Physical and Chemical Characterization of Gasoline and Diesel Engine Carbonaceous Particulate

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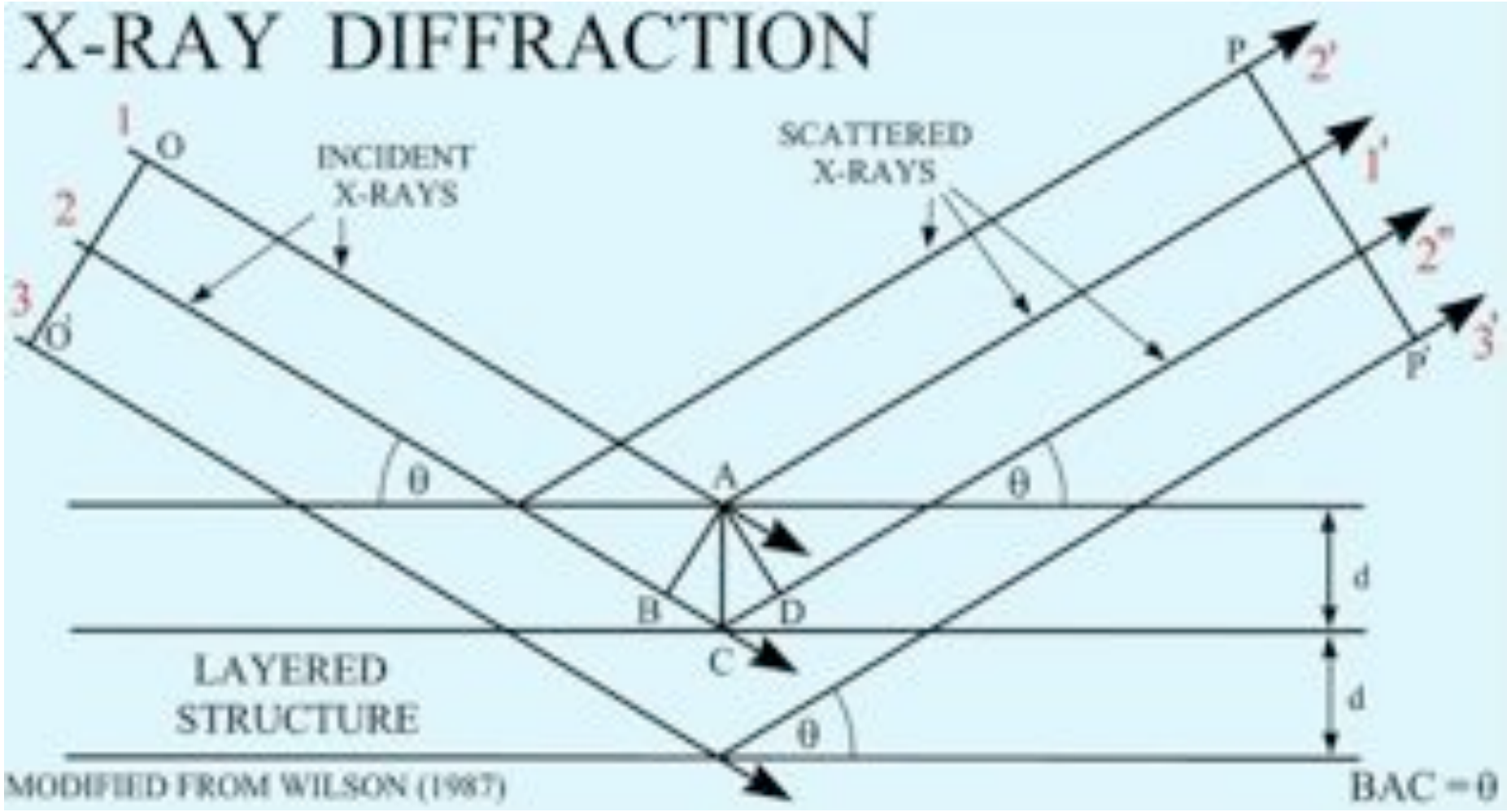
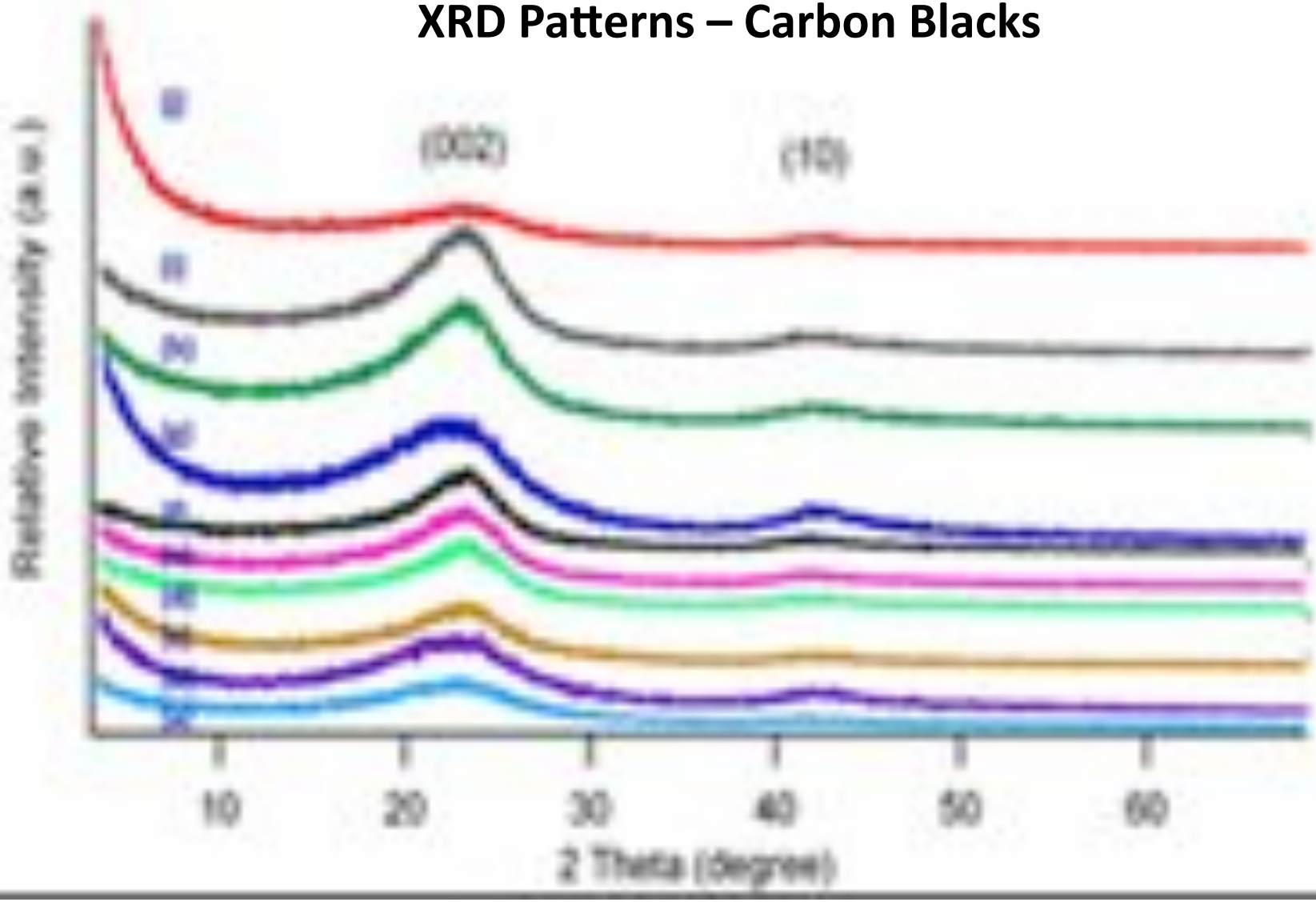
Outline

- **Introduction** Physical Analysis Techniques – XRD, Raman, HRTEM and Quantification
- **Results** Relevance to Biodiesel soot
- **Spectroscopic Analysis Techniques** – XPS, FTIR_ATR
- **Results** Relevance to Gasoline soot
- **Complimentary Aspects of Physical and Chemical Soot Forensics**

- **Addendum**: *Poster- Nanostructure as Indicator for Gas-phase Chemistry*


X-RAY DIFFRACTION
1
O
2
3
O'
INCIDENT
X-RAYS
SCATTERED
X-RAYS
P
2'
1'
2"
3'
P'
θ
A
θ
B
D
C
d
d
LAYERED
STRUCTURE
θ
MODIFIED FROM WILSON (1987)
BAC = θ

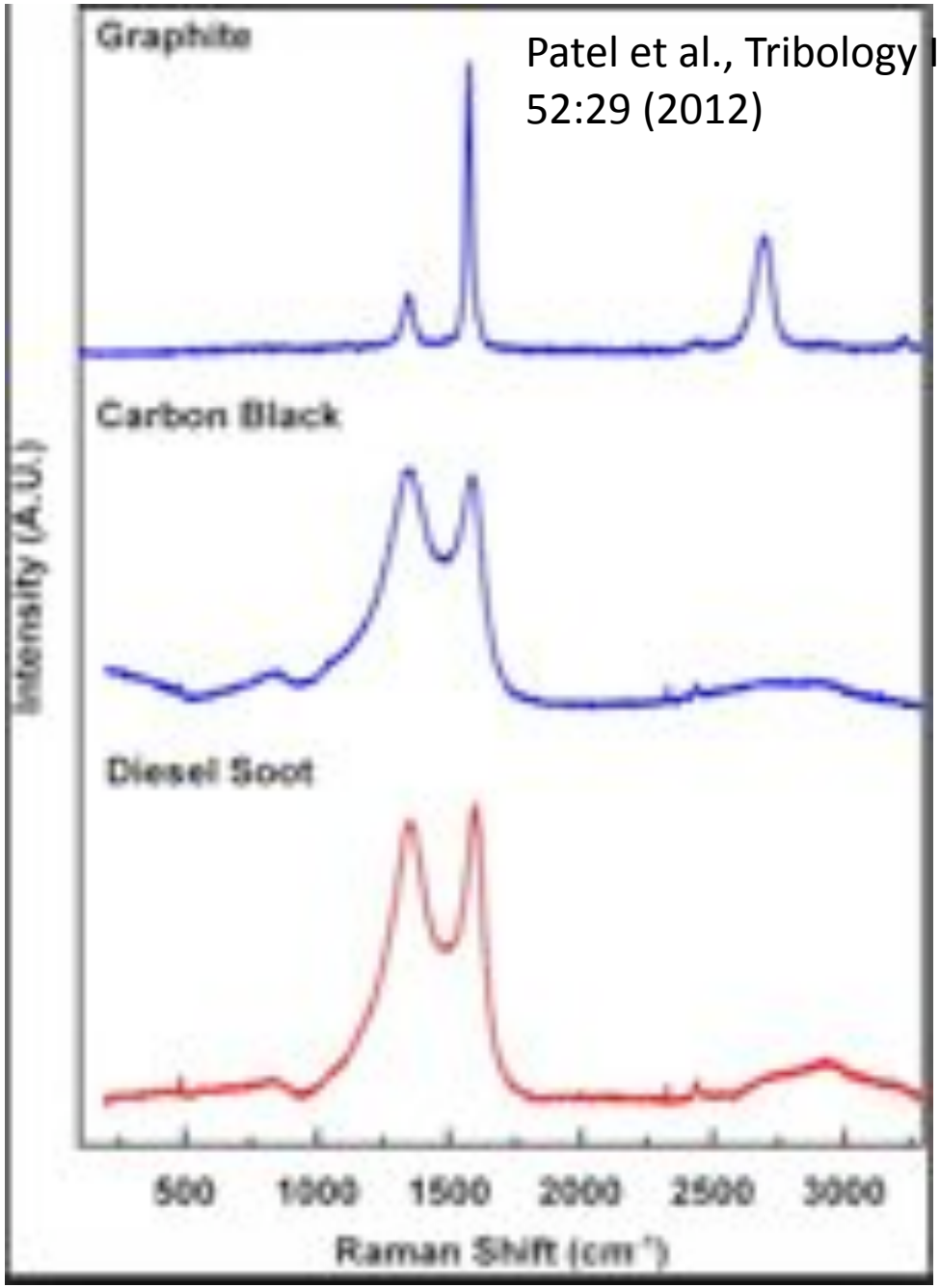
XRD Patterns – Carbon Blacks



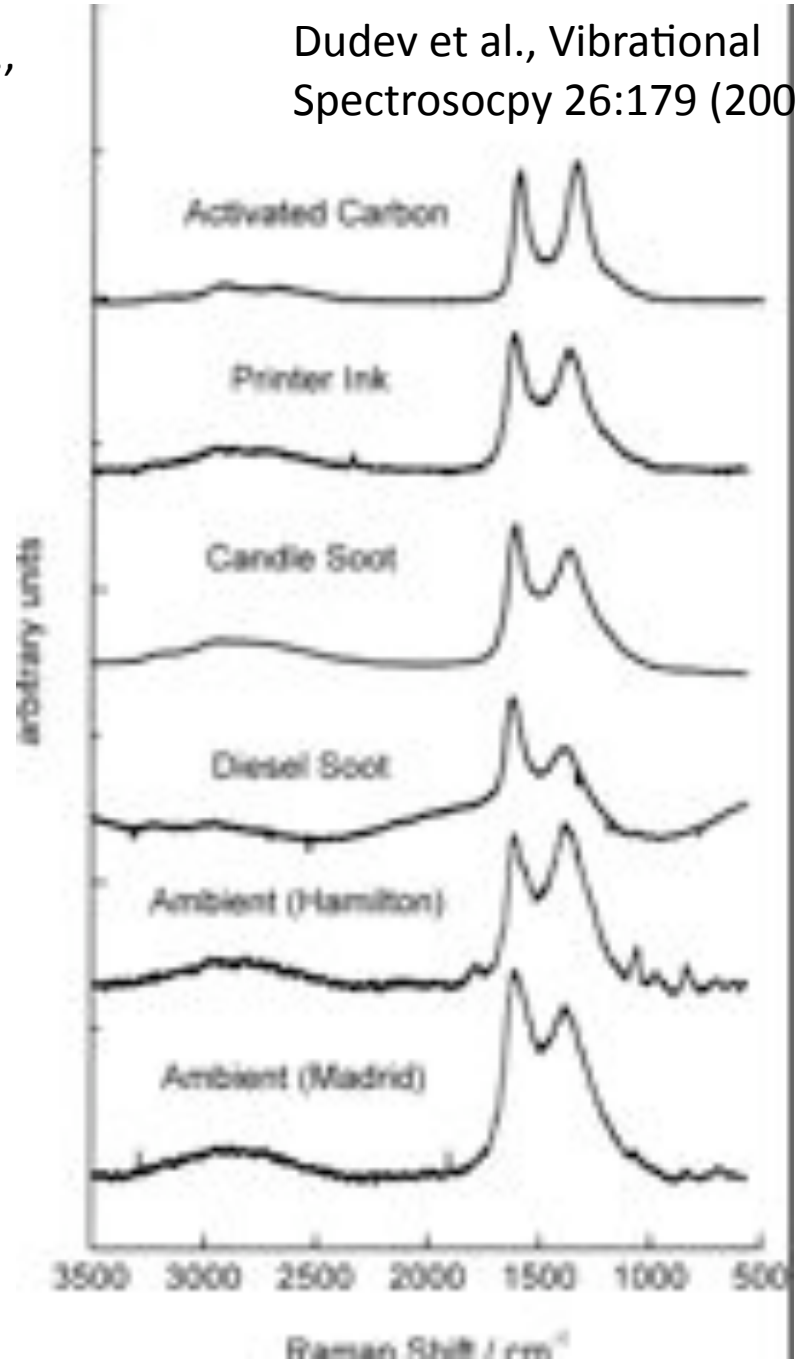
XRD patterns of a) Printex U, b) Monarch 1300, c) Vulcan XC72R, d) Monarch 280, e) Regal 330R, f) Printex G, g0 Monarch 1400, h) Regal 400 R, i) Mogul E, and j) Pintex XE-2.
Pahalagedara, et al., University of Connecticut

