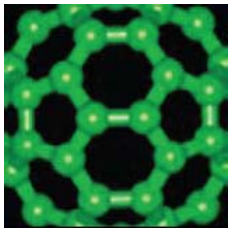
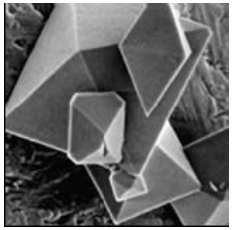
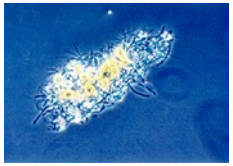
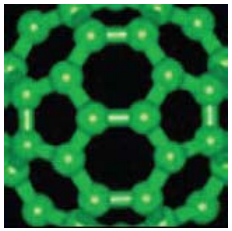


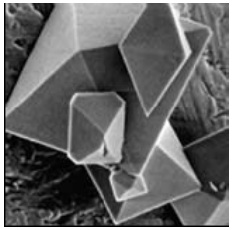


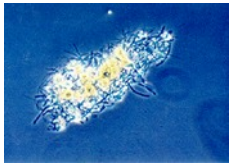


# Soot: Formation, Destruction and Environmental Implications

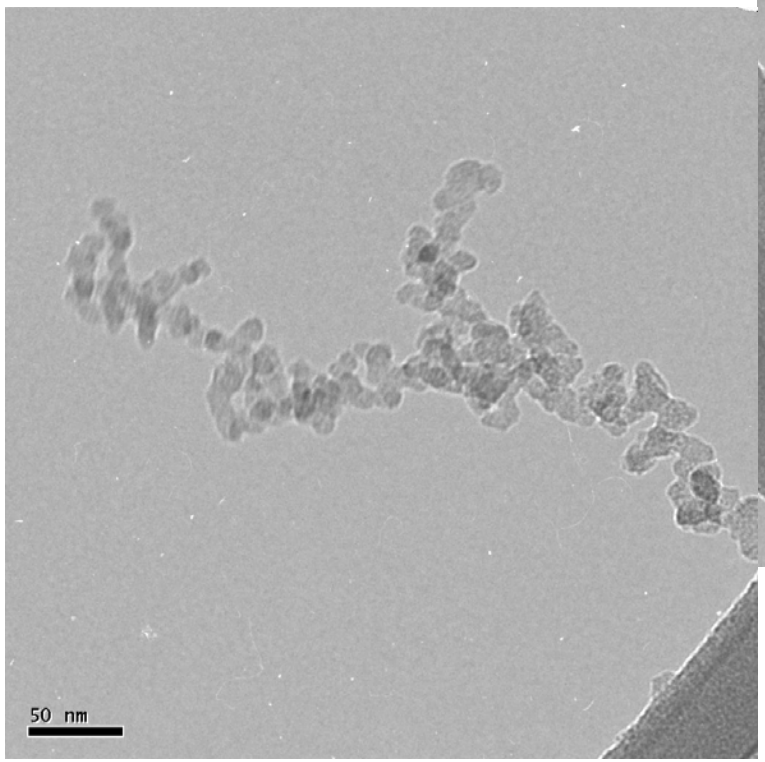
**JoAnn S. Lighty**
**Professor and Chair**
**Department of Chemical Engineering**
**Institute for Clean & Secure Energy**
**University of Utah**



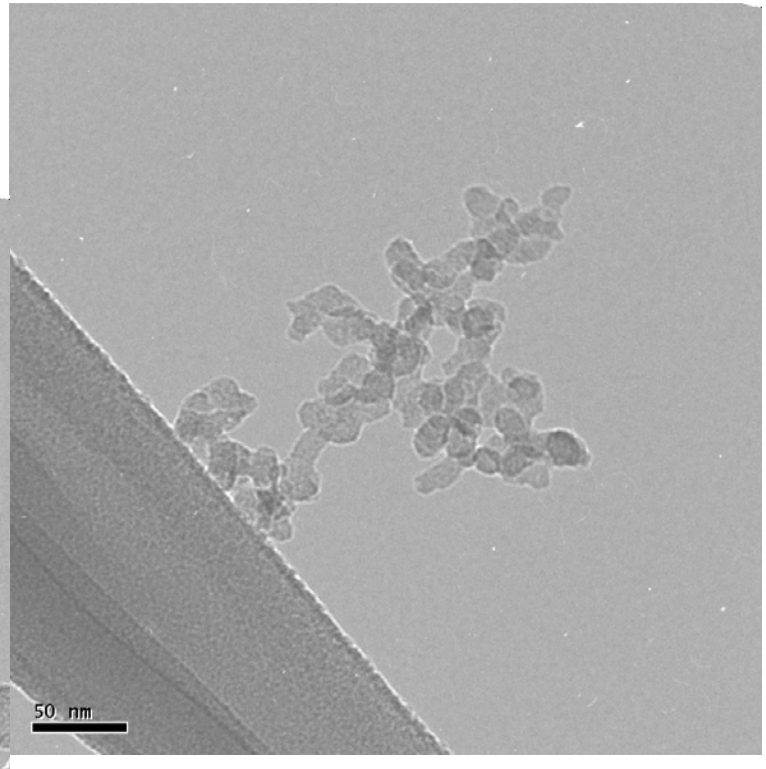




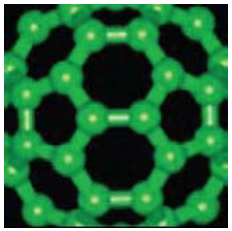
# What is Soot?

