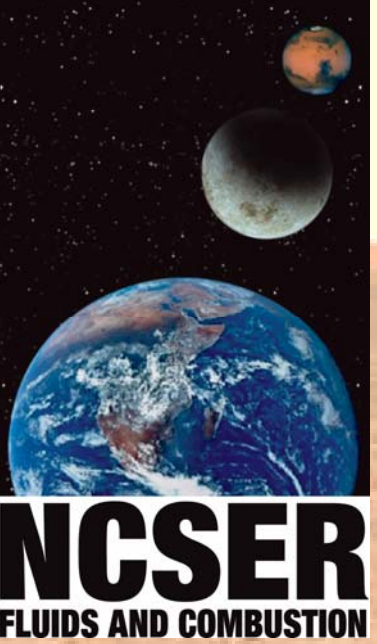

Soot Nanostructure: Definition, Quantification and Implications

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David R. Hull
William K. Thompson

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University of Michigan, Dearborn March 17th, 2005

NATIONAL CENTER FOR SPACE EXPLORATION RESEARCH

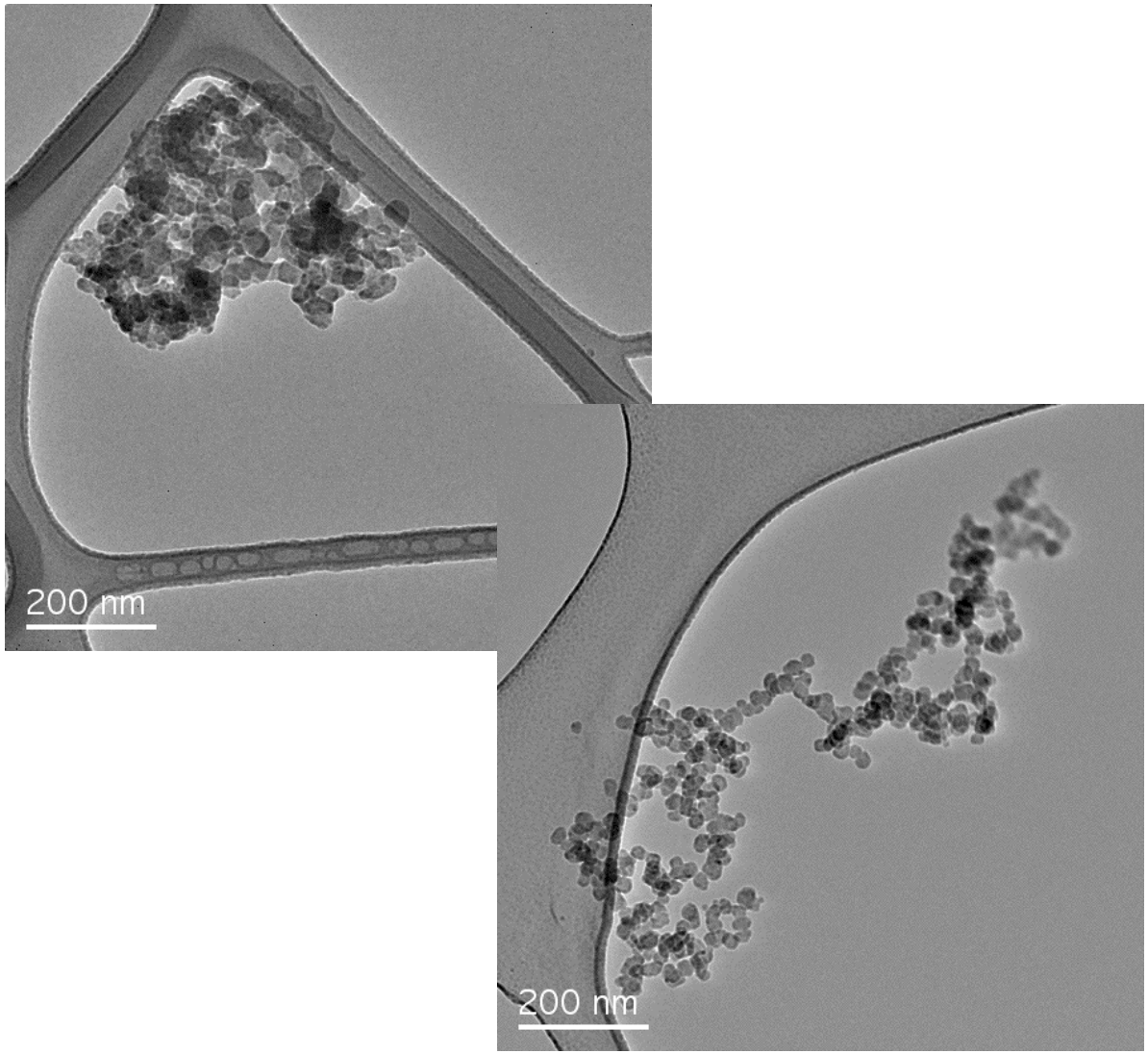
NCSER

FLUIDS AND COMBUSTION

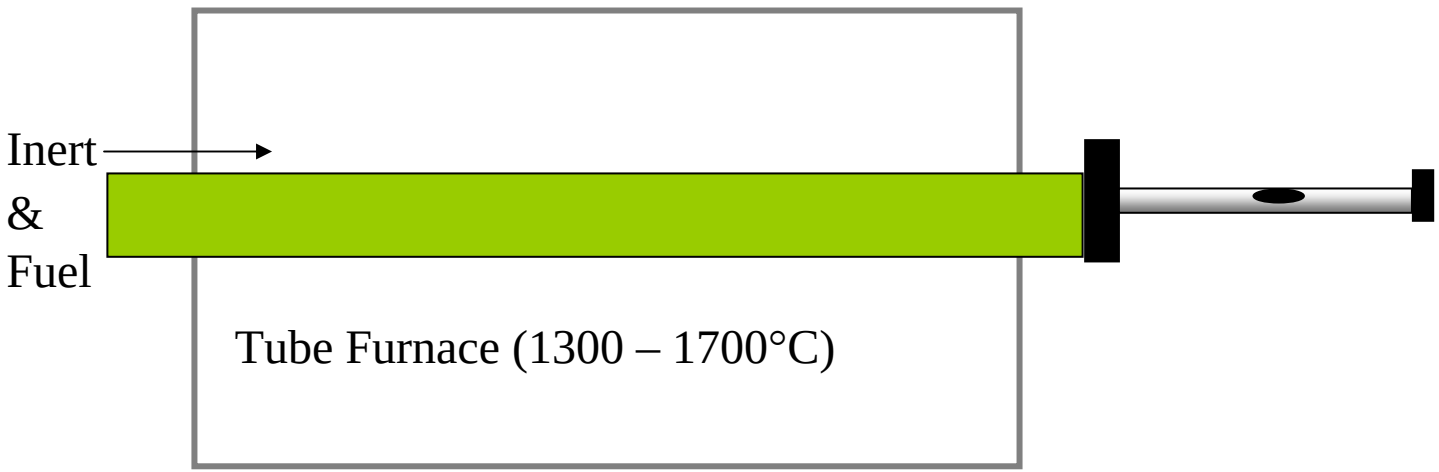
Outline

- Introduction
- Definition: Carbon (Soot) Nanostructure
- Quantification: Analysis of Soot Nanostructure (Lattice Fringe Analysis)
- Implications: Soot Oxidation Rates (Variability)
- Real examples

Soot Macrostructure: Aggregate Size and Morphology



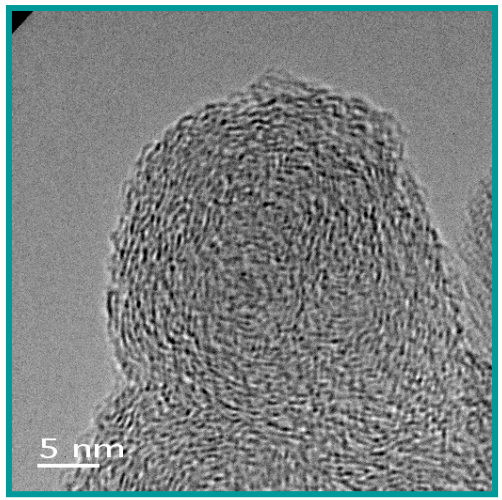
Soot Nanostructure: Experimental Apparatus (for producing soot)



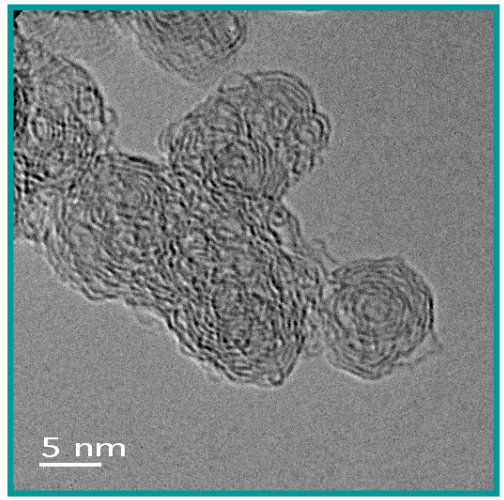
Dependence of Nanostructure on Temperature

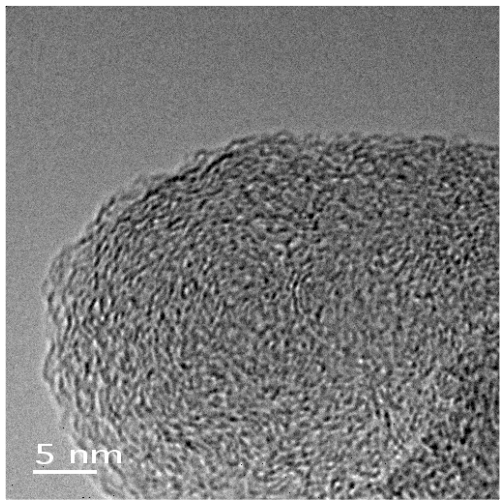
1250°C

1650°C

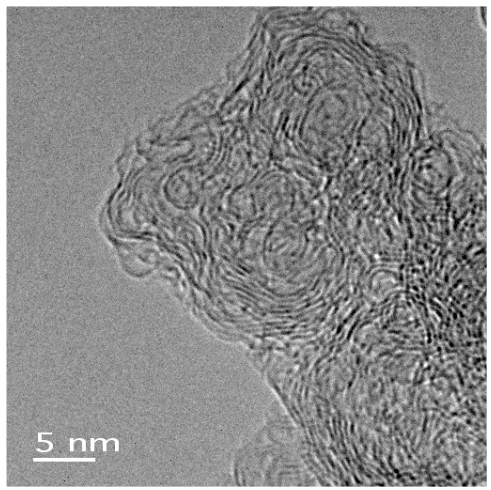


Acetylene





Benzene

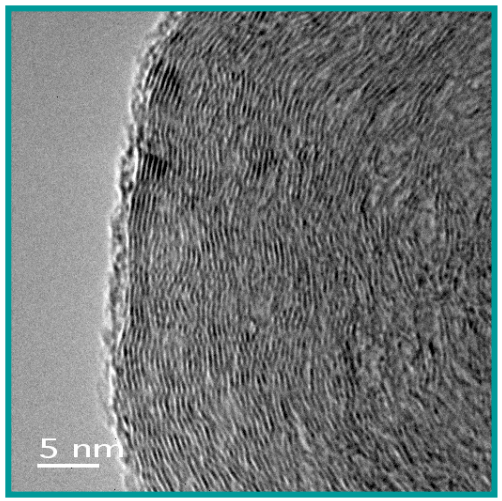


Flow Rate Constant

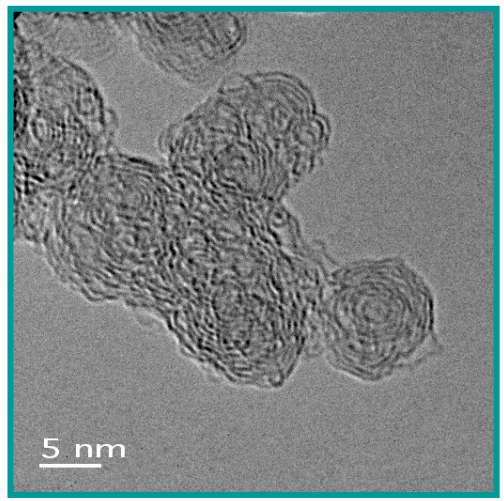
Dependence of Nanostructure on Flow Rate

