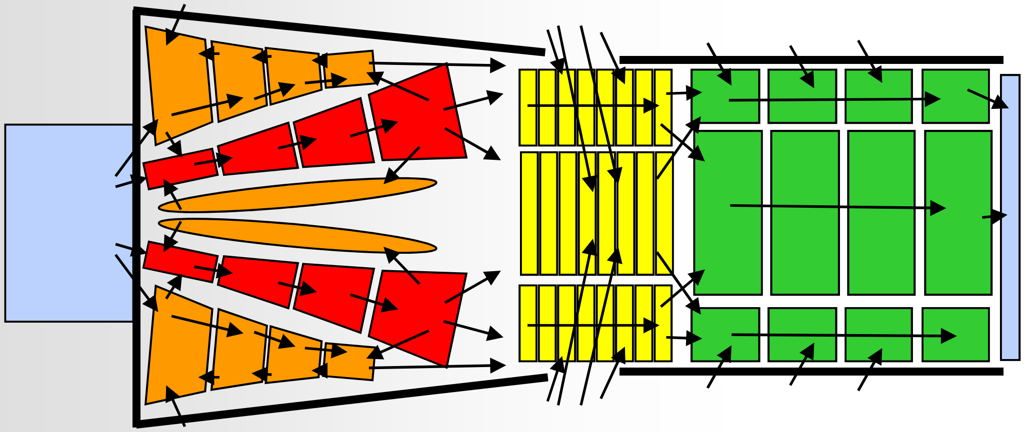
* Sectional equations allow predictions of particle size distributions. Size classes divided by logarithmic scale.

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

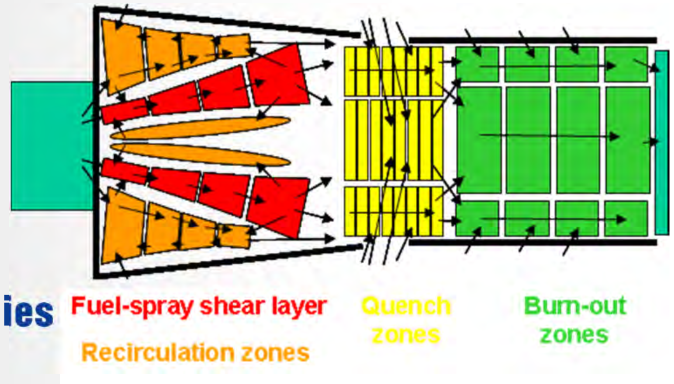
- Plotted as function of local equivalence ratio (phi)

Computations of typical particle size distribution and its evolution through combustor

