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# Nuclear and Volcanic Ash, Dust and Debris TIM

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## Soot from Solid Materials

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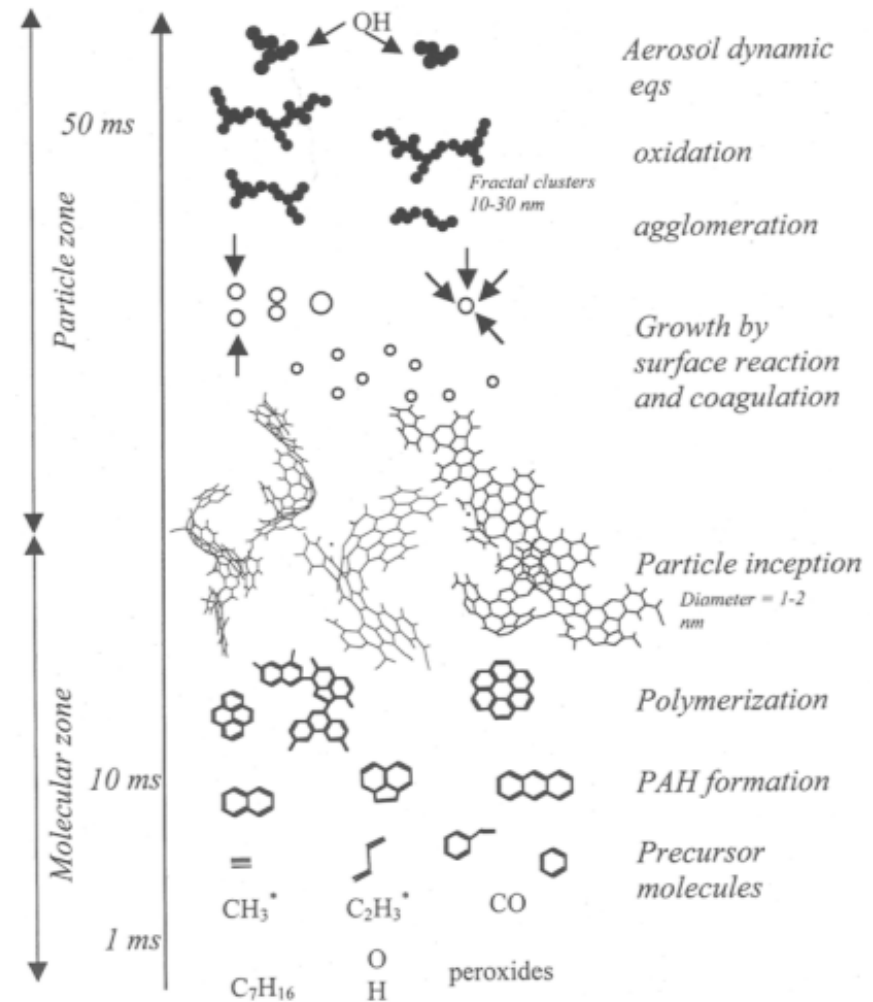
SAND2015-???? C

# Outline

- Soot Background
  - What it is
  - Why we care about it
  - How it behaves
- Soot Properties
  - Physical properties
  - Optical Properties
- How we model it
  - Two equation models
  - Detailed kinetics
  - Optical effects
  - Aerosol behavior
- Soot from an NW event
  - Conjecture on what occurs