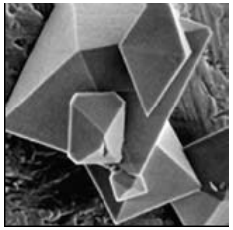


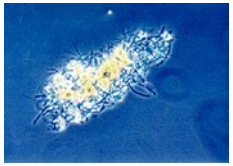

Benzene



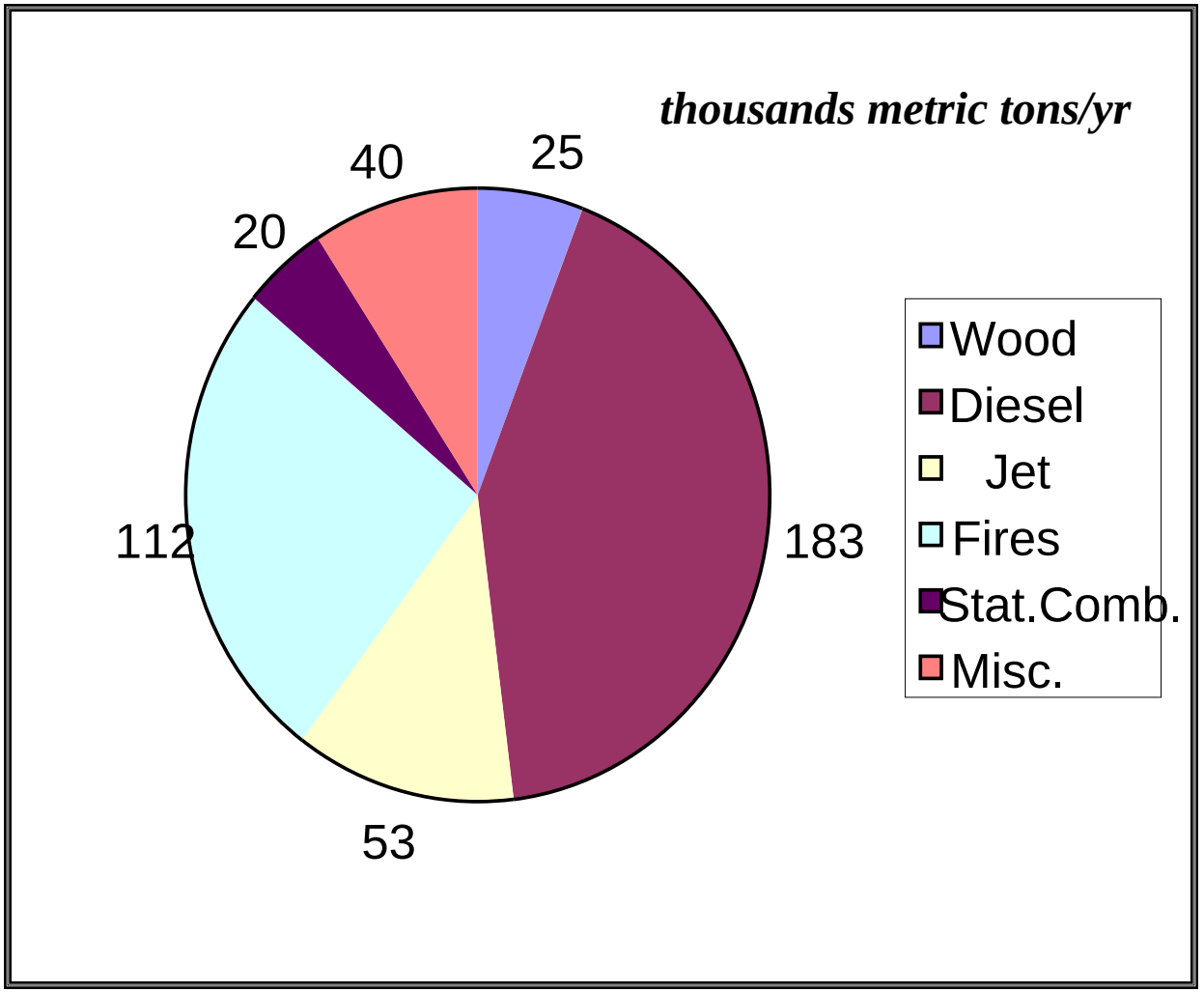

Ethylene

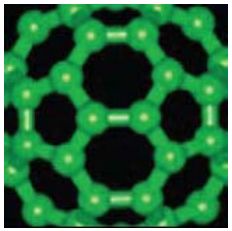


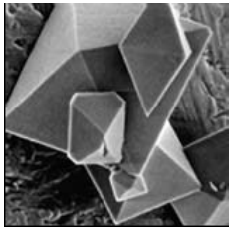


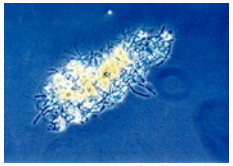


# Sources of Soot
## (EPA, 2002)



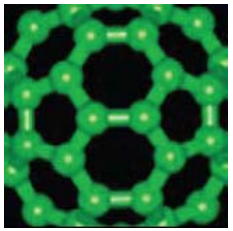


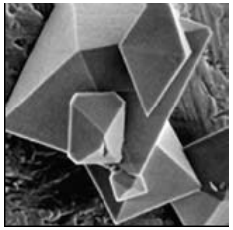


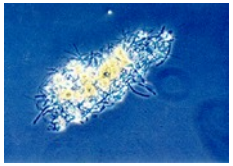


# Environmental Implications

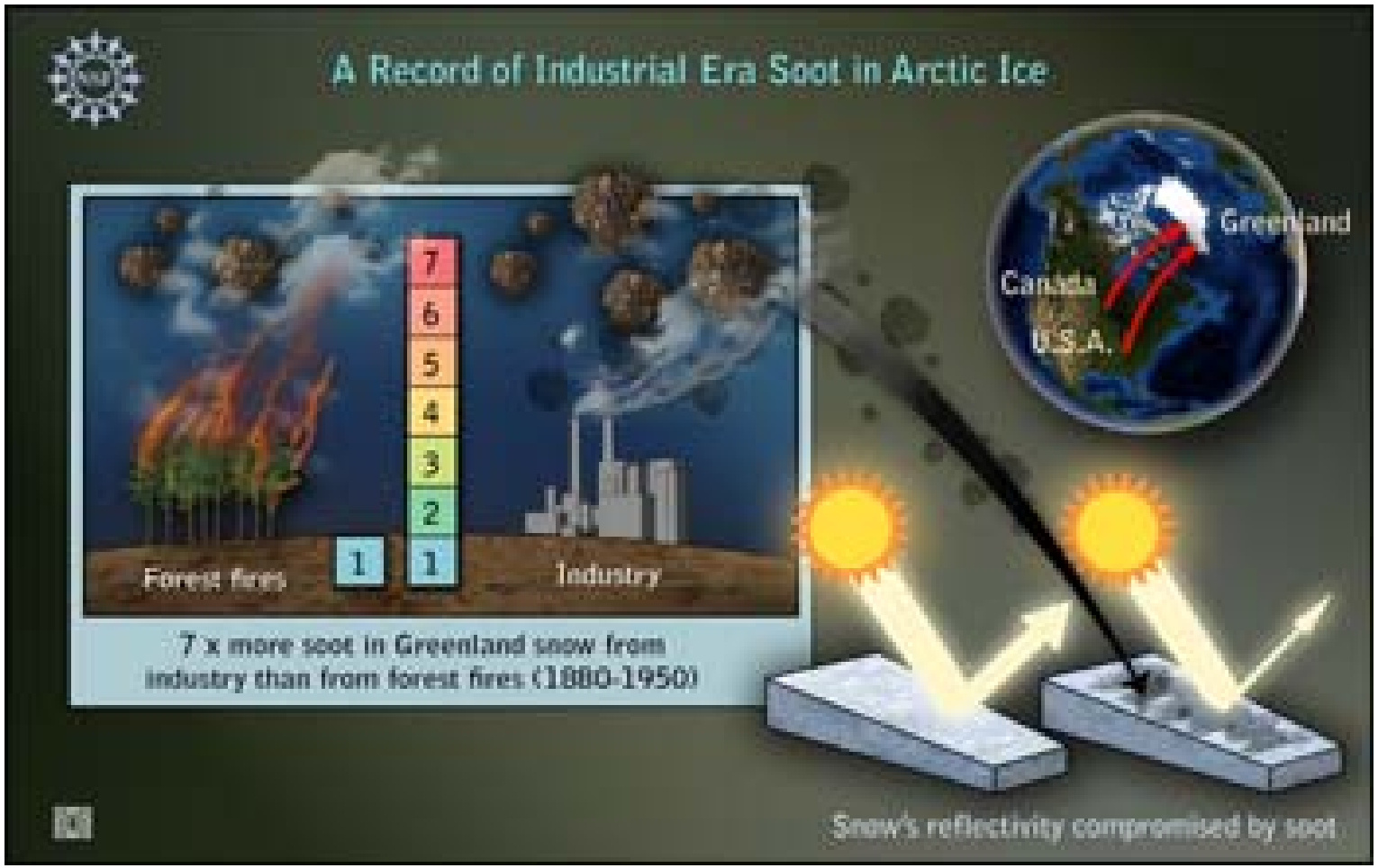
- **Warming effect (International Panel on Climate Change (IPCC))**
- **By reducing the ability of snow and ice to reflect sunlight (NASA, 2003), melts more rapidly, which in turn further increases temperatures**

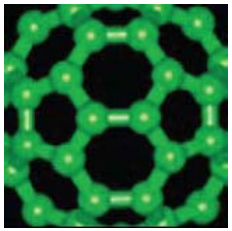


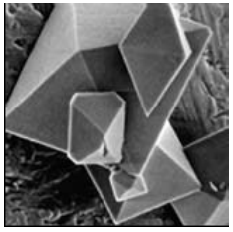


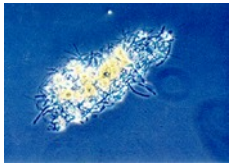


# Increase in soot changes the reflectivity of the snow/ice

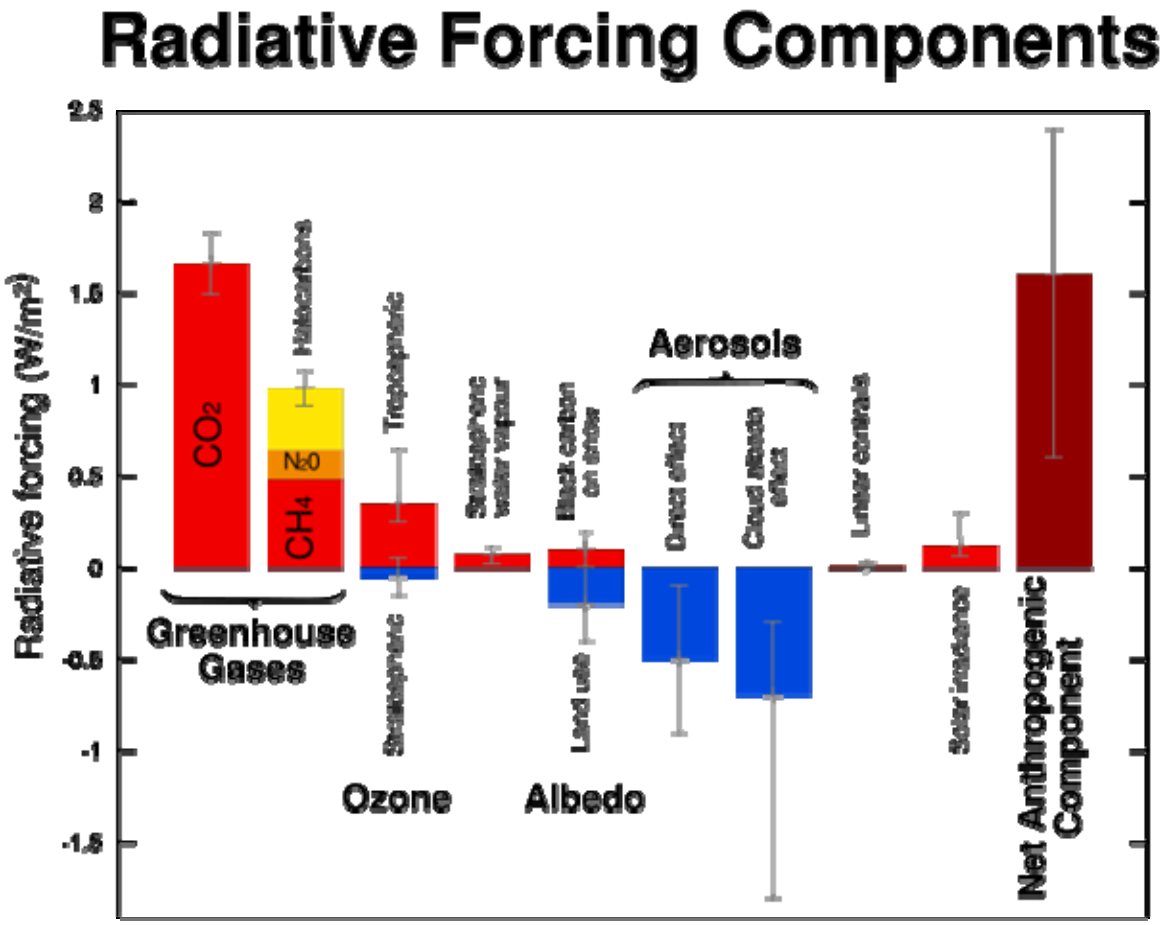




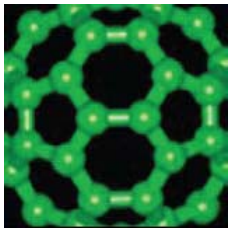


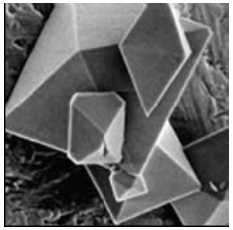


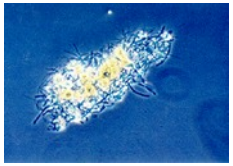
# IPCC implicates black carbon




**Changes in radiative forcings between 1750 and 2005**

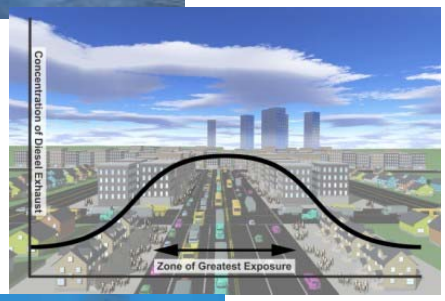


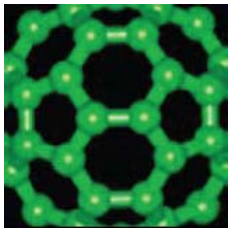


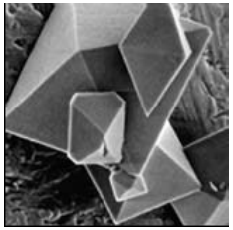


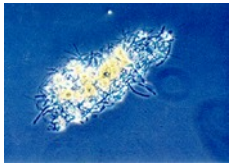
# Health Effects

Respiratory illness, cancer, heart attacks and premature death (Clean Air Task Force)