Raman Spectra – Varied Carbons

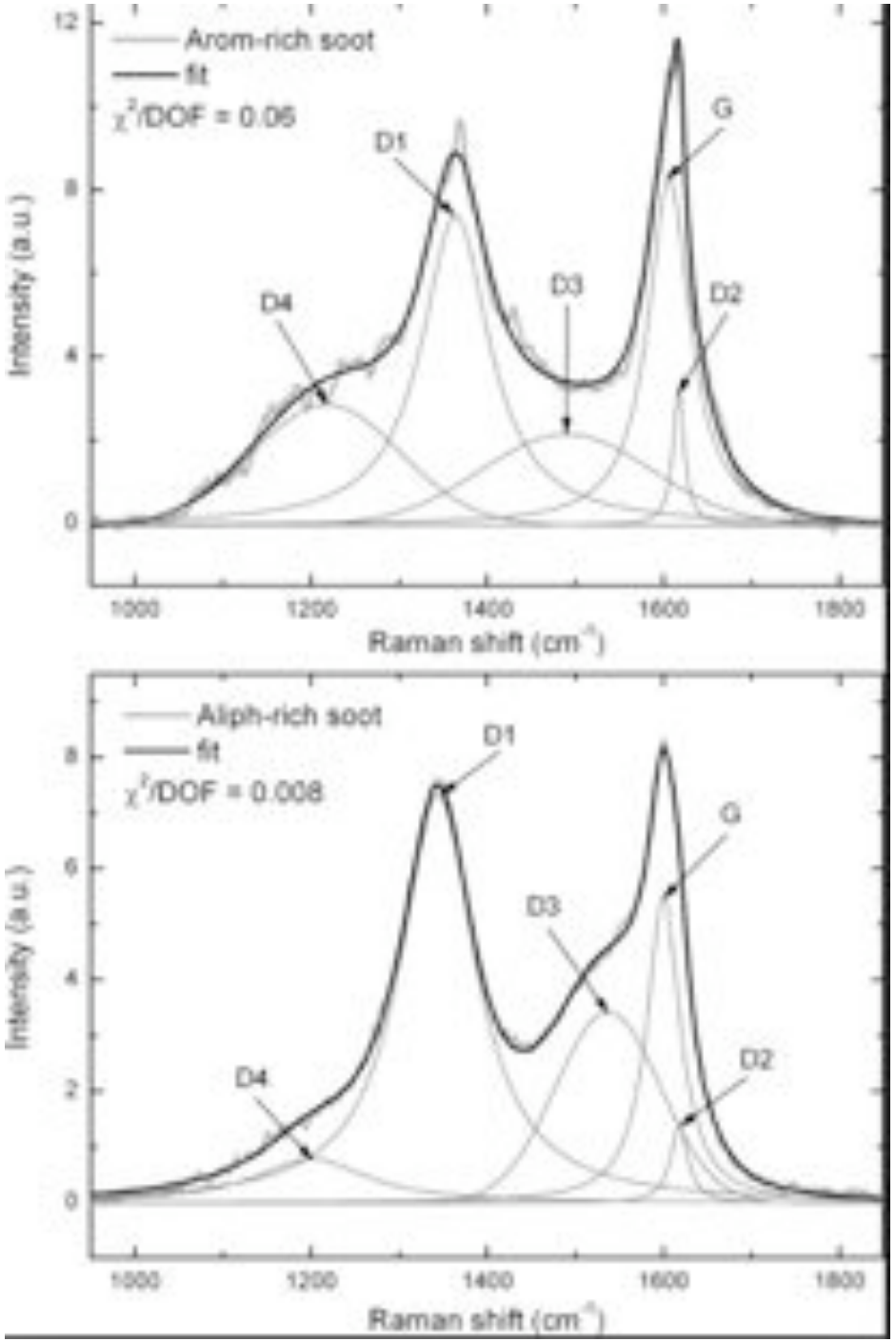
Patel et al., Tribology Int., 52:29 (2012)



Dudev et al., Vibrational Spectrosocpy 26:179 (2001)

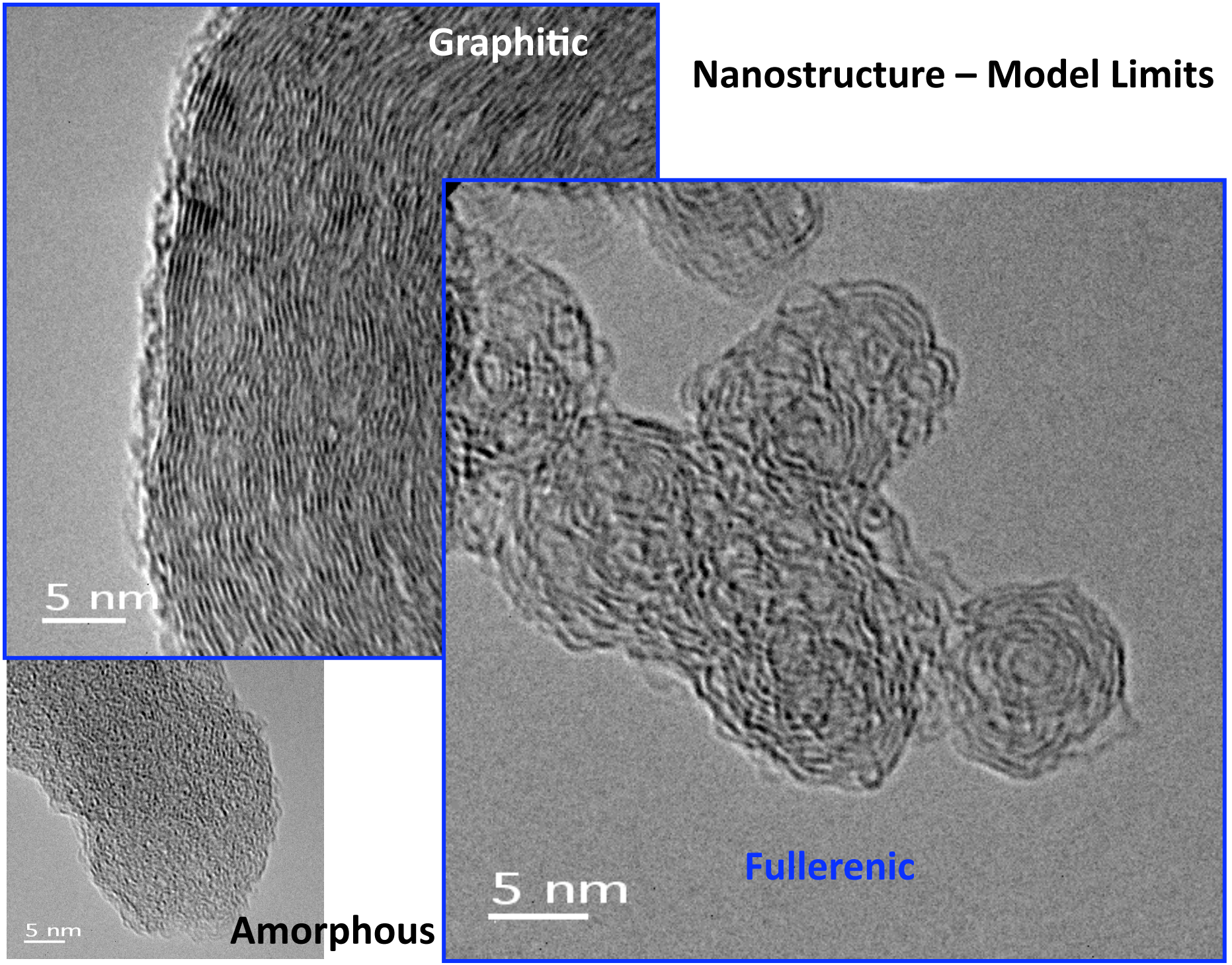


Raman Spectra Deconvolution

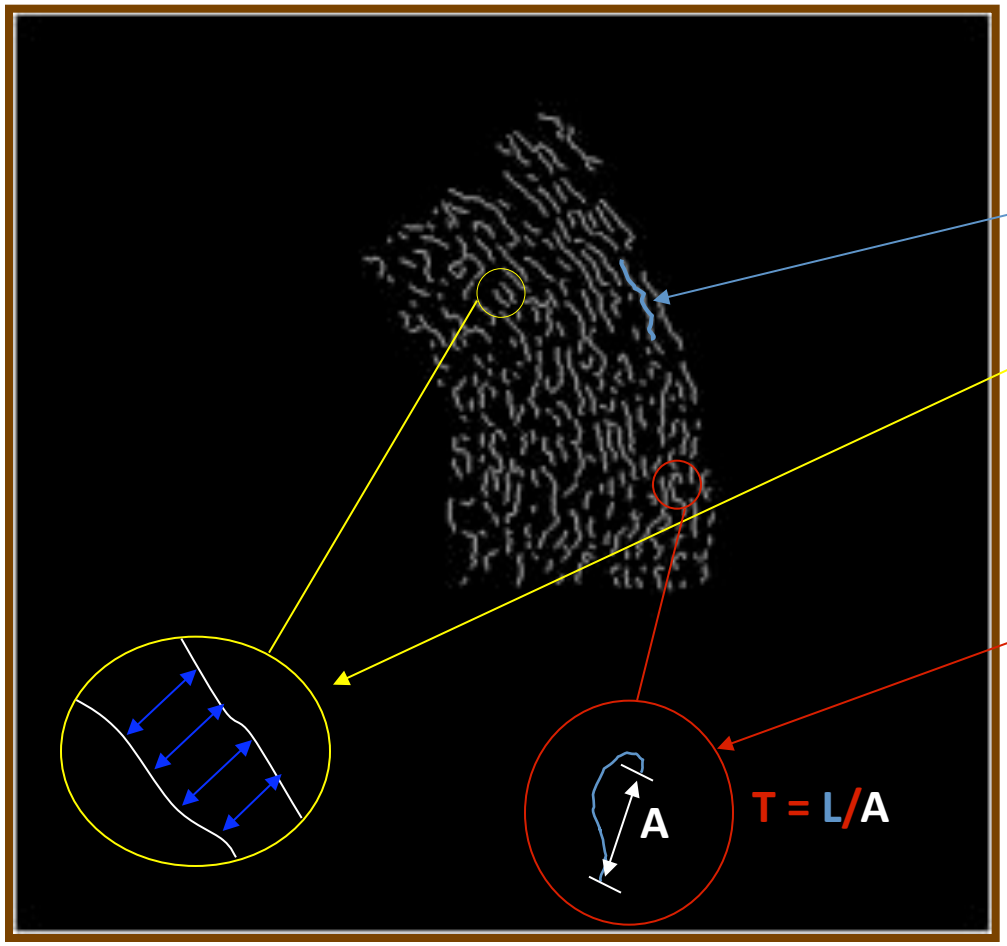


Sadezky et al., (2005)

Nanostructure – Model Limits



Statistical Properties Extracted From HRTEM Images (of soot nanostructure)



Position

Length

Fringe Separation

Orientation

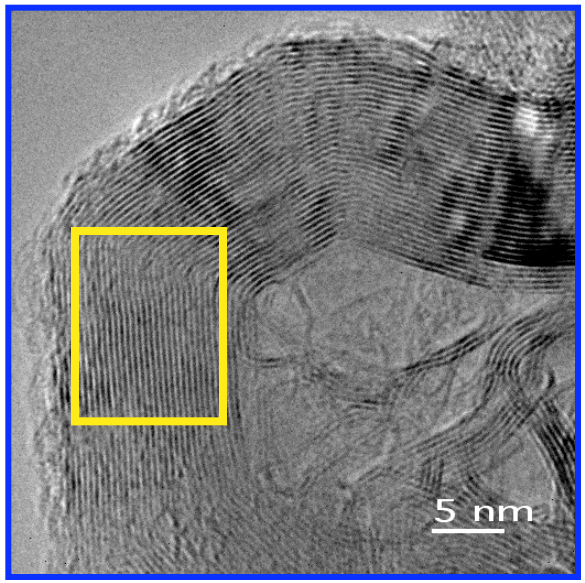
Tortuosity

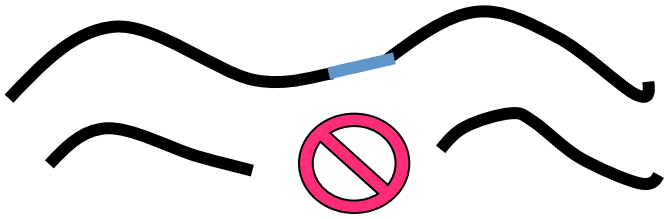
Fringe Density

Soot Nanostructure: Quantification via Fringe Analysis

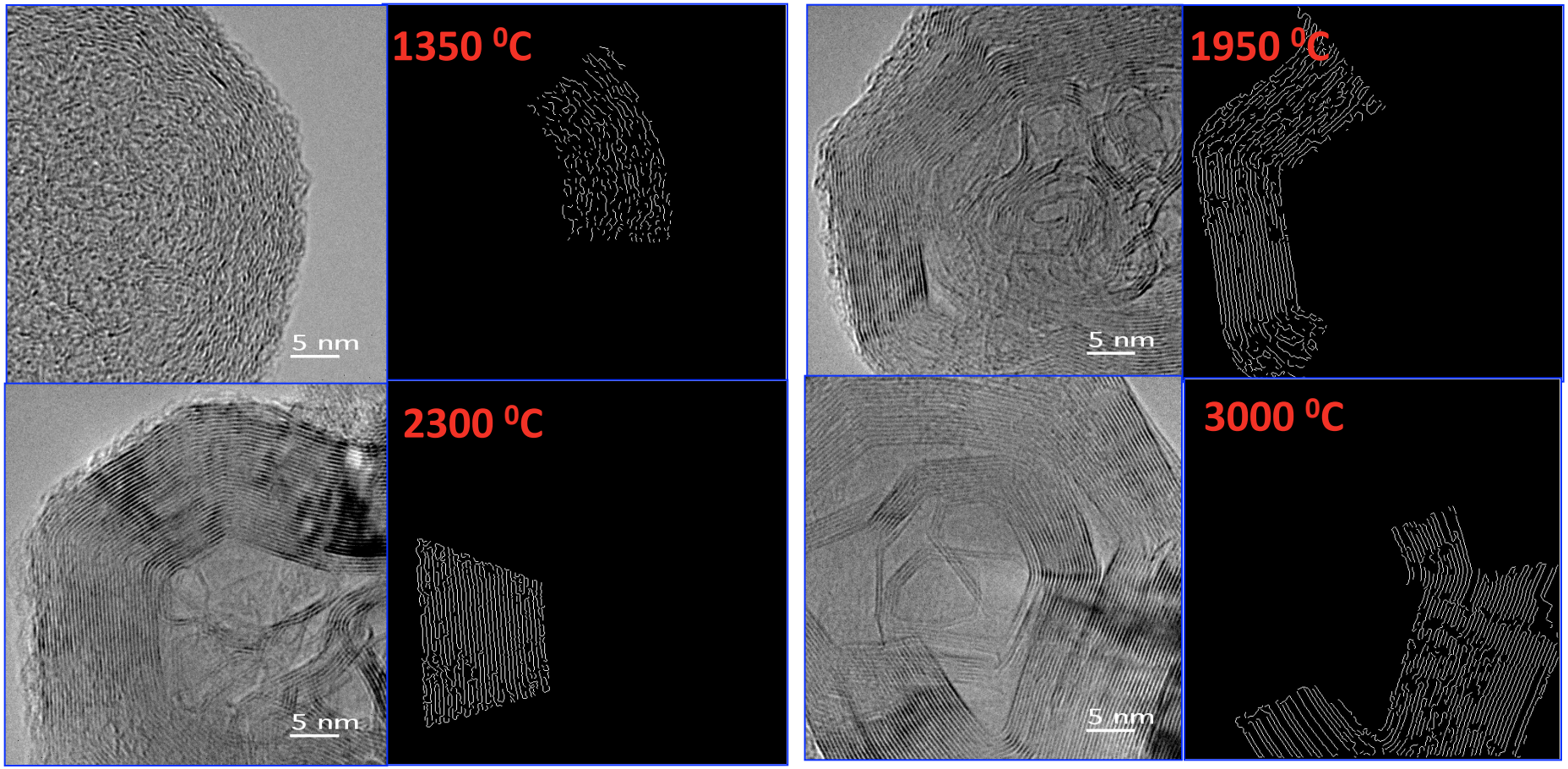
* **Image refinements - To overcome HRTEM image limitations**
  - **Region of interest**
  - **Spatial filtering**
  - **Binary thresholding**