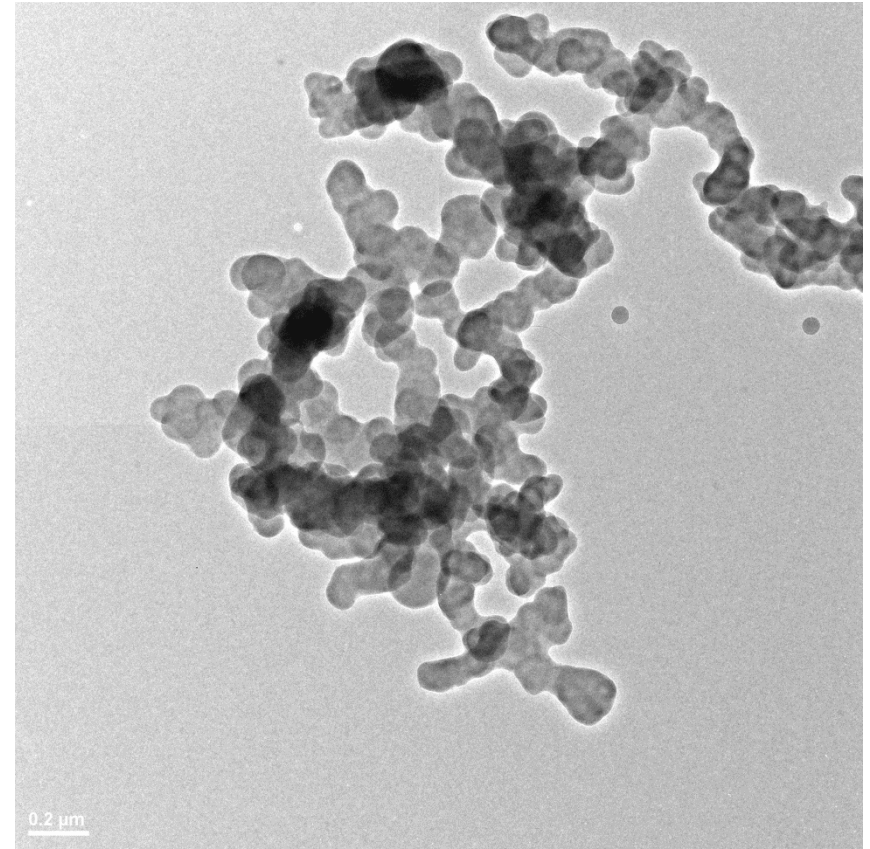
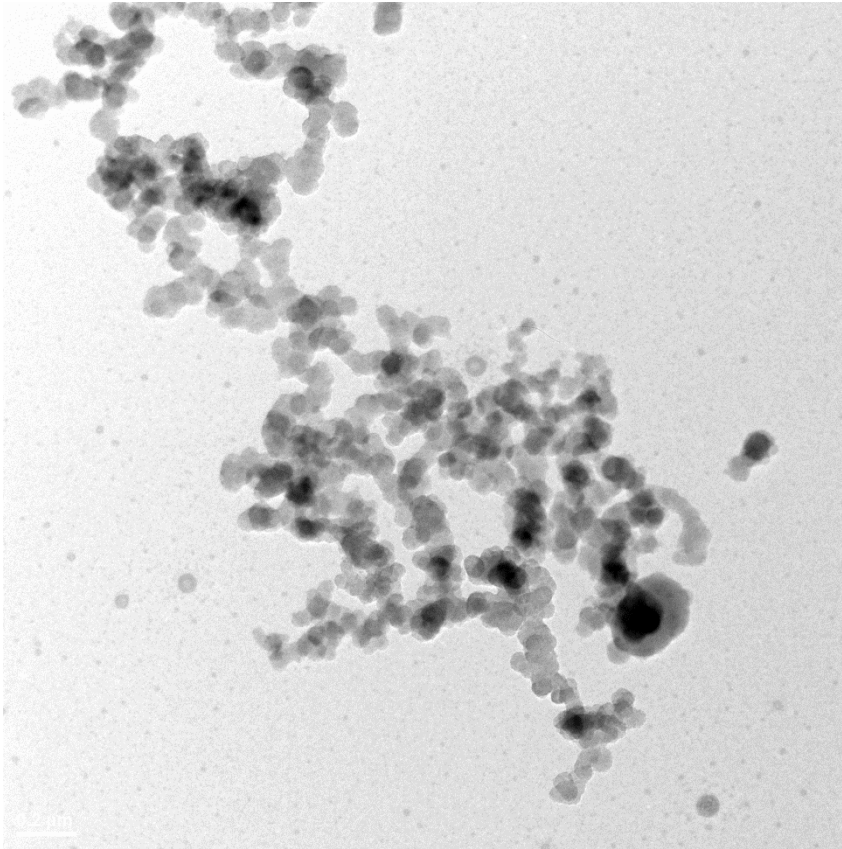
# Soot Background-Molecular Description

- Soot: A high carbon product of incomplete combustion
- Soot is still a difficult problem
- We understand much about the molecular zone from precursor to PAH formation
- We can reasonably well model the aerosol regime
- The transition (particle inception) regime is least understood