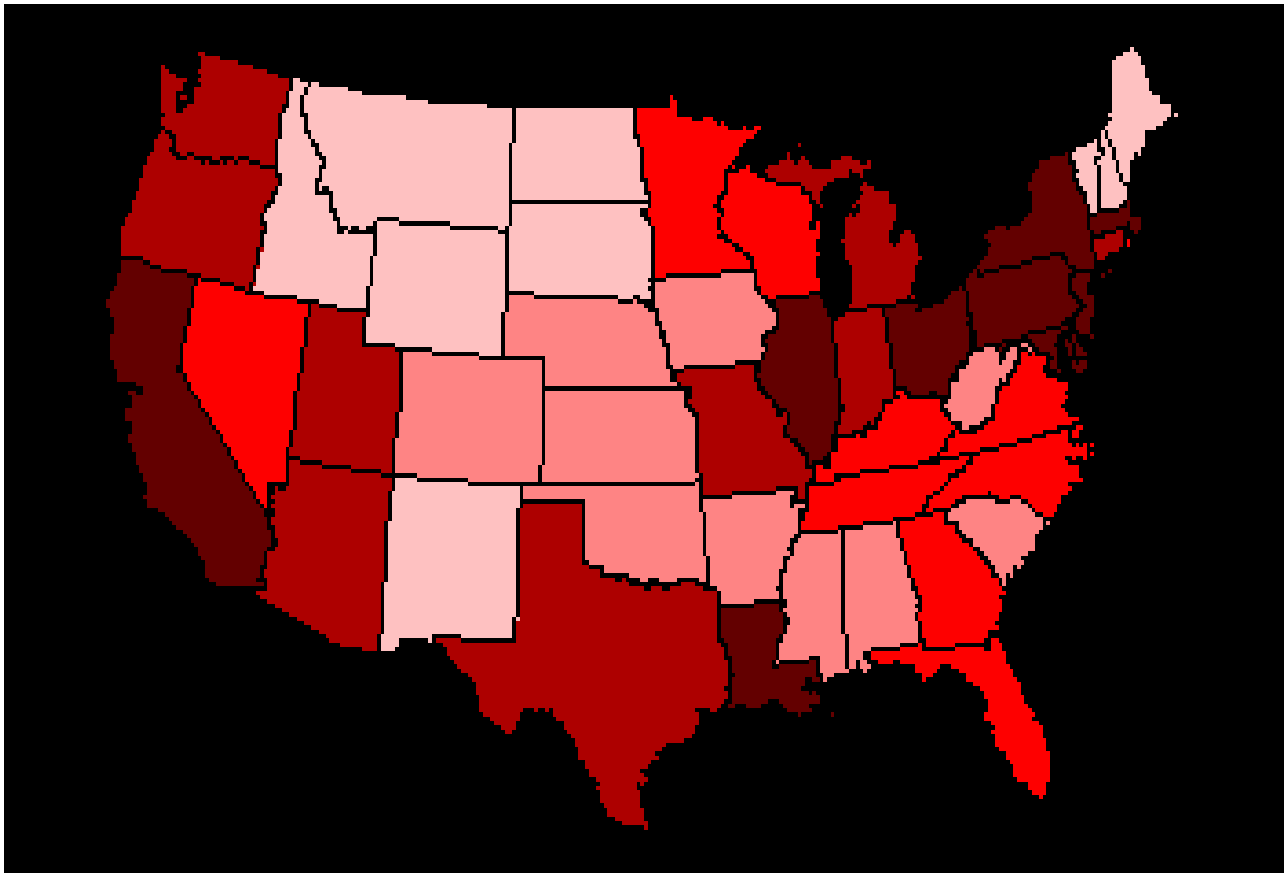



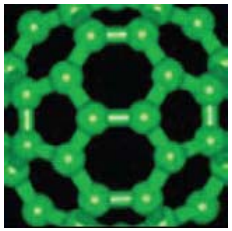



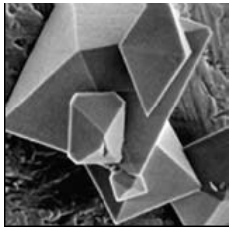


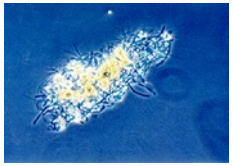


# Darker Color Indicates Higher Health Risk

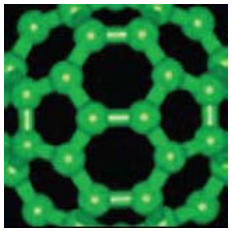


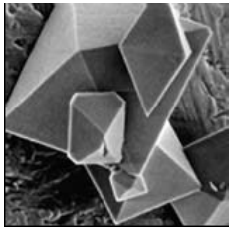


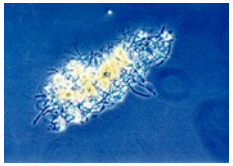


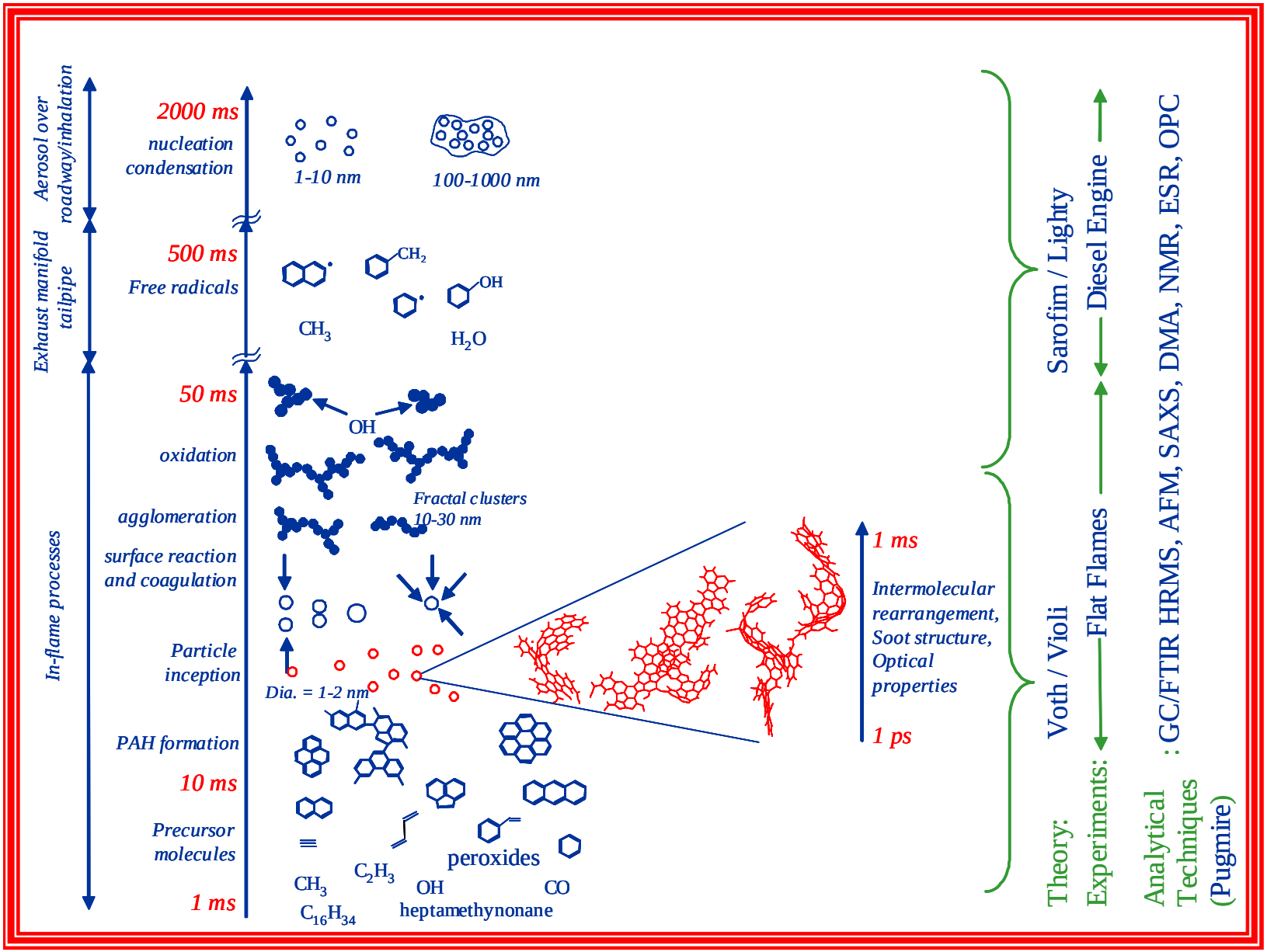


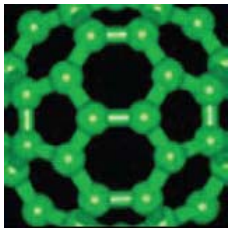
# Soot Formation

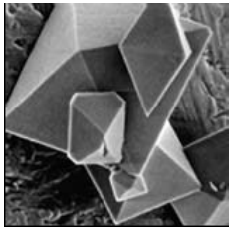


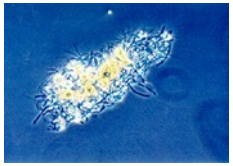





Aerosol over roadway/inhalation
Exhaust manifold tailpipe
In-flame processes
2000 ms
nucleation
condensation
1-10 nm
100-1000 nm
500 ms
Free radicals
CH3
CH2
OH
H2O
50 ms
OH
oxidation
agglomeration
Fractal clusters
10-30 nm
surface reaction
and coagulation
Particle
inception
Dia. = 1-2 nm
PAH formation
10 ms
Precursor
molecules
CH3
C16H34
C2H3
OH
peroxides
CO
heptamethynonane
1 ms
1 ms
Intermolecular
rearrangement,
Soot structure,
Optical
properties
1 ps
Sarofim / Lighty
Diesel Engine
Voth / Violi
Flat Flames
Theory:
Experiments:
Analytical
Techniques
(Pugmire)
: GC/FTIR HRMS, AFM, SAXS, DMA, NMR, ESR, OPC

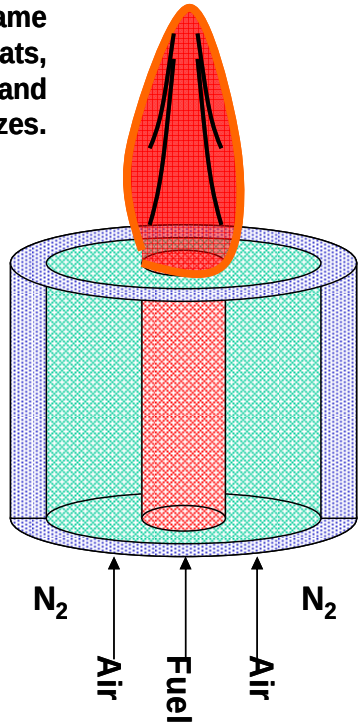




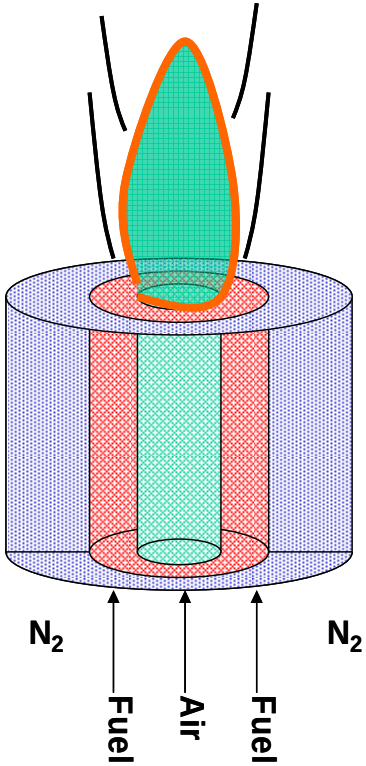


# Experimental System: IDF for young soot

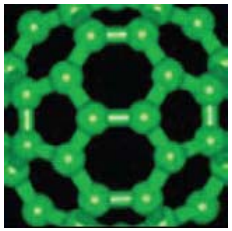
**Normal Diffusion Flame: Soot passes through the flame and heats, carbonizes, and oxidizes.**

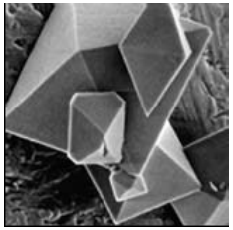


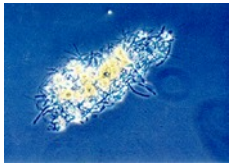

**Inverse Diffusion Flame: Soot is driven away from the flame into cool fuel/$N_2$: no carbonization or oxidation.**



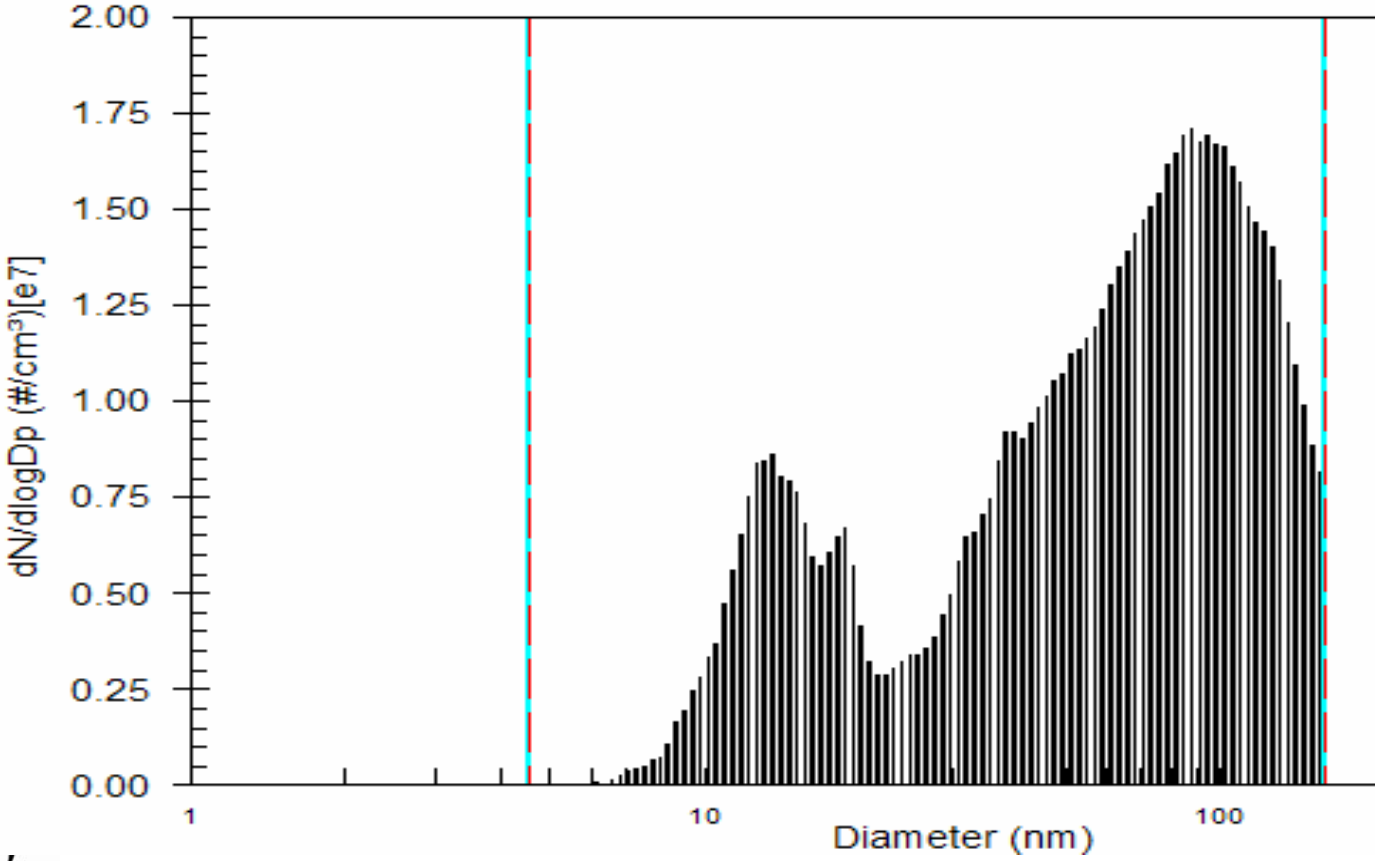

**Samples are taken and analyzed using a nano-SMPS system**

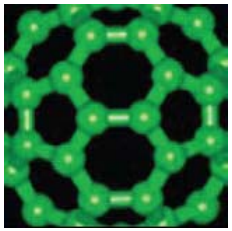


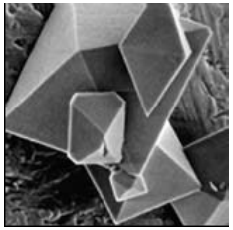


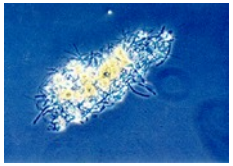


**<u>High in the Flame</u> – At significant dilution, there are 2 peaks. The small peak is assumed to be similar to the primary particles found low in the flame while the large peak is assumed to be an agglomeration peak.**

