Effect of Alternative Fuels on Soot Properties and Regeneration of Diesel Particulate Filters

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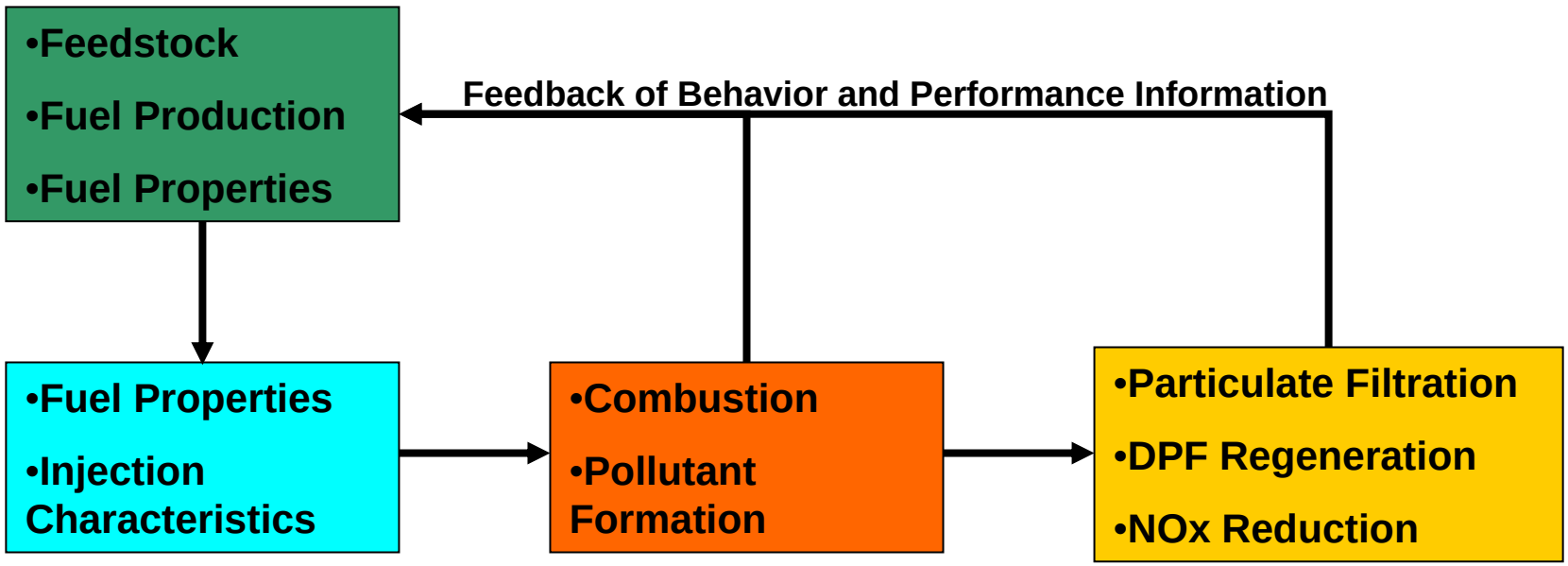
Background

- **Observations of a soot nanostructure-oxidative reactivity relationship, reported at DEER 2004, evidenced by lower regeneration temperature for biodiesel (B20) blends and greater oxidation rates in TGA/DSC measurements as well as in on-engine DPF regeneration tests – what is the source of this difference in PM regeneration process and how do these soots behave during oxidation ?**
- **Vander Wal et al. published in *Combustion & Flame* in 2003 and 2004 papers demonstrating: (1) differences in the structure within soot primary particles with benzene, ethanol and acetylene, and (2) particles with less ordered structure provided higher oxidative reactivity**

Objectives
Ultra Clean Fuels Project

- **Determine the Interaction between Formulation of Conventional, Renewable and Synthetic Diesel Fuels and their Injection Characteristics**
- **Measure Physical Properties of Fuels that Can Provide Support for Understanding Injection, Combustion and Emissions Performance of Diesel Fuels**
- **Use Injection Studies, Physical Properties, Emissions Measurements and In-Cylinder Visualization to Determine Optimal Fuel Formulations**
- **Link Feedstock and Fuel Production Process to Physical Properties and, Thereby, Injection, Combustion and Emissions Performance - *Characteristics of Soot from Different Fuels – Considering Neat Alternative Fuels, B100 and FT100***