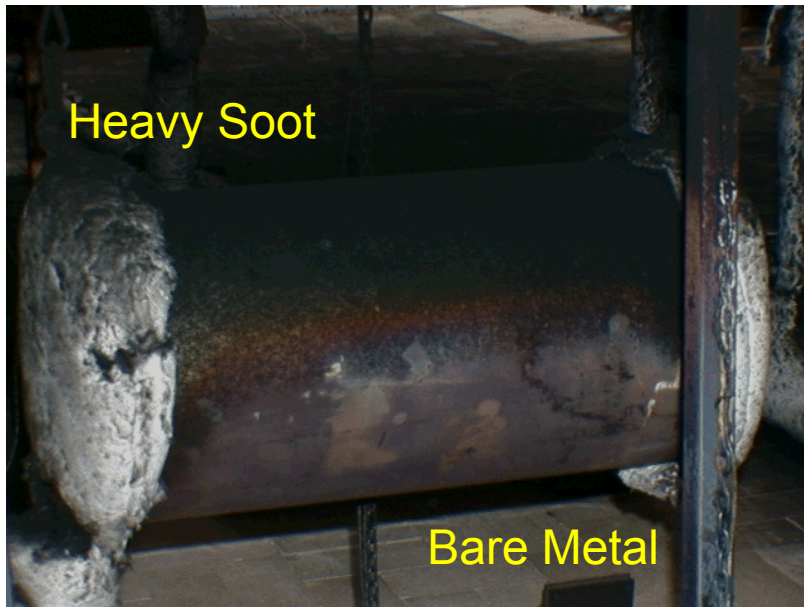
# TEM of Soot from Epoxy Composites

Soot forms complex agglomerate chains



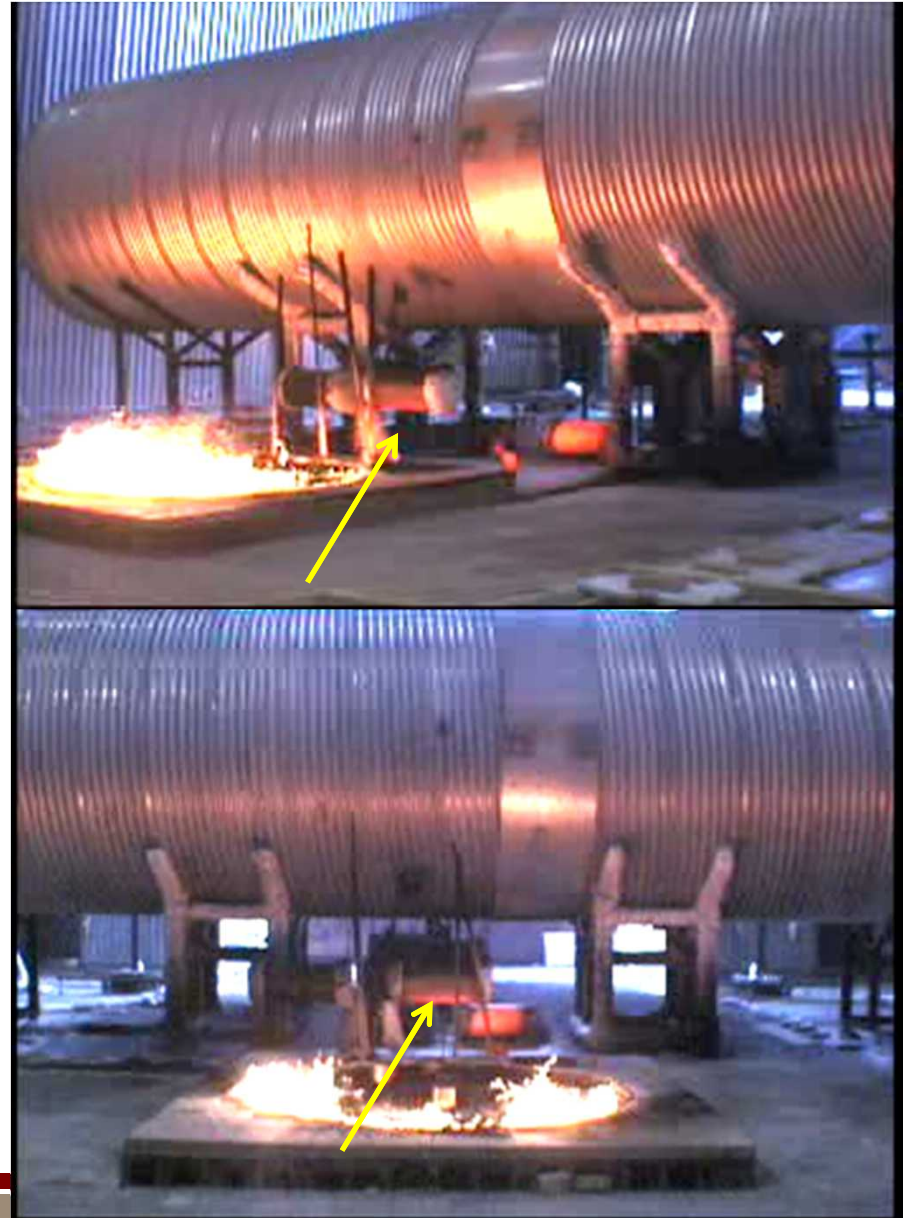
Brown A.L., A.B. Dodd, and B.M. Pickett, "Intermediate Scale Composite Material Fire Testing," The ASME 2011 International Mechanical Engineering Congress & Exposition, November 11-17, 2011, Denver, CO, USA, IMECE2011-63725.

# Surface Deposition of Soot Can Be Complex



In a series of fire tests, a complex deposition pattern was found on a calorimeter where there was significant soot on the top and not on the bottom. This related to the immersion in the flame, as the flames tended to burn under the calorimeter.

From SAND2008-0919



# Soot radiative heat flux is the dominant risk driver in fire environments

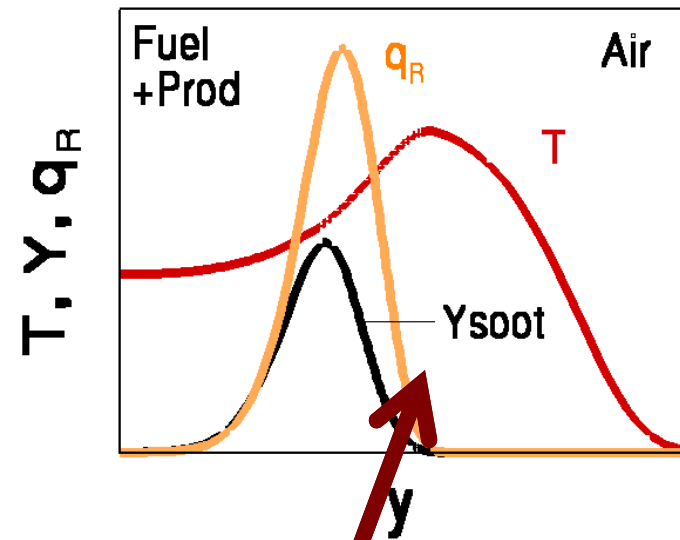
## Radiative Transfer Equation (RTE)

$$\frac{d\overline{I_\lambda}}{ds} = \overline{\mu_\lambda I_{\lambda,b}(T)}_{\text{emission}} - \overline{\mu_\lambda I_\lambda}_{\text{absorption}}$$

$I_{\lambda,b}(T)$  = blackbody at temperature,  $T$

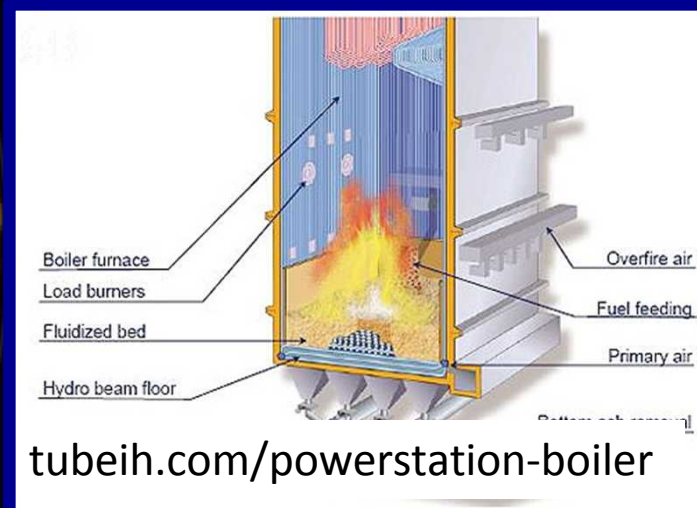
$\mu_\lambda = \frac{f_v}{\lambda} g(n, k)$  = soot absorption coeff.