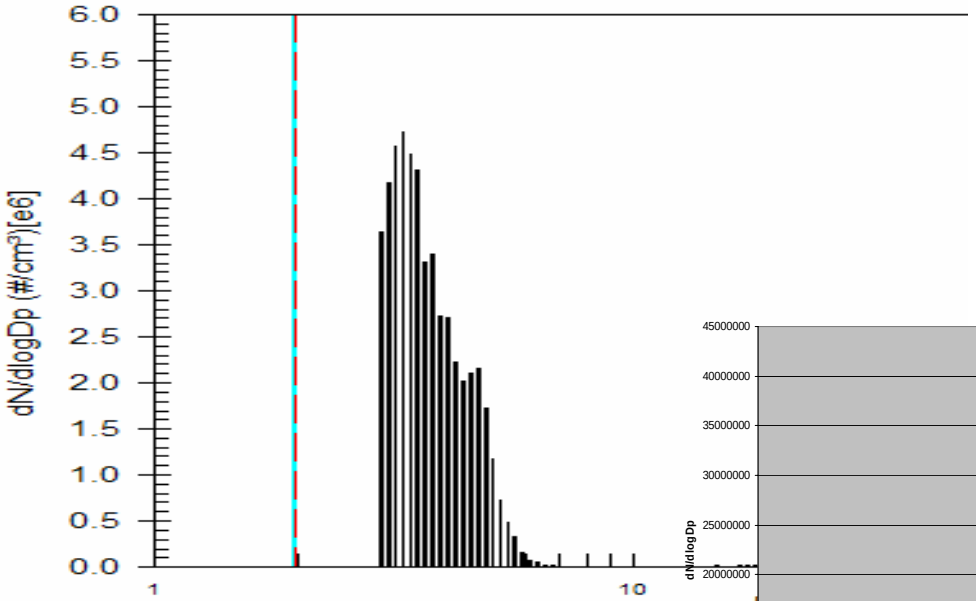


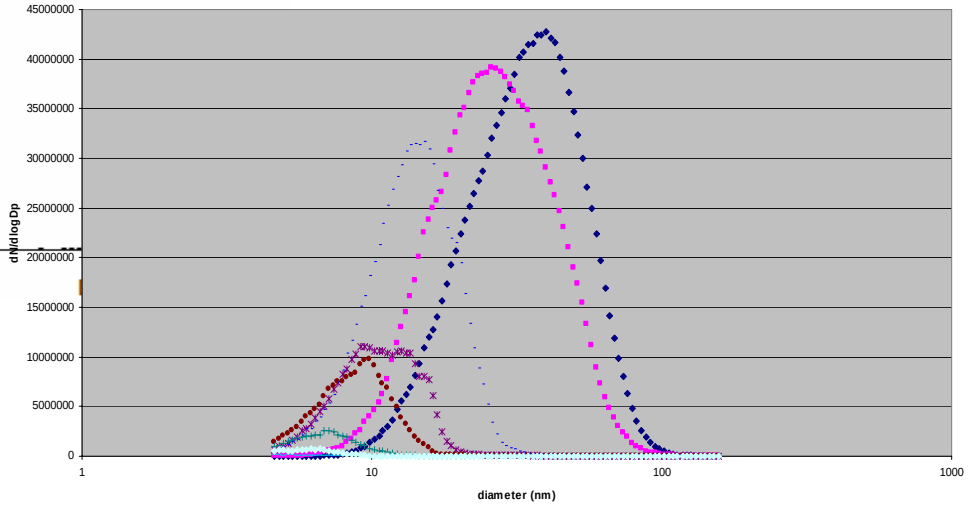


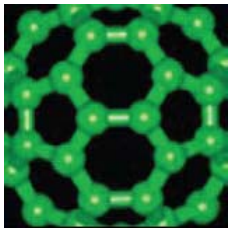


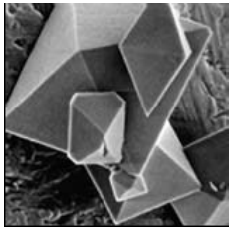


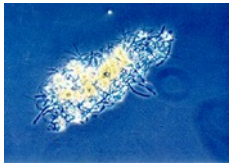
**<u>Low in the Flame</u> - With increasing dilution, the size distribution shifts past the lower detection limit indicating that the particles are all smaller than 3 nm.**





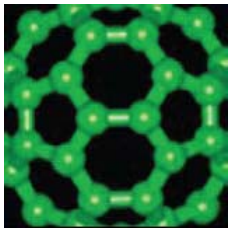


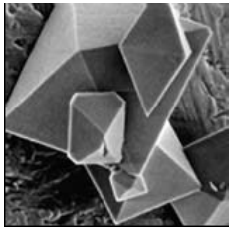


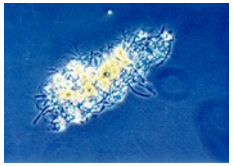
# Photoacoustic measurements & filter analysis showed that the absorption was less for IDF soot as compared to premixed.

| Flame | Position | Mass Specific Absorption Coefficient ($m^2/gm$) |
|---|---|---|
| Premixed | Exhaust | 4.37 |
| IDF | Exhaust | 2.63 |
| IDF | 20 mm HAB | 1.16 |

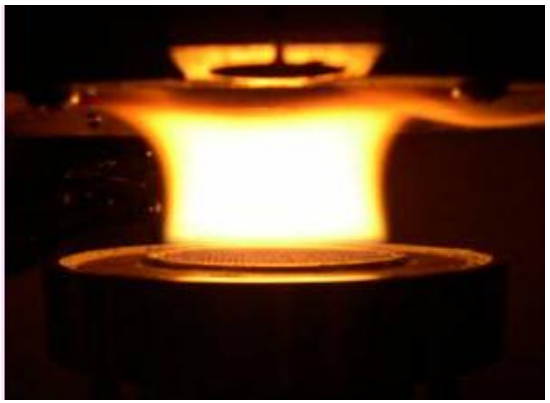
Black carbon is assumed to be 5 $m^2/gm$

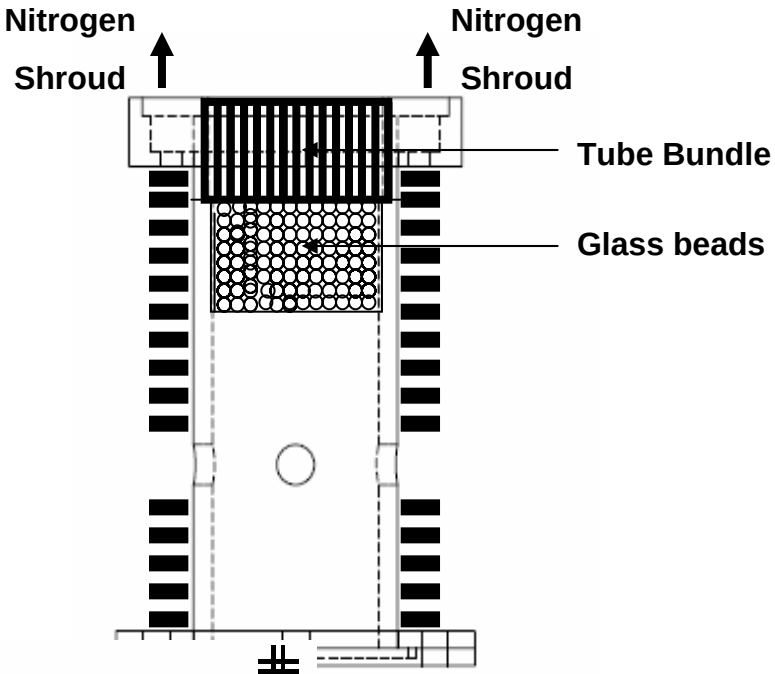


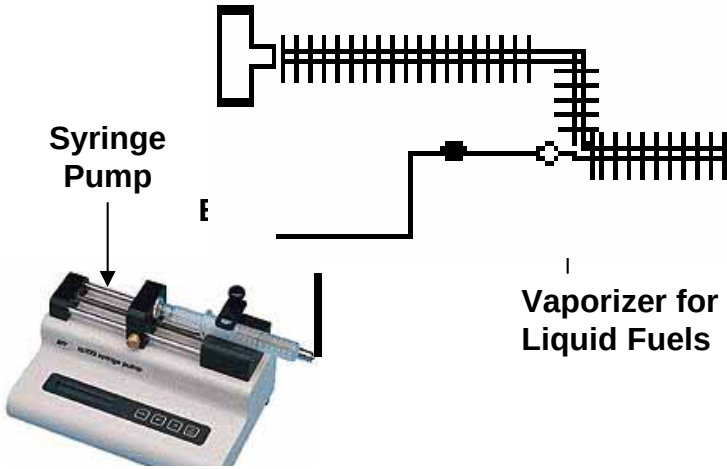


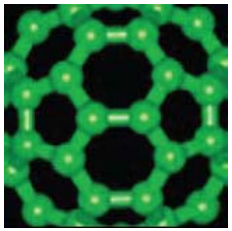


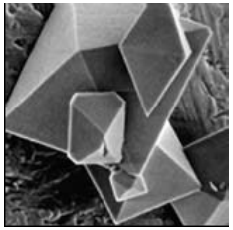
# Experimental Procedure: Premixed, Flat Flame

