HRTEM and XPS Analyses of Soot: Microscopic and Spectroscopic Observations

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Definitions

Soot nanostructure refers to the physical characteristics and arrangements of carbon lamellae within primary particles.

Lattice fringe length is the linear distance traversed by the atomic carbon layer planes.

Fringe separation is the mean distance between adjacent planes.

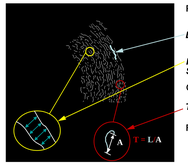
Tortuosity is the ratio of the actual fringe length relative to the straight-line distance between its endpoints. This provides a measure of the undulation of the layer planes.

Implications of Soot Nanostructure and Surface Chemistry

Oxidation—Oxidation rates depend strongly upon soot nanostructure.
Source Identification—Pollution source models could be based on real data, and emissions compliance could be monitored.
Atmospheric—Soot particles may act as cloud condensation nuclei and participate in NOx regeneration.
Health—Currently debate centers on the structural parameter (size for soot, aspect ratio for carbon nanotubes (CNTs)); nanostructure remains to be explored.

Soot Nanostructure: Quantification via Fringe Analysis[1,2]

Statistical Properties Extracted From High-Resolution Transmission Electron Microscopy (HRTEM) Images (of soot nanostructure)

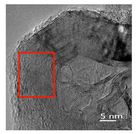


Position
Length
Fringe Separation
Orientation
Tortuosity
Fringe Density

Soot Nanostructure: Quantification via Fringe Analysis

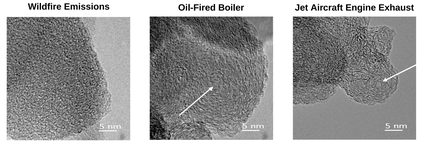
* Image refinements—To overcome HRTEM image limitations
  - Region of interest
  - Spatial filtering
  - Binary thresholding

* Other inputs
  - Maximum join distance
  - Minimum fringe length

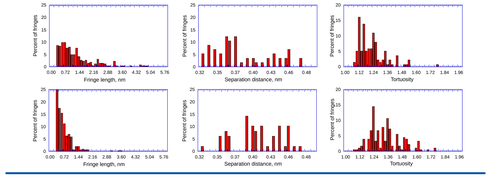


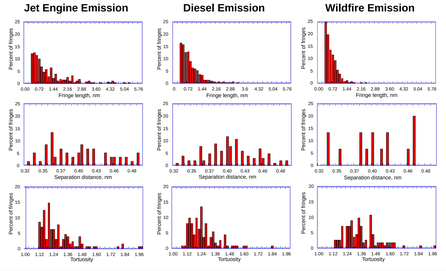
Operations:
1. Switches 256 grayscale image to binary
2. Removes all pixels not above threshold
3. Removes remaining pixels and groups of pixels that do not form extended lines
4. Uses position of pixels within lines to determine length, curvature, etc. of fringes

Application II: Source Identification[4]



Comparison Between Soot Nanostructure From Oil-Fired Boilers

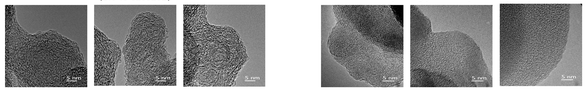




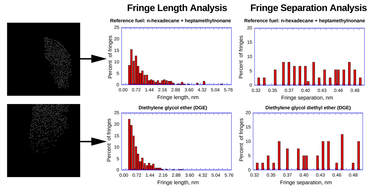
Application I: Emissions Reduction[3]

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

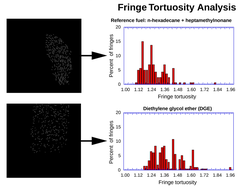
Diethylene glycol diethyl ether (DGE)



Processed Images (Fringe Length and Separation)



Processed Images (Fringe Tortuosity)



Conclusions for HRTEM and Image Analysis of Soot Nanostructure

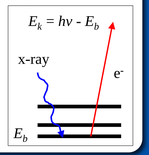
Soot Nanostructure (Definition):
* Soot nanostructure refers to carbon lamella (layer plane) length, orientation, separation, and tortuosity.
* Nanostructure is variable, dependent upon temperature, residence time, and fuel identity.

Fringe Analysis Algorithm (Quantification):
* Lattice fringe analysis can be used to analyze HRTEM image data and quantify carbon nanostructure through statistical analysis.

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?