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

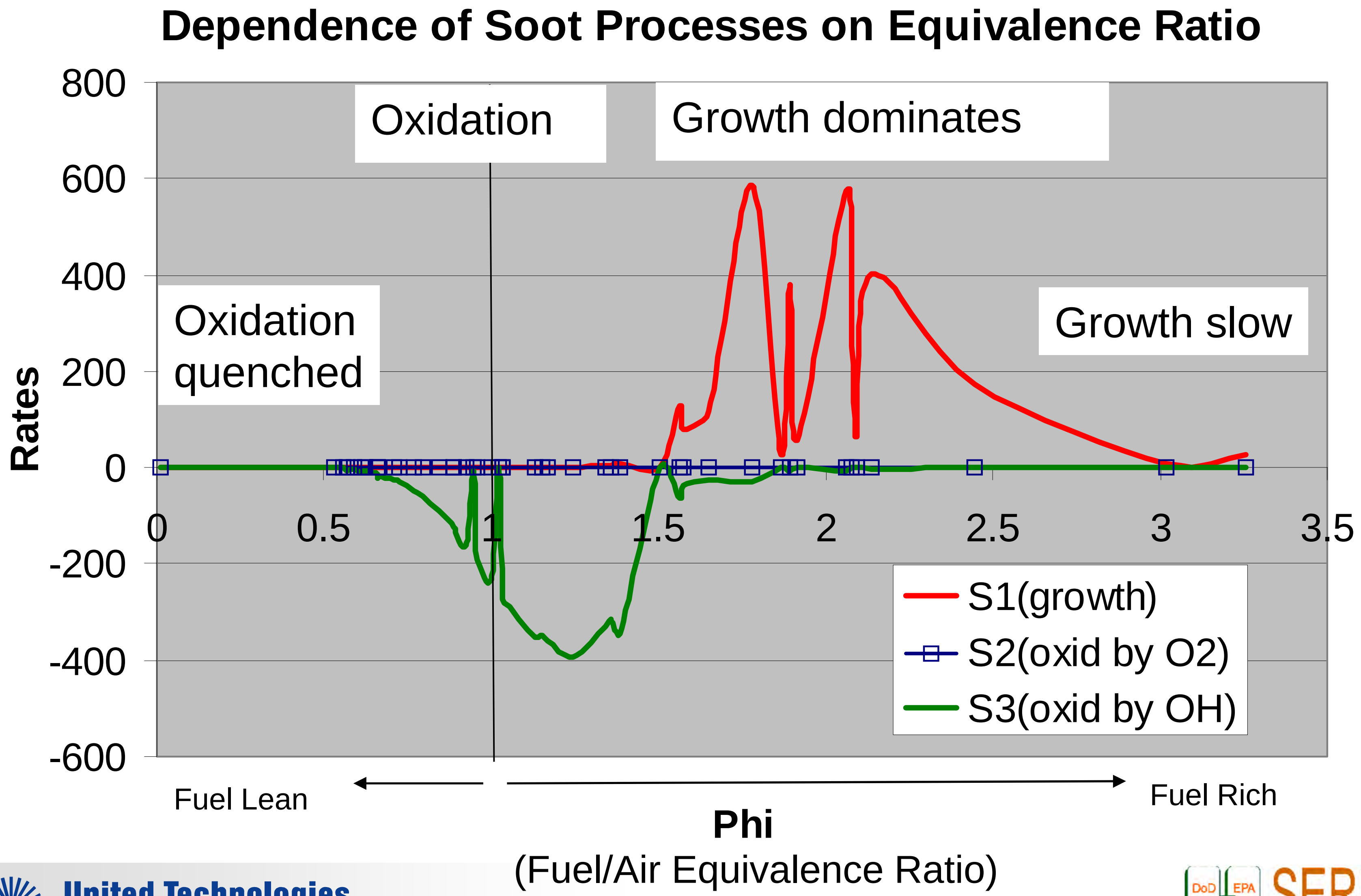
Burner conditions:

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



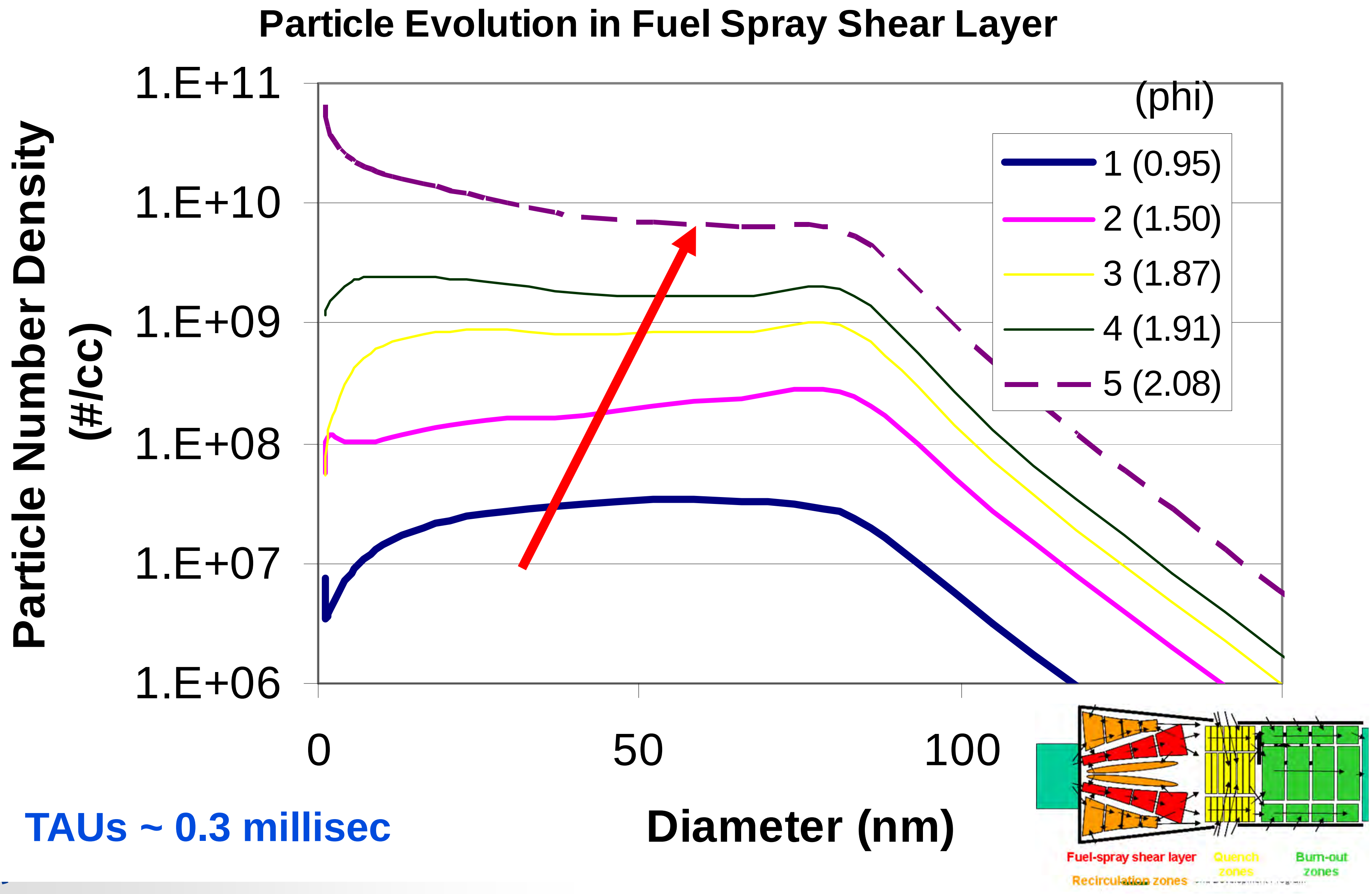
General Formation Characteristics

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

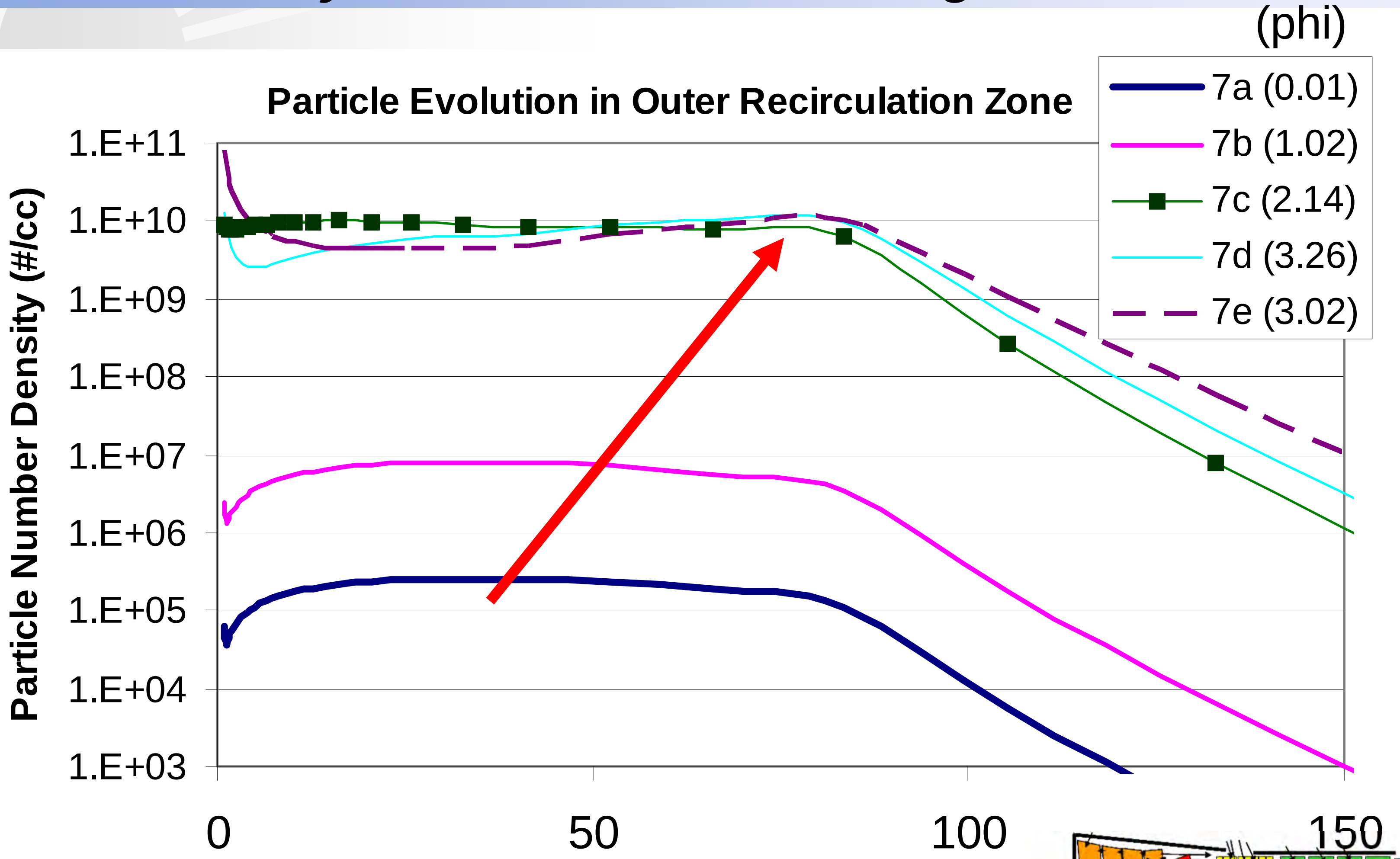