- Turbulent flame is an assembly of strained and wrinkled flame sheets
- Direct validation of RTE and heat-transfer models require
  - Temperature and soot measurements
  - Time- and space-resolved
- Soot is formed on the fuel rich side of the flame



# Why we Care-Soot impacts a wide variety of engineering applications

- *Soot formation impacts a wide variety of combustion systems*
- *Fire is a dominant safety threat*
- *Propulsion and power generation systems efficiency*
- *Emissions/environment/health*
- *Heat transfer equipment*
  - *Furnaces, boilers*



# How Soot Behaves

- Like an aerosol according to the size
  - Dispersion, transport, thermophoresis, respiratory issues
- Persistent-Doesn't oxidize below 1000K
- Sticks to surfaces, contaminants stick to the soot
  - Grows at intermediate temperatures in the fuel rich part of the flame/products
  - Attracted to cold surfaces by thermophoresis
- Modifies radiation transport
  - Shields radiation at high ( $f_v > 1$  ppm by volume) concentrations
  - Dampens temporal and spectral variations in radiation emission
  - Affects local temperature
- Oxidizes relatively slowly
  - OH and O<sub>2</sub> are the main oxidizers normally considered
- The fraction of fuel carbon resulting in soot is often looked at as a parameter (generally below 20%)
- Pressure generally enhances formation pathway
- Soot yield is optimized at a temperature above and below which yields decrease<sup>1</sup>

1. Frenklach, M., S. Taki, M.B. Durgaprasad, R.A. Matula, "Soot formation in shock-tube pyrolysis of acetylene, allene, and 1,3-butadiene," Combustion and Flame 54, 81-101, 1983.

# Physical Properties

- Specific Gravity: abt. 1.9
- Electrical and thermal conductivity: high ( $\sim 50 \text{ W}/[\text{mK}]$ )
  - Fires create havoc with electrical circuitry because soot deposits and creates conduction paths across dielectrics
- Size: 5-700 nm spheres, agglomerates up to hundreds +  $\mu\text{m}$
- Carbon mass content around 98% and below
  - Lower content reflects addition of impurities
- C/H ratios 72 to 168 by mass (one H for every 6-14 C)
- Soot is often confused/confounded with unburnt hydrocarbons, which have a lot lower C/H ratios, and less aromaticity
  - This results in a range of properties for soot-like particulates

# Optical Properties

- Participating Media Radiation (PMR) for a light beam  $I$  follows the Beer-Lambert attenuation law
 
$$I'_\lambda(S) = I'_\lambda(0) \exp \left[ \int_0^S K_\lambda(S) dS \right]$$
- Fundamental properties are comparatively simple
  - Carbon emits radiation much like a blackbody
  - Numerous studies measured indices of refraction for soot as a function of wavelength
  - Other models exist for property determination
- Scattering becomes complex for mature soot
  - Agglomerates have challenging morphology
  - Scattering depends significantly on the particle size and the wavelength of incident radiation ( $X = \pi d / \lambda$ ; Rayleigh for  $X < 0.3$ , Mie for  $X < 5$ )

$$\kappa_\lambda = \frac{C_\lambda f_v}{\lambda^\alpha}$$

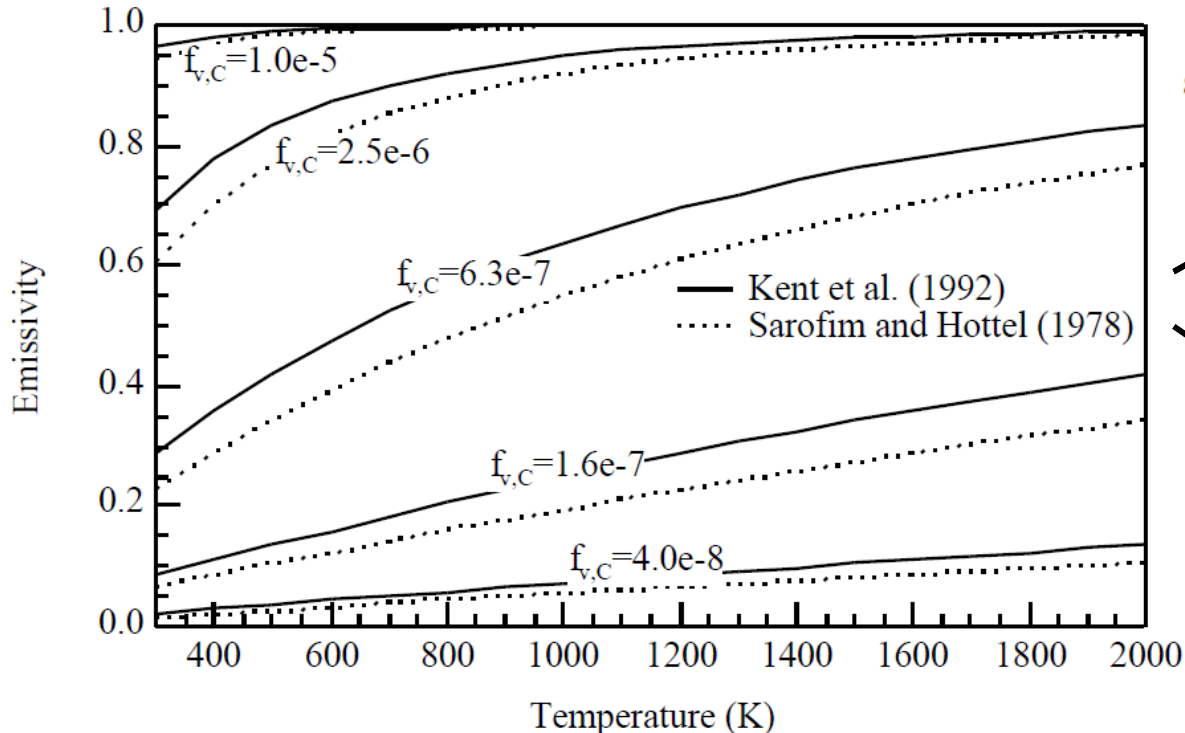
Siegel, R. and J. R. Howell, Thermal Radiation Heat Transfer Third Edition, Hemisphere Publishing Corporation (1992).