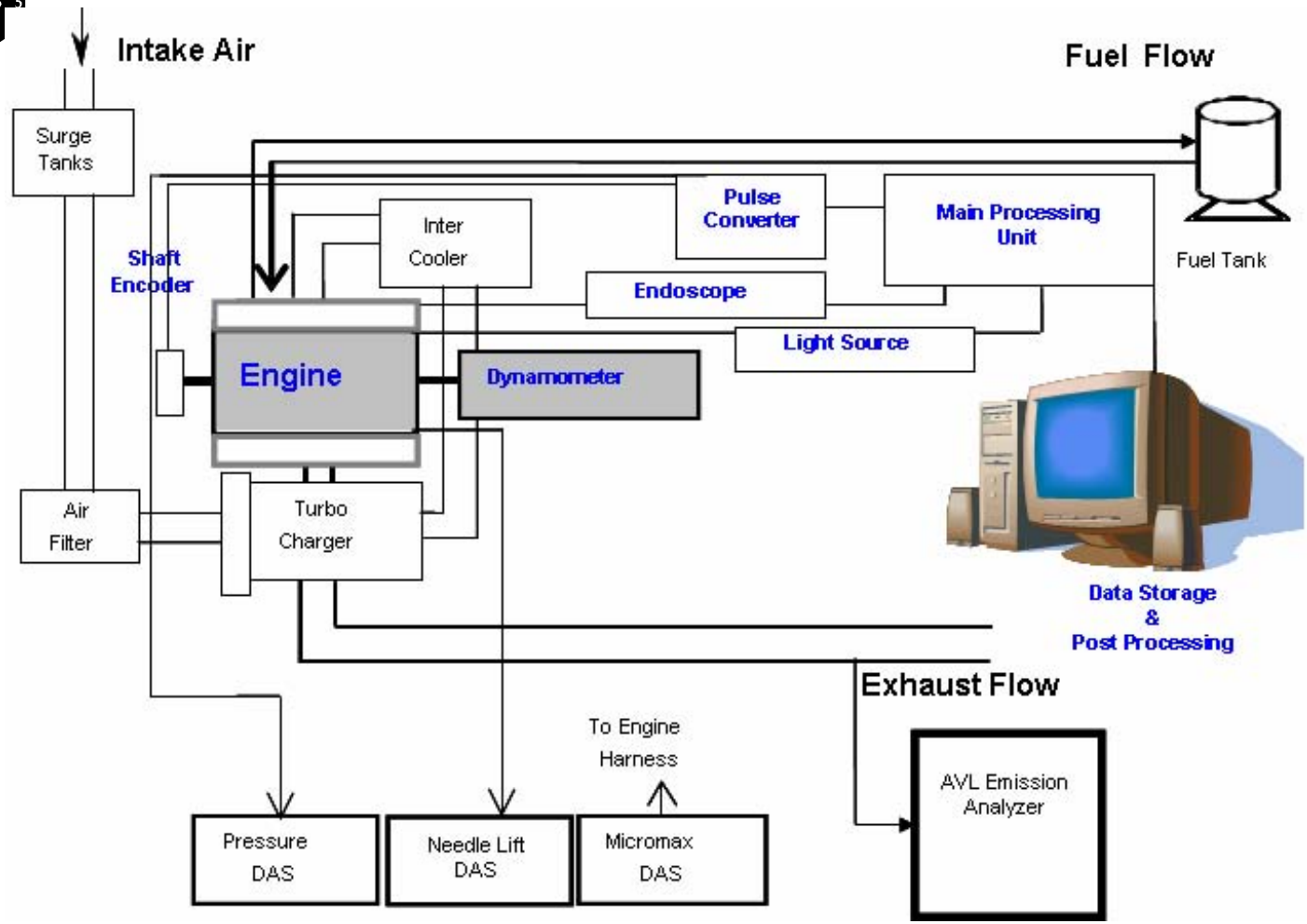
Research Strategy



- Spray Visualization Chamber
- Bulk Modulus of Compressibility

- AVL 513D Engine Videoscope
- Particulate and Gaseous Emissions

- Various Aftertreatment Strategies



Schematic diagram of the Cummins ISB test stand

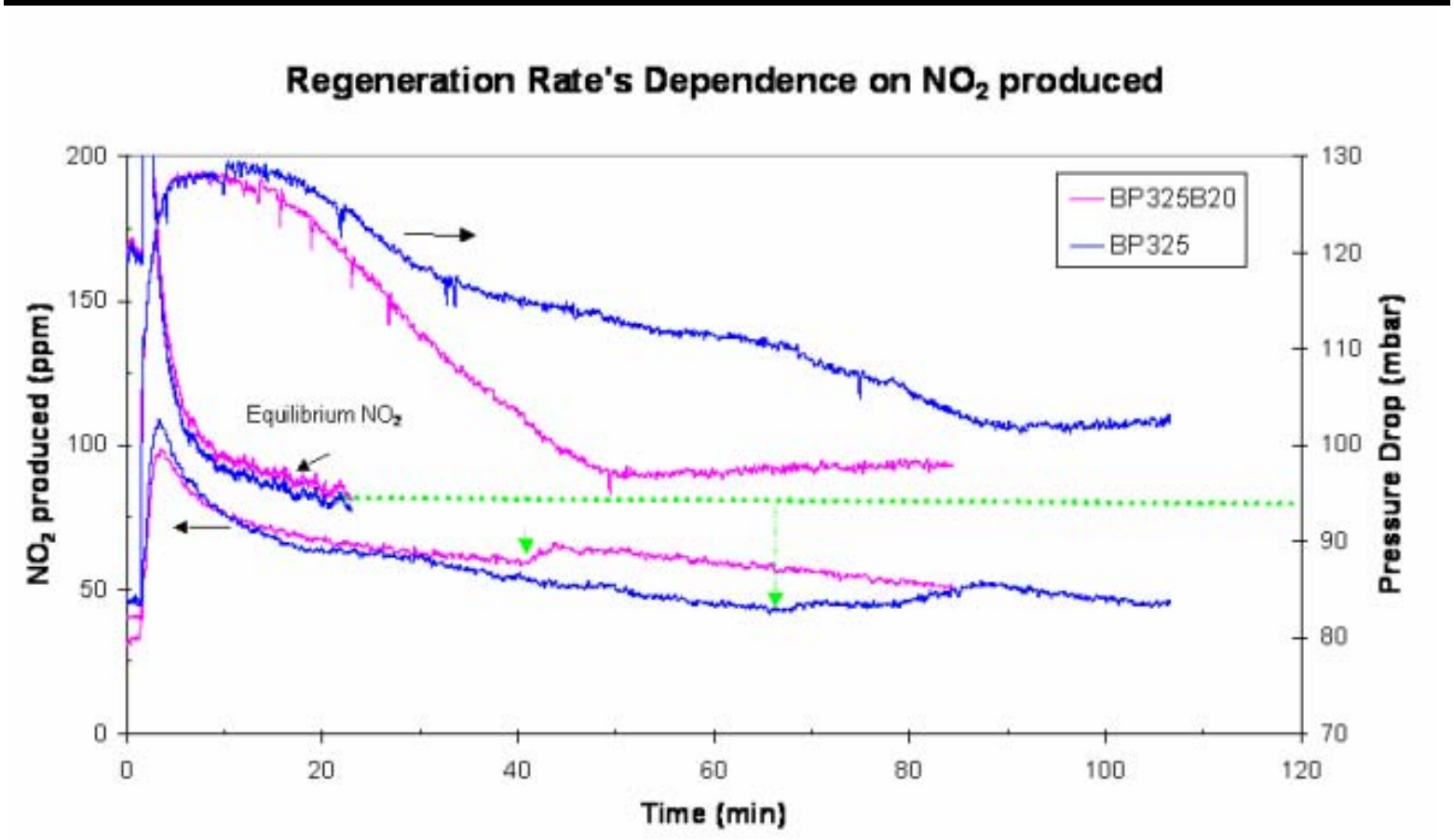
Outline

Ultra Clean Transportation Fuels from Natural Gas

- **Review of Key Observations Reported at DEER 2004**
- **Influence of Fuels, Injection Timing, Combustion and Emissions on the Performance of Aftertreatment Devices**
  → *Characteristics of Soot from Different Alternative Fuels*