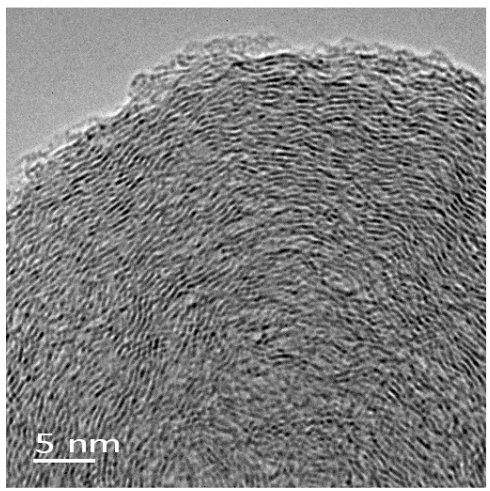
0.1 slpm

1.0 slpm

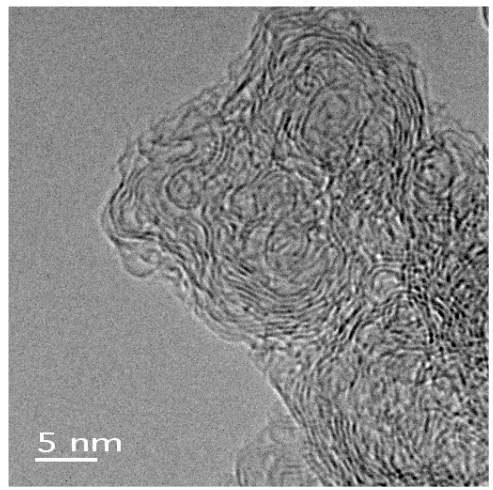


Acetylene





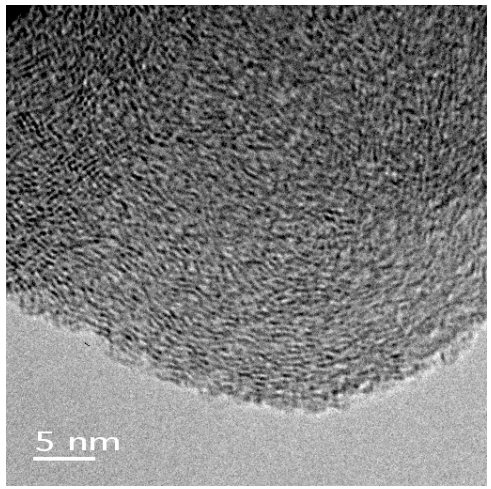
Benzene



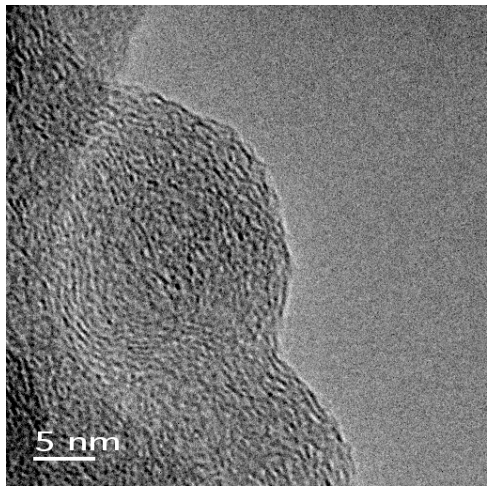
Temperature Constant

Temperature 1250 ^{0}C

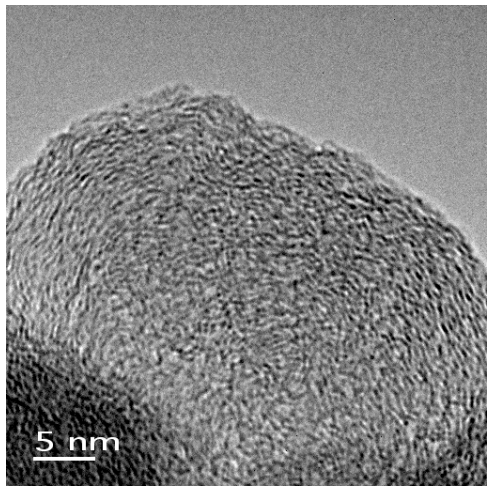
Acetylene



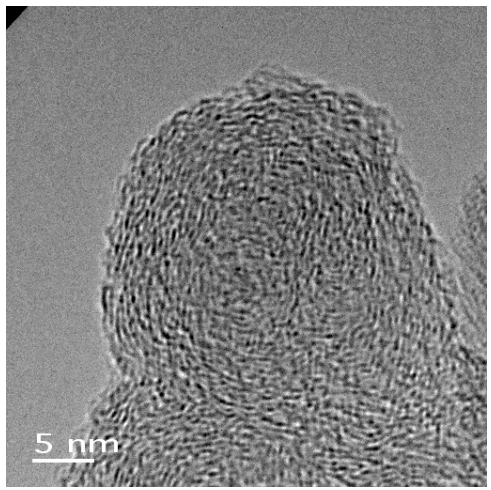
Benzene

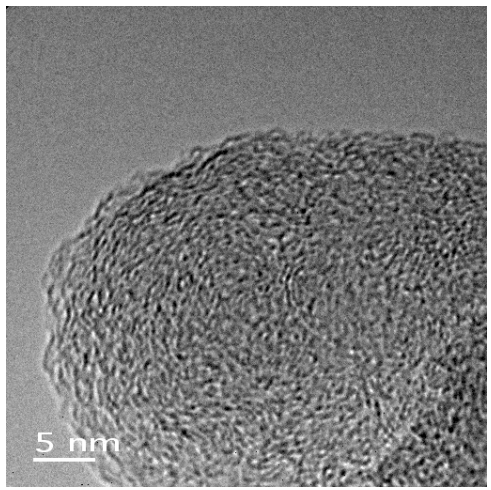


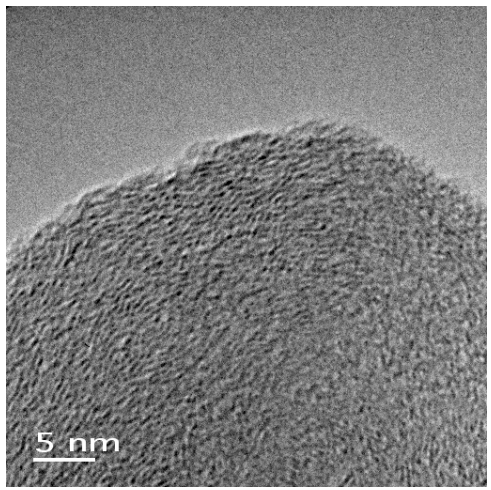
Pyrene



Flow Rate 100 sccm



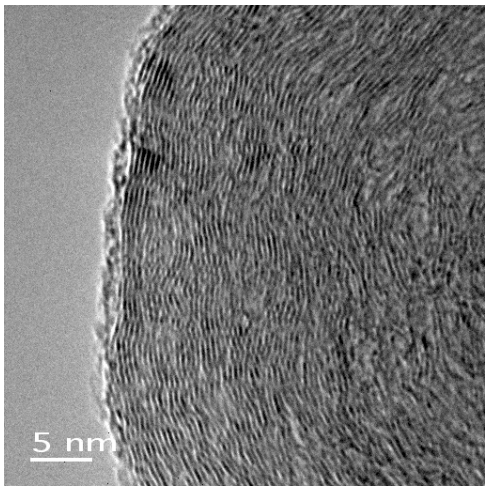




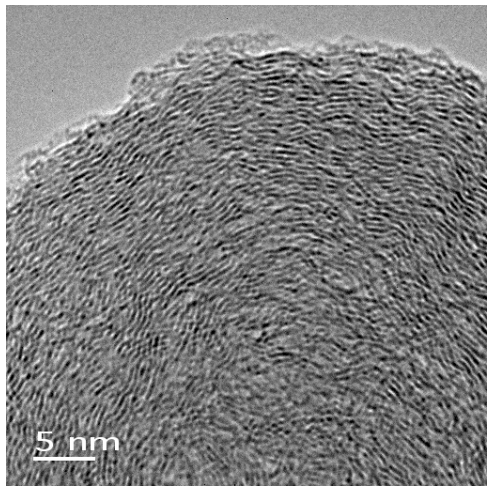
Flow Rate 1000 sccm

Temperature 1650 ^{0}C

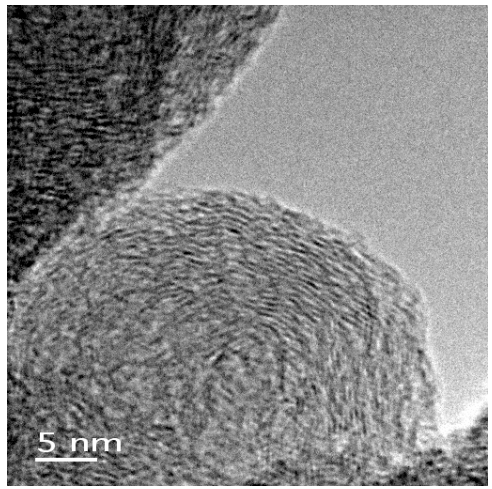
Acetylene



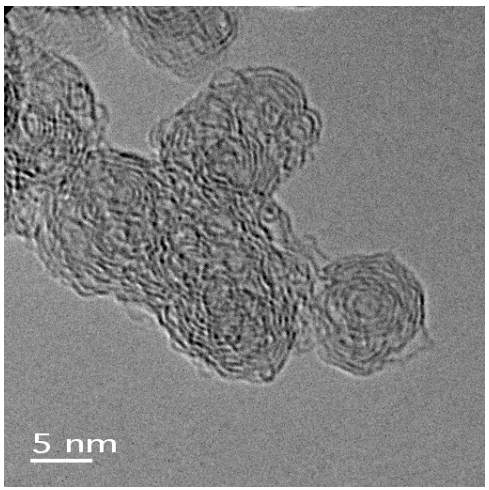
Benzene

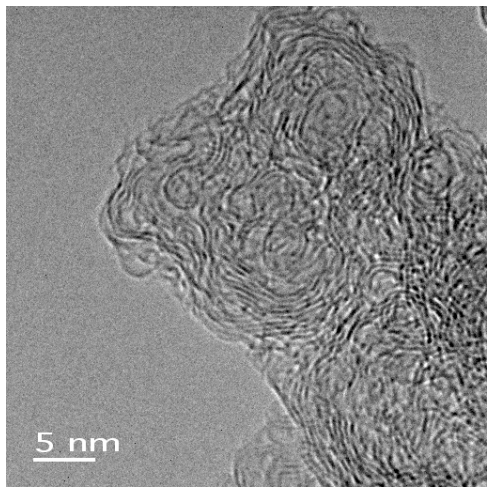


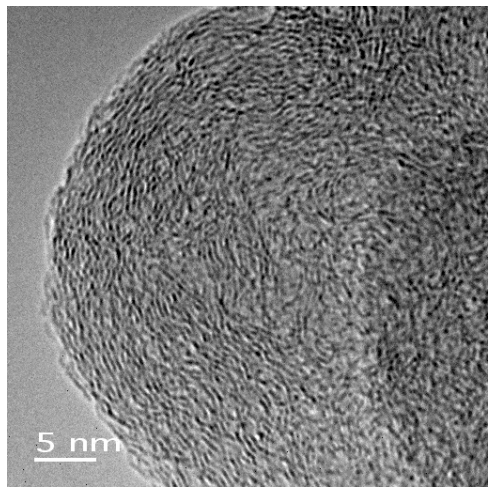
Pyrene