Sarofim, A. F.; Hottel, H. C. In Heat Transfer-1978; Hemisphere Publishing: Washington, DC, 1978; pp 199-217.

$C_\lambda$  is typically around 7,  $\alpha$  is a little below 1.

# Optical Properties

- Soot is fairly opaque at 1 m distances for 1 PPM



$$\epsilon_c = \frac{1}{\sigma T^4} \int_0^\infty E_{b\lambda} (1 - \exp(-\kappa_\lambda L_e)) d\lambda$$



$$\epsilon_c = 1 - (1 + 350 f_v T L_e)^{-1}$$

Figure 3.1 A comparison of two soot emissivity models ( $L_e=1.0$ ,  $C_\lambda=7.0$ )

Brown, A.L., "Modeling Soot in Pulverized Coal Flames," M. S. Thesis Brigham Young University, Department of Mechanical Engineering, (1997).

# Two Equation Models

- Transports the mass fraction ( $Y_c$ ) and number of particles ( $N_c$ )
- Particles nucleate and grow from fuel or fuel components
  - These model can accommodate a variety of combustion models
  - Variations in the literature are mostly in the source terms
- Particles oxidize with oxygen (and OH)
- Nuclei collide and are joined

Brown, A.L., Fletcher, T.H., "Modeling Soot in Pulverized Coal Flames," *Energy & Fuels*, **12**, 4, 745-757, (1998).

Fairweather, M., W. P. Jones and R. P. Lindstedt, "Predictions of Radiative Transfer from a Turbulent Reacting Jet in a Cross-Wind," *Combustion and Flame*, **89**, 45-63 (1992).

Leung, K. M., P. Lindstedt and W. P. Jones, "A Simplified Reaction Mechanism for Soot Formation in Nonpremixed Flames," *Combustion and Flame*, **87**, 289-305 (1991).

Sivathanu, Y. R., and J. P. Gore, "Coupled Radiation and Soot Kinetics Calculations in Laminar Acetylene/Air Diffusion Flames." *Combustion and Flame*, **97**, November, 161-172 (1994).

$$\bar{\nabla} \cdot (\rho_g \bar{u} Y_c) = \bar{\nabla} \cdot \left( \frac{\mu}{\sigma} \bar{\nabla} Y_c \right) + \rho_g S_{Y_c}$$

$$\bar{\nabla} \cdot (\rho_g \bar{u} N_c) = \bar{\nabla} \cdot \left( \frac{\mu}{\sigma} \bar{\nabla} N_c \right) + \rho_g S_{N_c}$$

# Two Equation Source Terms

$$S_{Y_c} = \text{Formation}_c - \text{Oxidation}_c$$

$$S_{N_c} = \frac{N_a}{M_c C_{\min}} \text{Formation}_c - \text{Agglomeration}_N$$

$$\text{Formation}_c = [c_T] A e_{FC}^{-E_{FC}/RT}$$

$$\text{Oxidation}_c = SA_{v,c} \frac{P_{O_2}}{T^{1/2}} A_{OC} e^{-E_{OC}/RT}$$

$$SA_{v,c} = \frac{6^{2/3} \pi^{1/3} (\rho_g N_c)^{1/3} Y_c^{2/3} \rho_g^{2/3}}{\rho_c^{2/3}}$$

$$\text{Agglomeration}_N = 2Ca \left( \frac{6M_c}{\pi\rho_c} \right)^{1/6} \left( \frac{6kT}{\rho_c} \right)^{1/2} \left( \frac{\rho_g Y_c}{M_c} \right)^{1/6} (\rho_g N_c)^{11/6}$$

# Modeling Detailed Kinetics

- The Gas Research Institute (GRI) at UC-Berkeley, Stanford, SRI International produced detailed gas-phase mechanisms incorporating much of the gas phase kinetics
  - Classical Hydrogen Abstraction by C<sub>2</sub>H<sub>2</sub> Addition (HACA) mechanism
  - More recently, recognition of propargyl (C<sub>3</sub>H<sub>3</sub>) as a precursor to benzene (C<sub>6</sub>H<sub>6</sub>)
  - Fuels with aromatic structures have a more direct route to soot
- Many reduced mechanisms are produced from GRI source material
- Equilibrium models are generally inadequate to predict soot, as soot is a non-equilibrium product of lean combustion
- Active work with molecular dynamics looks to better interrogate the intermediate scale molecular dynamics

# Detailed Soot Kinetics

- GRI participants have published a soot mechanism<sup>1</sup>.
  - HACA based
- More recently, Direct Numerical Simulations (DNS) of sooting flames have been simulated<sup>2</sup>
  - scalar dissipation rate affects nucleation and PAH growth
- Others have shown PAH growth to be well predicted by existing reaction mechanisms<sup>3</sup>

1. Appel, J., H. Bockhorn, and M. Frenklach, "Kinetic modeling of soot formation with detailed chemistry and physics: Laminar premixed flames of C-2 hydrocarbons", *Combustion and Flame*, 121:1-2, 122-136, 2000.

2. Bisetti, F., G. Blanquart, M.E. Mueller, H. Pitsch, "On the formation and early evolution of soot in turbulent nonpremixed flames," *Combustion and Flame*, 159:1, 317-335, 2012.

3. Slavinskaya, N.A., U. Riedel, S. B. Dworkin, and M.J. Thomson, "Detailed numerical modeling of PAH formation and growth in non-premixed ethylene and ethane flames," *Combustion and Flame*, 159:3, 979-995, 2012.