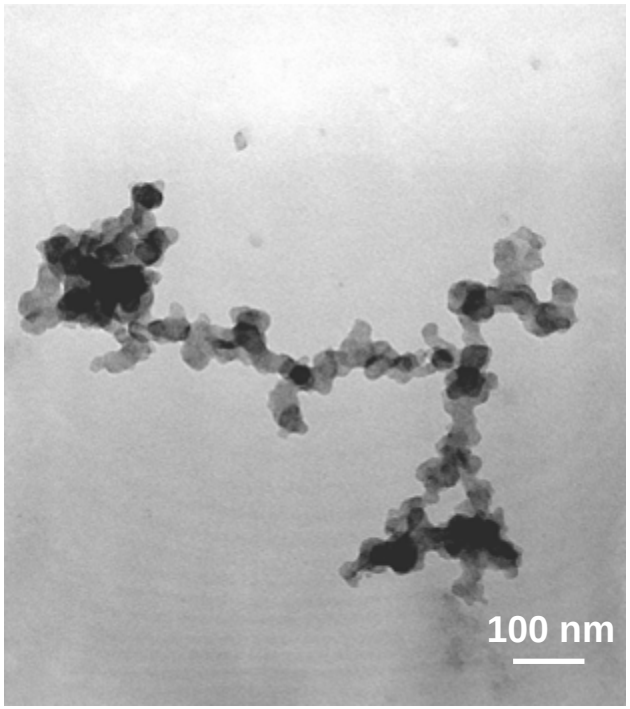
Fuel Composition Effects on Emissions

BP-325 and BP-325/B20 Test Fuels in a High Temp Regeneration

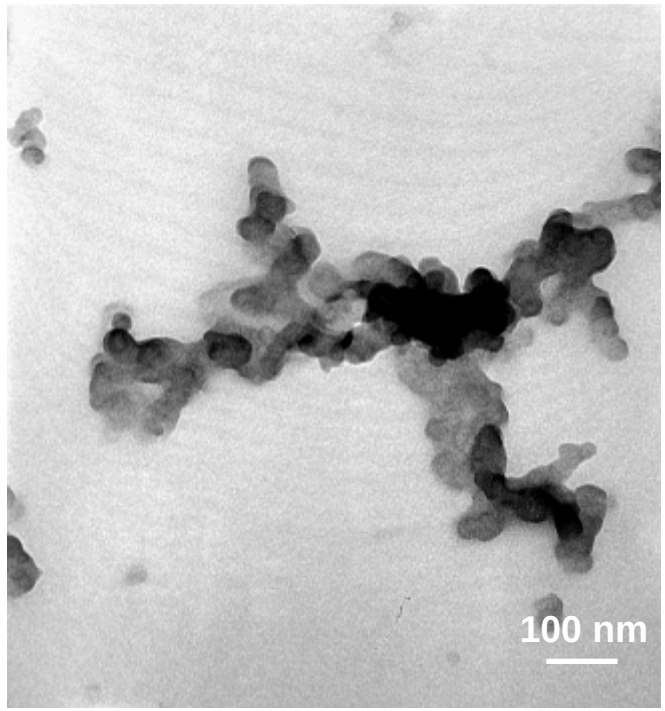


Variation in Heavy Hydrocarbon Fraction

Soot Morphology