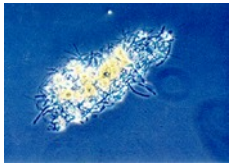








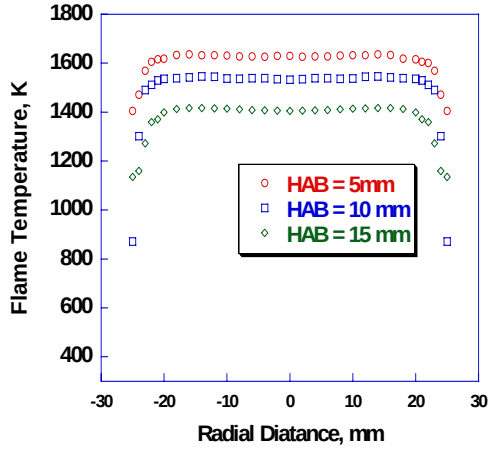


# TEMPERATURE PROFILES

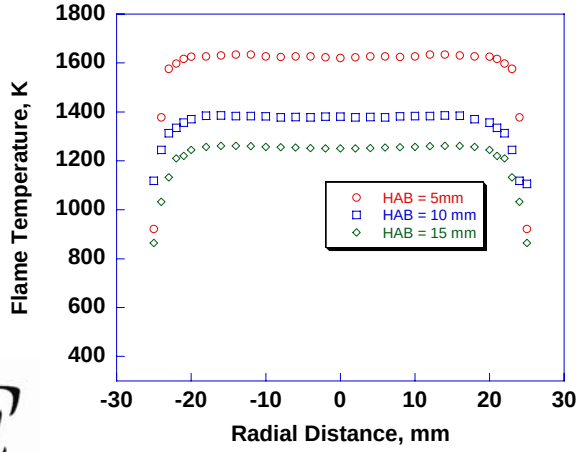
## with Radiation Correction

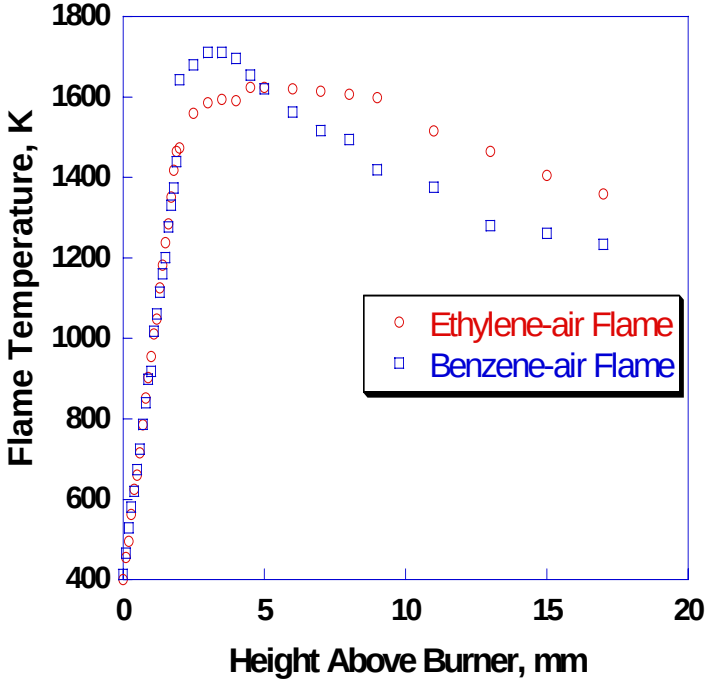
## C/O = 0.89

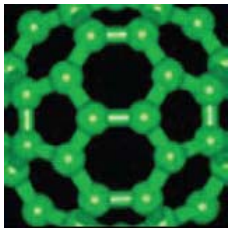
Ethylene_air Flame

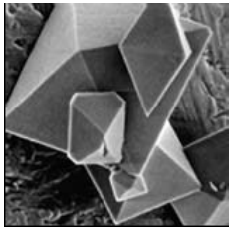


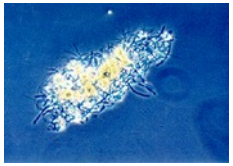

Benzene_air Flame



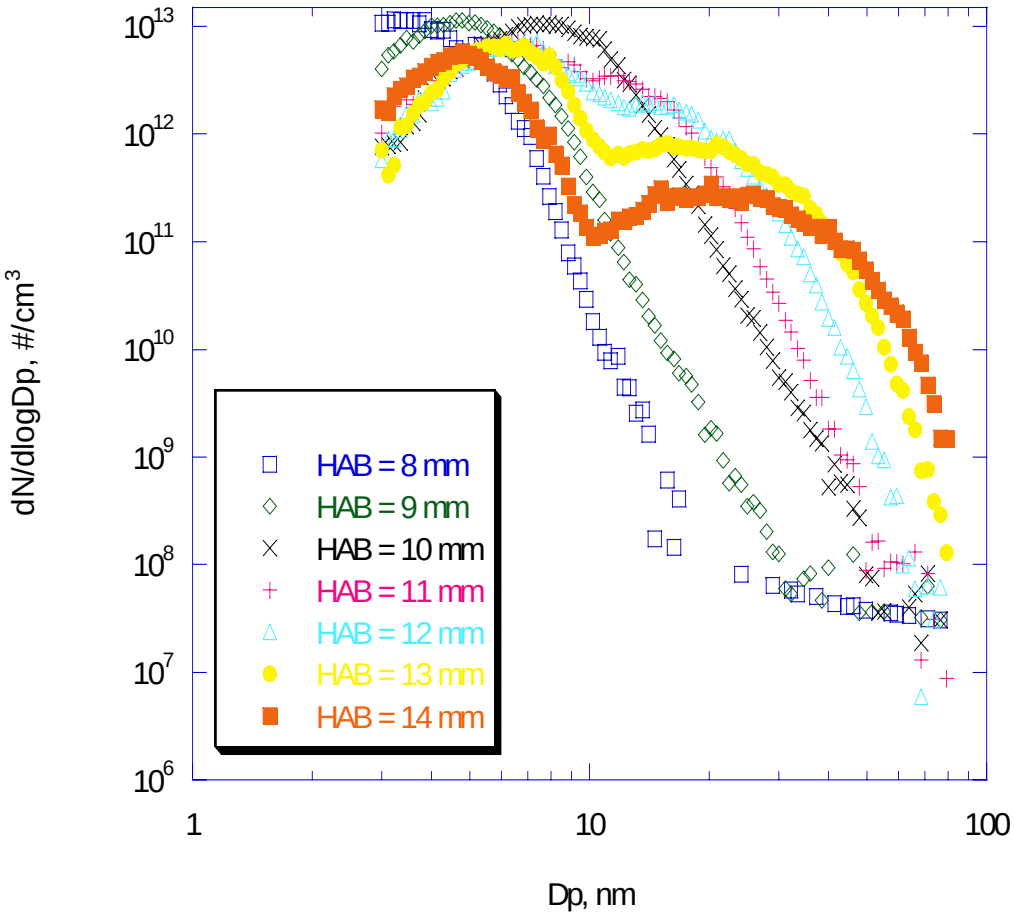



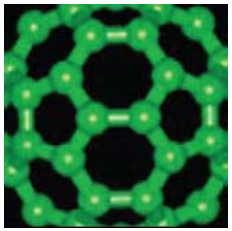


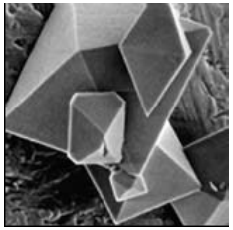


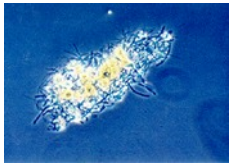


# Ethylene Flame, C/O=0.74, peak temp = 1661.5K

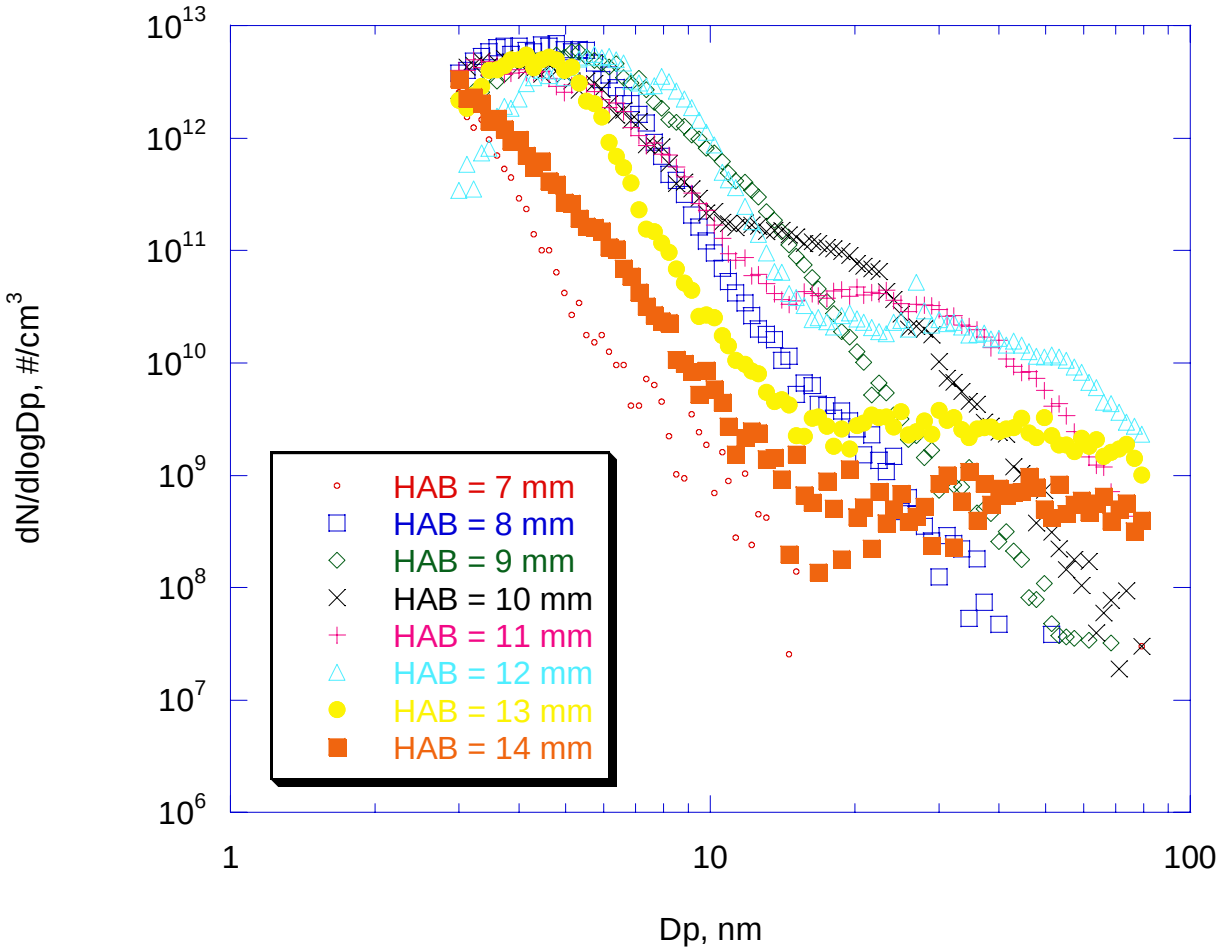


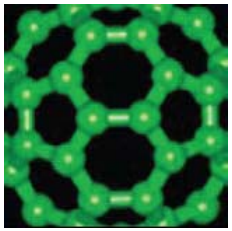


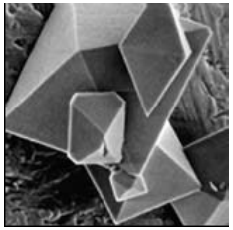


