Soot Nanostructure: Definition, Quantification and Implications

Randy L. Vander Wal*
and
Aaron J. Tomasek
Gordon M. Berger
Kenneth Street
David R. Hull
William K. Thompson

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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

Acetylene

Benzene

1650°C

Flow Rate Constant

5
Dependence of Nanostructure on Flow Rate

0.1 slpm

1.0 slpm

Acetylene

Benzene

Temperature Constant
Temperature 1250 °C

Acetylene

Benzene

Pyrene

Flow Rate 100 sccm

Flow Rate 1000 sccm
Temperature 1650 °C

Acetylene

Benzene

Pyrene

Flow Rate 100 sccm

Flow Rate 1000 sccm
Ethylene + Water

1650 °C

Flow Rate

100 sccm

1000 sccm
Acetaldehyde + Ethylene

Flow Rate

1:1

1650 °C

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

\[ T = \frac{L}{A} \]
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

1350 °C

1950 °C

2300 °C

3000 °C

Fringe Length (nm)

% of Fringes

Fringe Length (nm)

% of Fringes

Fringe Length (nm)

% of Fringes

Fringe Length (nm)

% of Fringes
Comparison to Benchmark Methods

Raman Spectra of Heat Treated Soot

- $E_{2g}$ 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

Integrated Intensity Ratio ($I_G / I_D$) vs. Fringe Length (nm) for Heat Treatment Temperature ($^\circ$C)

- Average G/D
- Median Fringe Length

Extended HT Samples
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$_2$O, 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

Inert Methane, Air and Oxygen Tube Furnace (1300 – 1700°C) McKenna Burner

TEM Grid Quartz Chimney C₂ Emission

Inert & Fuel

Tube Furnace (1300 – 1700°C) McKenna Burner

Nitrogen Co-Flow Methane, Air and Oxygen
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

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

Burnout Rate $w (g/cm^2 \cdot s) \times 10^3$

Percent (%) Excess Oxygen

- Ethanol
- Benzene
- Acetylene
- NSC
## Soot Oxidation Rates

### Average Burnout Rates $[\omega]$ (g/cm$^2$s)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Average $P_{O_2}$ atm</th>
<th>Average $\omega$</th>
<th>Average $[\omega/\omega_{NSC}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>0.005</td>
<td>1.02E-5</td>
<td>17.9</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.027</td>
<td>1.24E-5</td>
<td>6.7</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.007</td>
<td>1.43E-5</td>
<td>20.7</td>
</tr>
</tbody>
</table>
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?

Edge Site Carbon

Basal Plane Carbon
Nanostructure and Implications: Reactivity
Fringe Length Histograms

Benzene Derived Soot

Acetylene Derived Soot

Ethanol Derived Soot
Nanostructure and Reactivity
Fringe Separation Histograms

**Acetylene**

![Acetylene Fringe Separation Histogram]

**Ethanol**

![Ethanol Fringe Separation Histogram]

<table>
<thead>
<tr>
<th>Average [ω/ω_{NSC}]</th>
<th></th>
</tr>
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<td>17.9 Ethanol</td>
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</tr>
<tr>
<td>6.7 Acetylene</td>
<td></td>
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</tbody>
</table>
Soot Nanostructure: Interpretation of Reactivity via Nanostructure

Amorphous (Benzene)  Fullerenic (Ethanol)  Graphitic (Acetylene)
Diesel Engine Soots

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

Courtesy Sandia Nat. Labs

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?