# Modeling Optical Effects

- Soot is often not the only participating medium
  - In combustion, H<sub>2</sub>O and CO<sub>2</sub> are the other major participants
  - Spectral interactions with other species can be complex
- Transport via Radiative Transport Equation (RTE) solvers
  - Difficult integro-differential equation solve
  - Challenging to integrate the thermal transport spectrum ( $\lambda$  200nm-20 $\mu$ m)
- Common RTE Methods
  - Monte Carlo
  - Discrete Ordinates Method (DOM)
  - Diffusion Approximations (P<sub>n</sub>)

Fiveland, W., "Discrete Ordinates Solutions of the Radiative Transport Equation for Rectangular Enclosures," *Journal of Heat Transfer*, vol. 106, no. 4, 699-706, (1984).

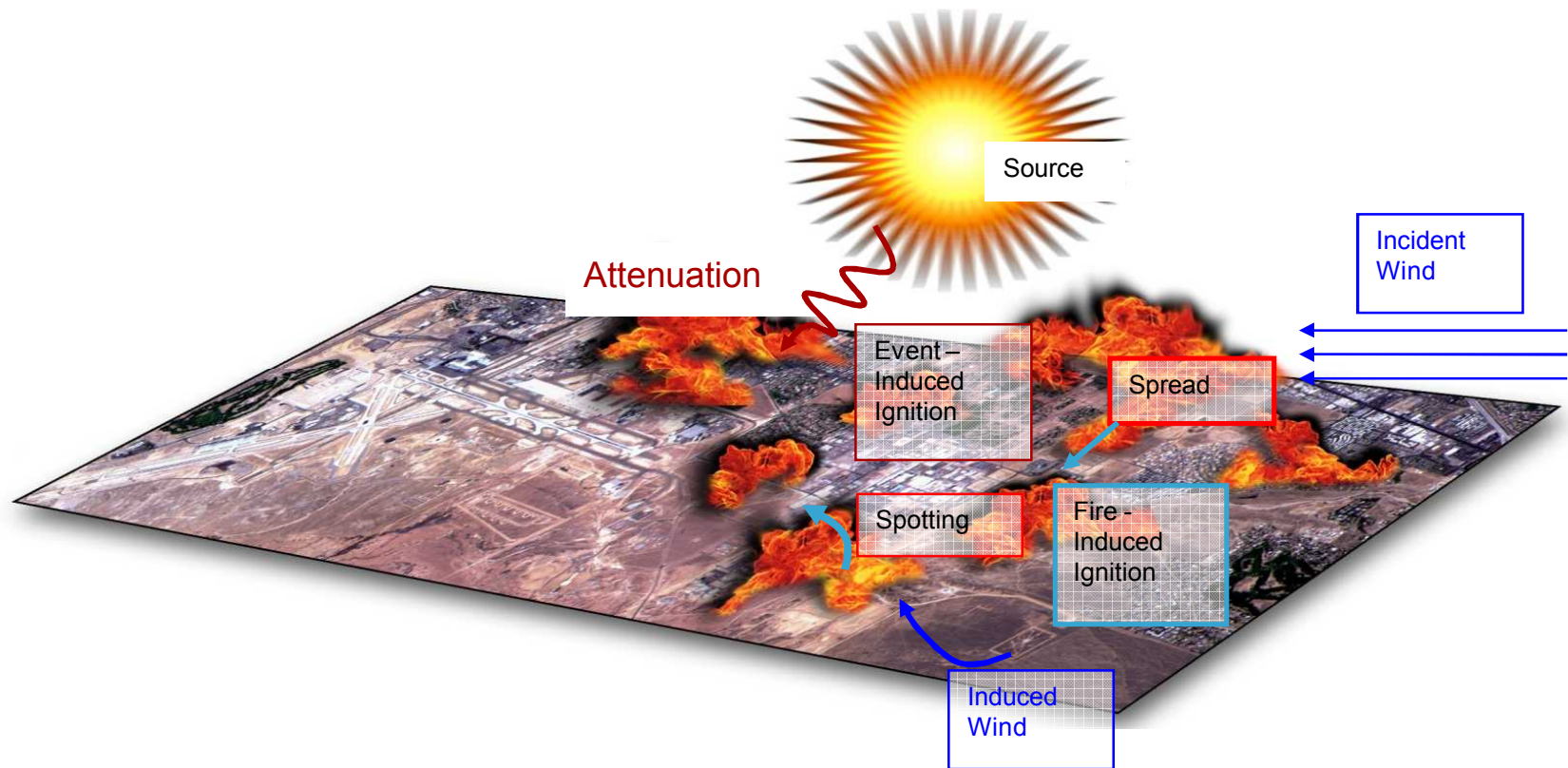
Siegel, R. and J. R. Howell, Thermal Radiation Heat Transfer Third Edition, Hemisphere Publishing Corporation (1992).