Particle Evolution in Fuel Spray Shear Layer

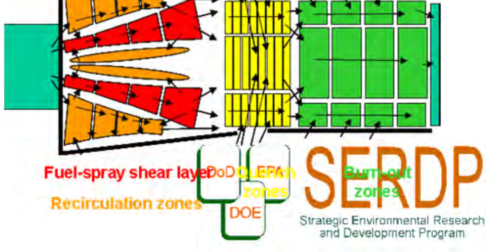
TAUs ~ 0.3 millisec

Particle Formation in Outer Recirculation Zone

Number density saturates due to long residence times

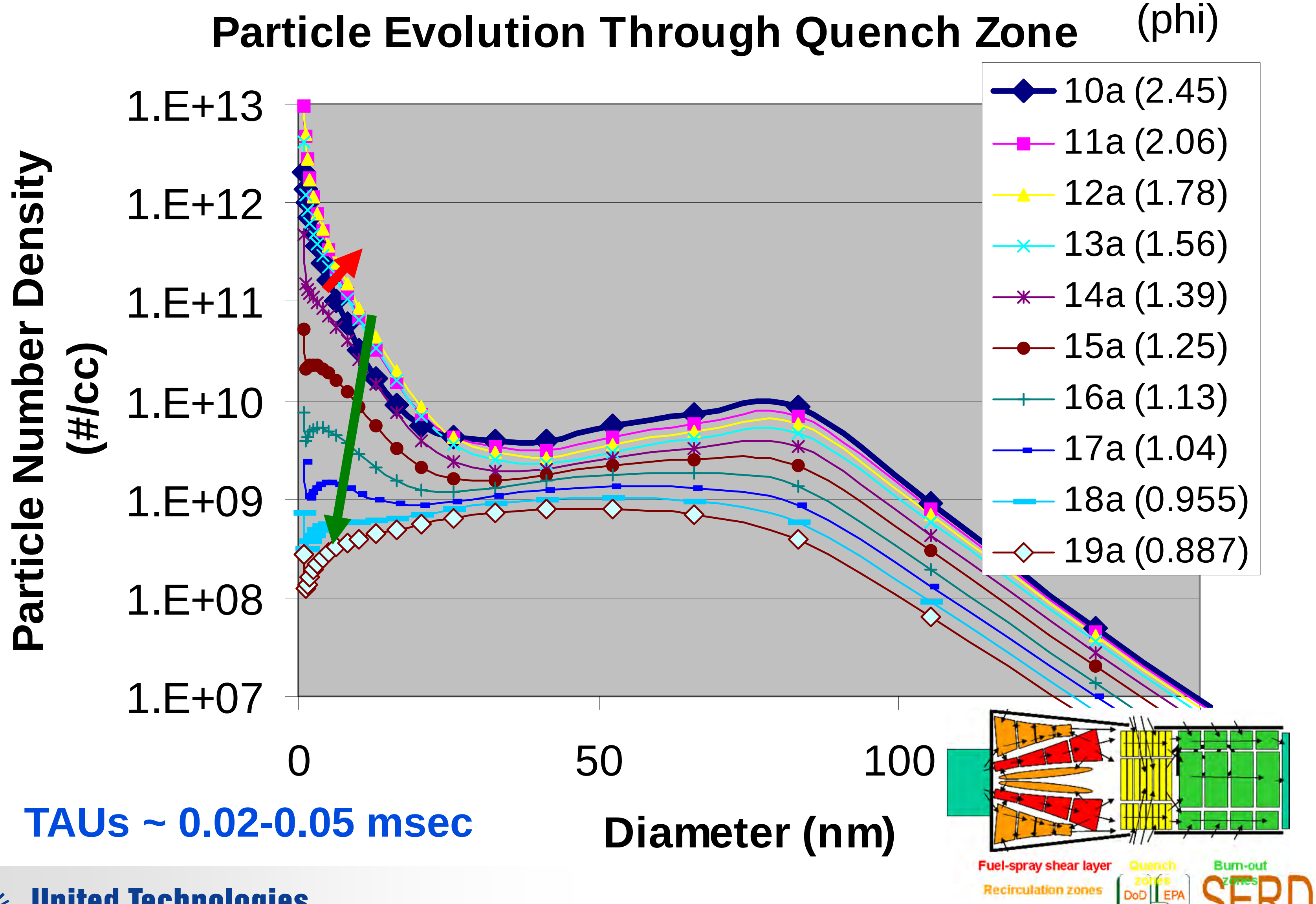


TAUs ~ 0.7-1.7 msec



Particle Evolution Through Quench Zone

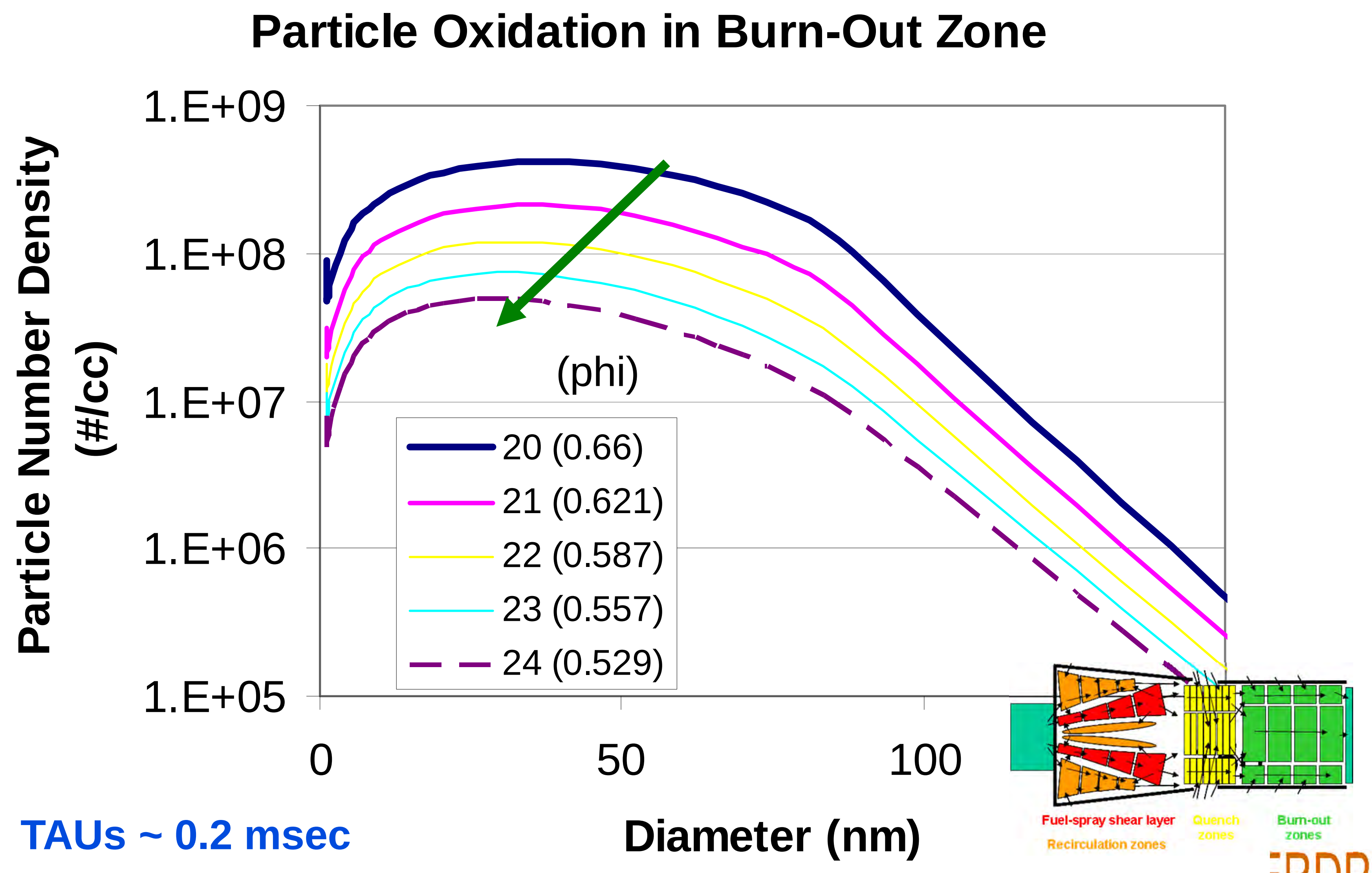
Particles first increase and then decrease: fastest changes in small particles