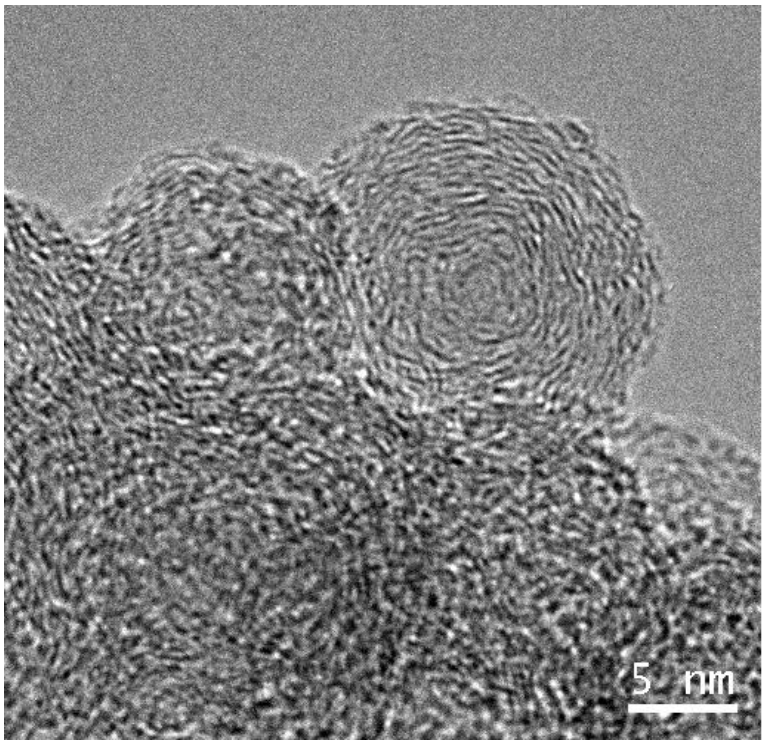
(c) BP15 Derived PM



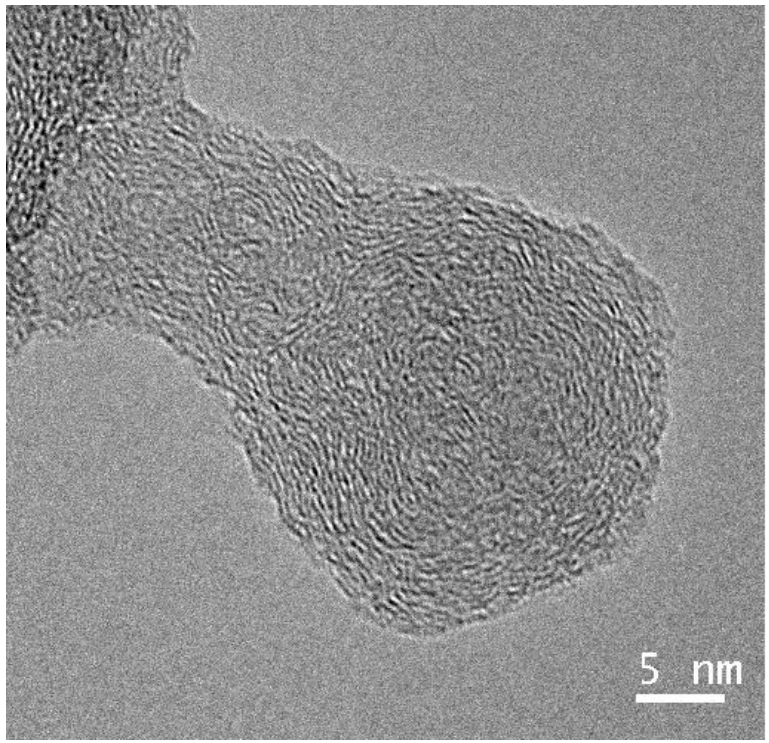
(d) BP15B20 Derived PM

Initial Results – Comparing Diesel and B20

Soot Nanostructure – Less Ordered Nanostructure Corresponds to Enhanced Reactivity