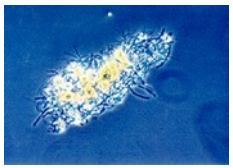


# Ethylene Flame, C/O=0.89 peak temp = 1654.7K

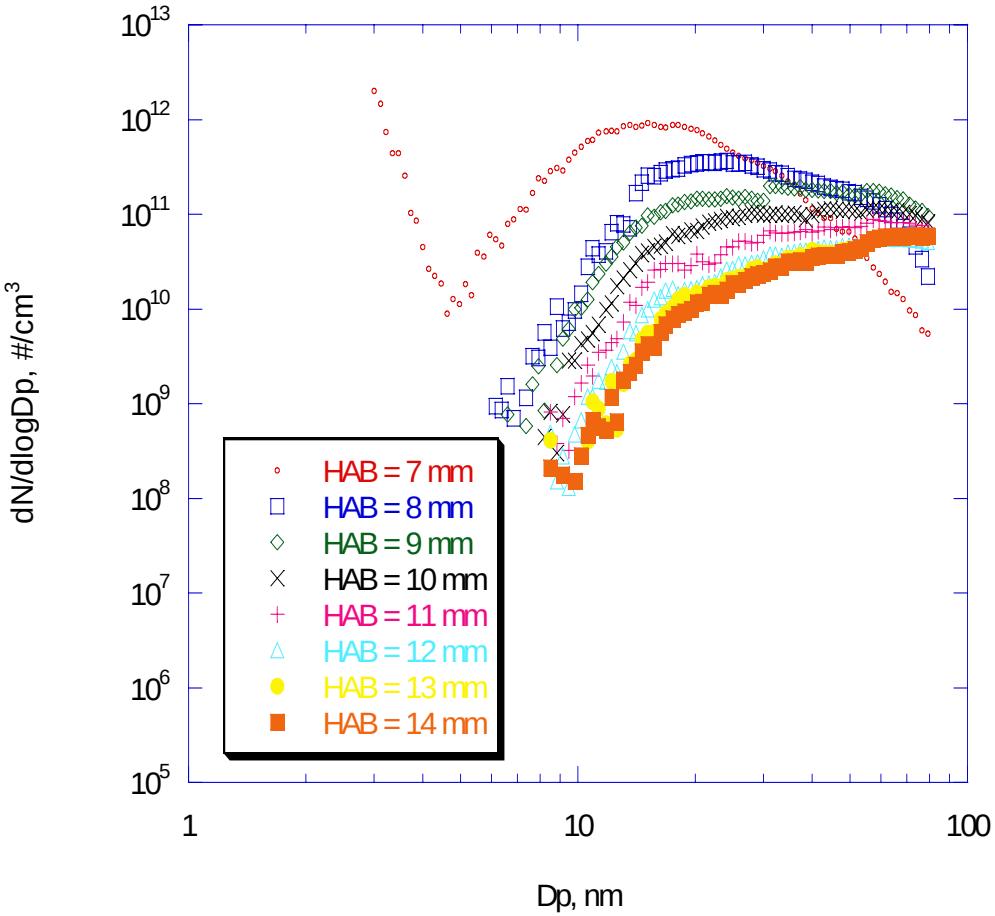


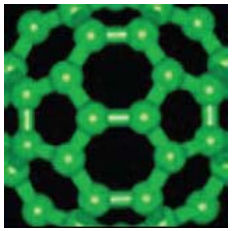


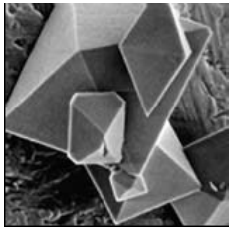


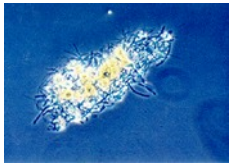


# Benzene Flame C/O=0.89 peak temp = 1706K

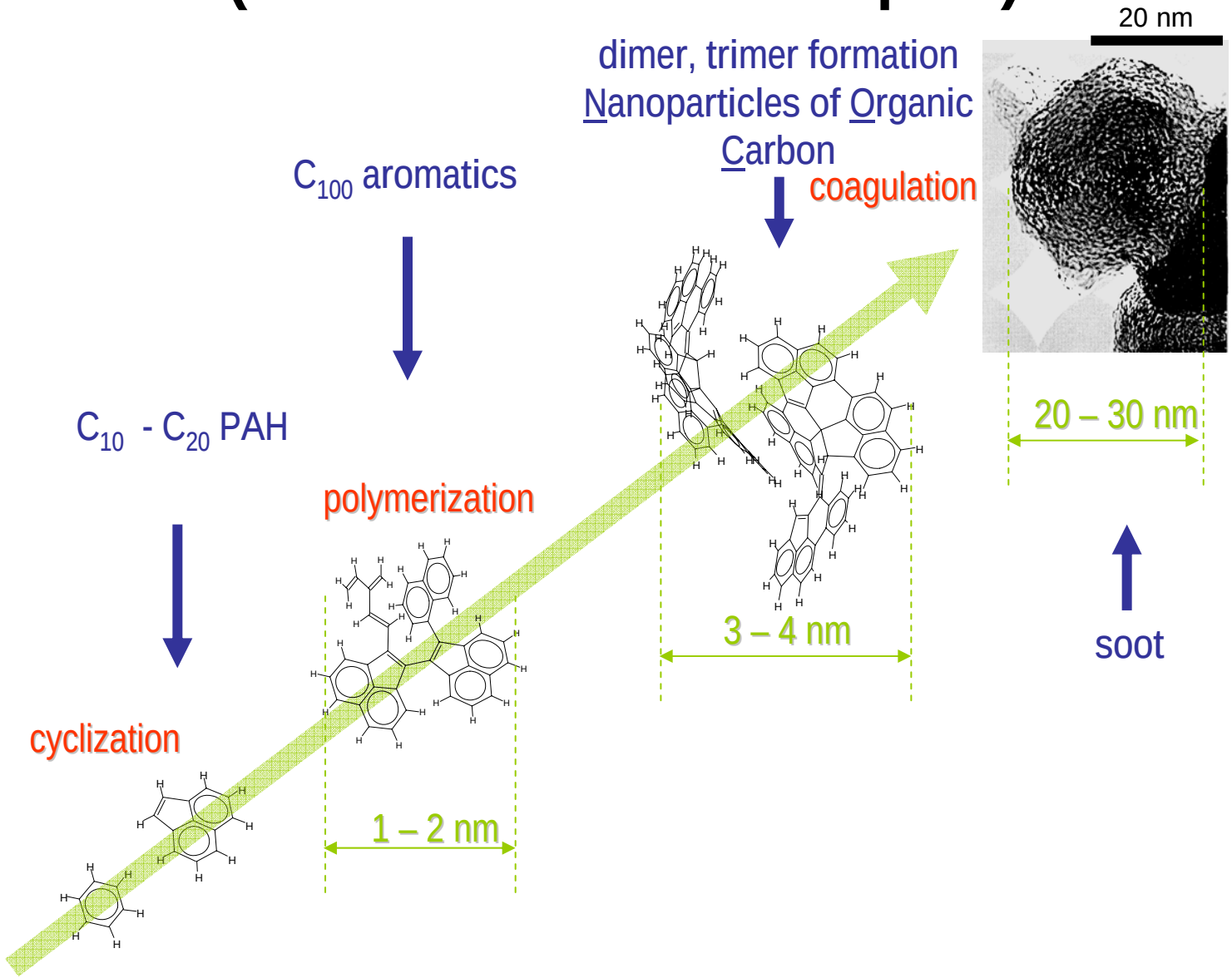


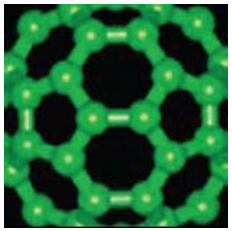


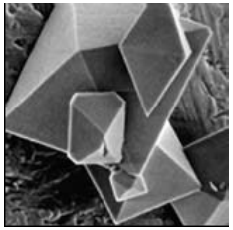


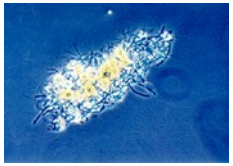


# Model (collaboration with Naples)

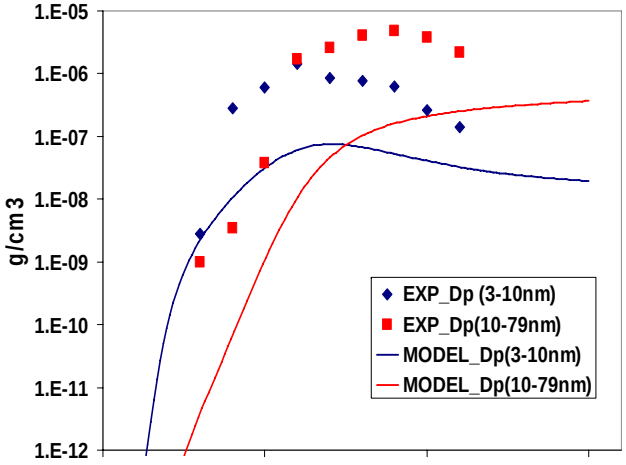


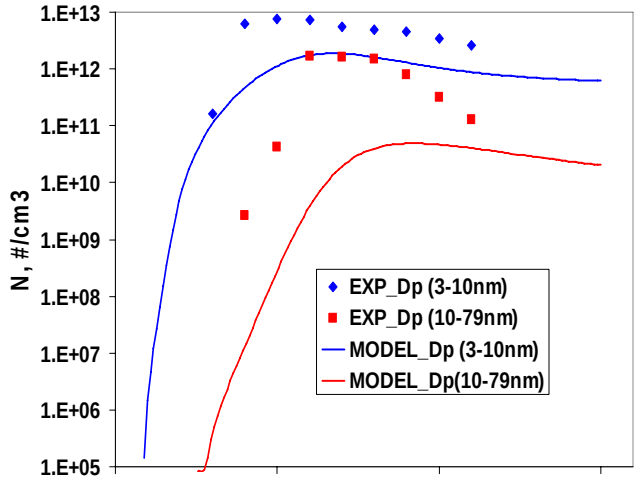


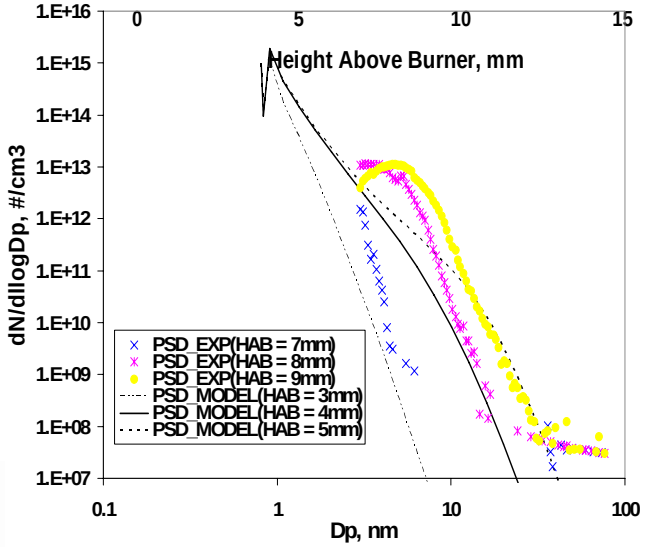


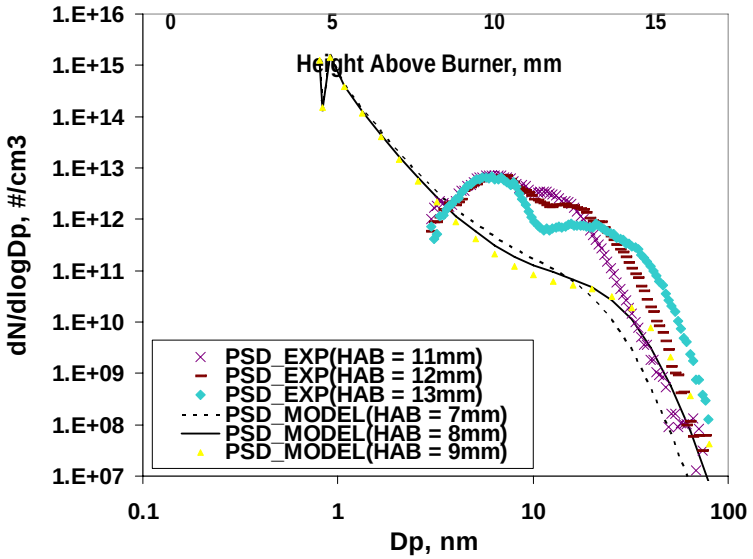


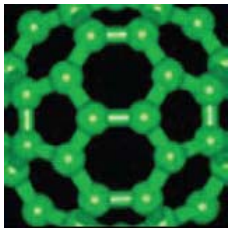
# Model predictions for the C2H4 flame C/O=0.74