TAUs ~ 0.02-0.05 msec

Particle Oxidation in Burn-Out Zone

Oxidation reduces number density and size (and mass)



TAUs ~ 0.2 msec

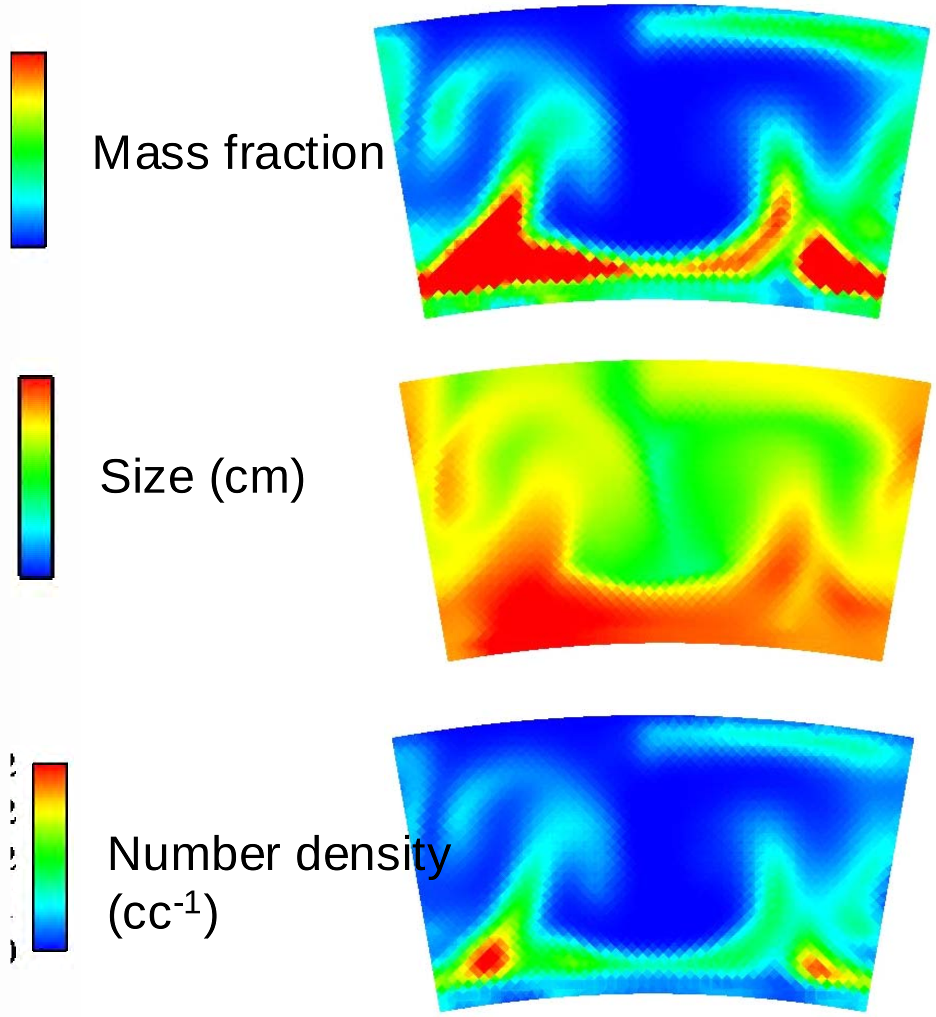
Simulations of Soot at Combustor Exit Plane

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