(a) BP15 Derived PM

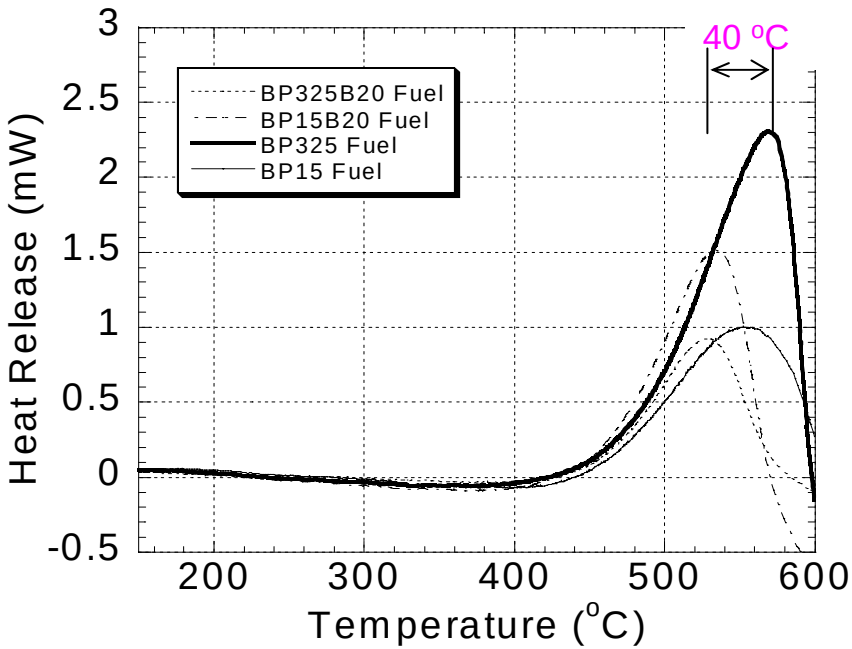


(b) BP15B20 Derived PM

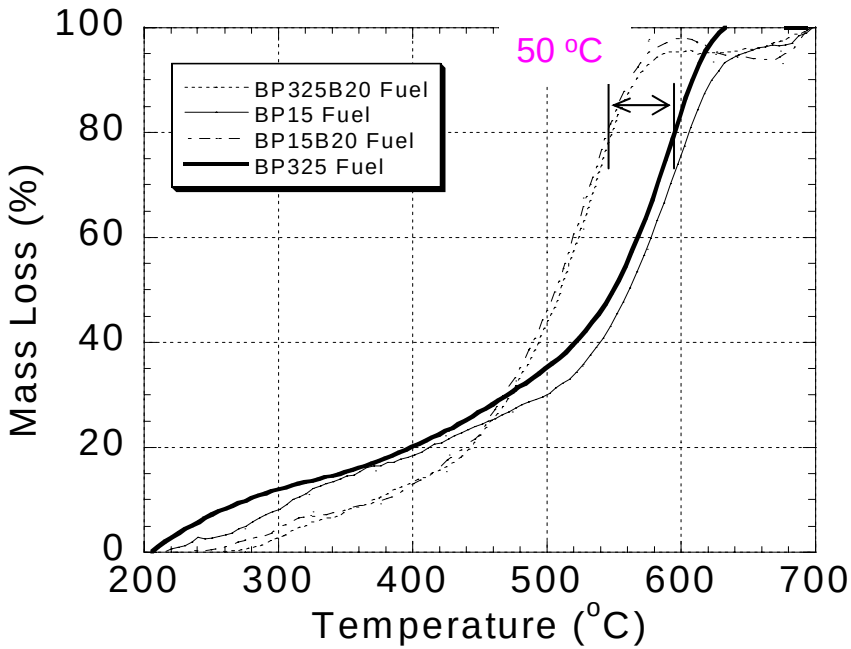
Soot Nanostructure and Its Effect on Reactivity