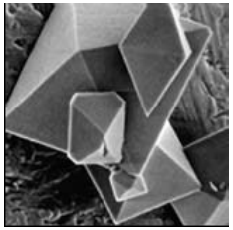


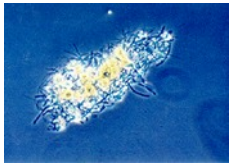



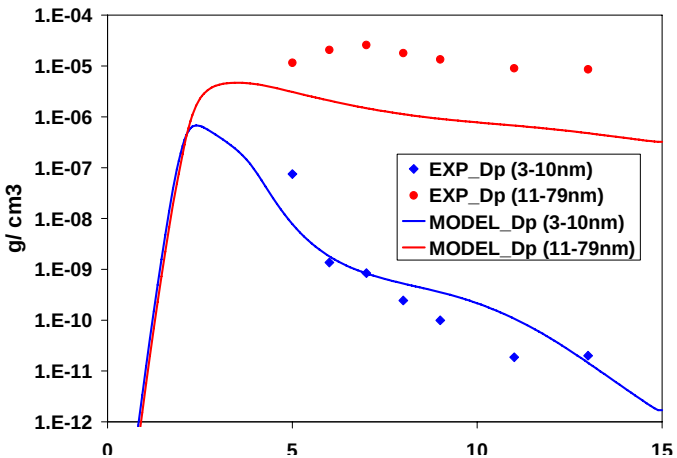



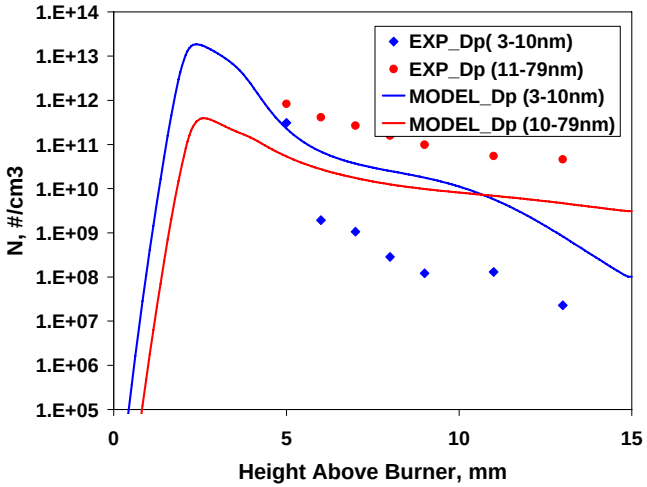


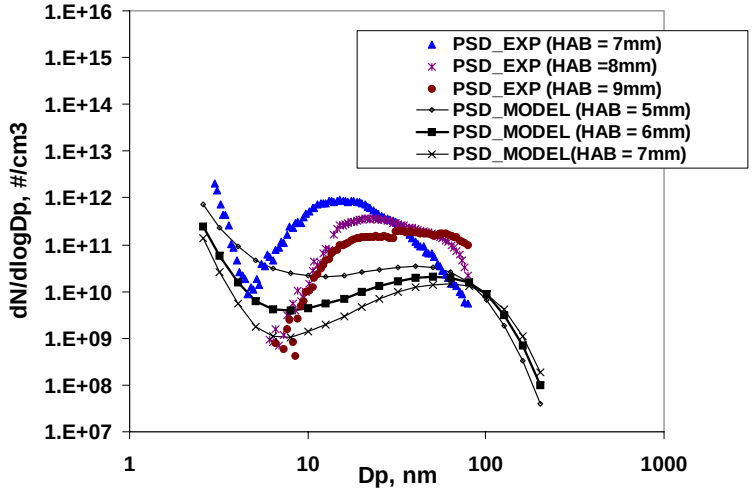


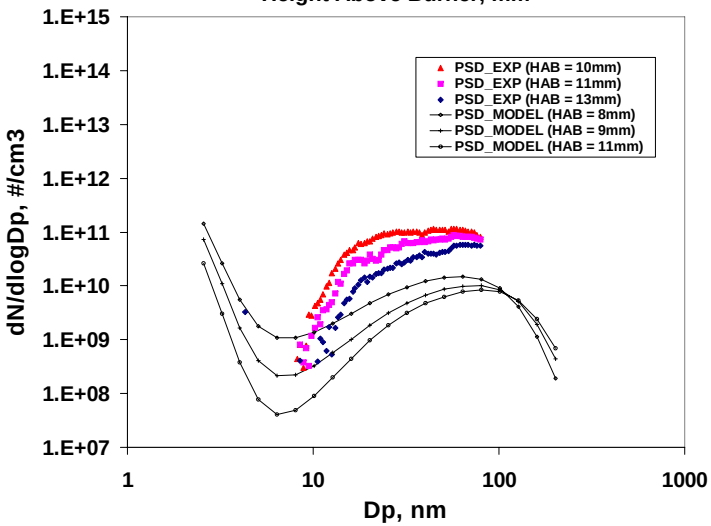


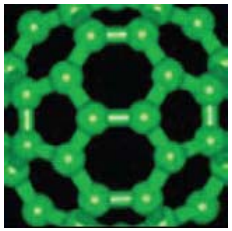
# Model Predictions for the C6H6 flame C/O=0.89

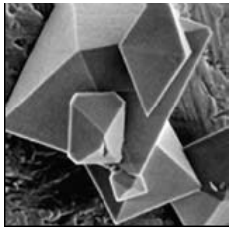


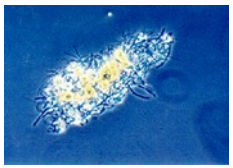



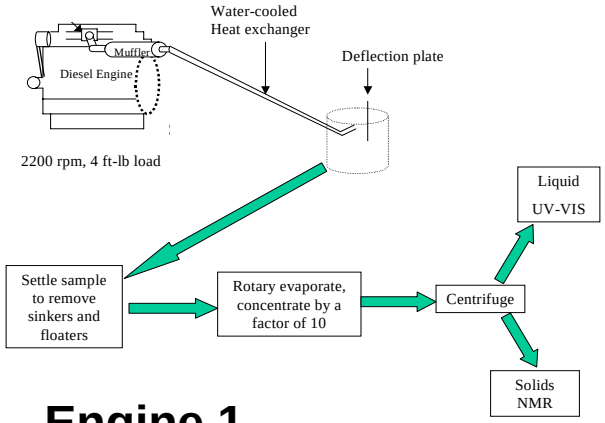





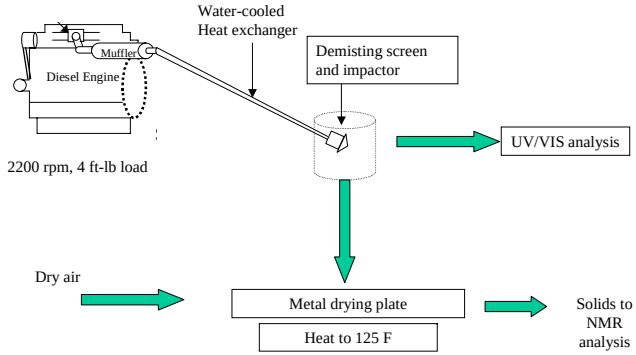




# Nano-Organic Carbon Particles (NOC) (collaboration with Naples)

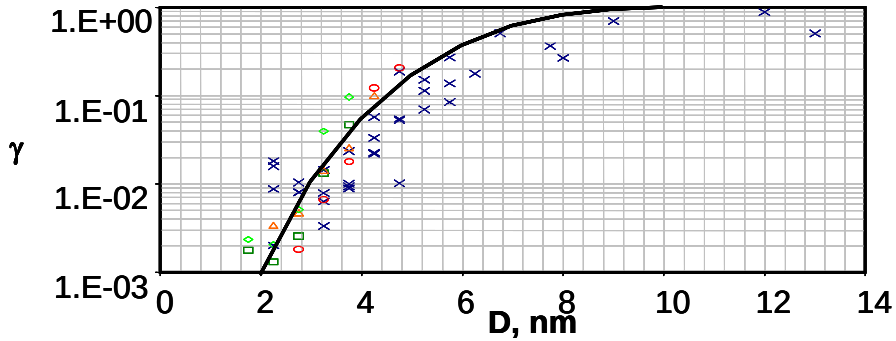


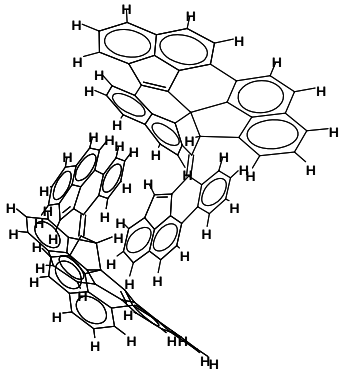

**Engine 1**



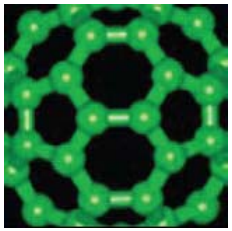

**Engine 2 & 3**

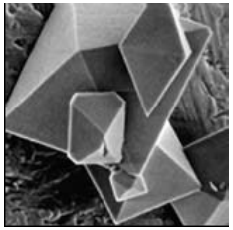
Size-dependent coagulation efficiency

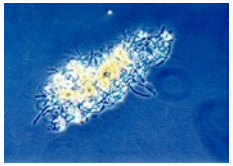


D'Alessio et al. *Proc. Combust Inst.* 30(2):2595-2603 (2004)

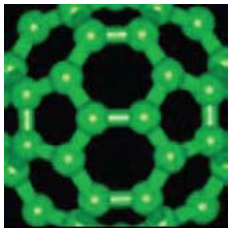


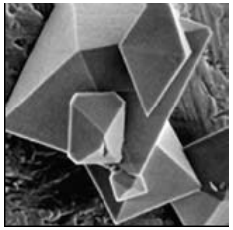


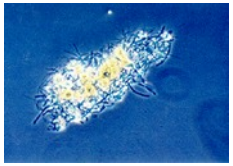


# Elemental Analysis of NOC

| Sample | Engine 1 | Engine 2 | Engine 3 |
|---|---|---|---|
| Carbon % | 63.66 | 40.14 | 65.43 |
| Hydrogen% | 5.72 | 5.88 | 9.11 |
| Oxygen% | 25.7 | 34.62 | 17.72 |
| Sulfur% | 0.49 | 3.16 | 1.35 |
| Ash% | 1.69 | 16.70 | 5.66 |

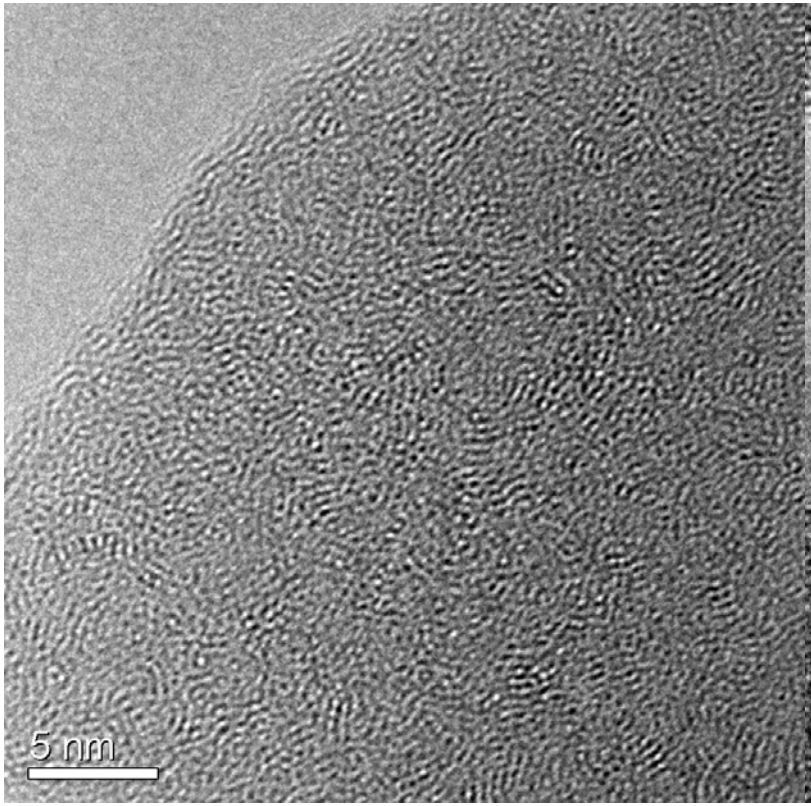




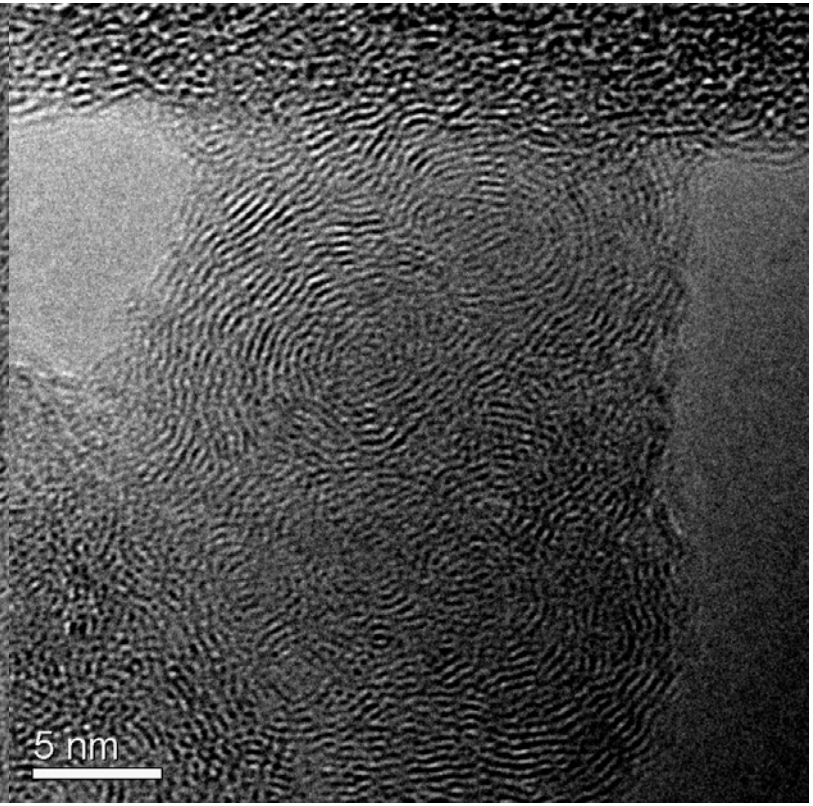


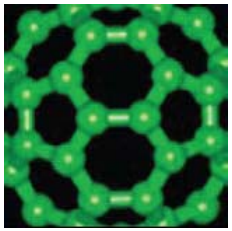
# HR-TEM micrographs

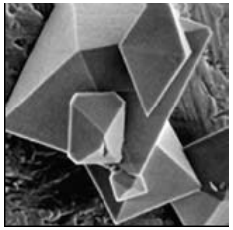
***ETHYLENE FLAME ,C/O = 0.89***
***HAB = 10 mm***