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



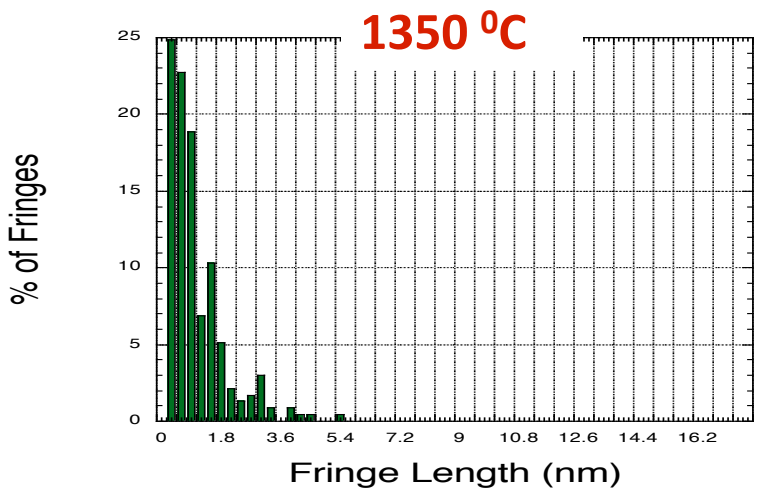


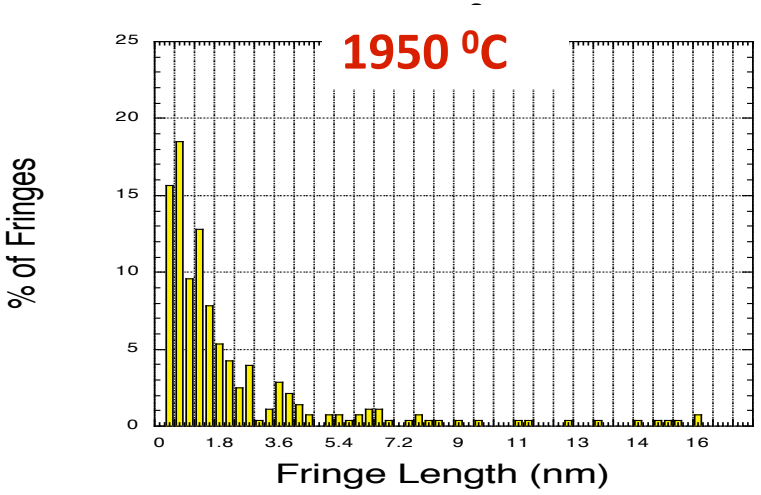
Comparison of Input (HRTEM) and Output (Binary-Fringe) Images

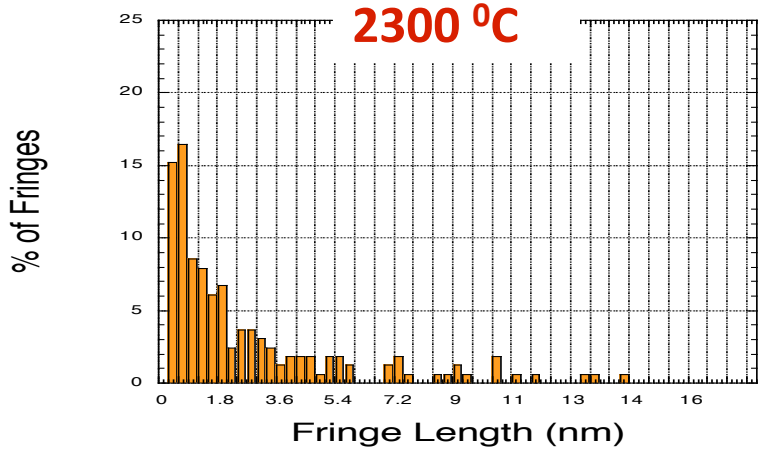


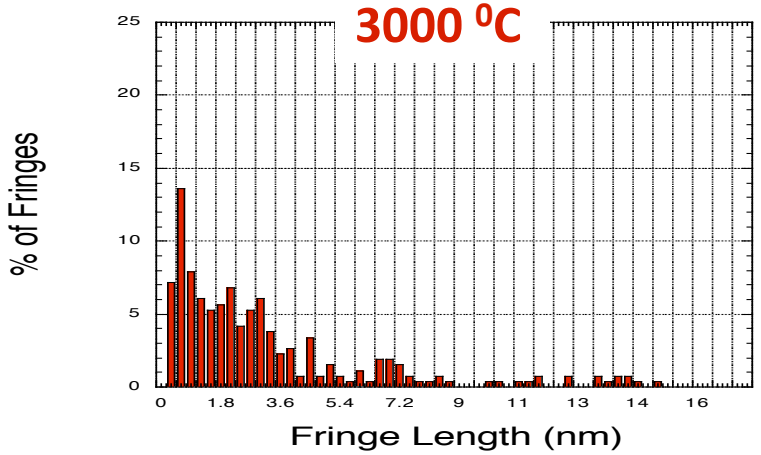
Selected samples of heat-treated carbon black

Fringe Analysis Output Data - Fringe Length Histograms

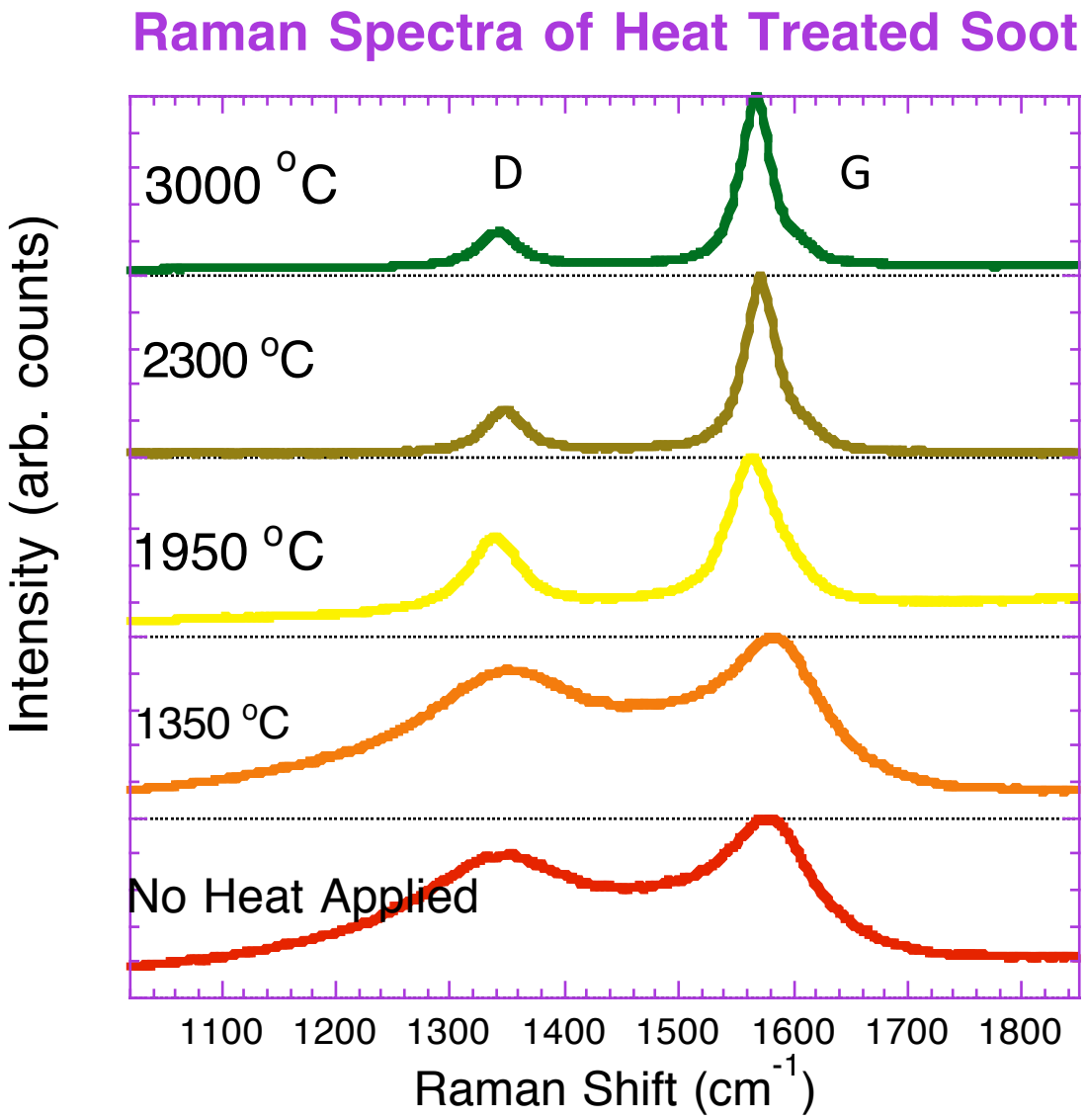






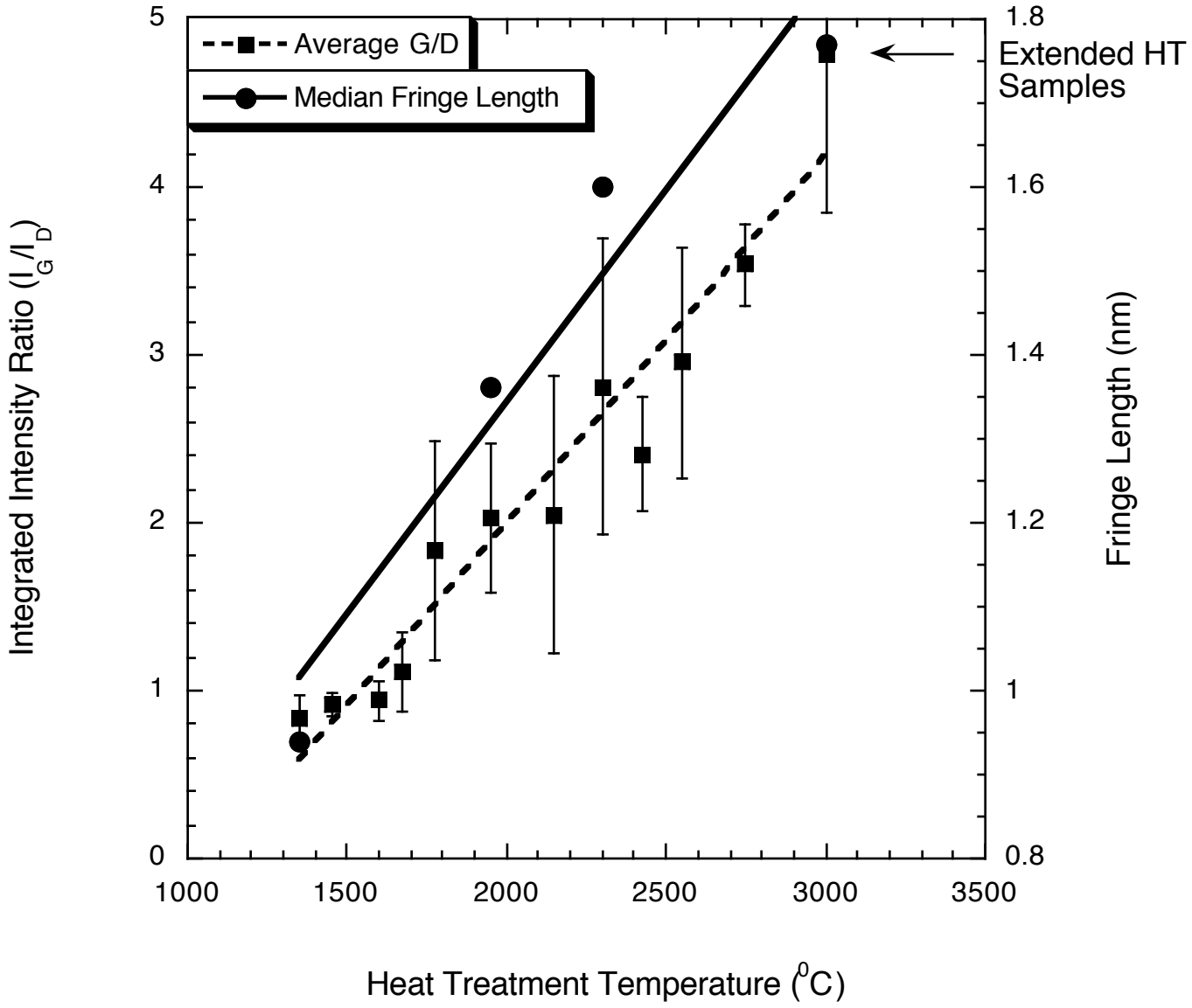


Comparison to Benchmark Methods



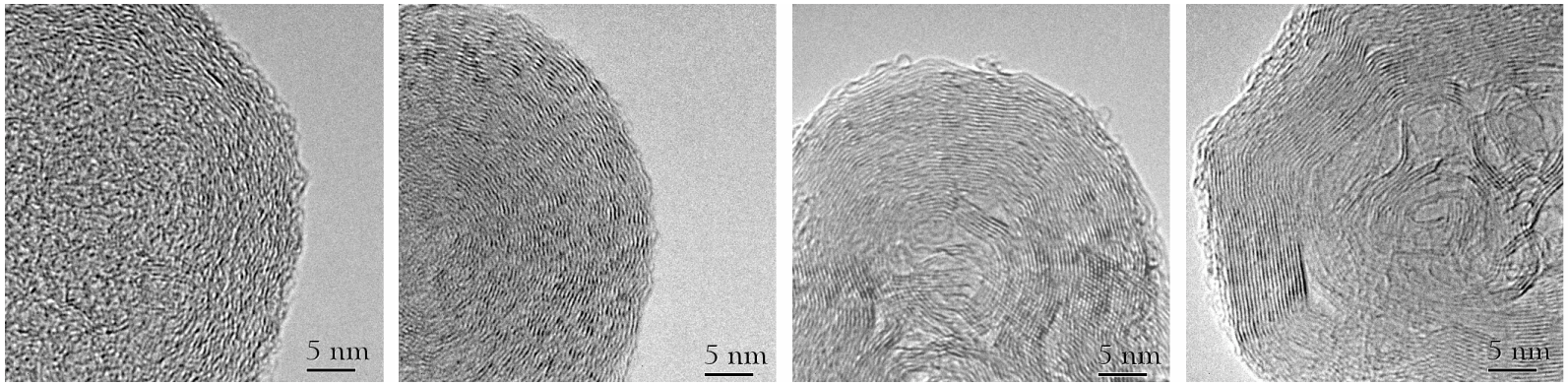
- E_{2g} or (G) peak at 1580 cm^{-1} (Graphitic)
- A_{1g} or (D) peak at 1360 cm^{-1} (Disordered)
- Intensity ratio have been used to measure in-plane dimensions