Low temperature Reactivity from DSC/TGA test

- under 21% oxygen gas with treated samples



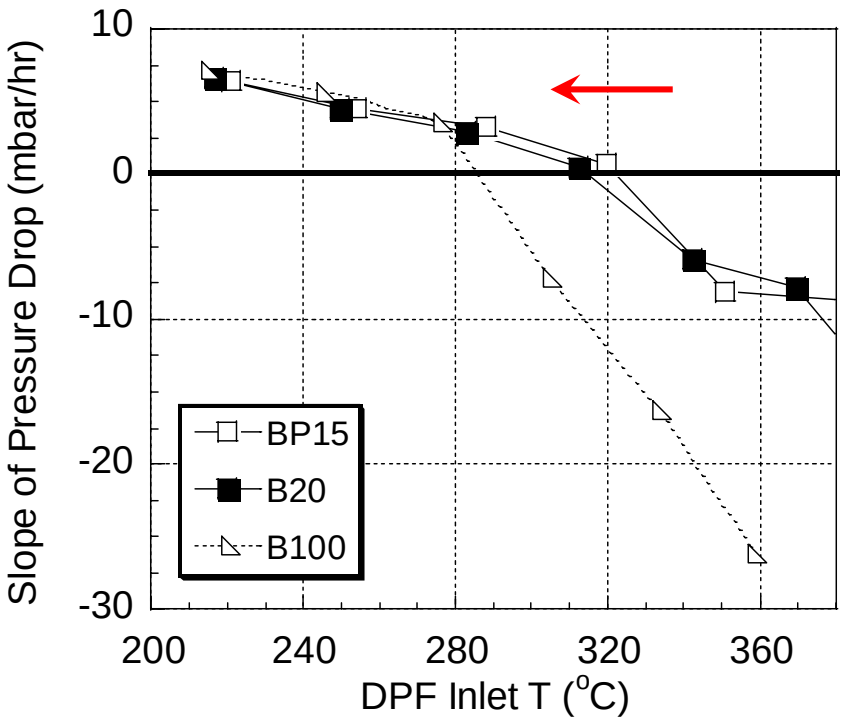
(a) Burning rate DSC curve

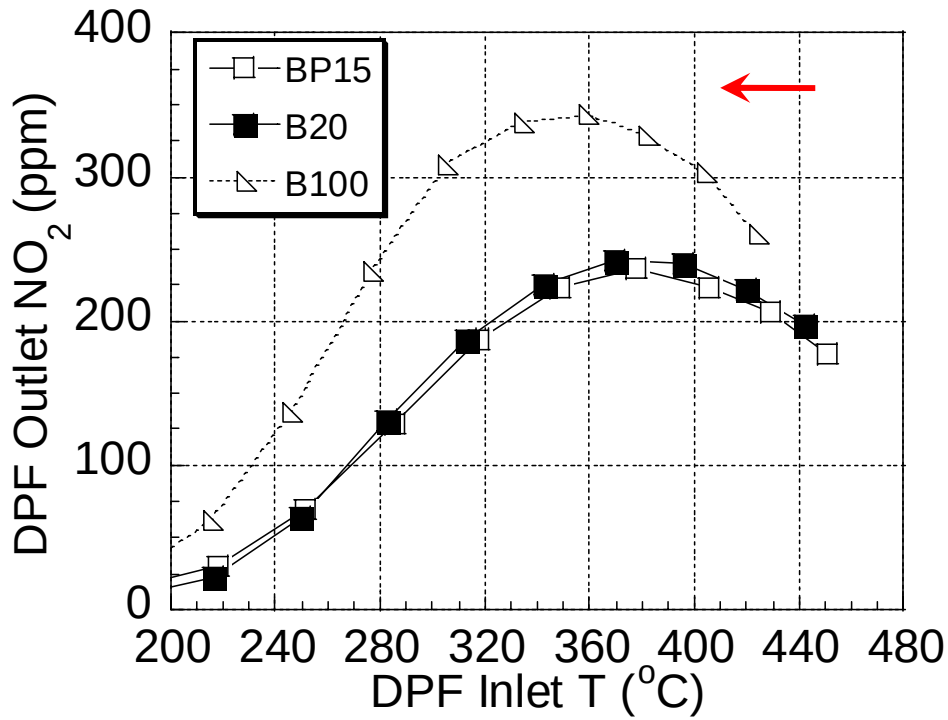


(b) Mass reduction TGA curve

Expanded Results – Comparing Diesel, F-T and B100

Low Temperature Regeneration