Flow Rate 100 sccm







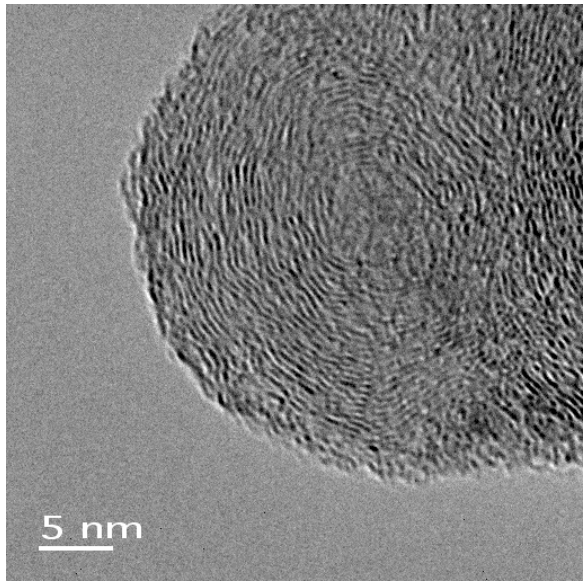
Flow Rate 1000 sccm

Ethylene + Water

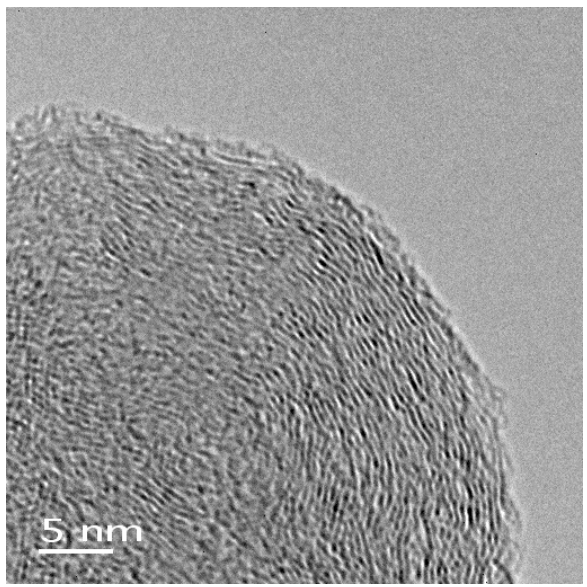
1650 ^{0}C

Flow Rate

100 sccm

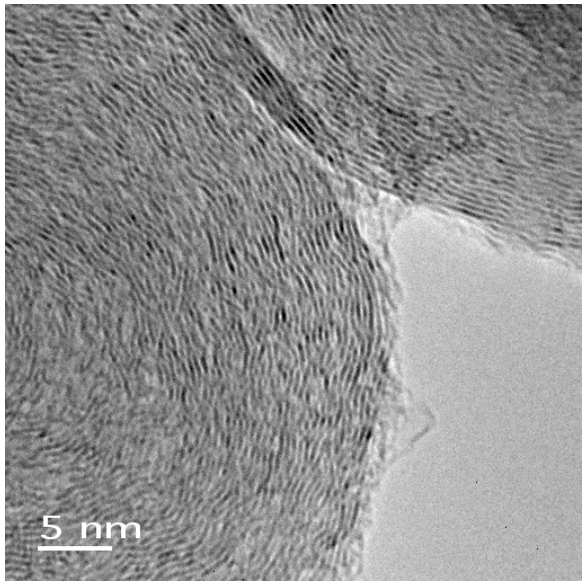
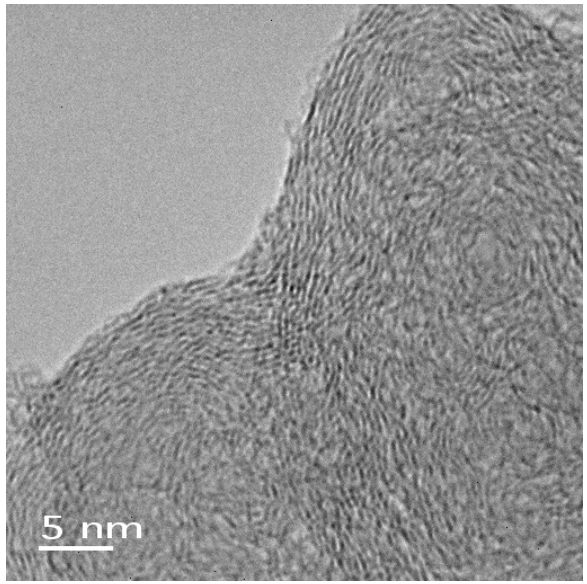
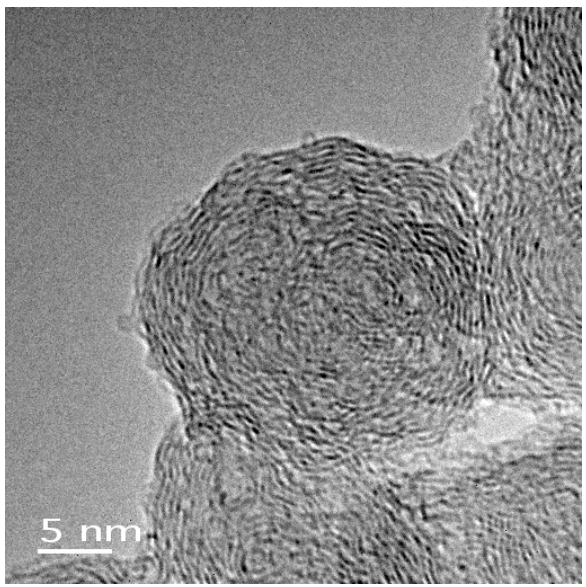
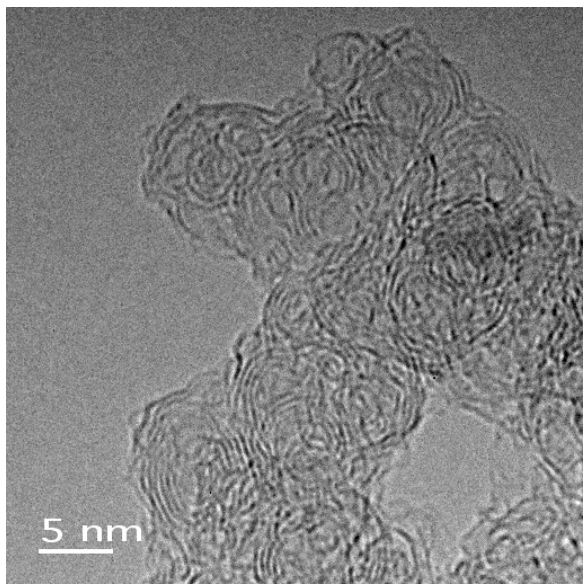


1000 sccm

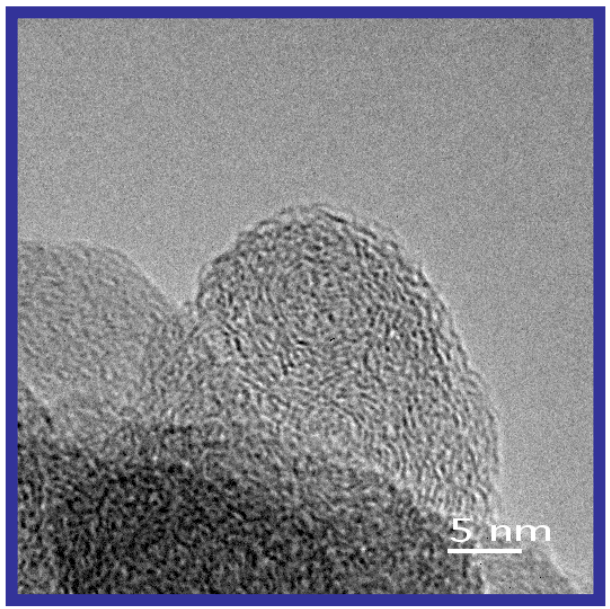


Acetaldehyde + Ethylene

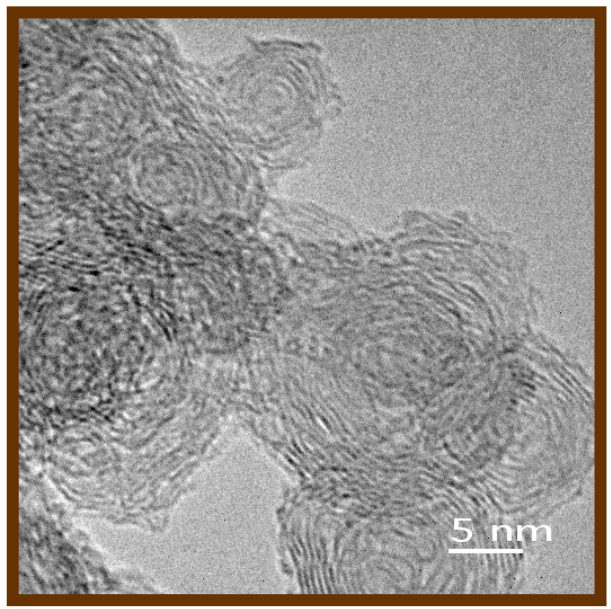
1650 ^{0}C

Flow Rate	1:1	10:1
100 sccm		
1000 sccm		

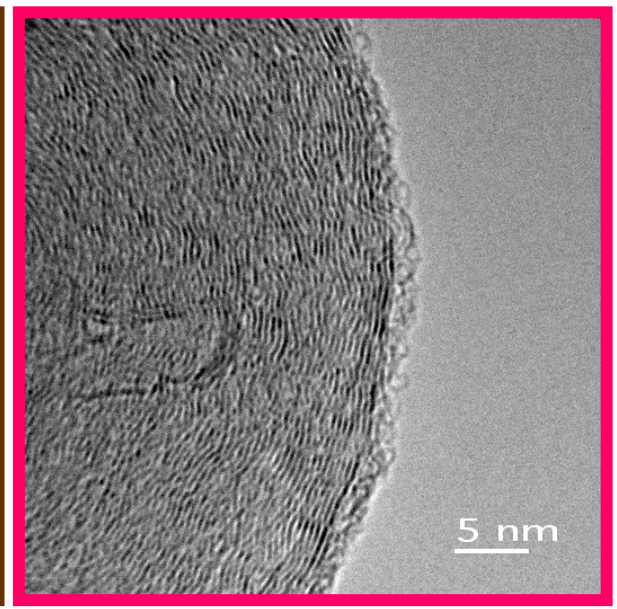
Soot Nanostructure: Definition using HRTEM: Images of Primary Particle (Internal) Structure



Amorphous (Benzene)



Fullerenic (Ethanol)



Graphitic (Acetylene)

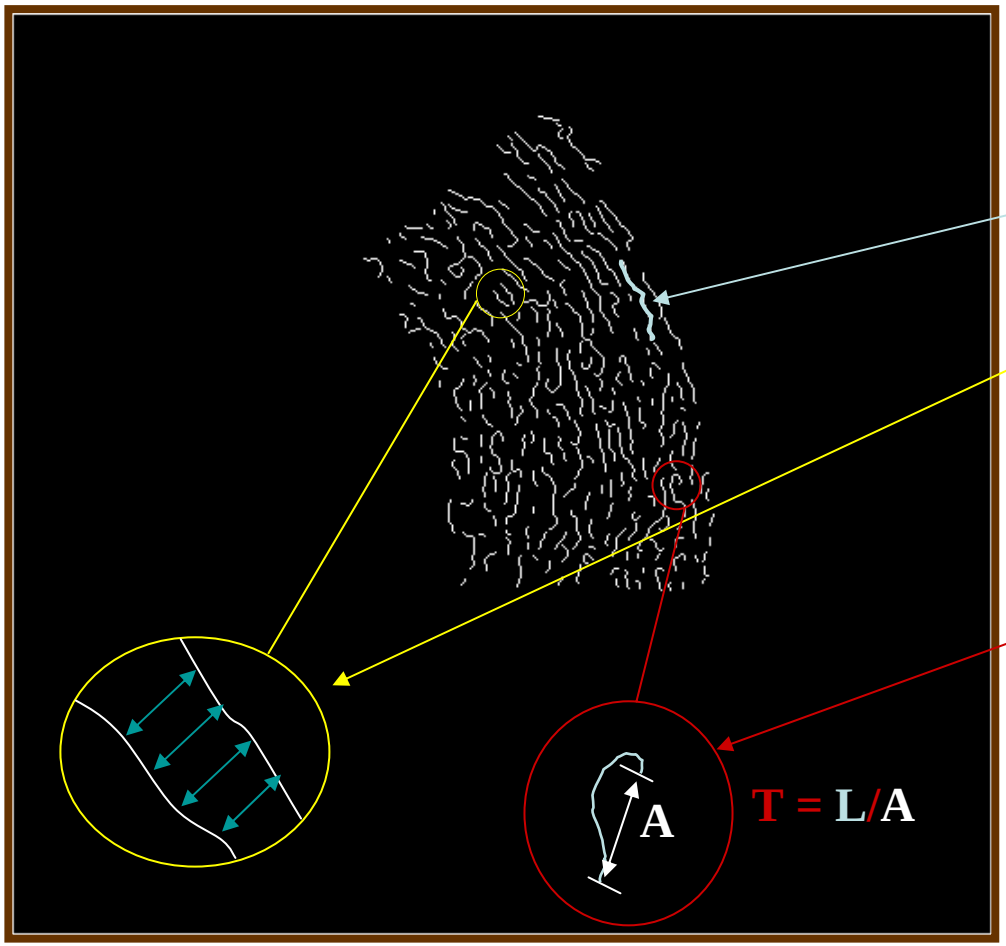
Soot Nanostructure: Quantification via Fringe Analysis