Ratios of Integrated Raman Intensities for Heat Treated Carbon Soots

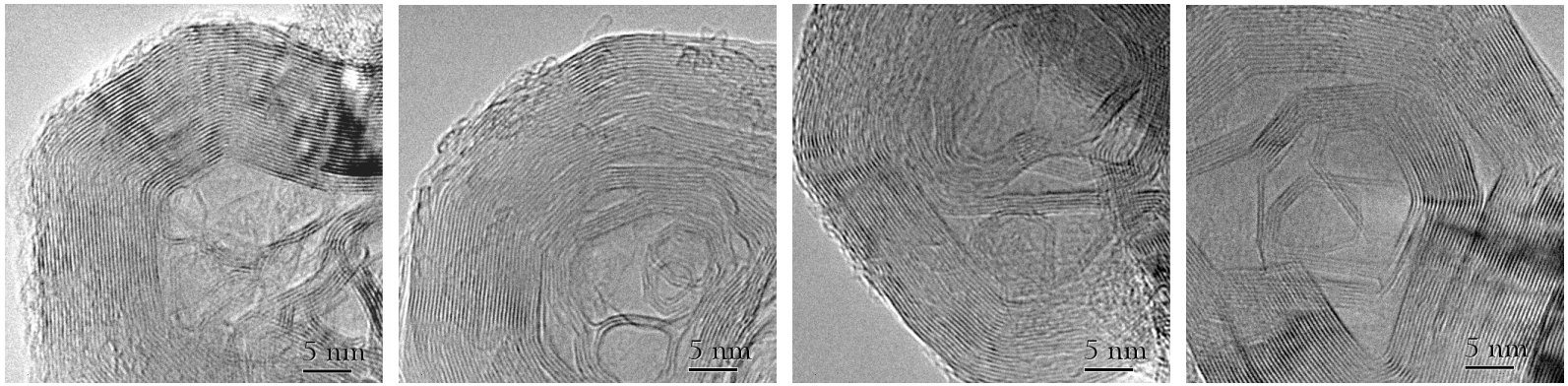


HRTEM Images of Heat Treated Carbon Black

1350°C 1575 °C 1675 °C 1950 °C

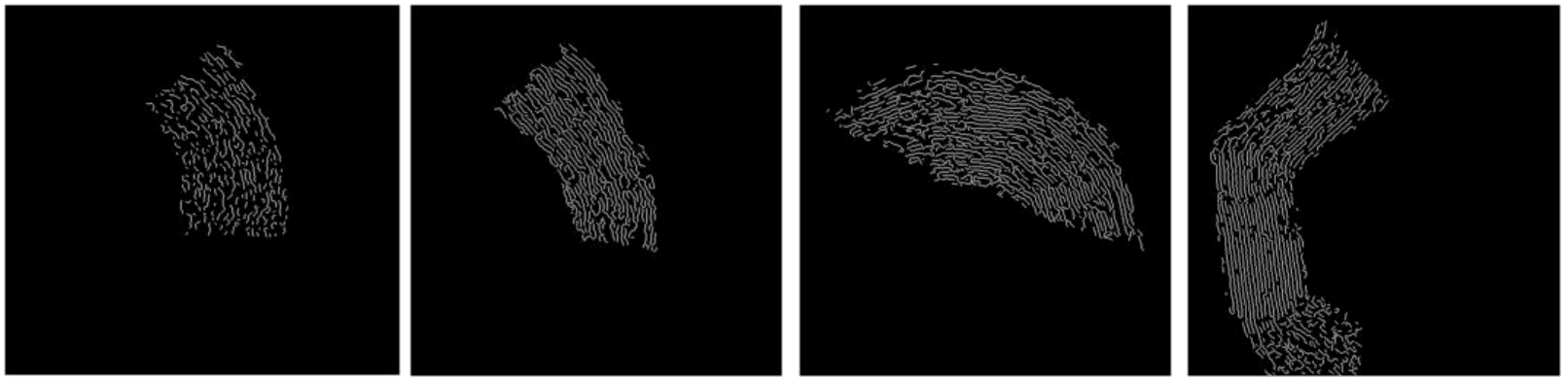


2300°C 2425 °C 2750 °C 3000 °C

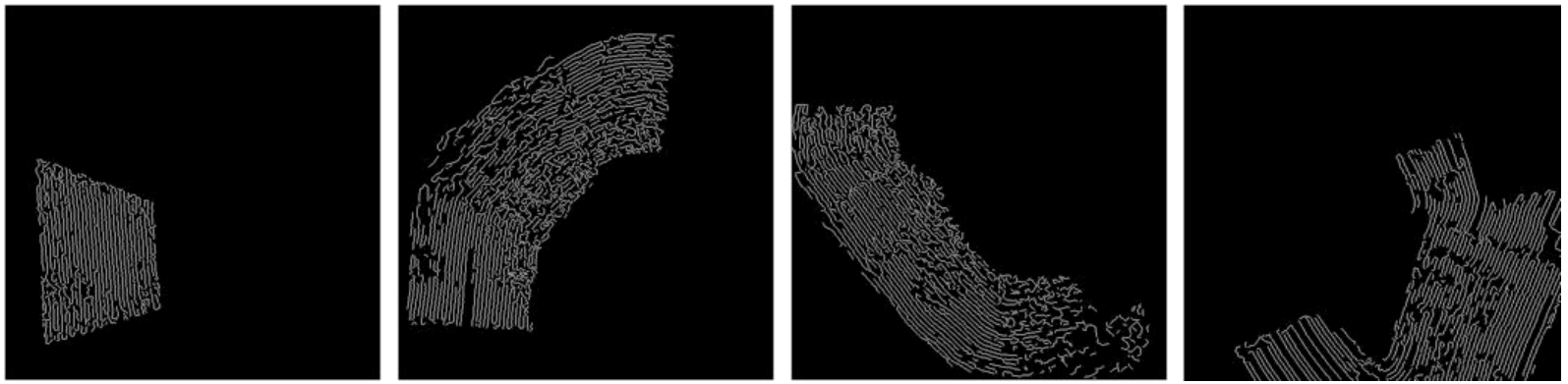


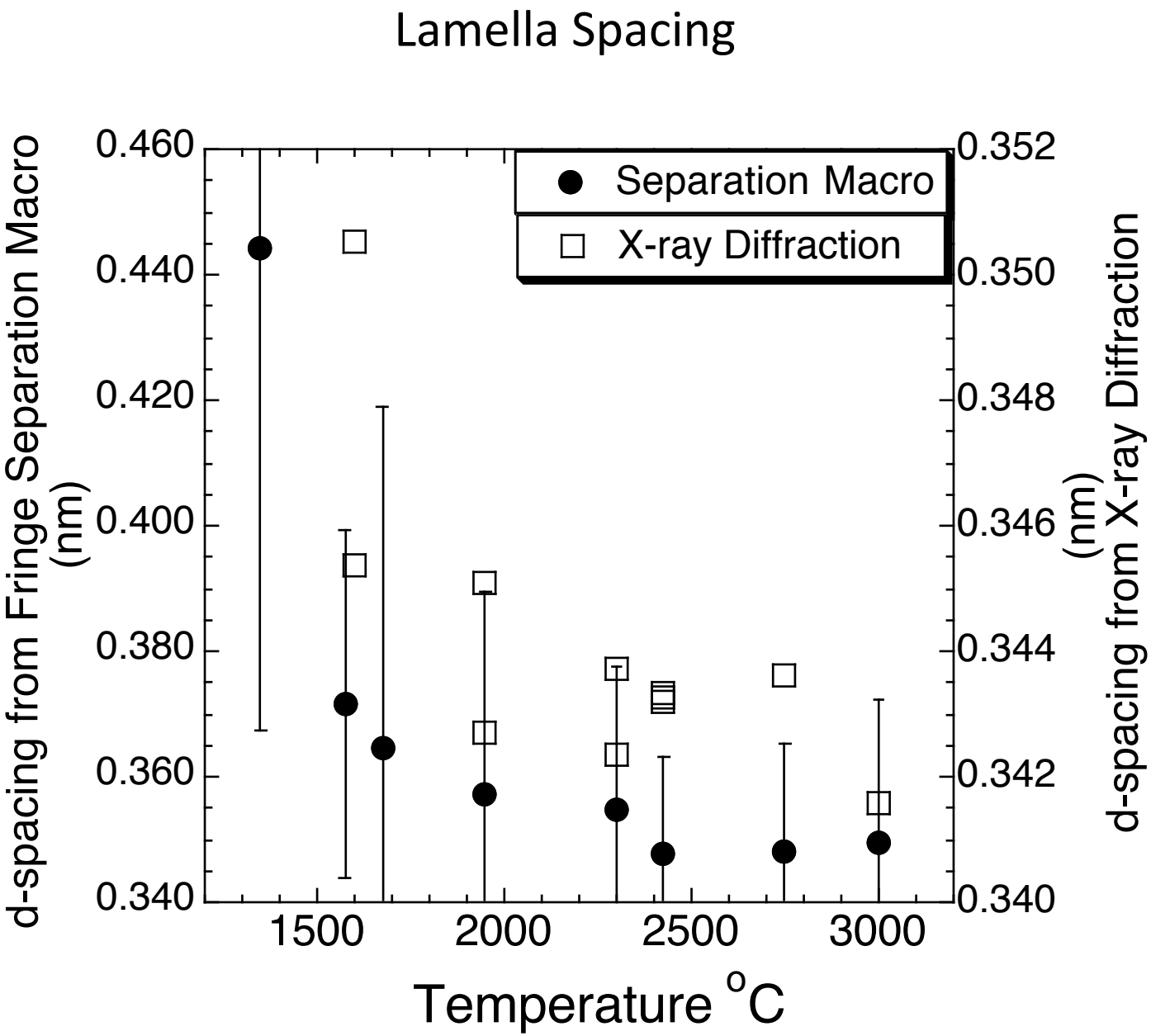
Skeleton Images of the Bright Field HRTEM

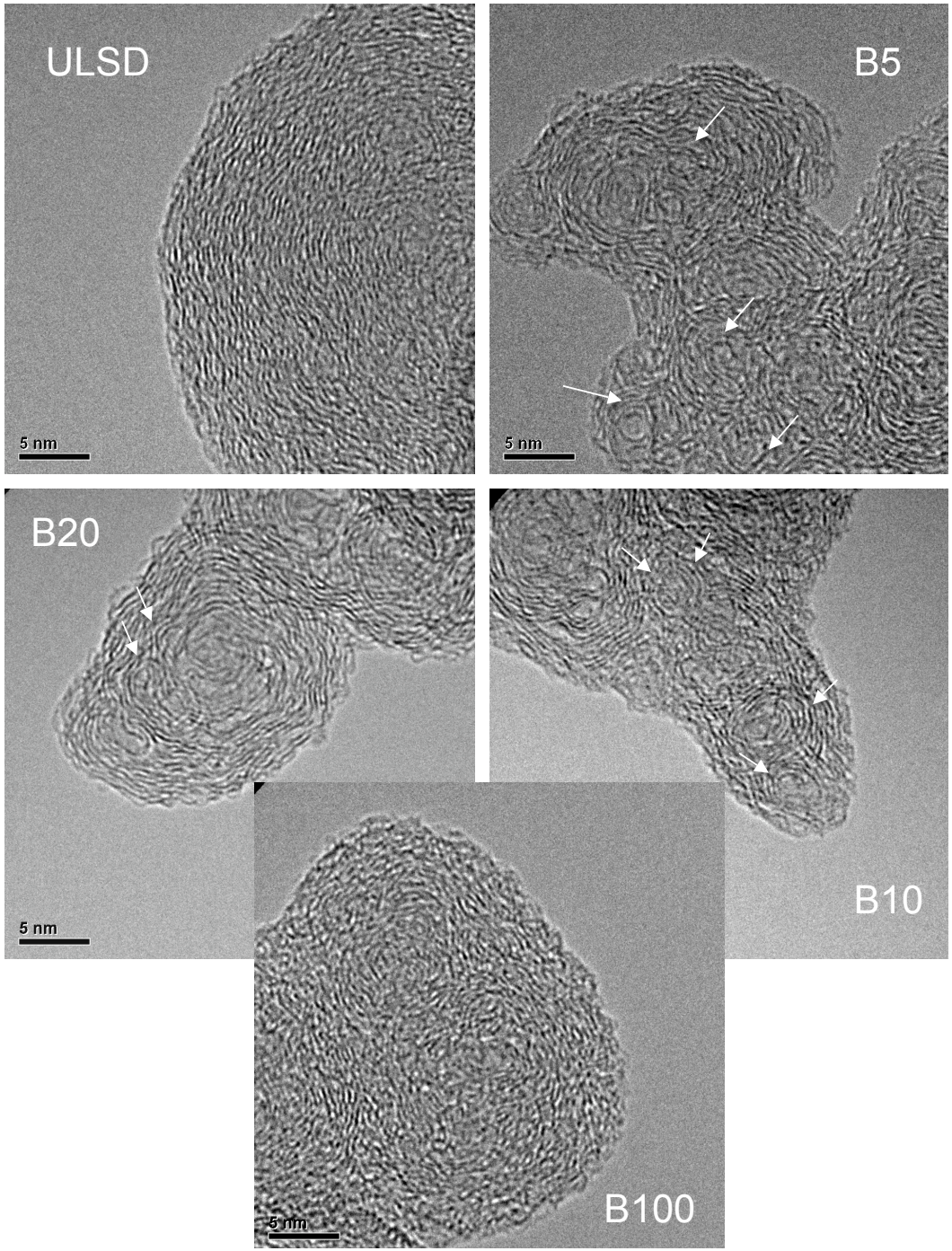
1350°C 1575 °C 1675 °C 1950 °C



2300°C 2425 °C 2750 °C 3000 °C

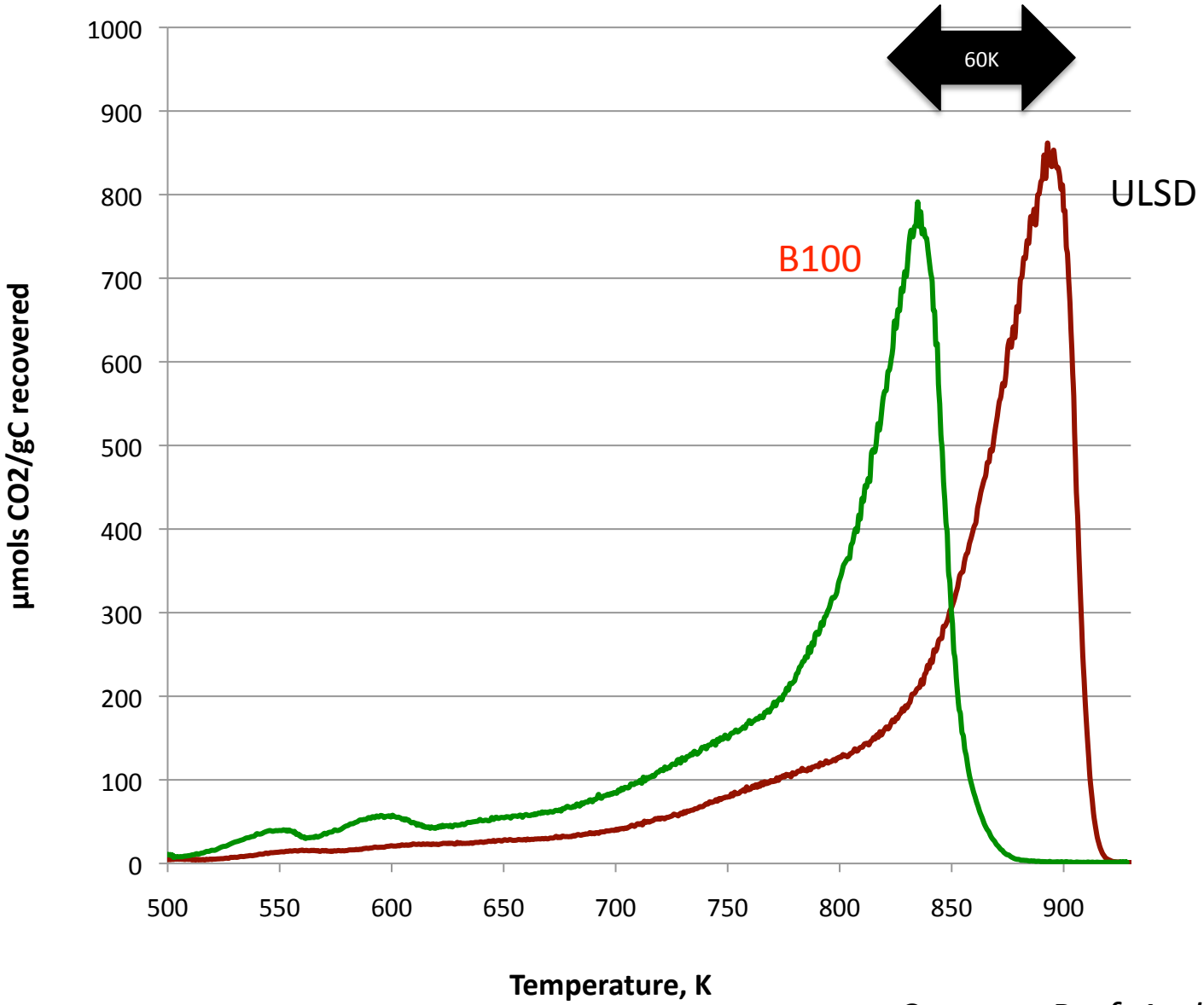



Lamella Spacing
Separation Macro
X-ray Diffraction
d-spacing from Fringe Separation Macro (nm)
d-spacing from X-ray Diffraction (nm)
0.460
0.440
0.420
0.400
0.380
0.360
0.340
0.352
0.350
0.348
0.346
0.344
0.342
0.340
1500
2000
2500
3000
Temperature °C