# Modeling Aerosol Behavior

- Methods besides two-equation models
  - Moment methods for particle size and composition
  - Modeling individual particles (detailed method)
  - Correlation based models
  - Smoke point models
- Other methods and technologies for other applications
  - Boundary layer deposition models
  - Optimization of soot yields for coke generation
  - Electrostatic precipitators and scrubbers for smoke removal
  - EGR HCCI for clean automotive applications
  - Overfire air for power plants

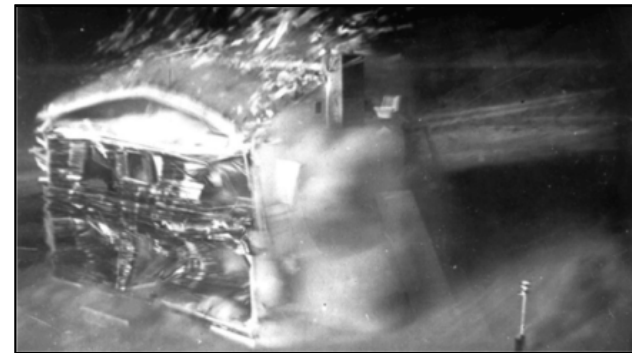
# Consider a Nuclear Detonation

- Characterized by intense thermal radiation that melts sand and vaporizes most solids
- Extremely high temperatures at and near the source



# Conjecture: Soot formation relates to proximity

- Near the Detonation:
  - Radiation vaporizes nearby organic materials and many inorganics
  - Temperatures can be too high for traditional combustion and flaming near the detonation point; traditional soot mechanisms less relevant
  - Soot may form as the ion/plasma cools
  - Affinity to radioactive and fall-out materials?
- Intermediate range
  - Dust/debris interactions?
  - Role of unburnt HCs?
- Outside the blast damage
  - In a more traditional range of combustion studies
  - Soot will form at longer time scales under more traditional mechanisms



# Combustion Theory: Heats of Formation Sandia National Laboratories

- Oxygen will tend to the lowest energy state

TABLE 1.6 Free Energy of Formation<sup>a</sup>  $\Delta g_f^\circ$  (kcal / mole) at 298 K

<i>Gases</i>		<i>Solids</i>	
H <sub>2</sub> O	-54.64	AgCl	-26.22
H <sub>2</sub> O <sub>2</sub>	-24.7	AgBr	-22.39
O <sub>3</sub>	39.06	AgI	-15.81
HCl	-22.77	BaO	-126.3
HBr	-12.72	BaSO <sub>4</sub>	-350.2
HI	0.31	BaCO <sub>3</sub>	-272.2
SO <sub>2</sub>	-71.79	CaO	-144.1
SO <sub>3</sub>	-88.52	CaCO <sub>3</sub>	-269.8
H <sub>2</sub> S	-7.89	Ca(OH) <sub>2</sub>	-214.3
N <sub>2</sub> O	24.9	SiO <sub>2</sub>	-192.4
NO	20.72	Fe <sub>2</sub> O <sub>3</sub>	-177.1
NO <sub>2</sub>	12.39	Al <sub>2</sub> O <sub>3</sub>	-376.8
NH <sub>3</sub>	-3.97	CuO	-30.4
CO	-32.81	Cu <sub>2</sub> O	-34.98
CO <sub>2</sub>	-94.26	ZnO	-76.05
<i>Organic Compounds</i>			
<i>Gases</i>			
Methane, CH <sub>4</sub>	-12.14	Ethylene, C <sub>2</sub> H <sub>4</sub>	16.28
Ethane, C <sub>2</sub> H <sub>6</sub>	-7.86	Acetylene, C <sub>2</sub> H <sub>2</sub>	50.00
Propane, C <sub>3</sub> H <sub>8</sub>	-5.61	1-Butene, C <sub>4</sub> H <sub>8</sub>	17.09
<i>n</i> -Butane, C <sub>4</sub> H <sub>10</sub>	-3.75	<i>cis</i> -2-Butene, C <sub>4</sub> H <sub>8</sub>	15.74
Isobutane, C <sub>4</sub> H <sub>10</sub>	-4.3	<i>trans</i> -2-Butene, C <sub>4</sub> H <sub>8</sub>	15.05
<i>n</i> -Pentane, C <sub>5</sub> H <sub>12</sub>	-2.0	Isobutene, C <sub>4</sub> H <sub>8</sub>	13.88
Isopentane, C <sub>5</sub> H <sub>12</sub>	-3.5	1,3-Butadiene, C <sub>4</sub> H <sub>6</sub>	36.01
Neopentane, C <sub>5</sub> H <sub>12</sub>	-3.6	Methyl chloride, CH <sub>3</sub> Cl	-14.0
<i>Liquids</i>			
Methanol, CH <sub>3</sub> OH	-39.73	Benzene, C <sub>6</sub> H <sub>6</sub>	29.76
Ethanol, C <sub>2</sub> H <sub>5</sub> OH	-41.77	Chloroform, CHCl <sub>3</sub>	-17.1
Acetic acid, CH <sub>3</sub> COOH	-93.8	Carbon tetrachloride, CCl <sub>4</sub>	-16.4

- Will there be atmospheric oxygen available in the plume?

- Excess carbon may find its way to soot

Kuo, K.K., Principles of Combustion, John Wiley & Sons, 1986.