Algorithm-Optimas® Version 6.5

Operations:

1. **Switches 256 grayscale image to binary**
2. **Removes all pixels not above threshold**
3. **Removes remaining pixels and groups of pixels that do not form extended lines**
4. **Uses position of pixels within lines to determine length, curvature, etc. of fringes**

Statistical Properties Extracted From HRTEM Images (of soot nanostructure)



Position

Length

Fringe Separation

Orientation

Tortuosity

Fringe Density

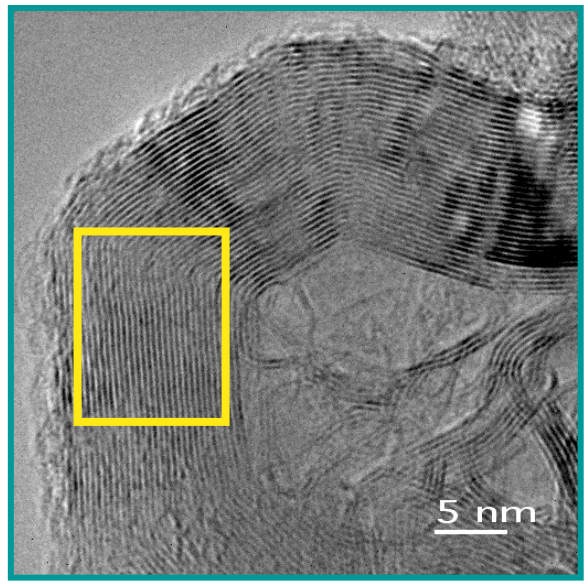
Soot Nanostructure: Quantification via Fringe Analysis

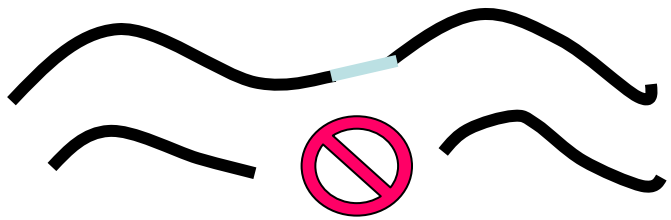
*** Image refinements - To overcome HRTEM image limitations**

- **Region of interest**
- **Spatial filtering**
- **Binary thresholding**

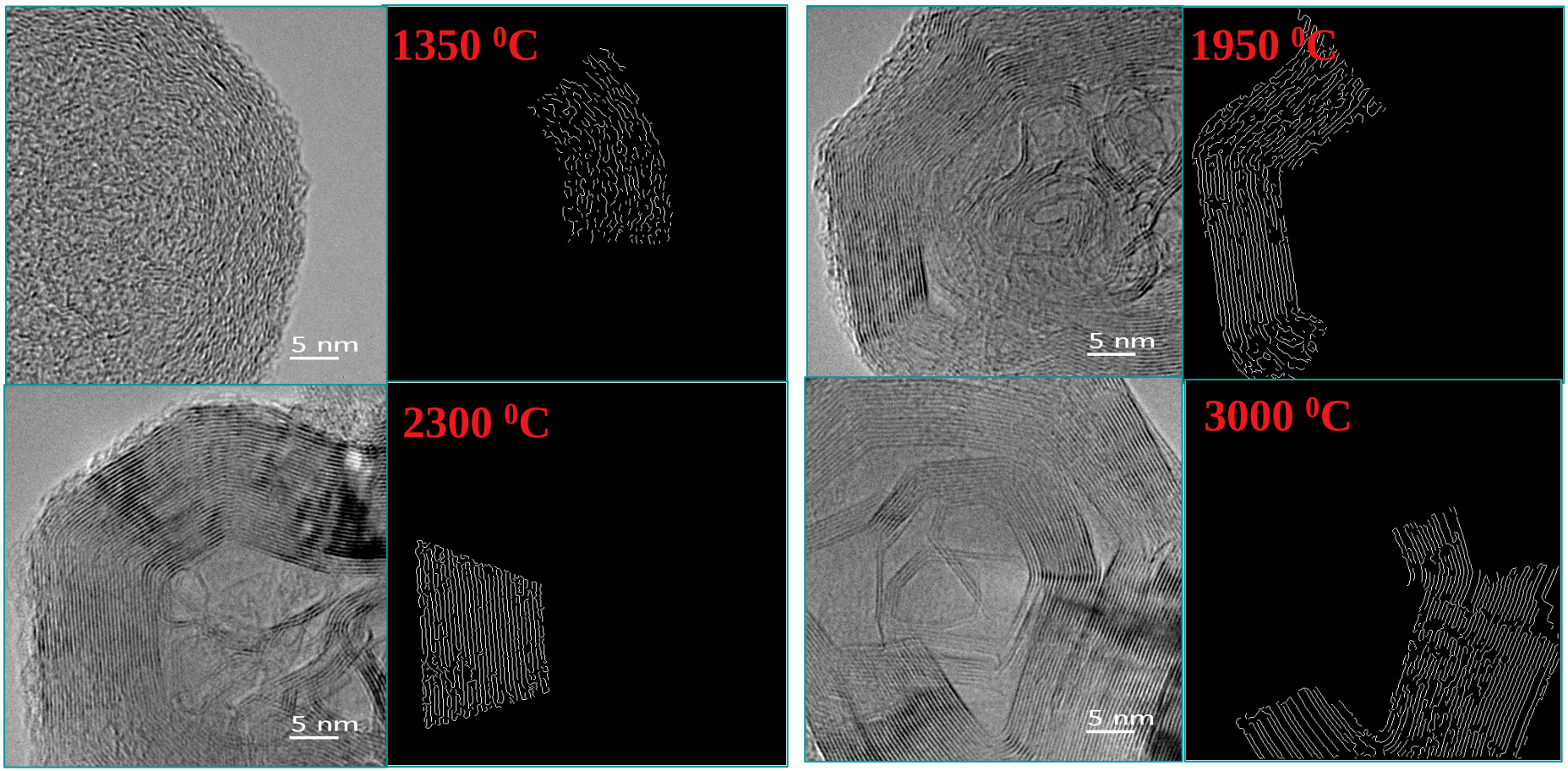
*** Other inputs**

- **Maximum join distance**
- **Minimum fringe length**



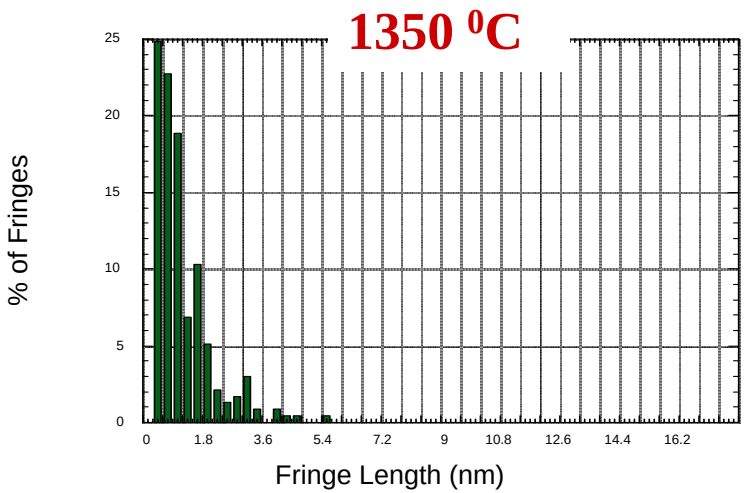


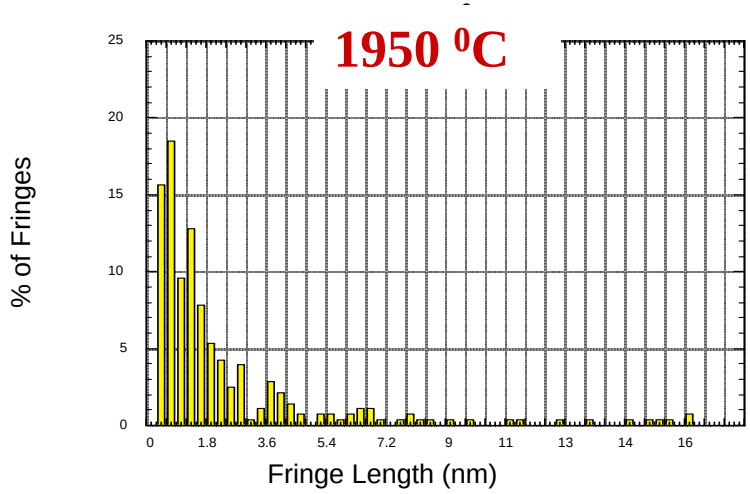
Comparison of Input (HRTEM) and Output (Binary-Fringe) Images

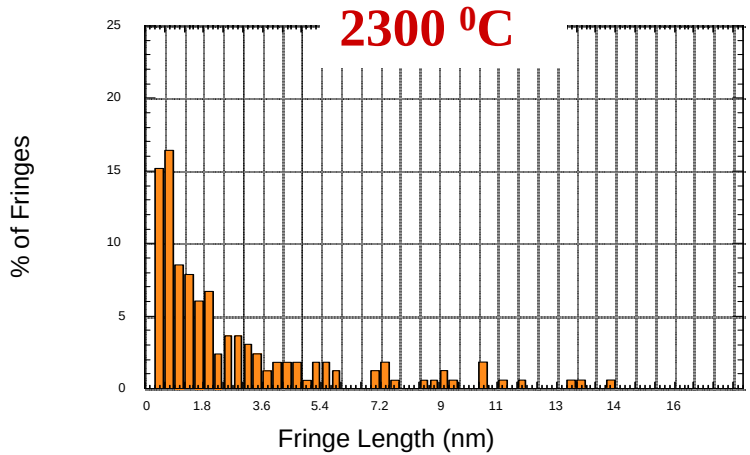


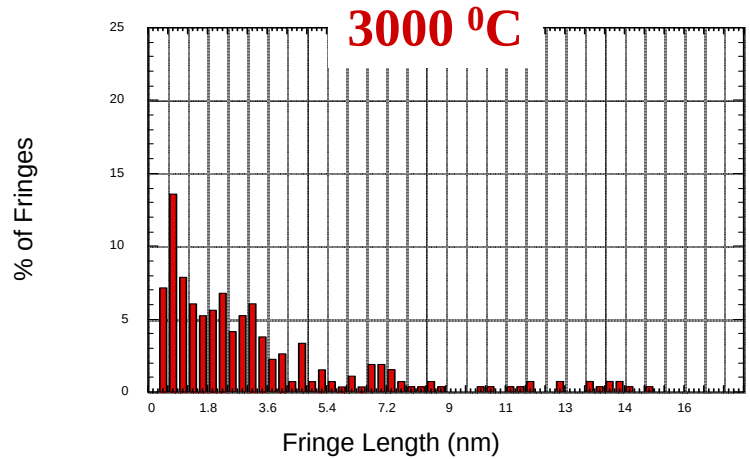
Selected samples of heat-treated carbon black