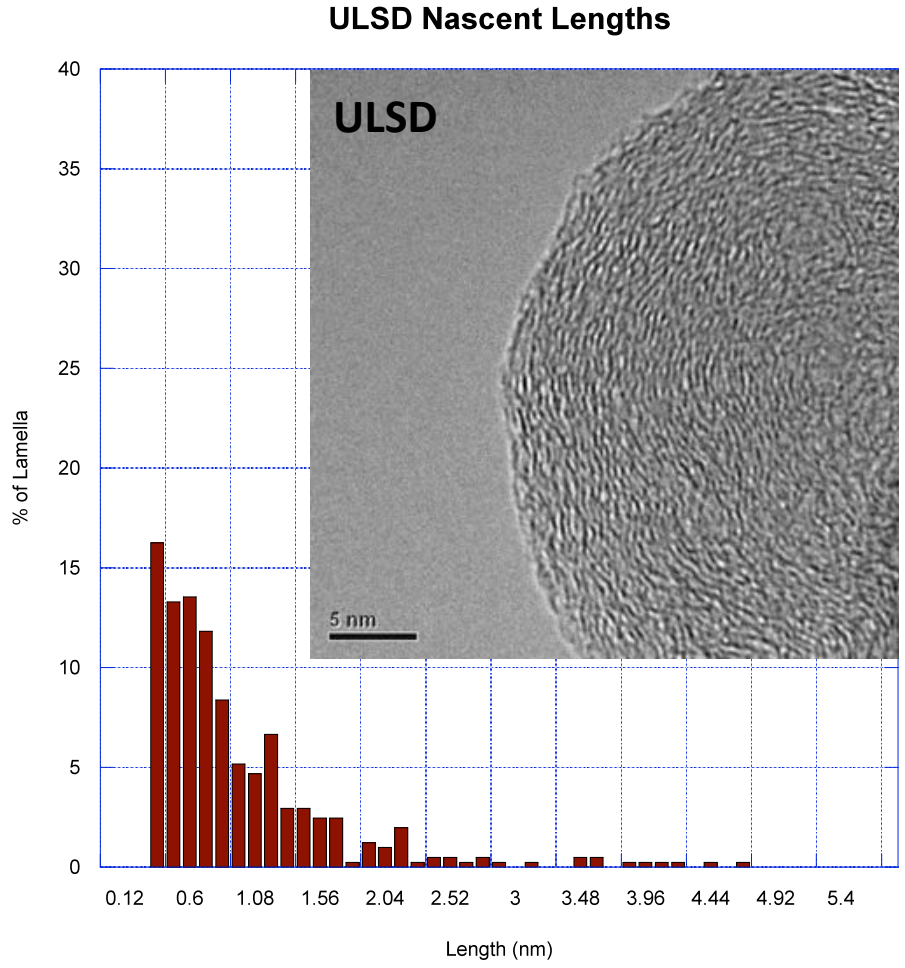
- PM generation on Diesel engine dynamometers
- Mercedes Benz 1.7L (LD) Diesel engine
- Multiple fuel blends (conventional and biodiesel)
- Steady operation at different speeds/loads
- Highly controlled PM sampling protocols

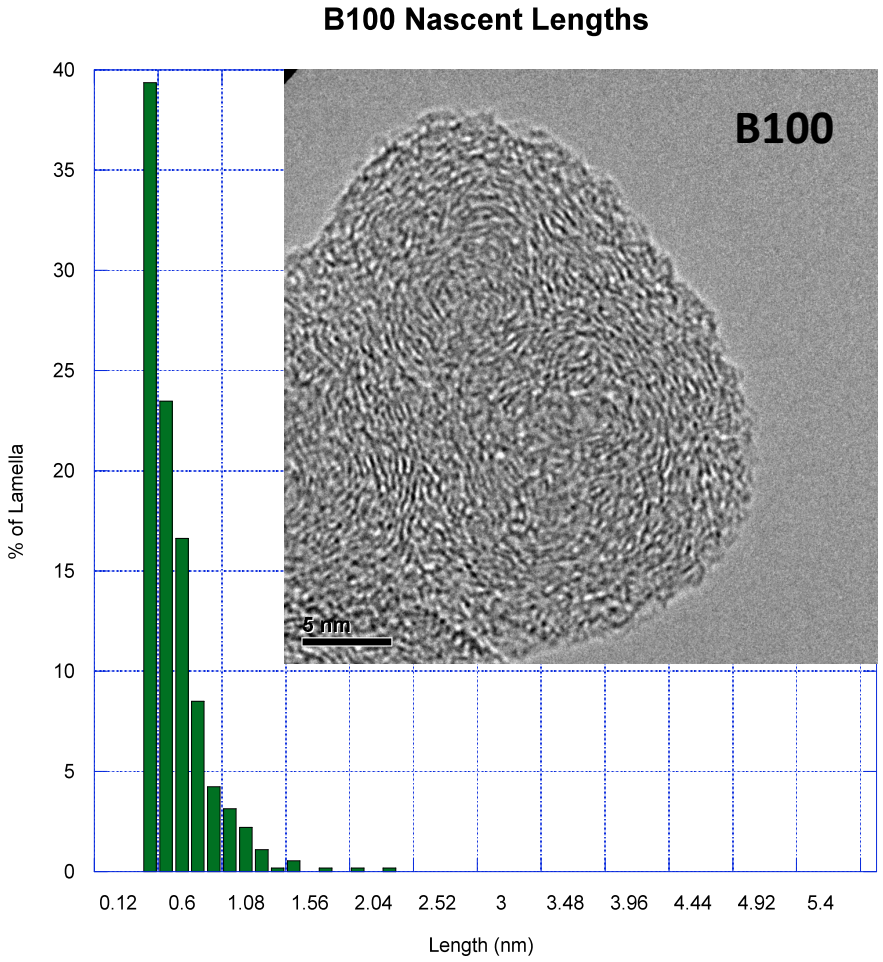
Temperature Programmed Oxidation



Courtesy Prof. Andrea Strzelec & ORNL

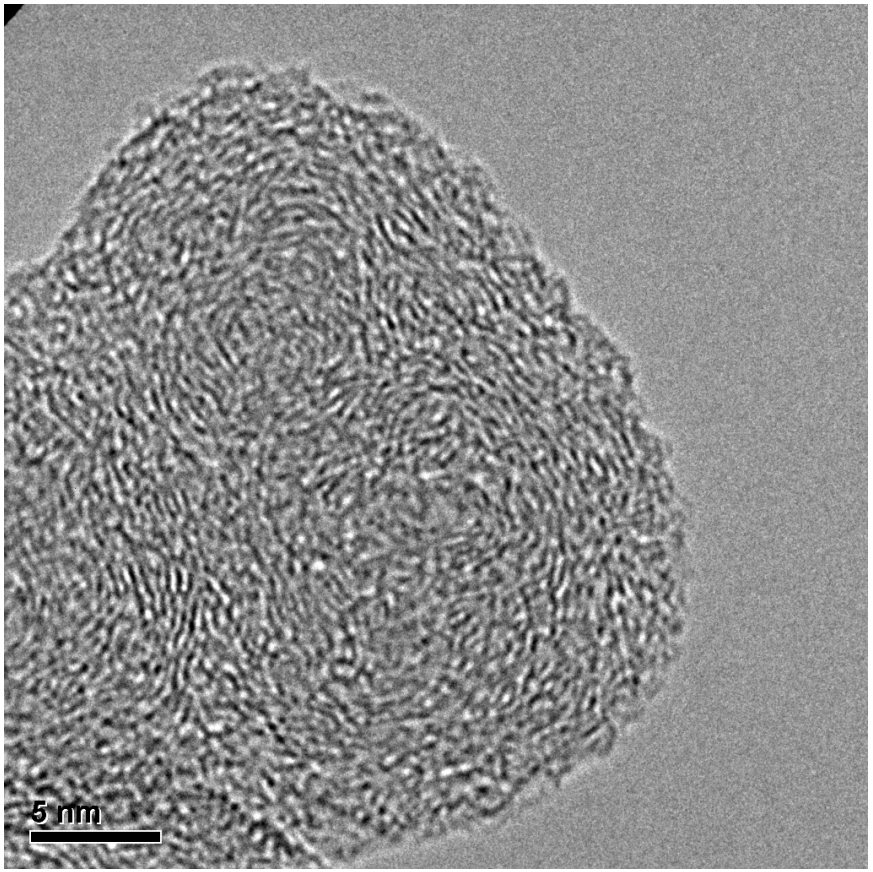
Lamella statistics do seem to correlate with fuel-related differences, *with significant implications for burnout!*



