Soot Nanostructure: Definition, Quantification and Implications

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Soot Macrostructure: Aggregate Size and Morphology
Soot Nanostructure: Experimental Apparatus

- Inert Methane, Air and Oxygen
- Nitrogen Co-Flow
- McKenna Burner
- TEM Grid
- Quartz Chimney
- C$_2$ Emission
- Tube Furnace (1300 – 1700°C)
- Methane, Air and Oxygen
Soot Nanostructure: Definition using HRTEM Images of Primary Particle (Internal) Structure

- Amorphous (Benzene)
- Fullerenic (Ethanol)
- Graphitic (Acetylene)
Statistical Properties Extracted from HRTEM Images (of soot nanostructure)
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
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
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

Int&aacutenity (arb. counts)

Raman Shift (cm$^{-1}$)

3000 °C
2300 °C
1950 °C
1350 °C
No Heat Applied
Ratios of Integrated Raman Intensities for Heat-Treated Carbon Soots
Soot Nanostructure and Implications: Reactivity

TEM images of partially oxidized benzene 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 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?

**Carbon Soot Nanostructure**

- **Edge Site Carbon**
- **Basal Plane Carbon**
Nanostructure and Implications: Reactivity

Fringe Length Histograms

Fringe Length (nm)

% of Fringes

Benzene Derived Soot

Acetylene Derived Soot

Ethanol Derived Soot

Nanostructure and Implications: Reactivity
Nanostructure and Implications: Reactivity

Fringe Separation Histograms

Acetylene

Ethanol

Average
\[
\frac{\omega}{\omega_{NSC}}
\]

17.9 Ethanol
6.7 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?