Fringe Analysis Output Data - Fringe Length Histograms

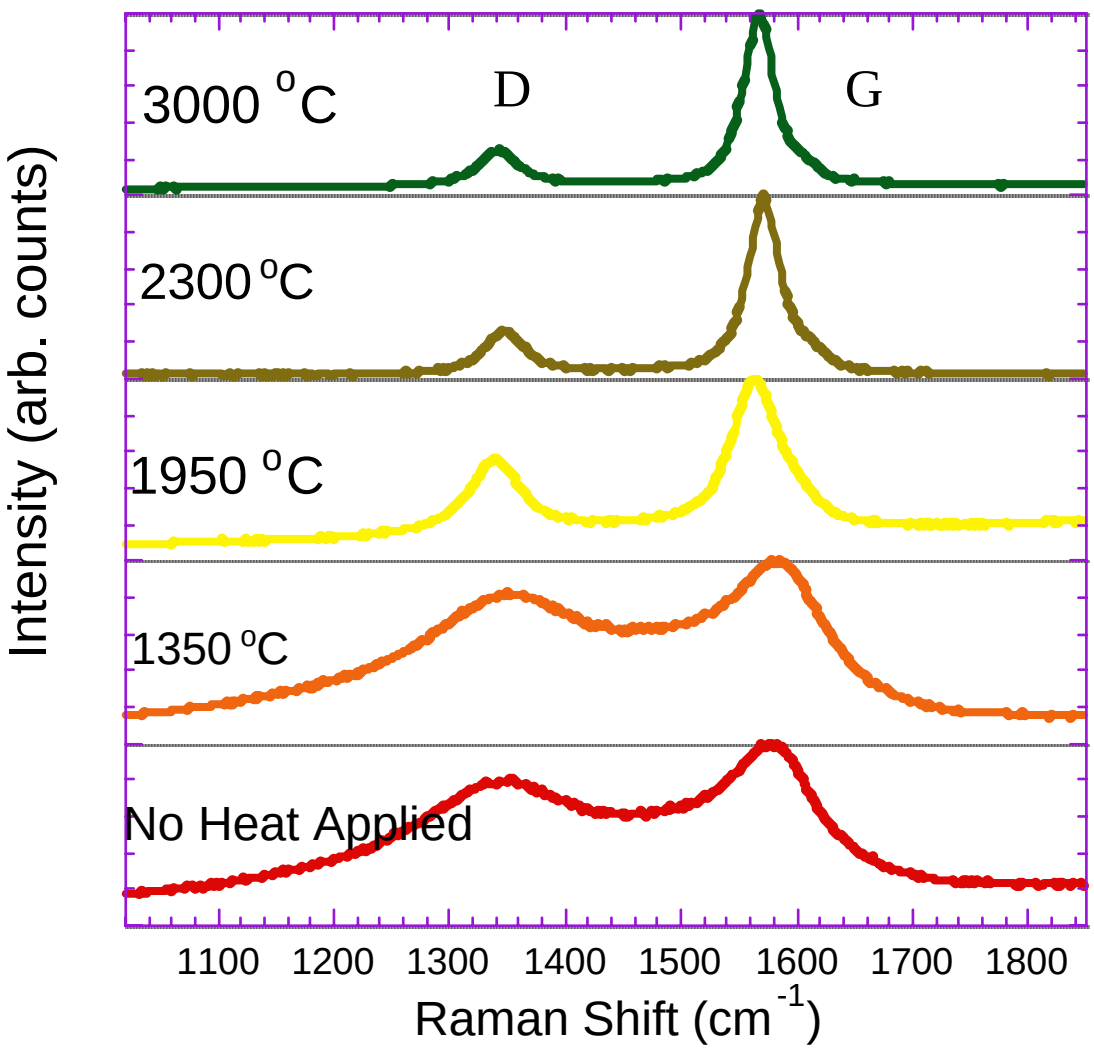






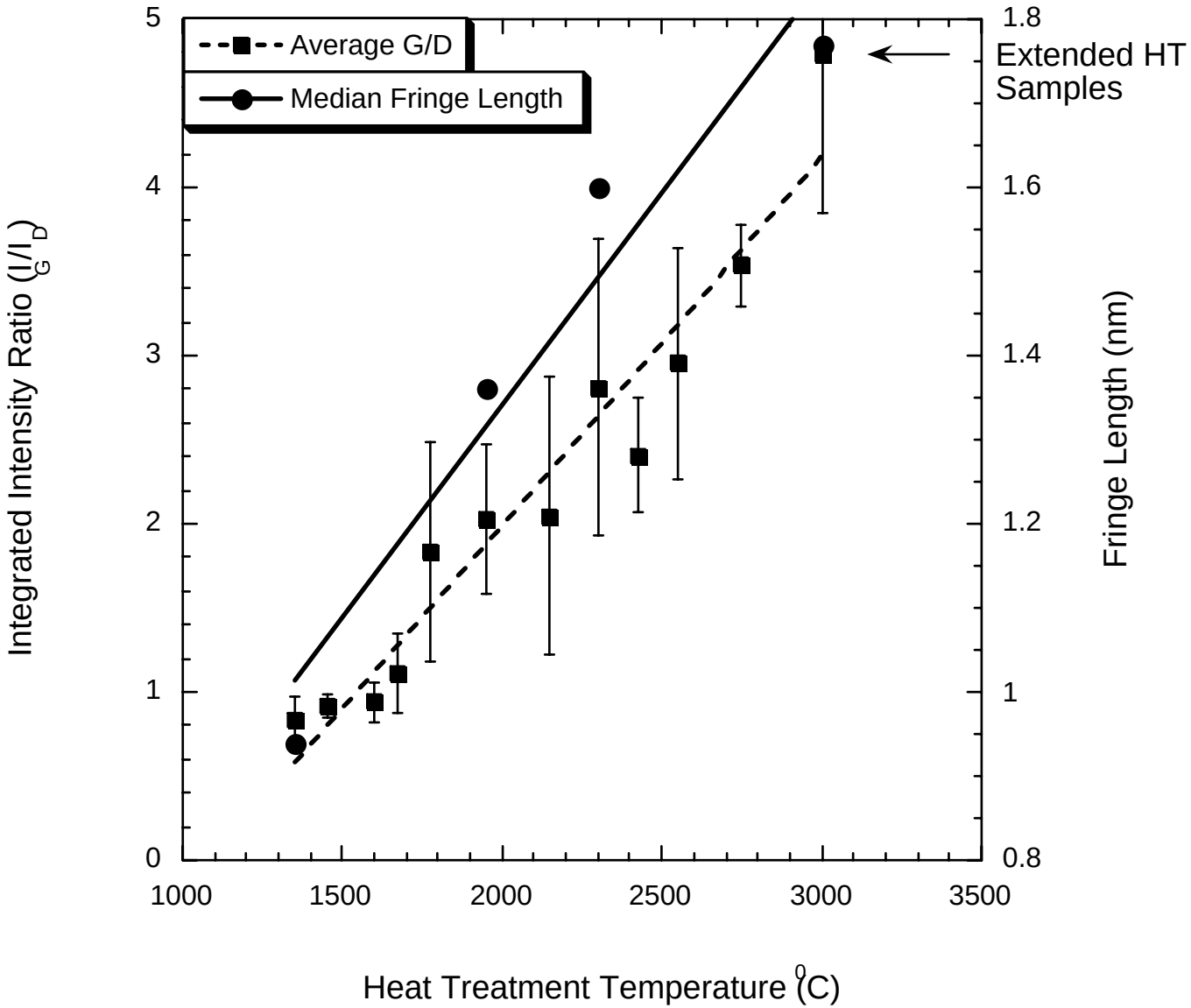


Comparison to Benchmark Methods



- E_{2g} or (G) peak at 1580 cm^{-1} (Graphitic)
- A_{1g} or (D) peak at 1360 cm^{-1} (Disordered)
- Intensity ratio have been used to measure in-plane dimensions

Ratios of Integrated Raman Intensities for Heat Treated Carbon Soots



Soot Oxidation-Prior Studies

* Soot oxidation rates vary widely--10-fold
* Comparing literature oxidation rates difficult, as great number of conditions vary
    - Soot growth conditions
    - Oxidants (O_2, CO_2, H_2O, NO, OH...)
    - Temperature
    - Oxidant concentration
    - Residence times
* Past studies generally used light absorption and scattering

Studies to-date generally examined only 1 soot in any series of measurements

Analysis Methods--Optical vs. TEM

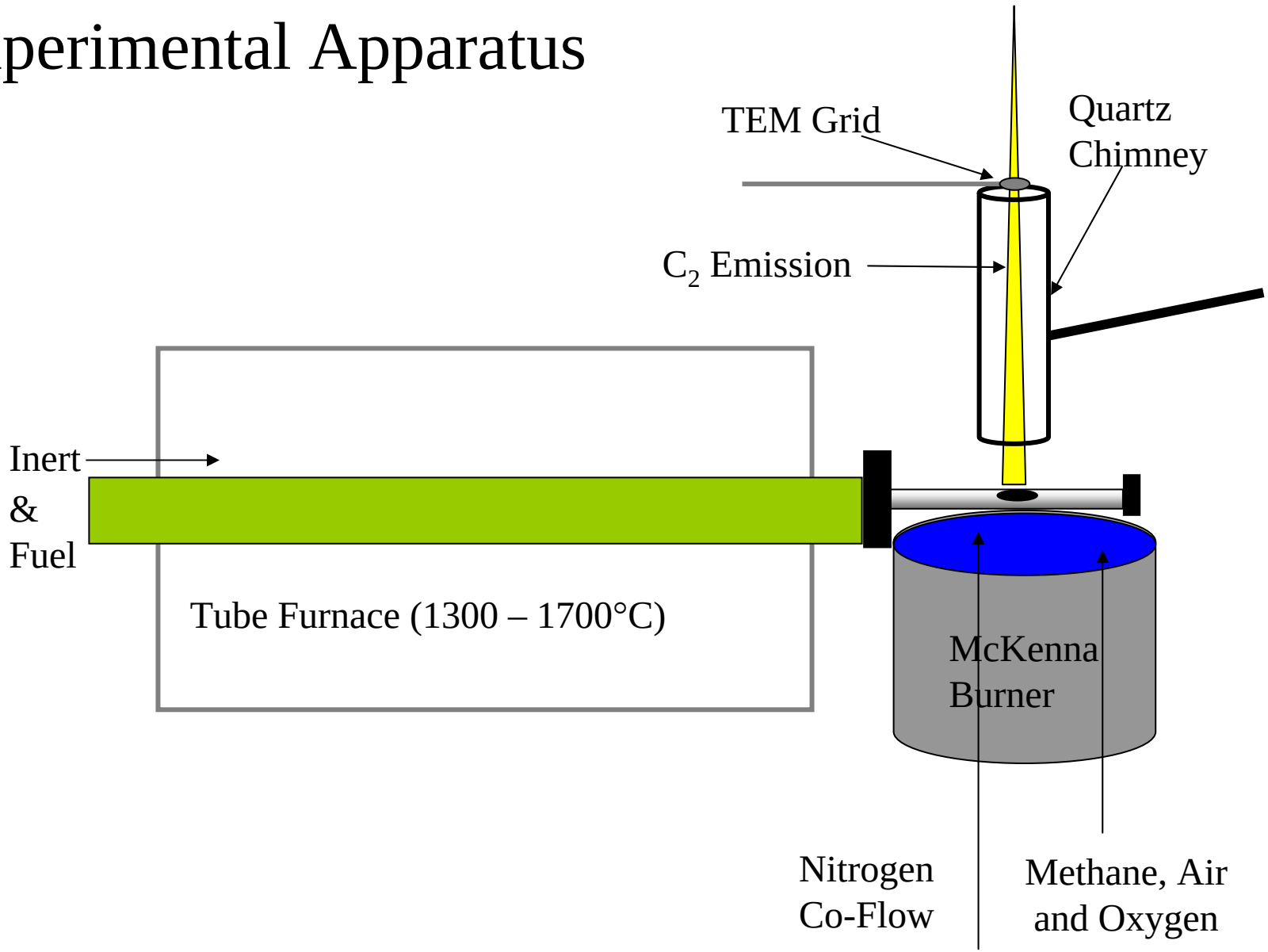
Optical Sizing

- Strengths
  - Real-time
  - Non-intrusive
- Drawbacks
  - Scattering
  - Refractive index issues

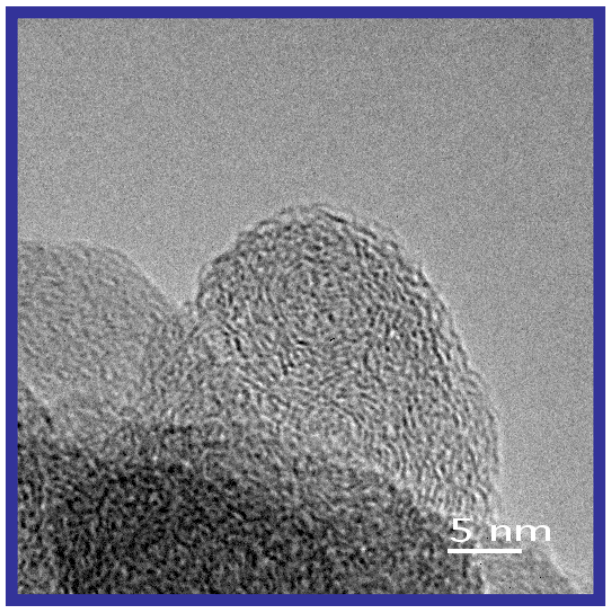
TEM Sizing

- Strengths
  - Direct visualization
  - No property assumptions
- Drawbacks
  - Time
  - Access