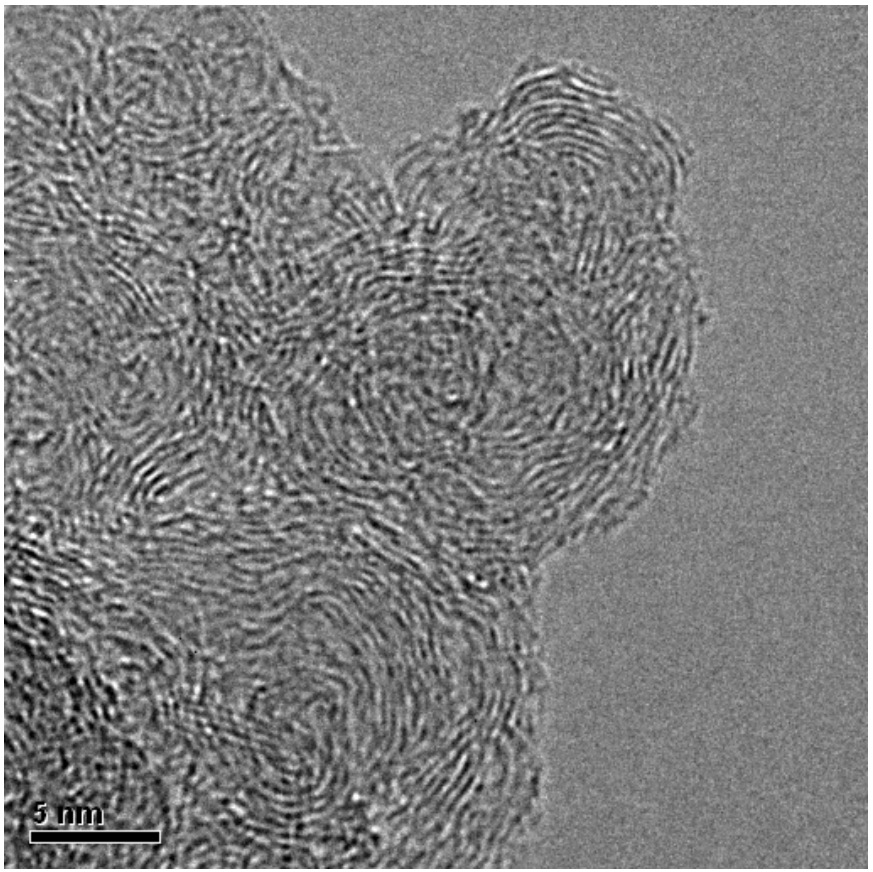


We speculate lamella spacing may relate to apparent 'porosity' in O_2 oxidation

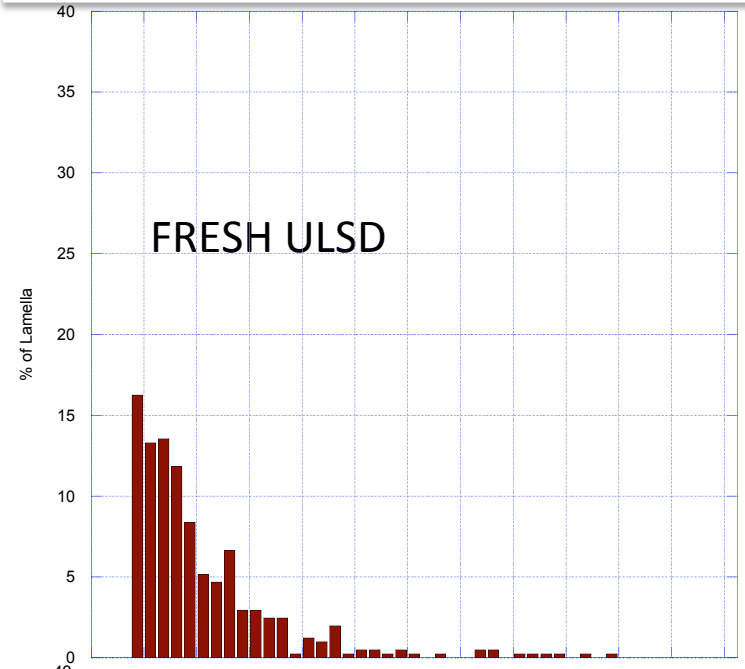
B100

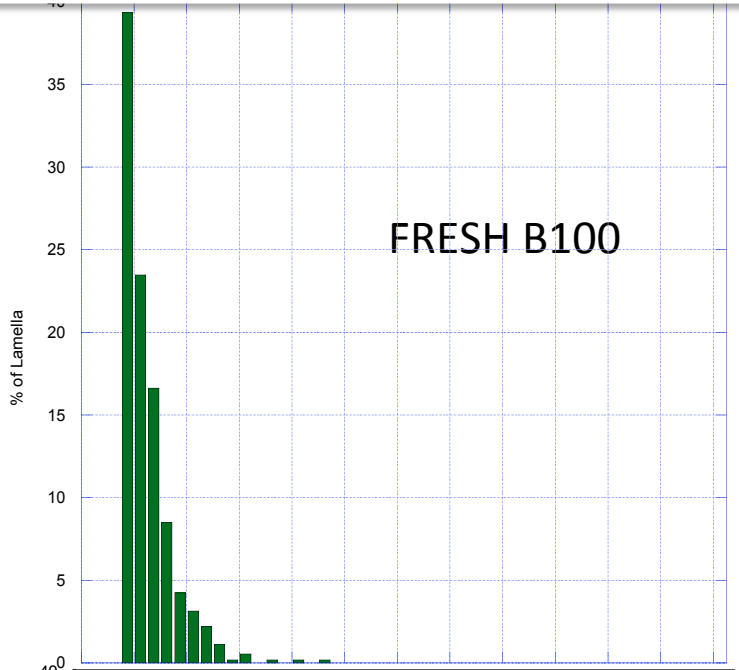


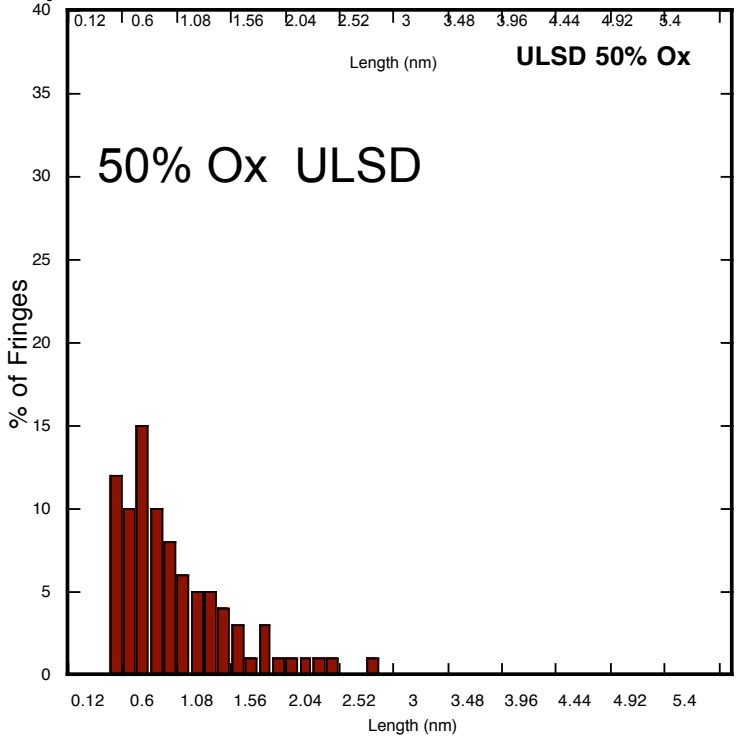
Fresh soot –B100 – 1500 rpm, 2.6 bar

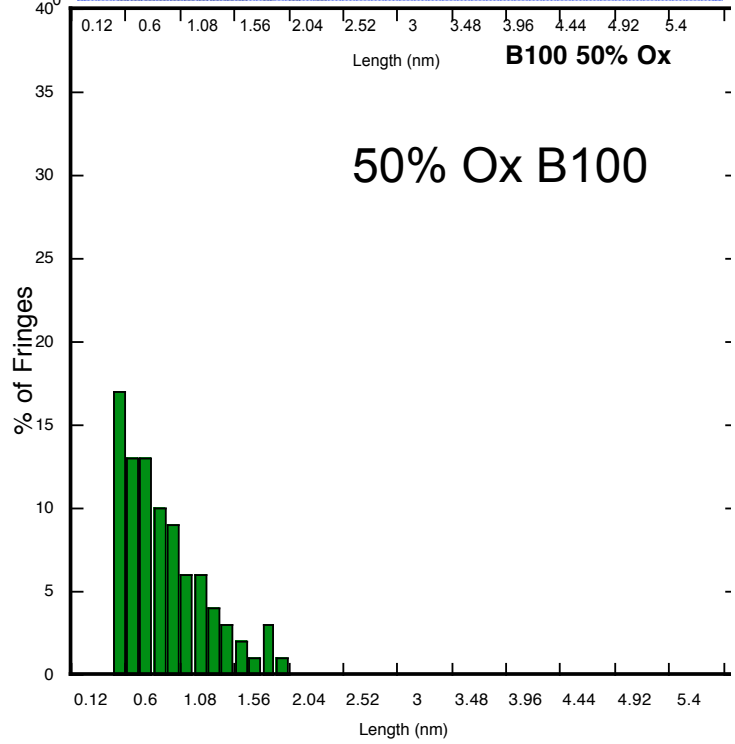


53% oxidized –B100 – 1500 rpm, 2.6 bar

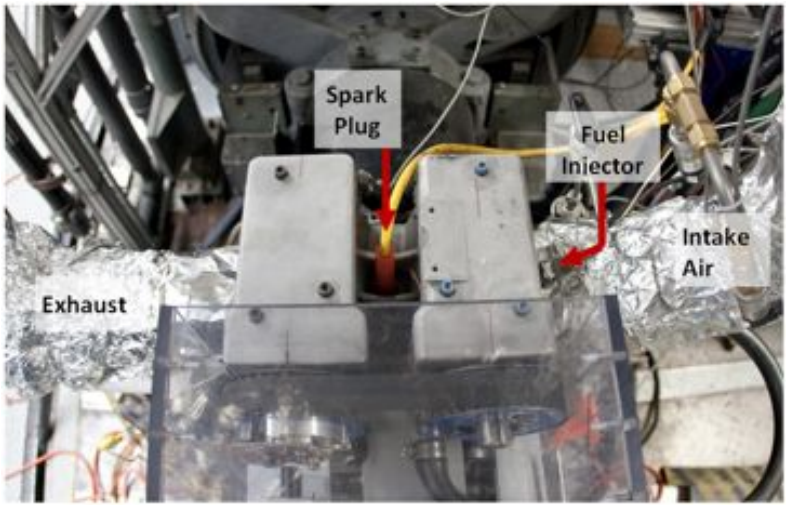

FRESH ULSD
% of Lamella
Length (nm)


FRESH B100
% of Lamella
Length (nm)


ULSD 50% Ox
50% Ox ULSD
% of Fringes
Length (nm)


B100 50% Ox
50% Ox B100
% of Fringes
Length (nm)

SIDI ENGINE



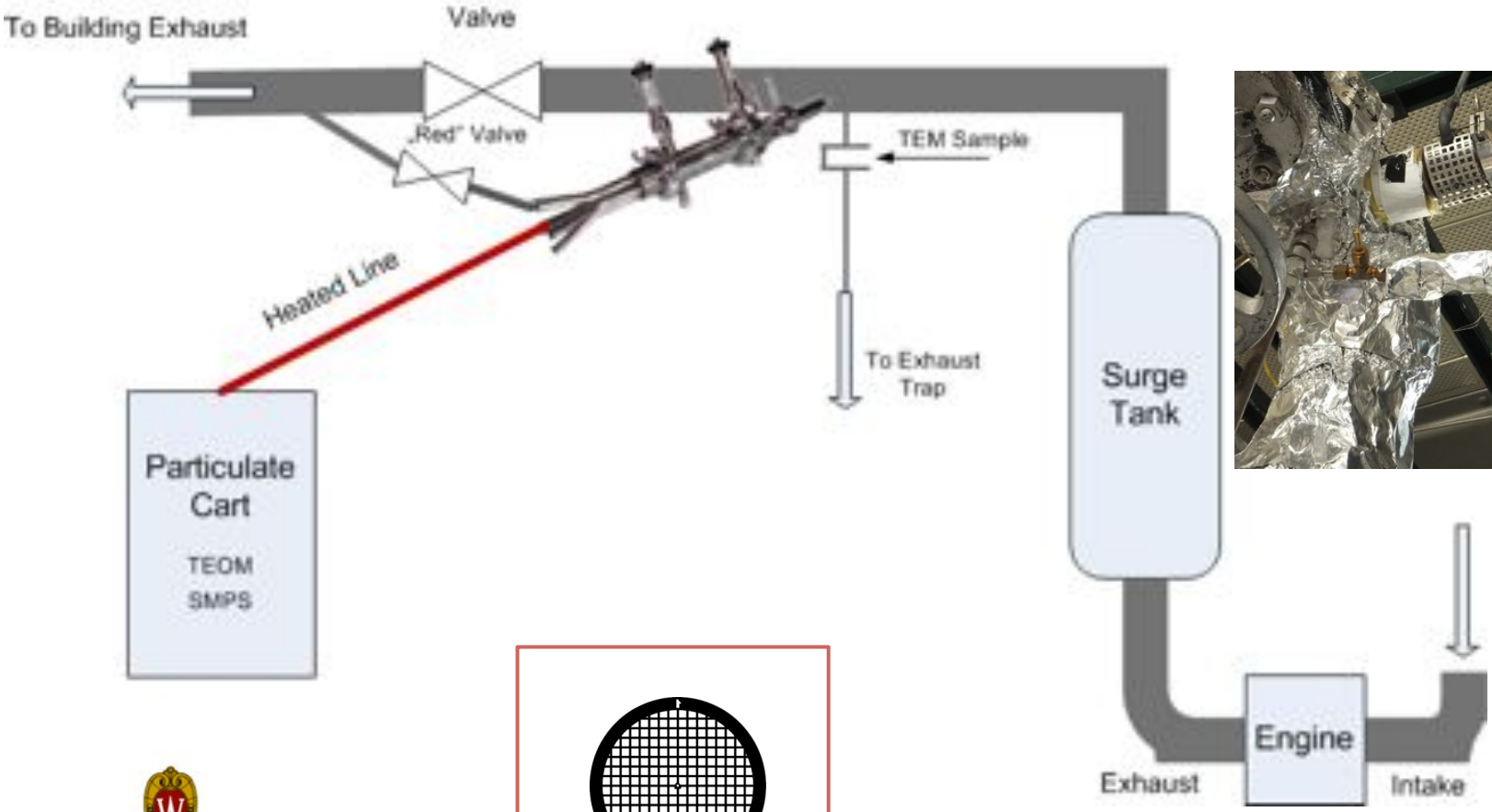
Gasoline direct injected Ricardo Hydra

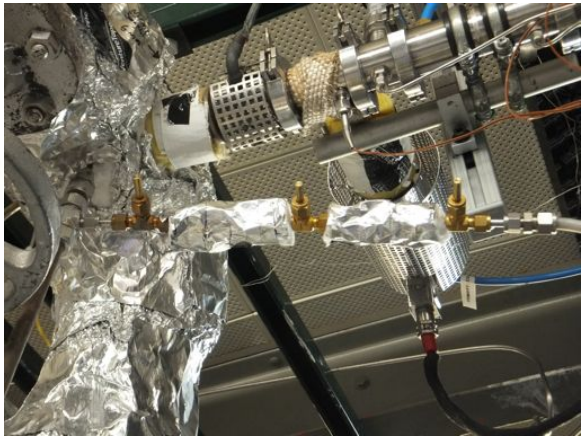
- Single cylinder research engine
- Four-stroke engine

Engine Parameter	Units	Value
Compression Ratio	[-]	11.97
Bore	[mm]	85.96
Stroke	[mm]	94.6
Displacement	[cm^3]	549
Clearance Volume	[cm^3]	50
Connection Rod Length	[mm]	152.4

Courtesy of Profs. Foster, Rothamer

EXPERIMENTAL SETUP





TESTED FUELS & TEST MATRIX

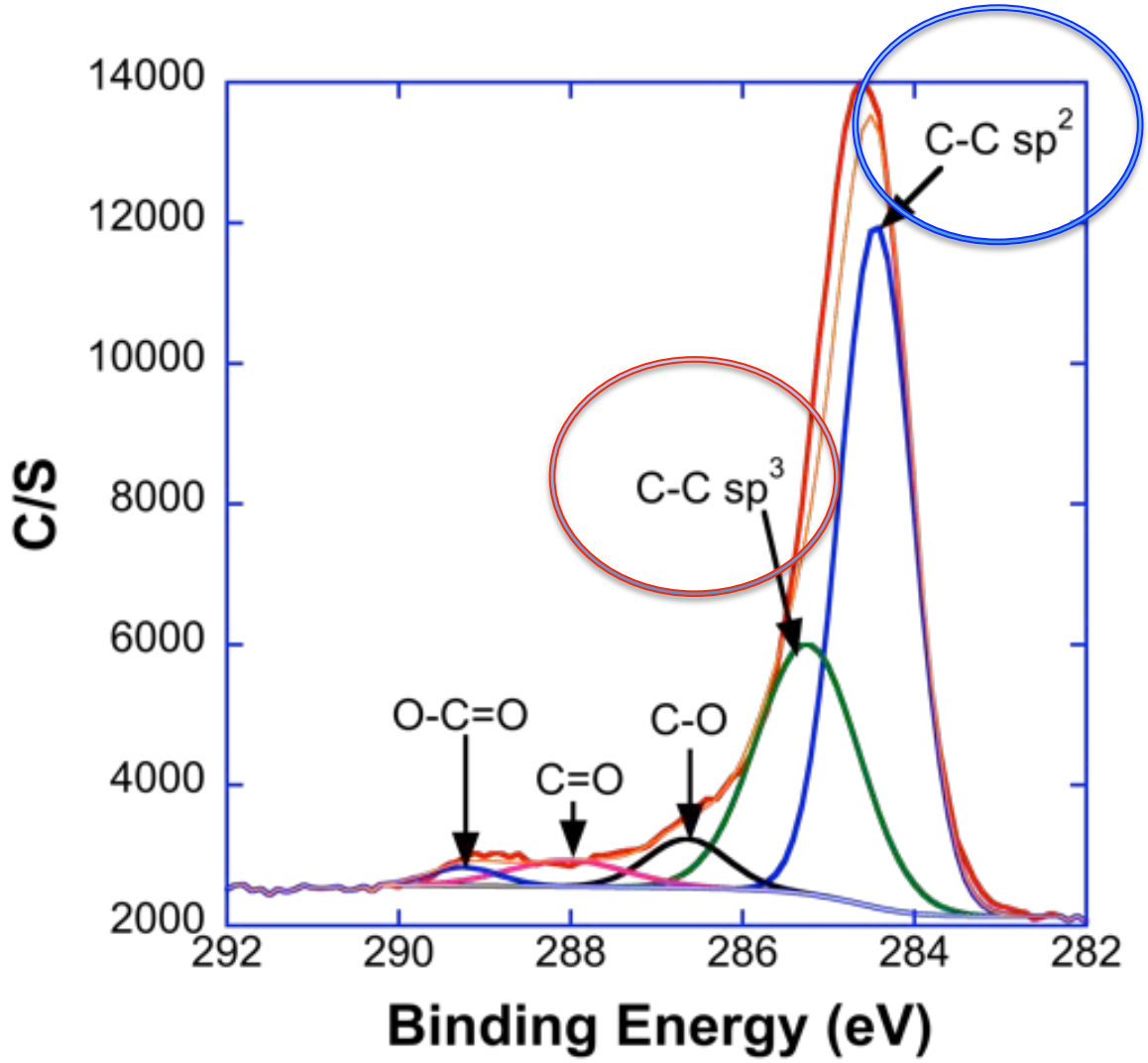
3 fuels tested

- EPA Tier II EEE
- E20 (denatured ethanol:EEE, 20%:80% by volume)
- E85 (denatured ethanol:EEE, 85%:15% by volume)

Operating Condition	Speed	Injection Timing	Fuel Quantity	AF	Spark Advance	Injection Pressure	Intake Temp.	Oil Temp.	Coolant Temp.
	[RPM]	[°bTDC]	[mg/cyc]	[-]	[°bTDC]	[MPa]	[°C]	[°C]	[°C]
EEE									
EOI 280	2100	280	11	15	25	11	45	90	90
Rich	2100	280	11	13	25	11	45	90	90
Lean	2100	280	11	17	25	11	45	90	90
Late EOI	2100	220	11	15	25	11	45	90	90
Heavy Load	2100	280	21	15	18	11	45	90	90