# Some recent test results

- Flash ignition at the solar furnace facility- significant unburnt HC



# Typical Fuel Loadings

## Urban<sup>1,2</sup>

English Units

Metric Units

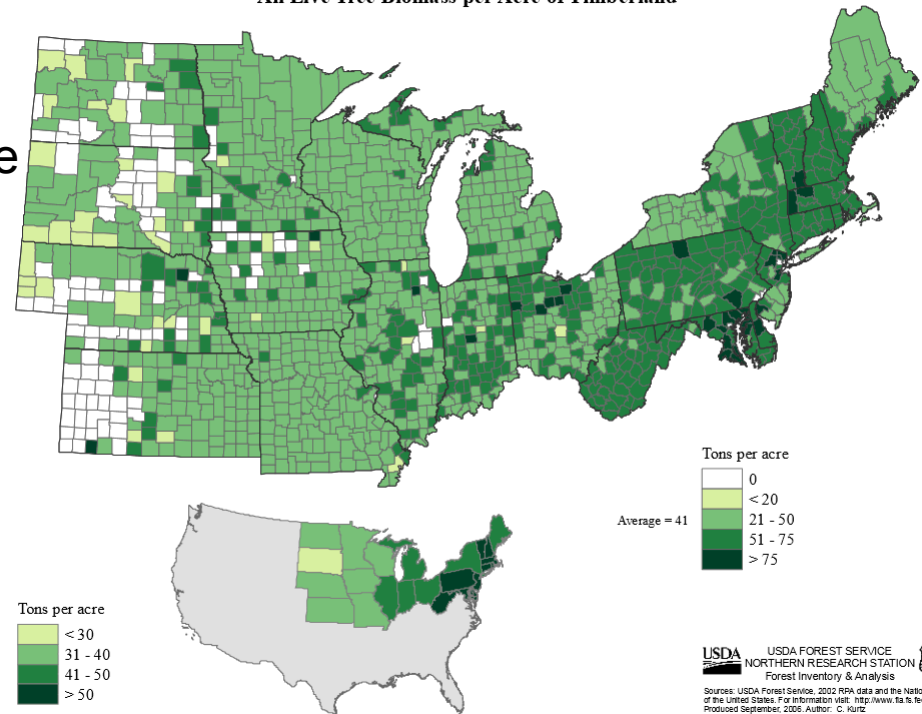
	W	M	E		W	M	E
	Low	Med	High		Low	Med	High
Fuel Loading	lb/ft <sup>2</sup>			Fuel Loading	kg/m <sup>2</sup>		
Central city	48	84	128	Central city	234.4	410.1	625.0
Inner belt	13.5	21.6	37.8	Inner belt	65.9	105.5	184.6
Outer belt	3.6	6.4	10	Outer belt	17.6	31.2	48.8

## Rural<sup>3</sup>

Dense live trees tend around 50 ton/acre  
 50 tons/acre = 11.2085 kg/m<sup>2</sup>

1. Larson, D.A. and Small, R.D., "Analysis of the Large Urban Fire Environment; Part II. Parametric Analysis and Model City Simulations," PSR Report 1210, November 1982.
2. DCPA Attack Environmental Manual Chap. 3, "What the Planner Needs to Know about Fire Ignition and Spread," U.S. Defense Civil Preparedness Agency and U.S. Department of Defense, Washington, D.C., June 1973
3. [http://www.nrs.fs.fed.us/fia/maps/nfr/Final\\_PDF/northern\\_100dpi/xlivebio\\_northern\\_100.pdf](http://www.nrs.fs.fed.us/fia/maps/nfr/Final_PDF/northern_100dpi/xlivebio_northern_100.pdf)

All Live Tree Biomass per Acre of Timberland



# Soot Yield Vaporizing a 300 m Circle

## Assumptions

Vegetation Density ( $\rho_v$ ) = 50 tons/acre = 11.2085 kg/m<sup>2</sup>

Area =  $\pi r^2 = 3.14159 \cdot (150 \text{ m})^2 = 70,690 \text{ m}^2$

Mass<sub>Combustible</sub> =  $\rho_v \cdot \text{Area} = 70,690 \cdot 11.2 = 792,280 \text{ kg}$

Soot Density ( $\rho_c$ ) = 1900 kg/m<sup>3</sup>

Volume =  $\frac{4}{3}\pi r^3 = \frac{4}{3} \cdot 3.14159 \cdot r^3 = \text{Mass}_{\text{Carbon}} / (f_v \rho_c) = 21 \text{ m}^3 / 1\text{e-}6$

All mass vaporized, ~50% of tree by mass is carbon (typical of dry wood), 396,000 kg of carbon could be in the atmosphere for a 300 m diameter vaporization event.

If 10% of the carbon ends up as soot, there might be 40 tons of soot dispersed in the plume from ground fuel.

40 tons of soot is 21 m<sup>3</sup> of soot, which perfectly dispersed would fill a 340 meter diameter sphere with 1 ppm volume fraction of soot (very opaque).

The chronology of this formation may significantly affect the optical signature of the blast.

# Summary

- Much is known about soot in the combustion/fire environment
  - Presented some general knowledge on the subject
- Little is known about soot formed in and around a nuclear detonation
  - Most historical data are from tests performed in the desert, over the ocean, may not be representative
  - This might be an area where the community is poorly informed based on models that do not consider this as a parameter
  - Soot may form in highly urban or heavily forested regions
- Soot participates in fall-out material transport
- Current weapons effects work may help provide additional information

# Acknowledgements

- Prepared with help from Josh Hubbard, Fred Gelbard, John Hewson, Sean Kearney

# City Data from Larson & Small\*

## City Data from Larson & Small\*

### City Dimensions\*

City			
Type	W	M	E
Radial Dimension (km)			
Central city	0 - 1	0 - 1	0 - 2
Inner belt	1 - 3	1 - 4	2 - 6
Outer belt	3 - 12+	4 - 12+	6 - 12+
Average Building Height (m)			
Central city	27	40	54
Inner belt	10	13	20
Outer belt	5	7	8

### City Fuel Loading & Burning Rate\*

	Degree of "built-up-ness" of city		
	W Low	M Med	E High
Total areal fuel loading (lb/ft <sup>2</sup> )			
Central city	48.0	84.0	128.0
Inner belt	13.5	21.6	37.8
Outer belt	3.6	6.4	10.0
Areal heating rate (kcal/m <sup>2</sup> -s)			
Central city	87.40	153.00	233.0
Inner belt	24.60	39.30	68.6
Outer belt	6.55	11.75	18.3
Areal heating rate (kW/m <sup>2</sup> )			
Central city	N/A	639	974
Inner belt	N/A	164	288
Outer belt	N/A	N/A	N/A

### Block shapes, sizes, street widths (internet):

	City type		
	W	M	E
Block shape	N/A	Square	Rectangular
Block sizes (m)	N/A	100 x 100 (Houston) to 201 x 201 (Chicago)	80 x 322 (NYC)
Avg. Street width (m)	N/A	70 (Chicago)	23 (Frankfurt)