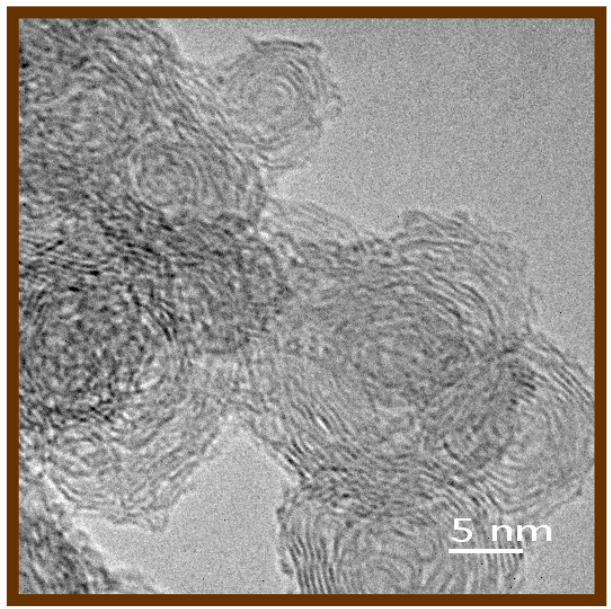
Soot Nanostructure: Experimental Apparatus



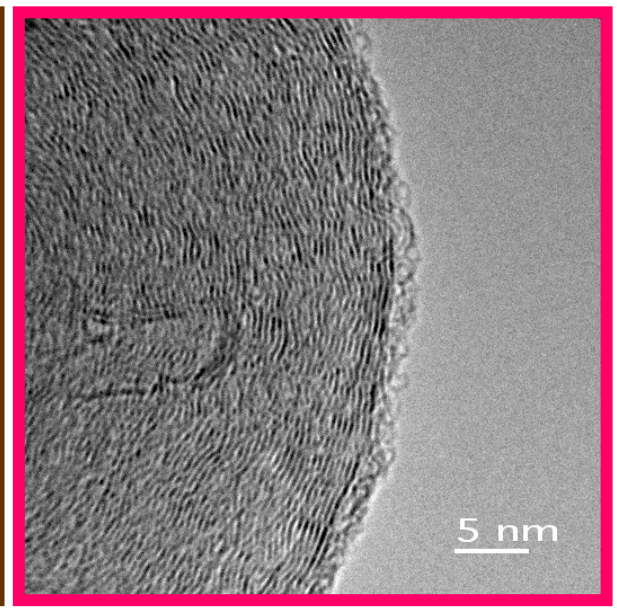
Soot Nanostructure: Model Soots for Oxidation Studies - Dependence Upon Nanostructure



Amorphous (Benzene)



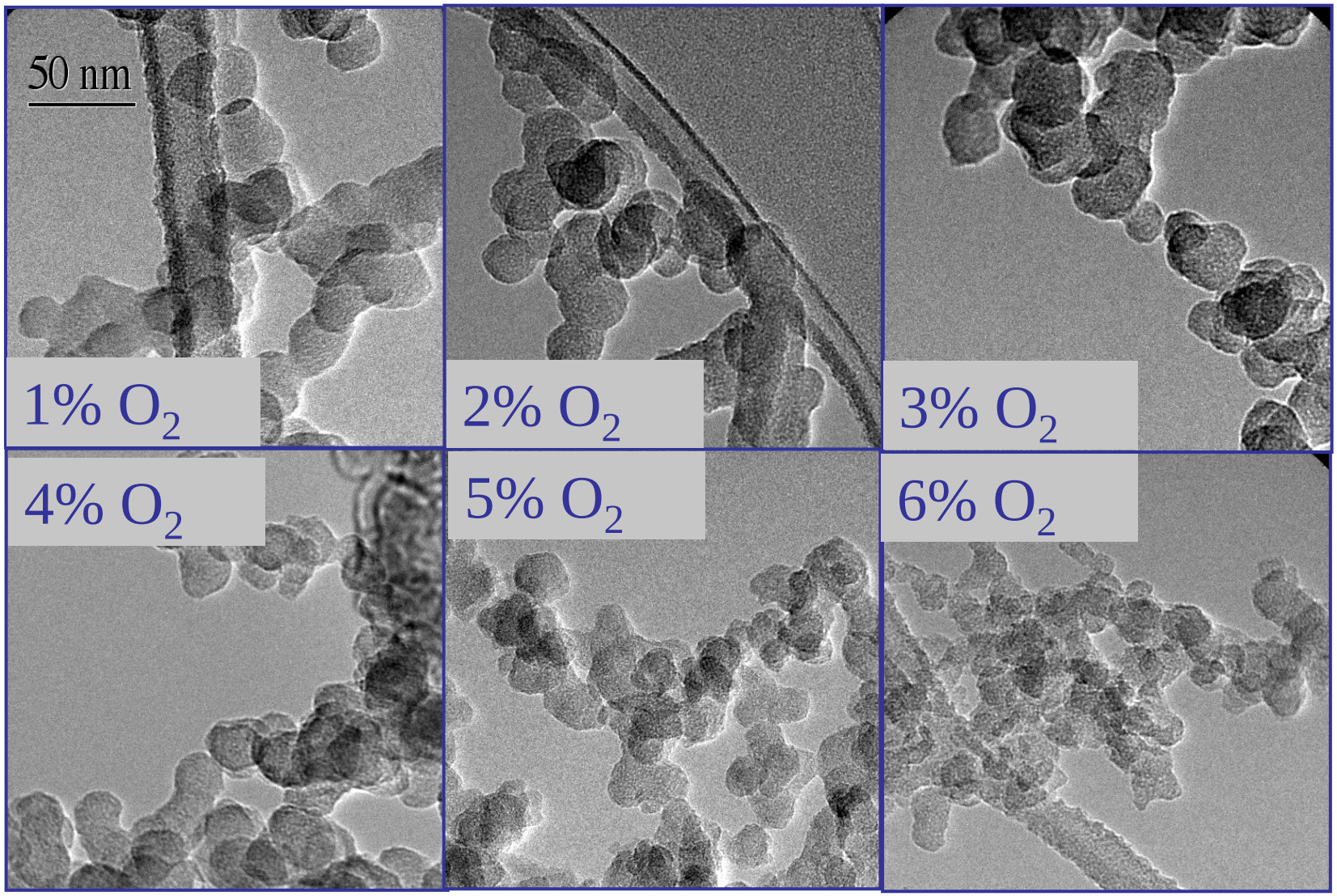
Fullerenic (Ethanol)



Graphitic (Acetylene)

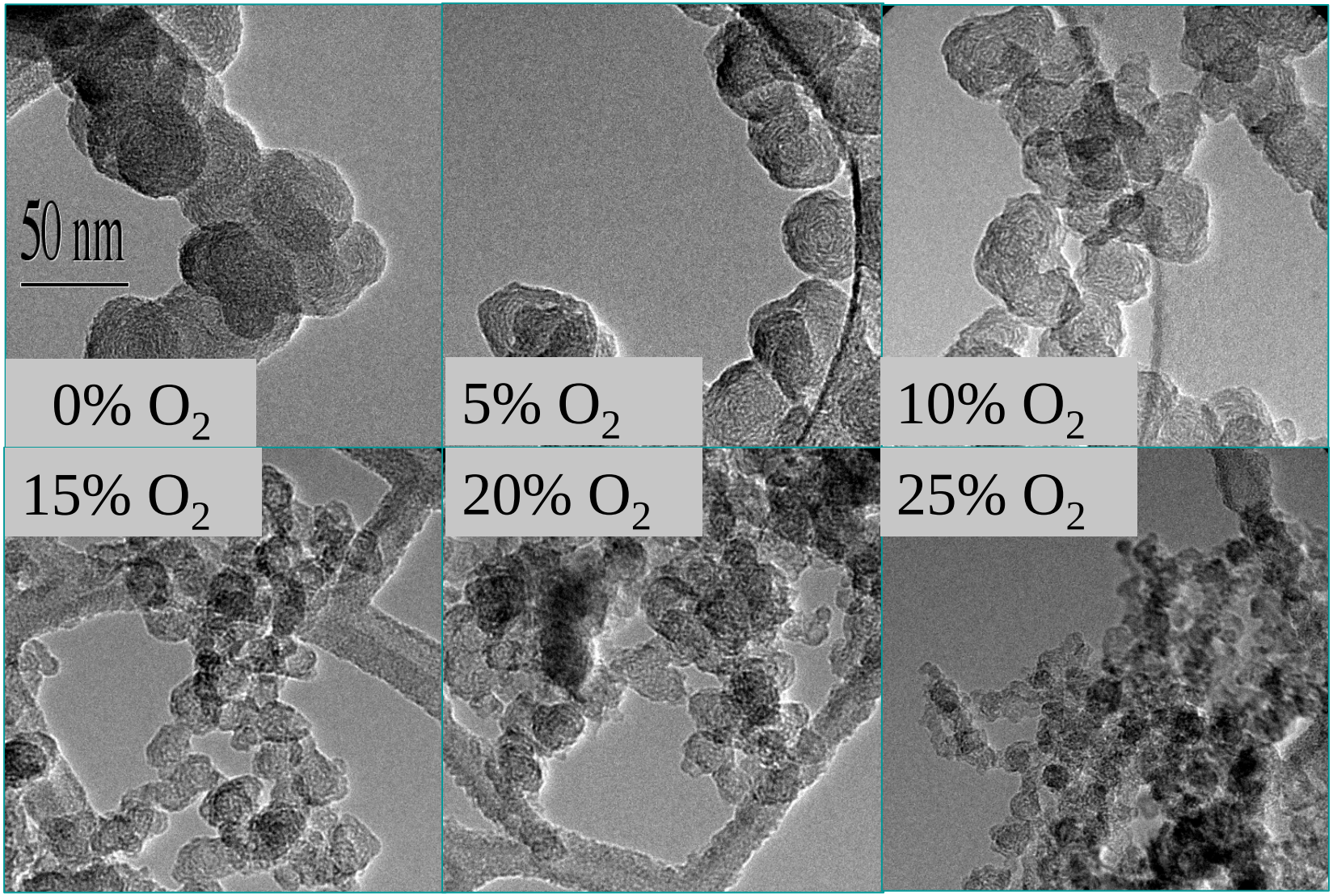
Soot Nanostructure and Implications: Reactivity

TEM images of partially oxidized Benzene soot



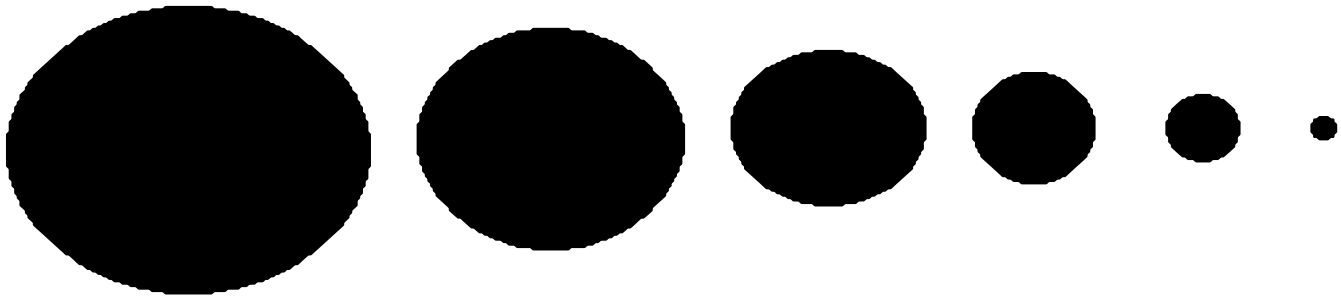
Soot Nanostructure and Implications: Reactivity