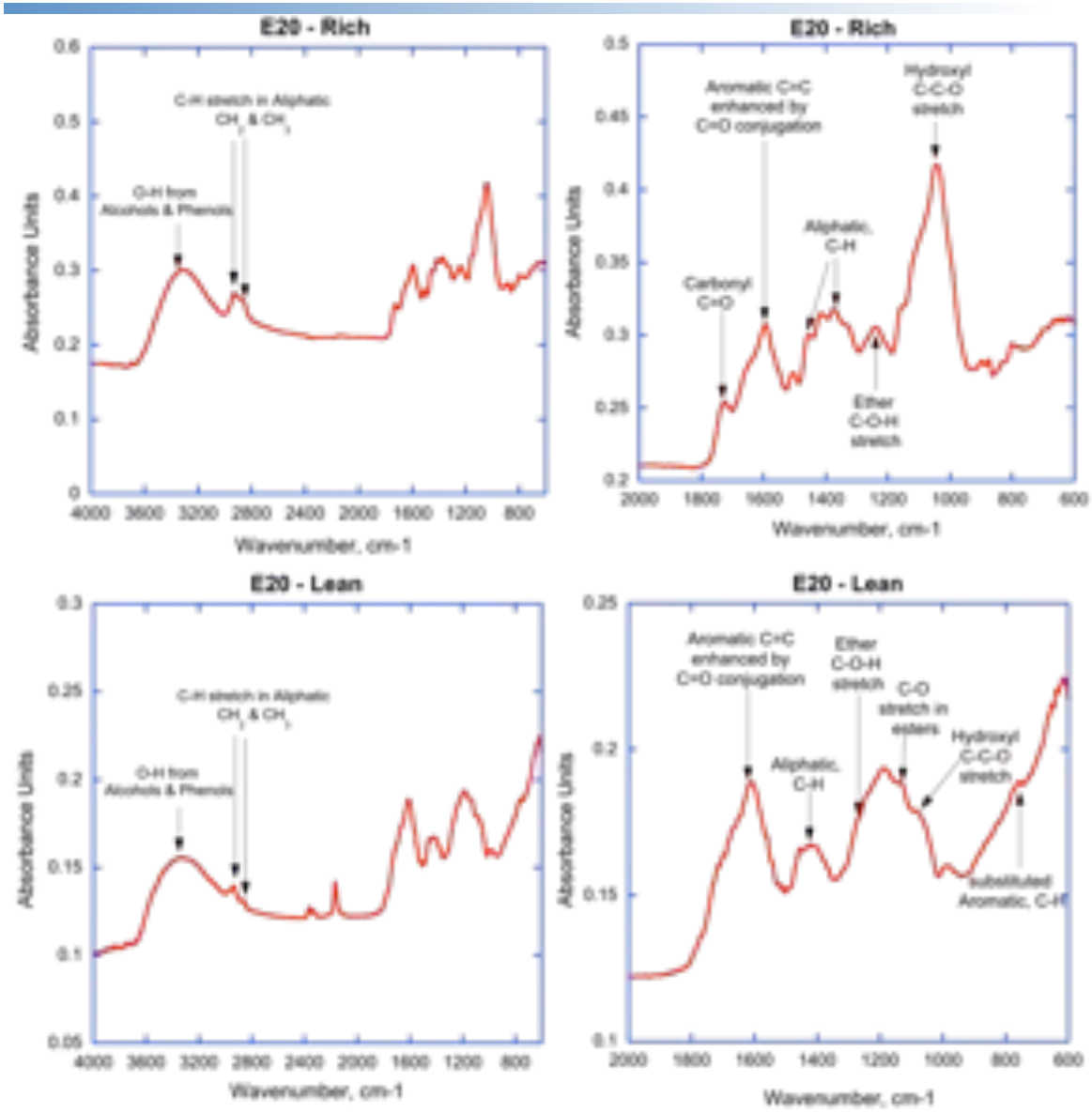
Engine Operating Conditions

- PM sampling was pre-planned
- Wide range of operating conditions with changes to A/F ratio, Load, Injection timing



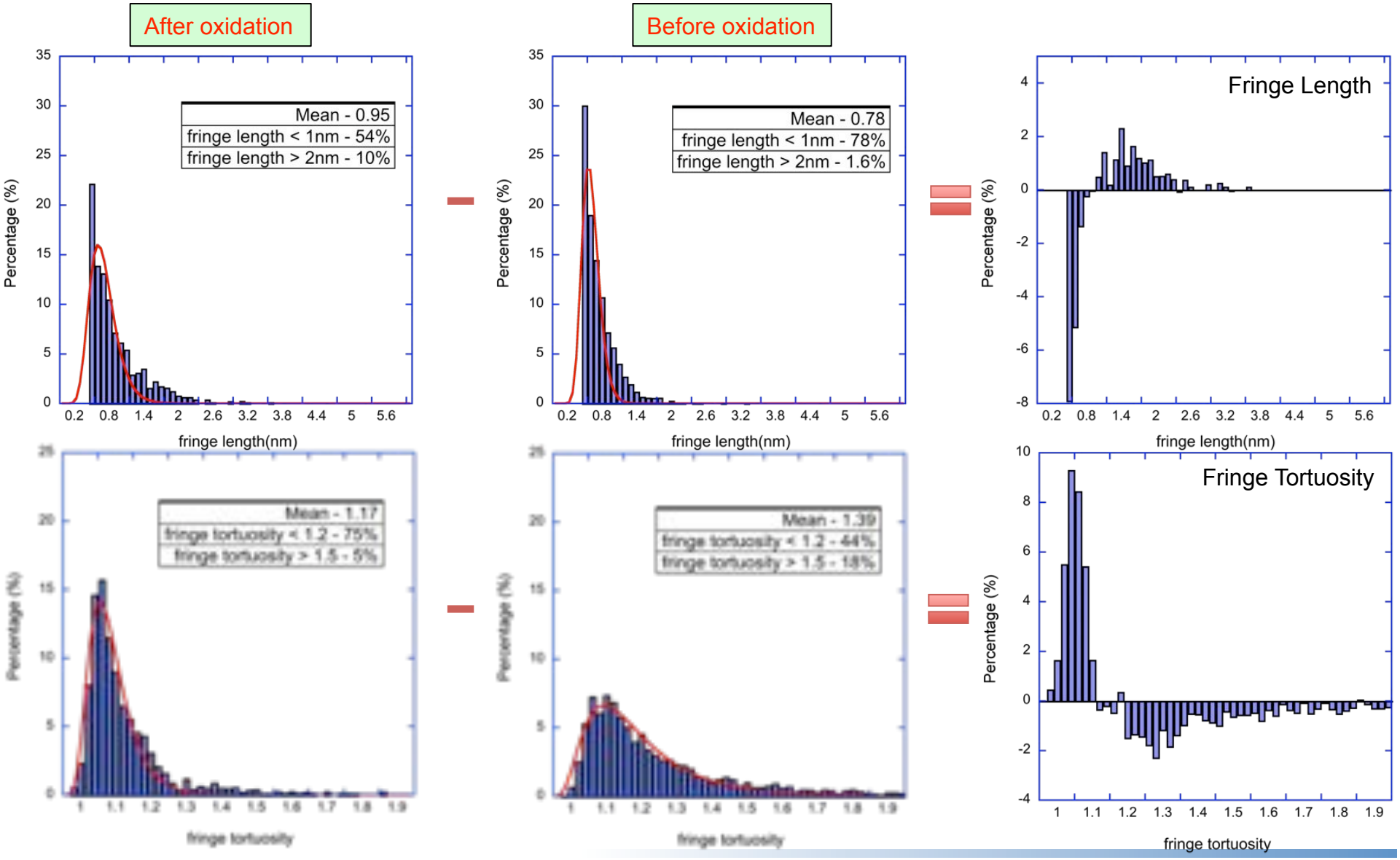
C 1s high res scan – SIDI engine/EEE fuel/Rich condition

FTIR-ATR Analysis



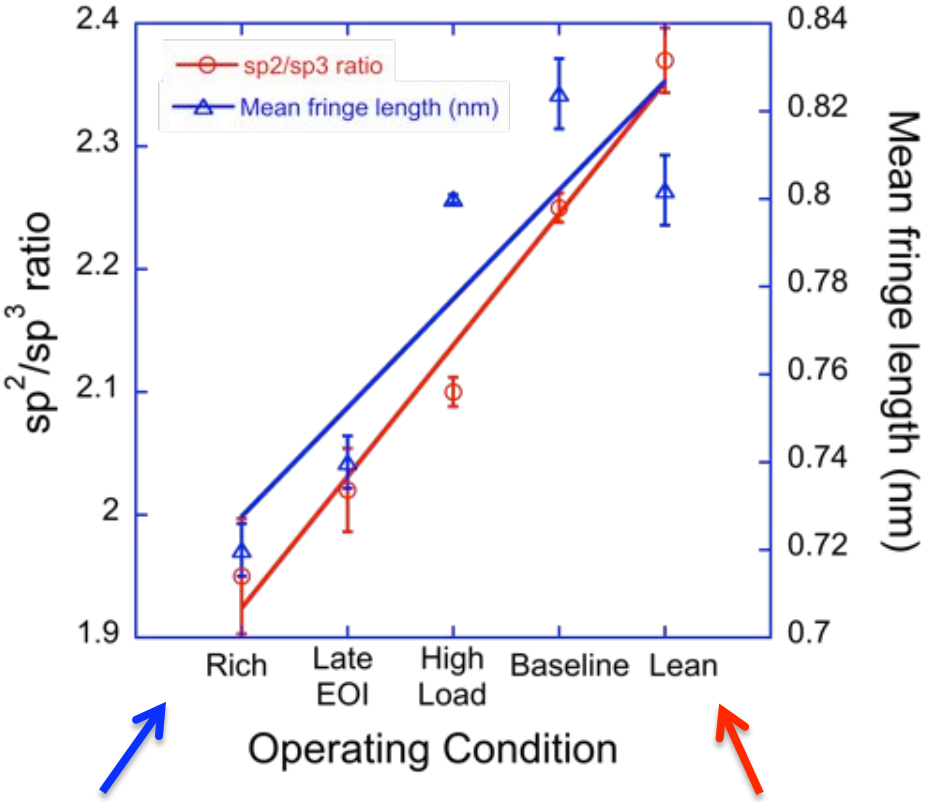
- Significant volume-averaged organic content
- Variation with condition – suggests different chemistries
  - More variation as a function of engine operation
  - Even within a single aggregate
- C-H (aliphatic) – more profound in Fuel-rich conditions

COMPARATIVE FRINGE ANALYSIS

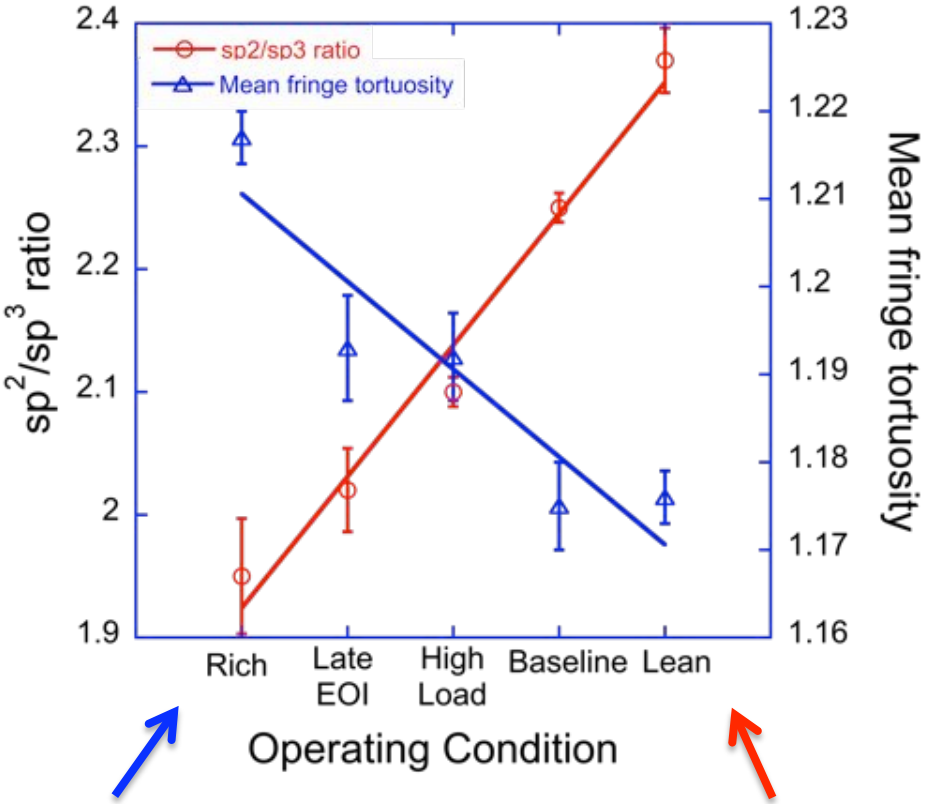


- Distinct change in nanostructure during oxidation
- Lamella become more longer, flattened

XPS vs.Lamella Length

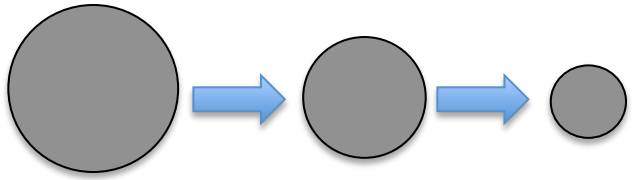


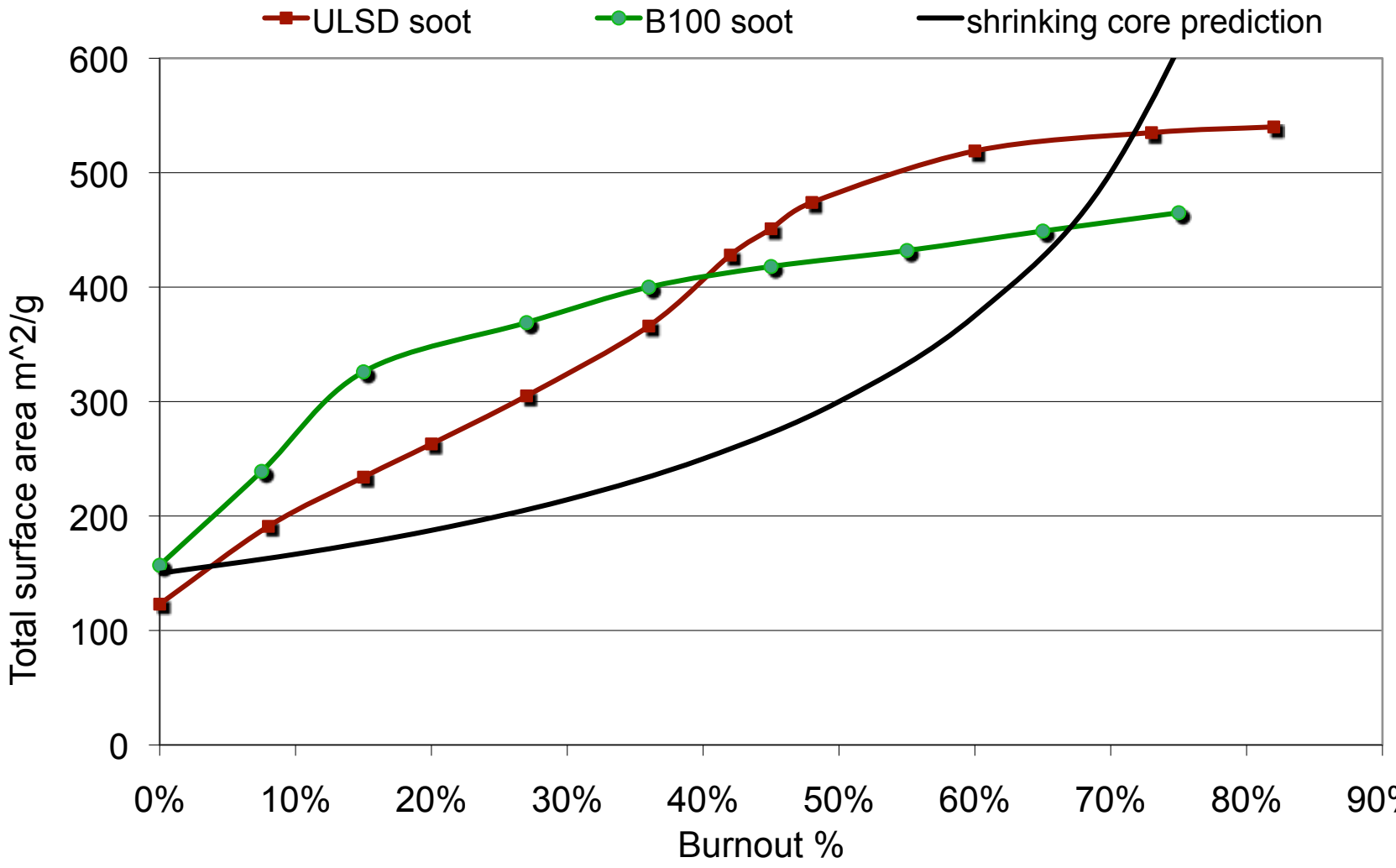
XPS vs. Lamella Tortuosity



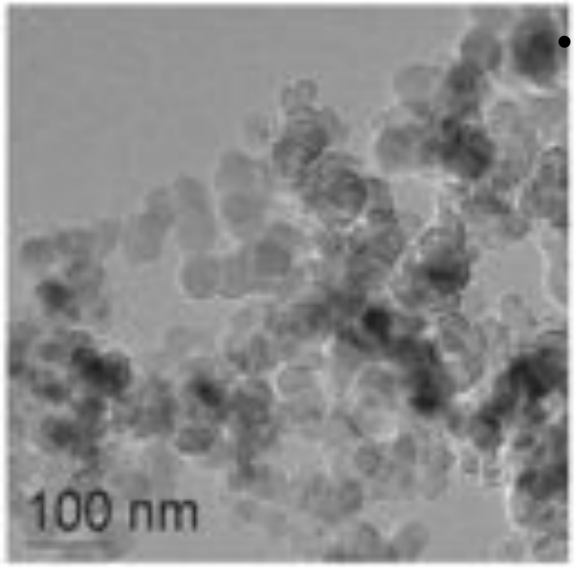
Neither particulate sample follows common model behavior for surface area evolution with burnout.