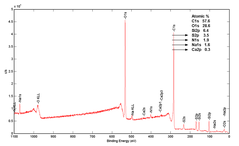
Introduction to X-Ray Photoelectron Spectroscopy (XPS)[5]

* XPS provides information about elemental composition and oxidation state of the surface.
* A monochromatic x-ray beam of known energy displaces an electron from a K-shell orbital.
* The kinetic energy of the emitted electron is measured in an electron spectrometer.
* The binding energy $E_b = h\nu - E_k$ is characteristic of the atom and orbital from which the electron is emitted.
* A low-resolution wide-scan (survey) spectrum serves as the basis for the determination of the elemental composition of samples.
* At higher resolution, chemical shifts are observed depending upon oxidation state.

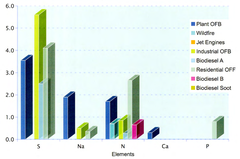


Elemental Composition

Low-Resolution Survey Scan - Plant Oil Fired Boiler

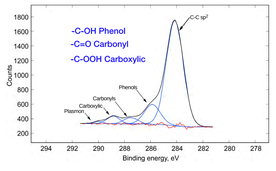


XPS - Survey Elemental Analysis

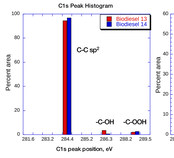


Carbon Oxidation State

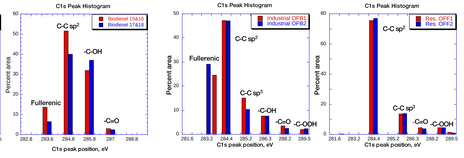
Identification of Oxygen Functional Groups



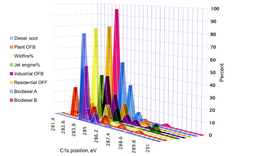
Comparison Between Biodiesel Soots



Oil Fired Boiler Versus Residential Oil-Fired Furnace

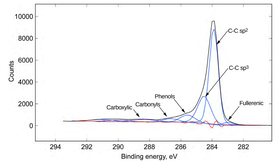


Comparative Peak Intensities—Oxygen Functional Groups

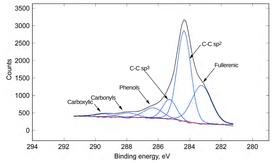


Carbon Nanostructure: Characterization of sp^2 and sp^3 Carbon

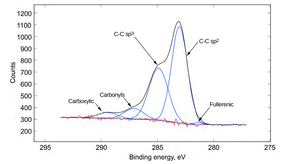
Carbon Nano-onions



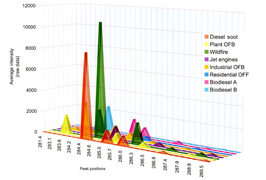
Oil-Fired Boiler



Diesel Engine



Comparative Peak Intensities—Carbon Nanostructure



Conclusions for XPS Analysis of "Real" Soots:

1. XPS analysis can identify and quantify trace elements.
   Utility: Can be used to identify source based on specific elements present and their distribution
   * Track fuel and/or oil elements
   * Analysis of engine wear

2. XPS can identify oxygen groups by bonding type: C-OH, C=O, and C-OOH. These reflect the soot oxidation history.
   Utility: Identify the occurrence and degree of oxidation

3. XPS can identify the types of carbon present: sp^2, sp^3, and fullerenic.
   Therein it can provide a complimentary method to HRTEM and image analysis.
   Utility: Correlate nanostructure with soot reactivity

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References:

1. Vander Wal, R. L., Tomasek, A. J., Pamphlet, M. I., Taylor, C. D., and Thompson, W. K., "Analysis of HRTEM images for carbon nanostructure quantification", J. of Nanoparticle Research 6:555-568 (2004).
2. Vander Wal, R. L., Tomasek, A. J., Street, K. W., Hull, D. R., and Thompson, W. K., "Carbon nanostructure examined by lattice fringe analysis of high resolution transmission electron microscopy images", Applied Spectroscopy 58:230-237 (2004).
3. Vander Wal, R. L., and Mueller, C. J., "Initial investigation of effects of fuel oxygenation on nanostructure of soot from a direct-injection diesel engine", Energy and Fuels (submitted).
4. Vander Wal, R. L., and Hays, M., "Source identification by quantification of HRTEM images", Energy and Fuels (submitted).
5. Vander Wal, R. L., and Hays, M., "Chemistry and nanostructure by XPS". Environmental Sci. and Technol. (to be submitted).