TEM images of partially oxidized Acetylene soot



Oxidation Analysis

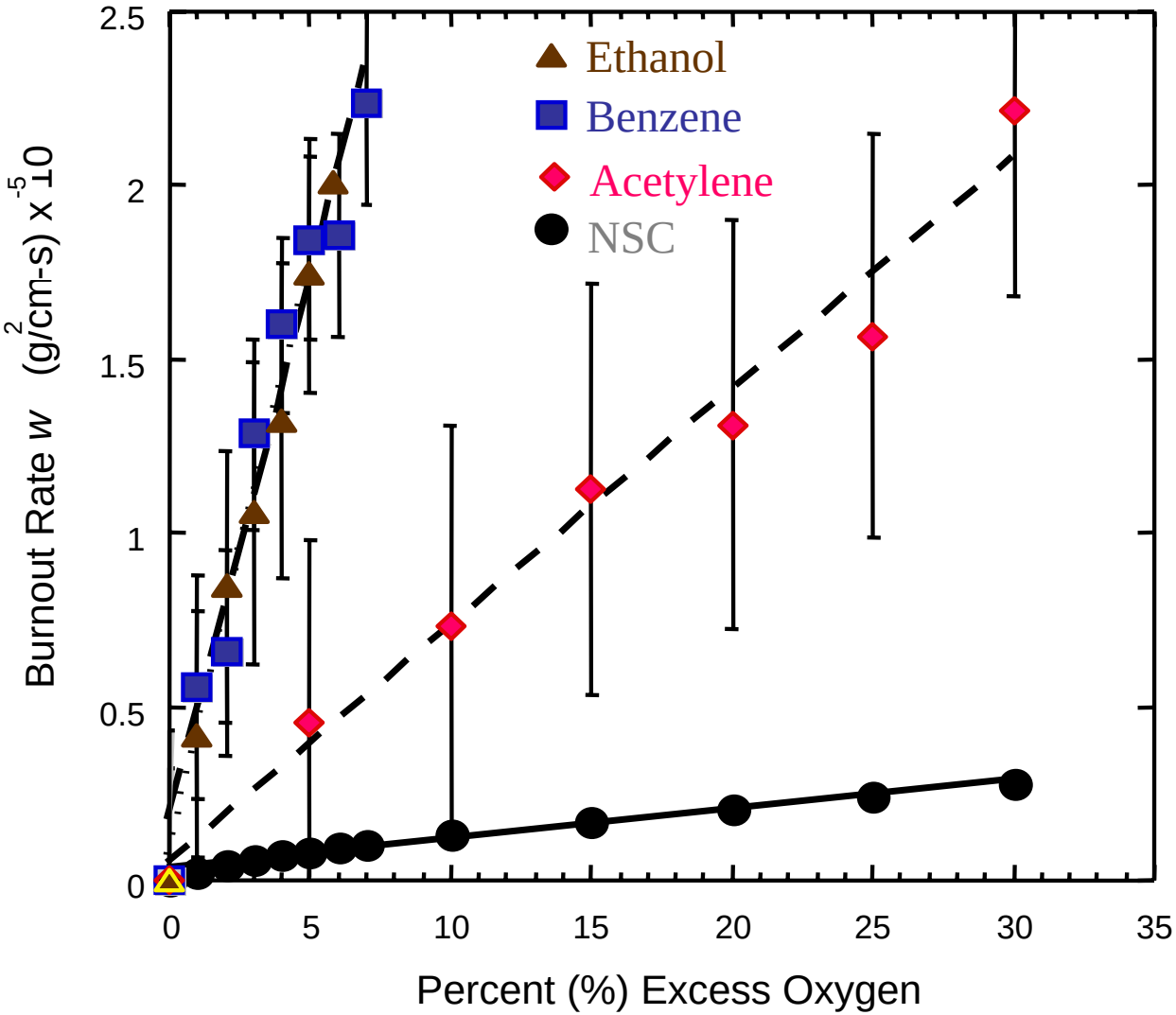
- **Shrinking Spheres Model**



- **Soot Burnout Rate Expression**

$$\omega(kg/m^2 s) = \frac{\rho r_0}{t}\left(1 - \frac{r_t}{r_0}\right) = \frac{1}{A}\frac{dm}{dt}$$

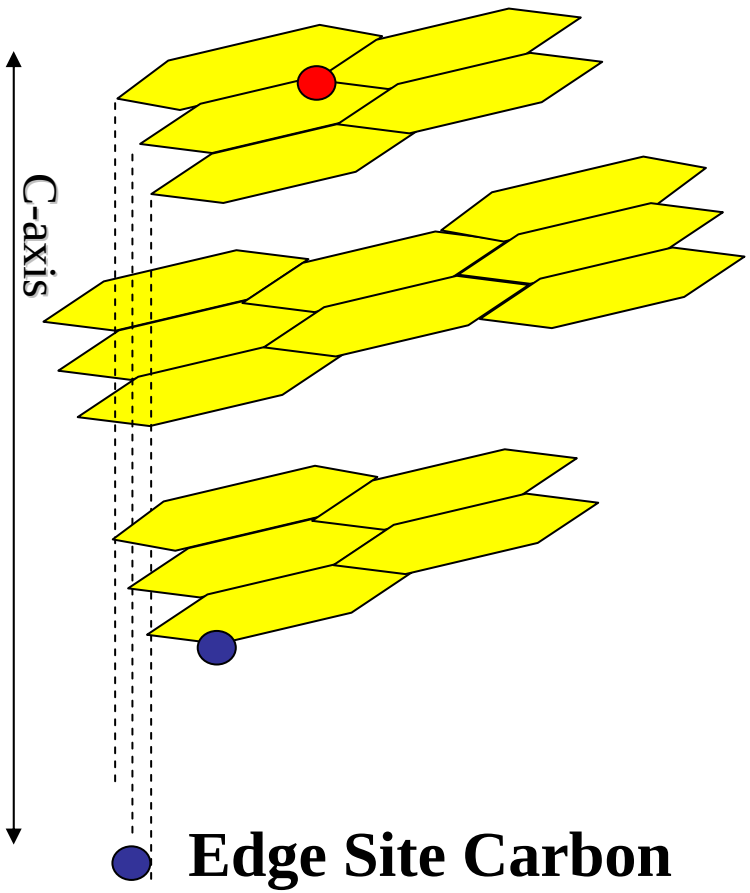
Soot Burnout Rates



Soot Oxidation Rates

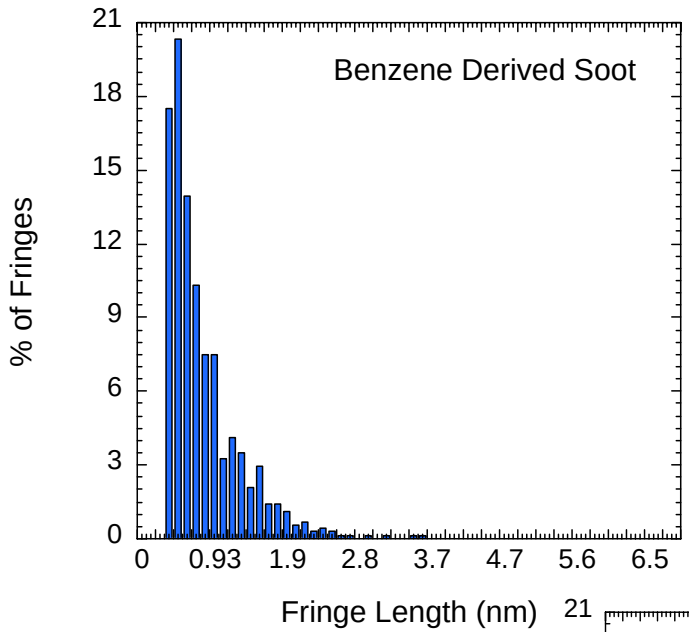
Average Burnout Rates [ω] (g/cm^2s)			
Fuel	Average P_{O2} atm	Average ω	**Average [ω/ω_{NSC}]**
Ethanol	0.005	1.02E-5	**17.9**
Acetylene	0.027	1.24E-5	**6.7**
Benzene	0.007	1.43E-5	**20.7**

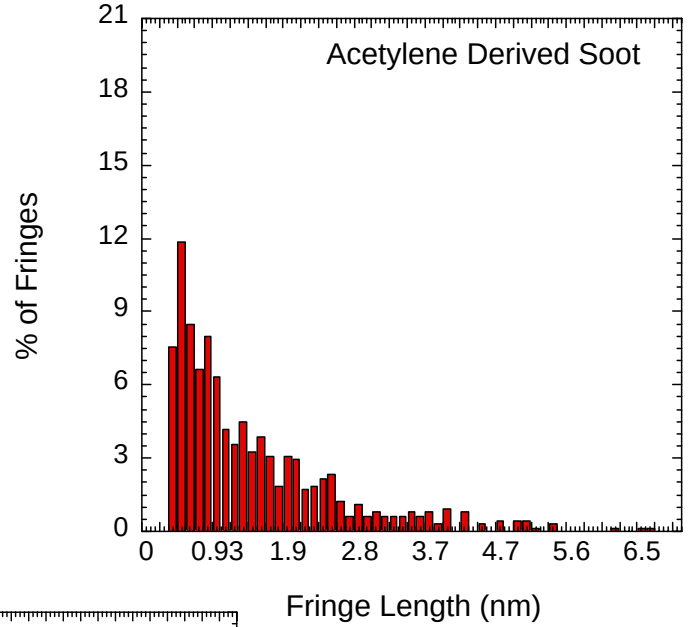
Carbon Soot Nanostructure

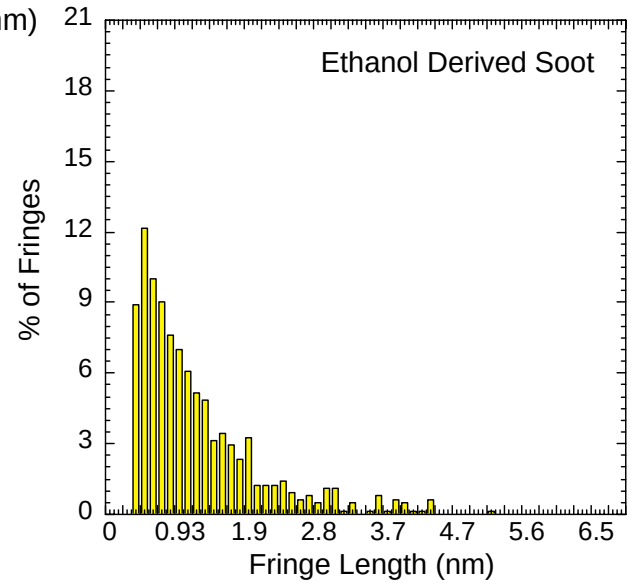


- **Soot oxidation rates are different. What is the cause?**
- **Previous studies ignored nanostructure.**
- **Graphitic carbons are less reactive than amorphous carbons.**
- **Is it just fringe length?**