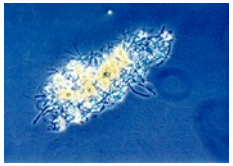



***BENZENE FLAME ,C/O = 0.89***
***HAB = 10 mm***

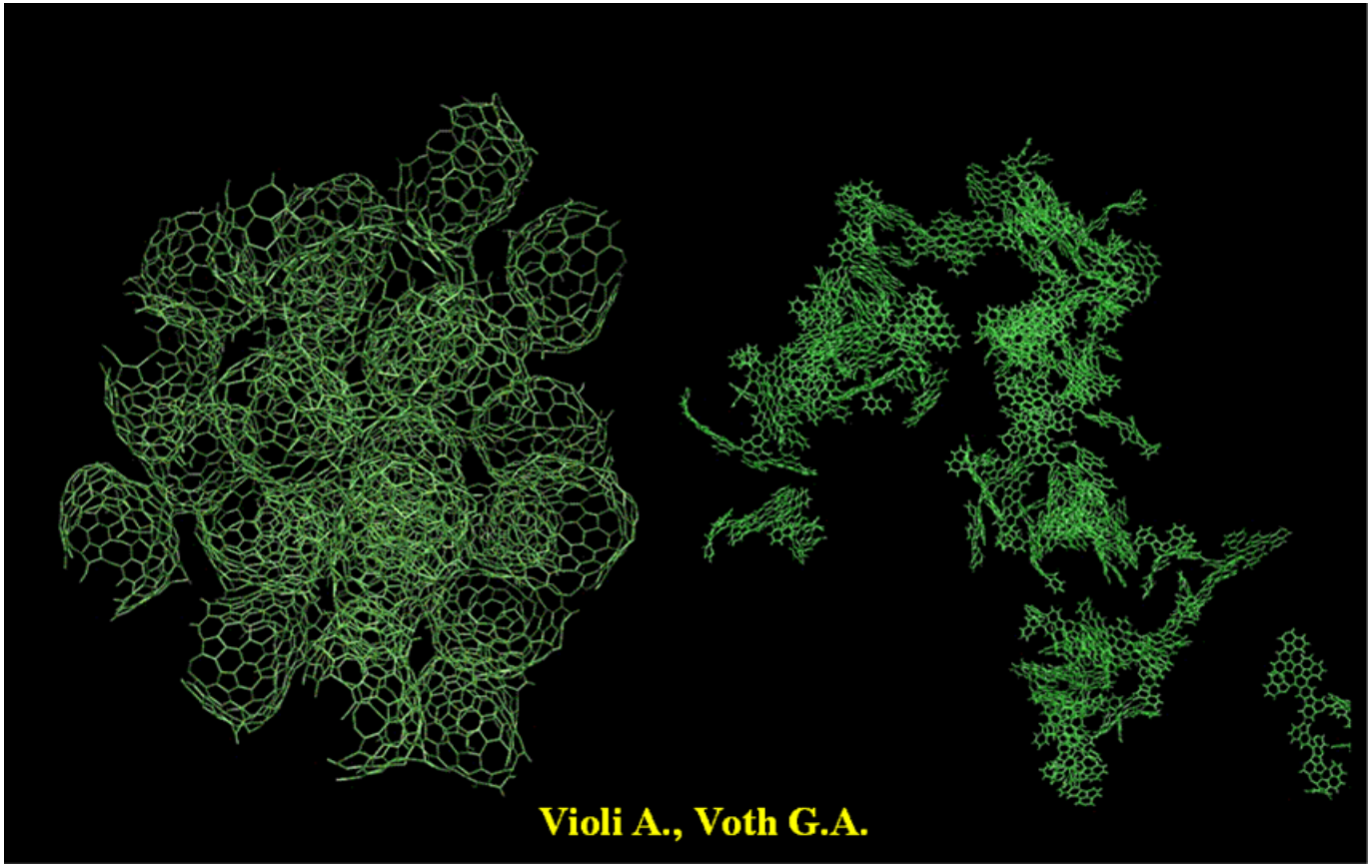




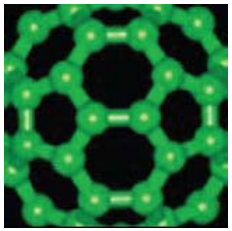


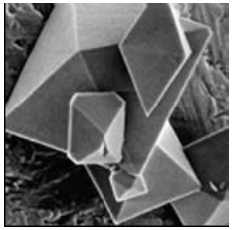


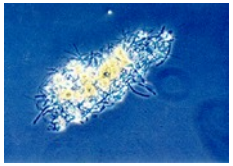
# Model Predicts Structure Differences



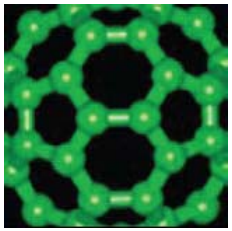

**MD simulation of agglomeration of nanoparticles formed with KMC/MD.**
**Round particles (from benzene, left) tend to cluster, while "flaky" particles subcluster (acetylene flames, right).**

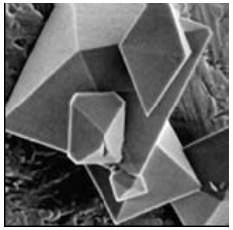


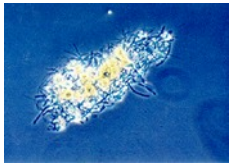




# Soot Destruction

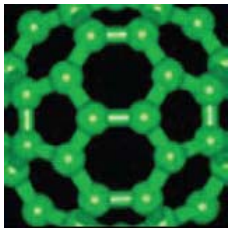


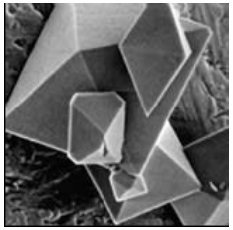


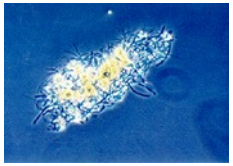


# Oxidation by OH, O, and $O_2$

- **A high percentage of soot formed in flames and engines is oxidized prior to emission (often >90%)**
  **(Stanmore, et al. 2001)**
- **Oxidation is dominated by OH in flames**
- **$O_2$ is important for burnout in diesel engines, gas turbine engines, and in the regeneration of diesel particulate filters**

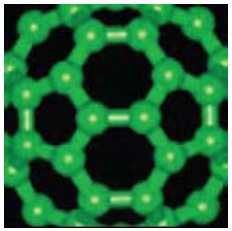


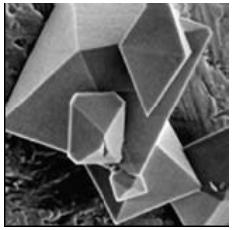


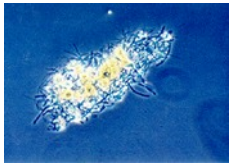


# Oxidation Kinetics

- **OH oxidation occurs due to a collision of OH radical with the soot surface. Studies show that collision efficiency is relatively independent of fuel and equiv. ratio**
- **$O_2$ kinetics appear to be a function of soot structure, porosity, etc. Power law kinetics have been used.**

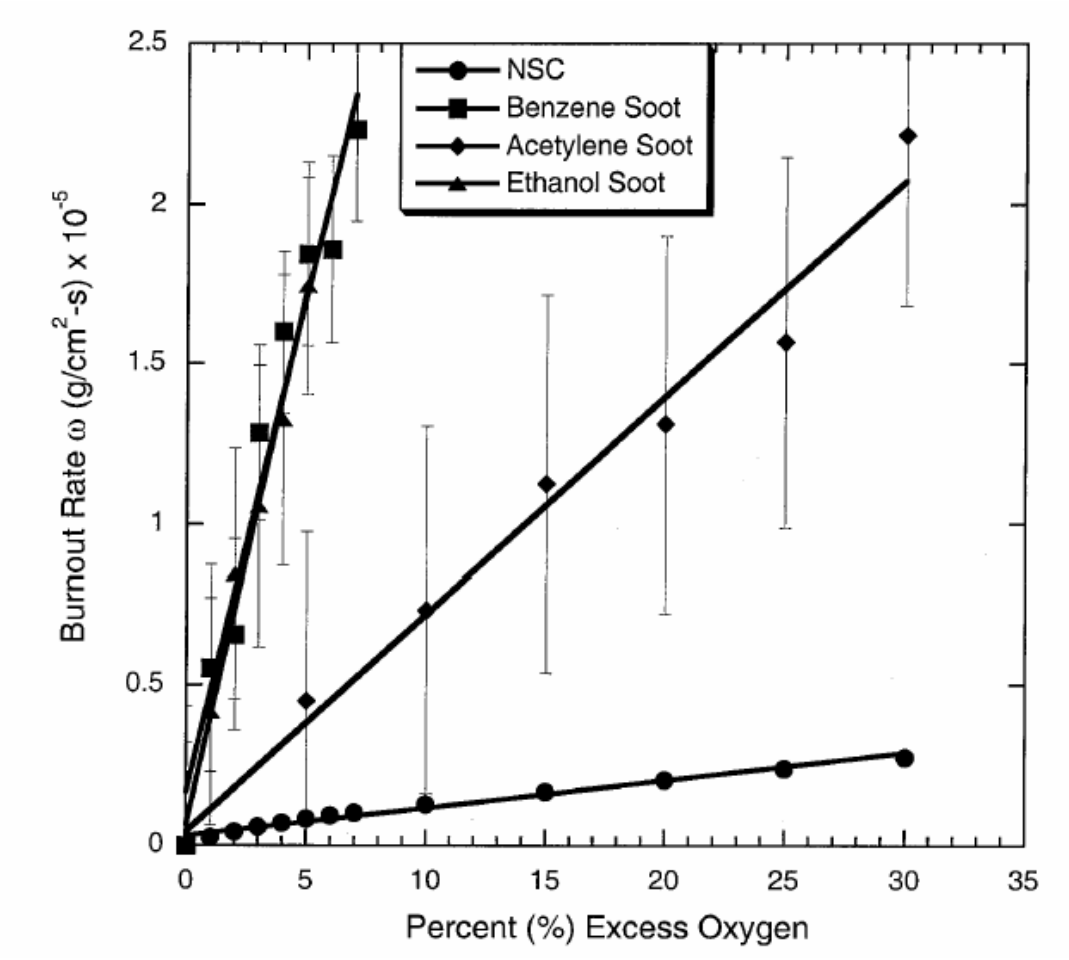


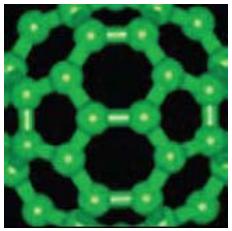


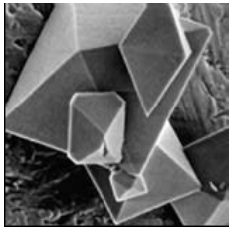


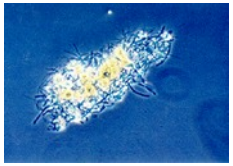
# Ordering provides an explanation for fuel effects on oxidation

**(Vander Wal and Tomasek, 2003 & 2004)**



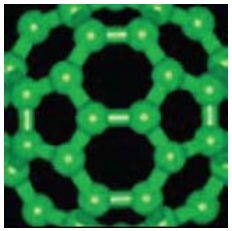


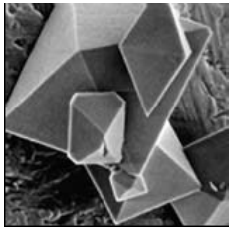


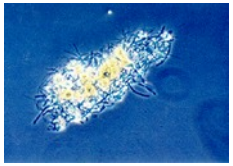


# Conclusions

- **Transportation is the primary cause of soot. As these sources are more highly regulated, fires will be increasingly important**
- **Soot has adverse environmental and health effects**
- **Understanding of soot formation mechanisms are important to enable predictions from engines; new models are needed to predict the particle size distributions**
- **There is evidence of the existence of nano-organic carbon particles which persist in the environment; these are not well understood**
- **Soot structure is dependent upon fuel, temperature history, etc. In turn, soot oxidation is likely dependent upon soot structure**







# Acknowledgments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