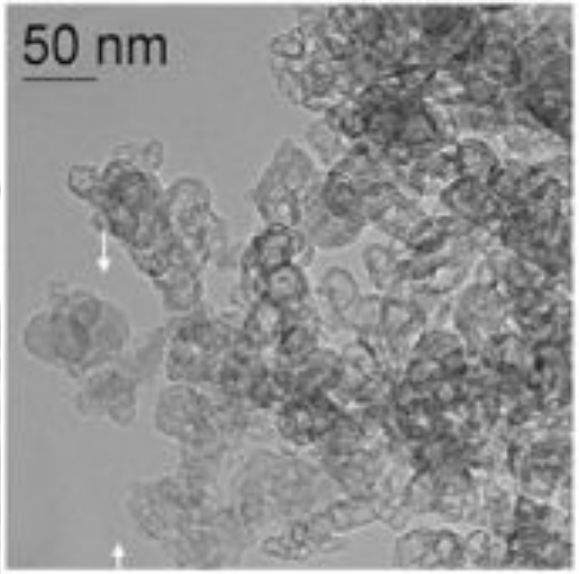
B100 initially has greater surface area, cross-over at ~40% burnout.



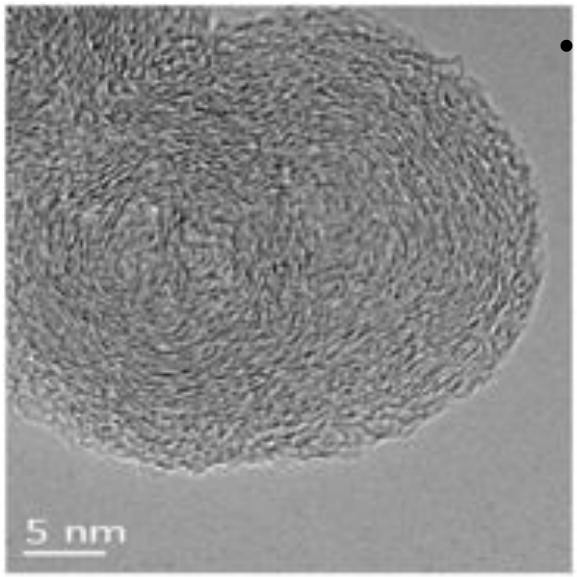


Internal Burning Mode - Diesel Soot

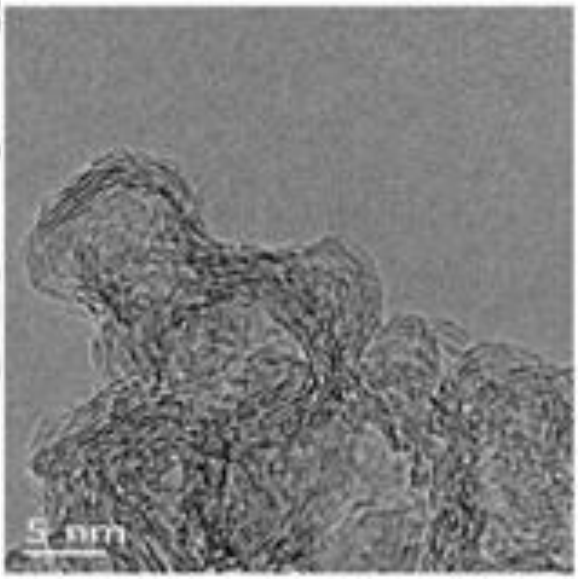




- Cummins ISB Diesel engine



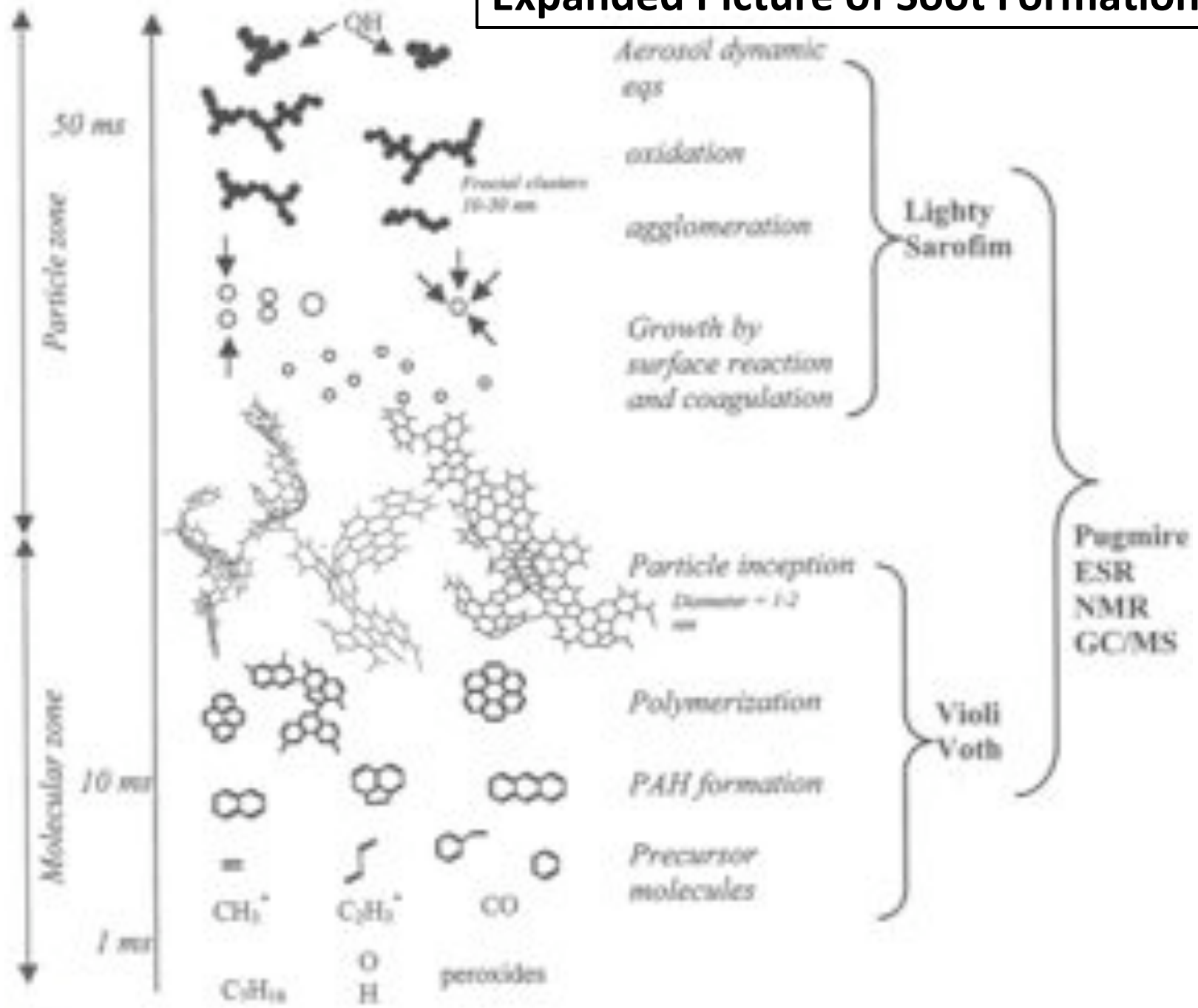
- Partial Oxidation (50%)
  - Hollow shells
  - Oxidation-induced graphitization[1]



low load (1500 rpm, 125 ft/lb)
exhaust temp. ~ 270 ^{0}C

R.L. Vander Wal et al. (2007), 1. R. H. Hurt et al. (1987), T.E. Easler et al. (1990)

Expanded Picture of Soot Formation



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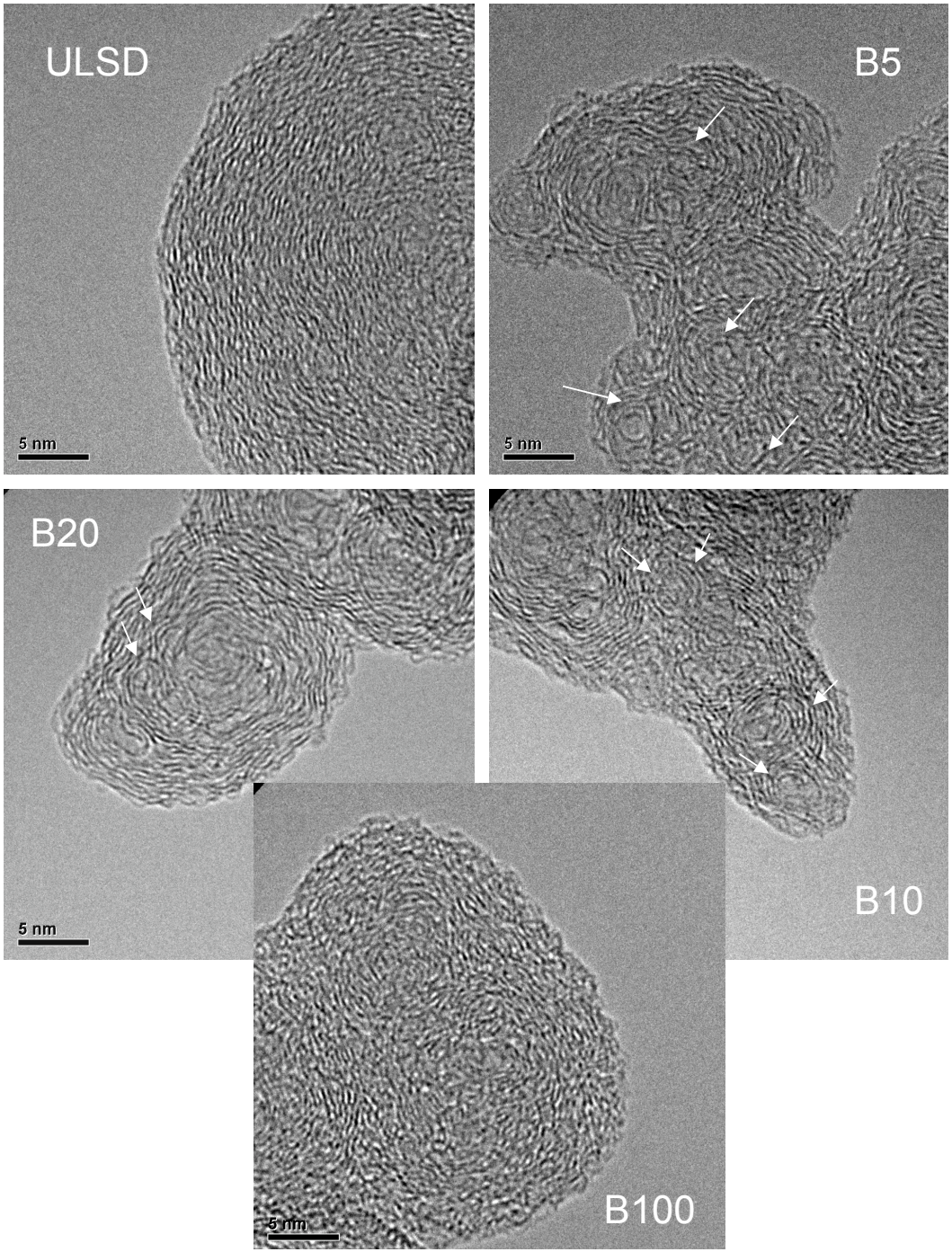
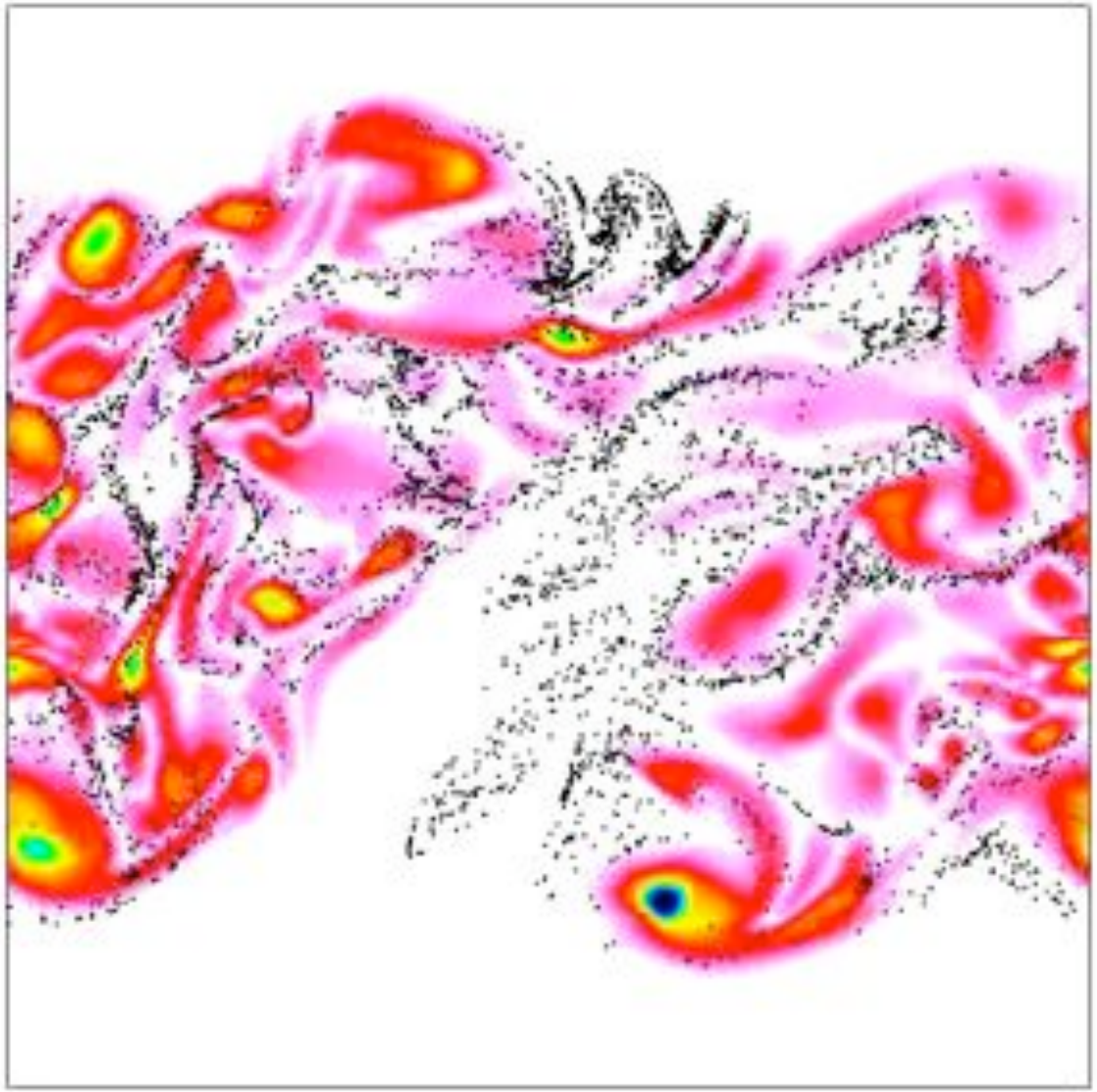
Dr. Joe Kulik (HRTEM), Dr. Trevor Clarke (TEM), Dr. Vince Bojan (XPS), Dr. Josh Stapleton (FTIR-ATR)

Chung-Hsuan Huang (data analysis & discussions), Dr. Boehman & Eduardo Barrientos (TGA)


ULSD
5 nm
B5
5 nm
B20
5 nm
B10
B100
5 nm

Schematic of Turbulence and Mixture Fraction



Illustrations of Curvature in Lamellae