Nanostructure and Implications: Reactivity
Fringe Length Histograms



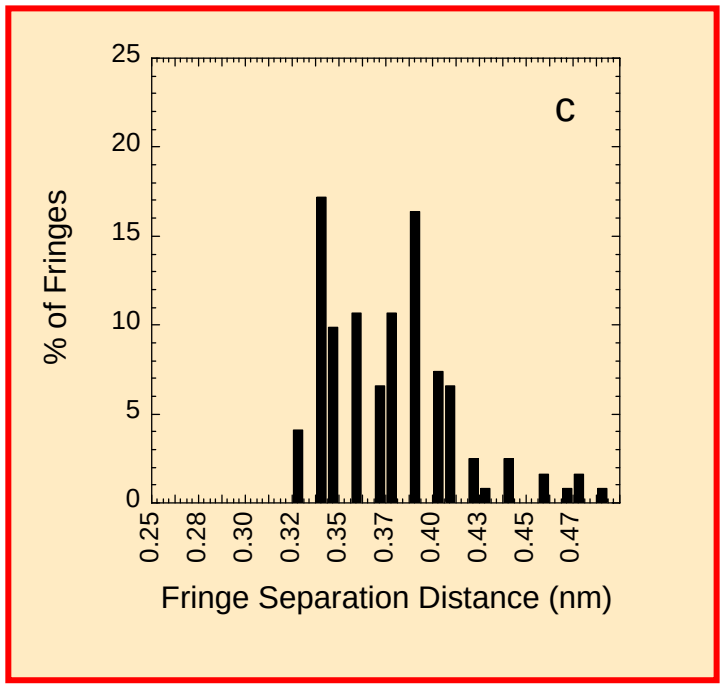




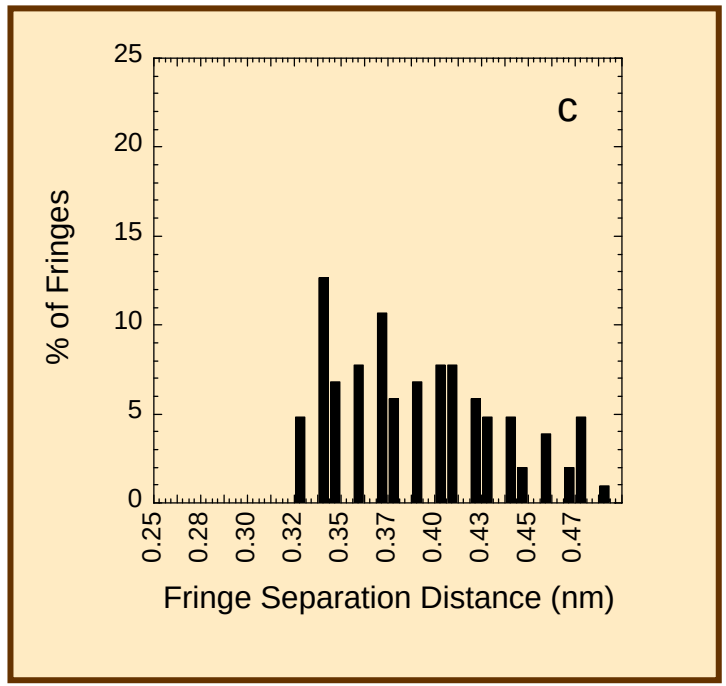
Nanostructure and Reactivity

Fringe Separation Histograms

Acetylene

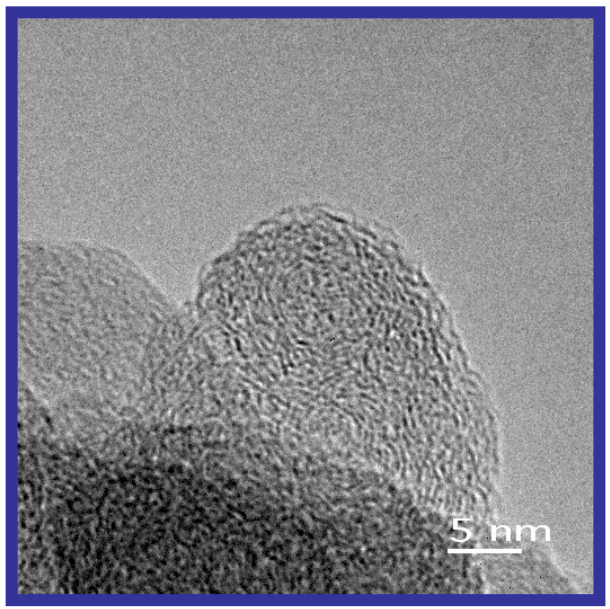


Ethanol

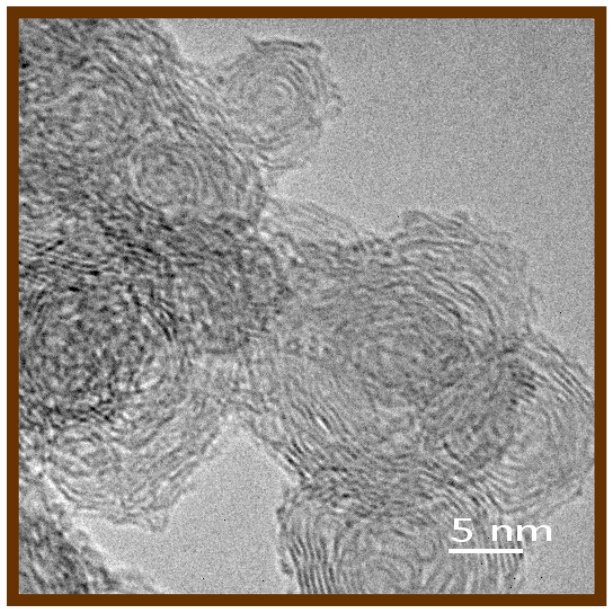


Average $[\omega/\omega_{NSC}]$
17.9 Ethanol
6.7 Acetylene

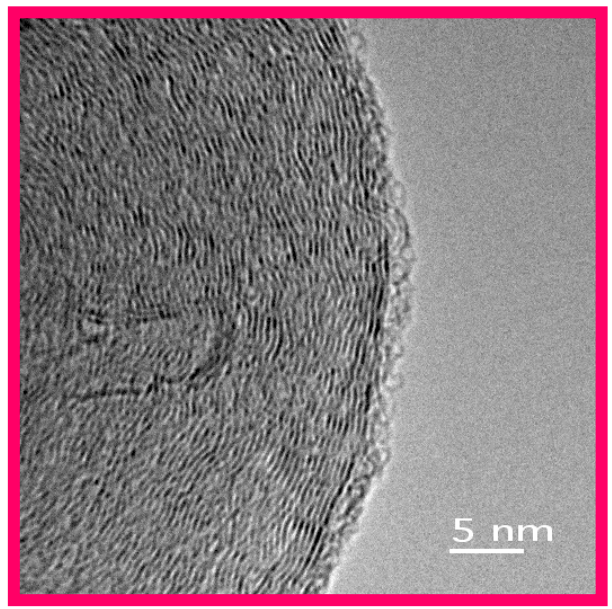
Soot Nanostructure: Interpretation of Reactivity via Nanostructure



Amorphous (Benzene)



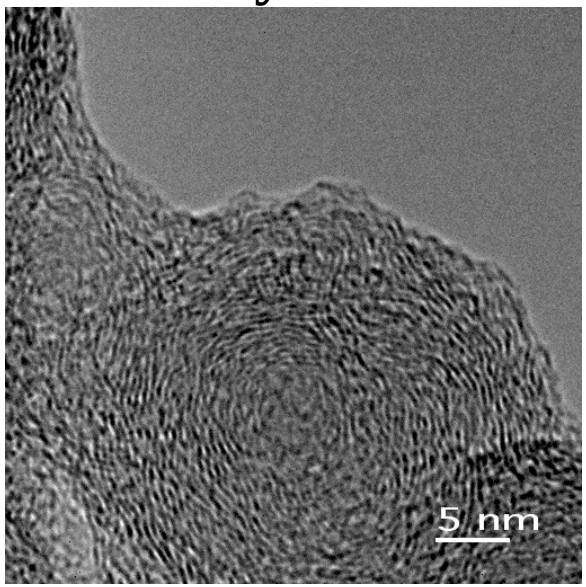
Fullerenic (Ethanol)

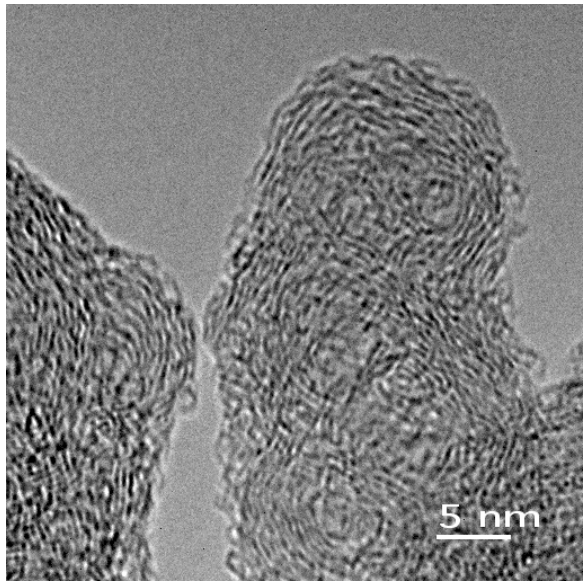


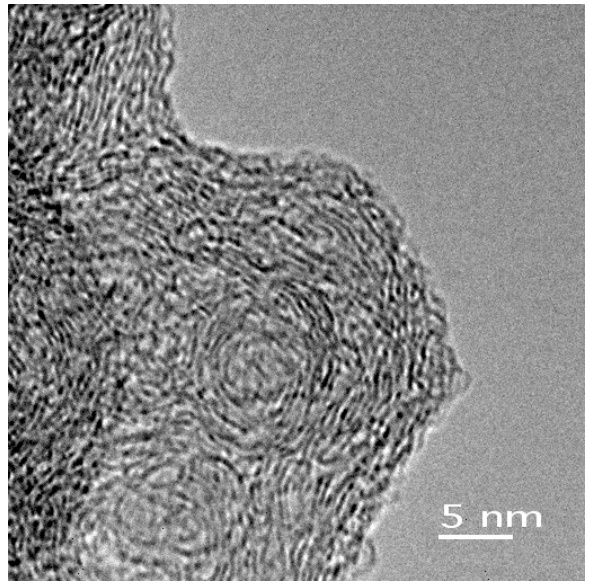
Graphitic (Acetylene)

Diesel Engine Soots
Courtesy Sandia Nat. Labs

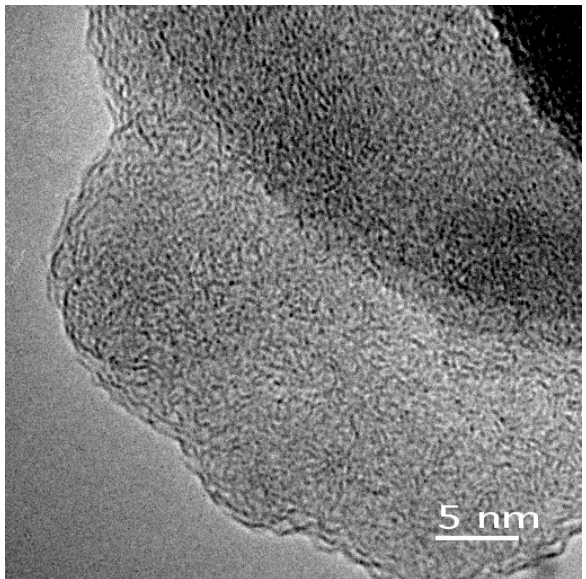
Reference Fuel - n-hexadecane + heptamethylnonane (CN 45-020926B)

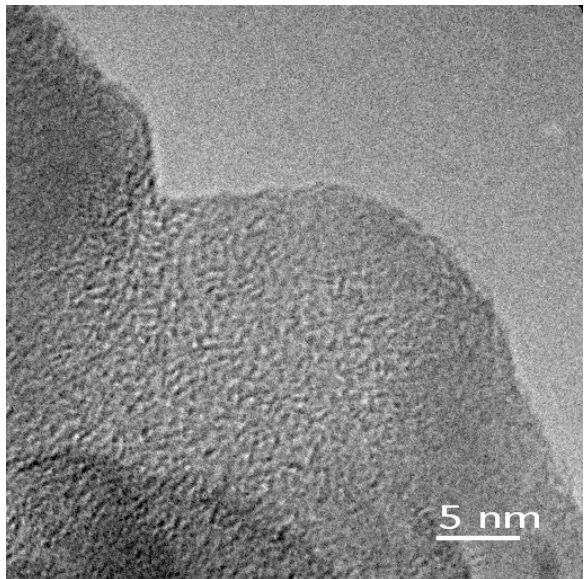


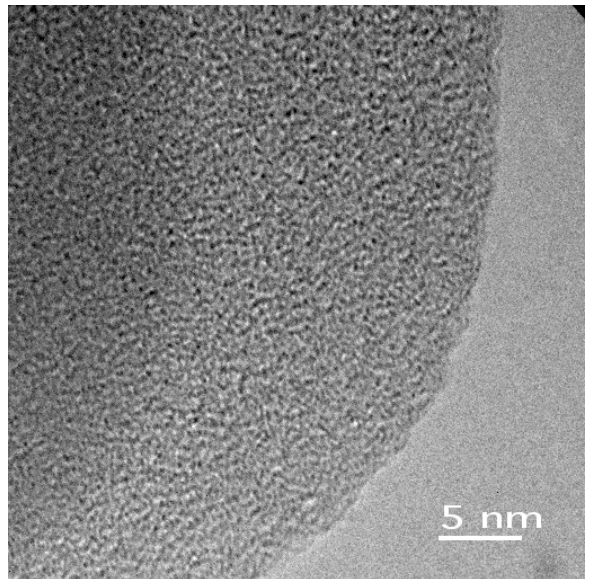




Diethylene glycol diethyl ether **(DGE)**







Conclusions

Soot Nanostructure: (Definition)

*** Soot Nanostructure refers to carbon lamella (layer plane) length, orientation, separation and tortuosity.**

*** Nanostructure is variable, dependent upon temperature, residence time and fuel identity.**

Fringe Analysis Algorithm: (Quantification)

*** Lattice fringe analysis can be used to analyze HRTEM image data and quantify carbon nanostructure through statistical analysis.**

Oxidation Rates: (Implications)

*** Oxidation rates are dependent upon nanostructure - suggests using nanostructure to control (accelerate) oxidation.**

*** Source apportionment via analysis of nanostructure?**

*** Health consequences related to nanostructure?**

*** Environmental impact dependent upon nanostructure?**