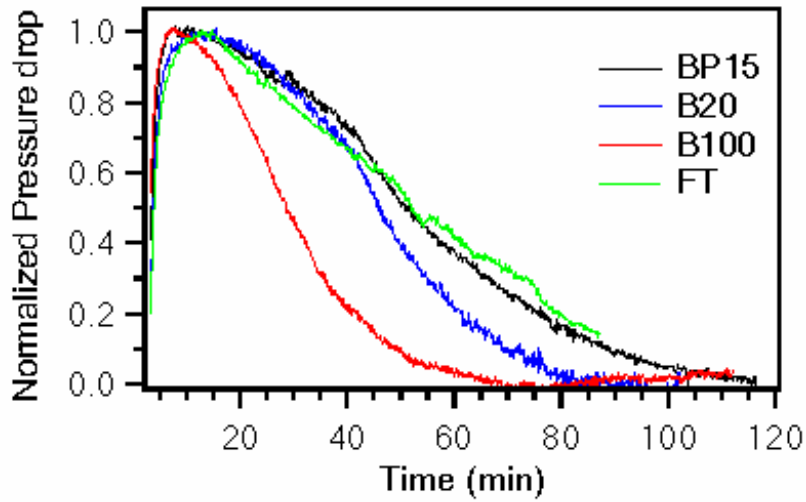


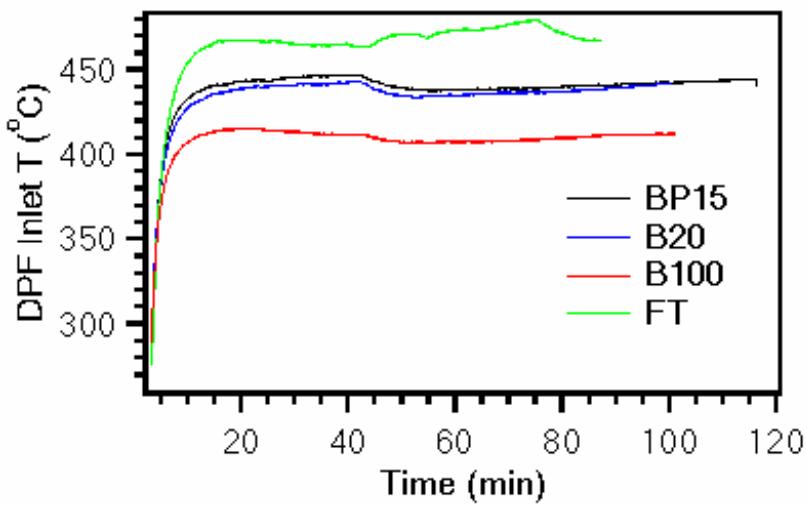


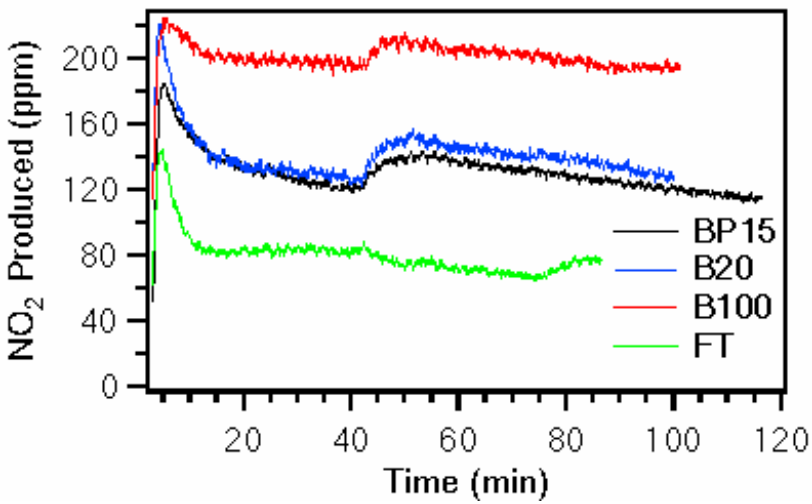
BET Temperature to be lower by **30 ºC** with B100

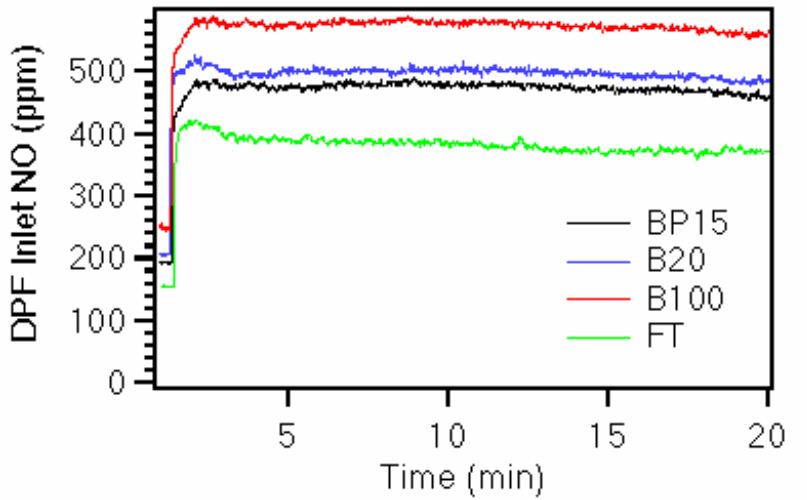
30 ºC shift of temperature where maximum NO_2 is produced over DPF

High Temperature Regeneration (from 280 to 450 ºC)

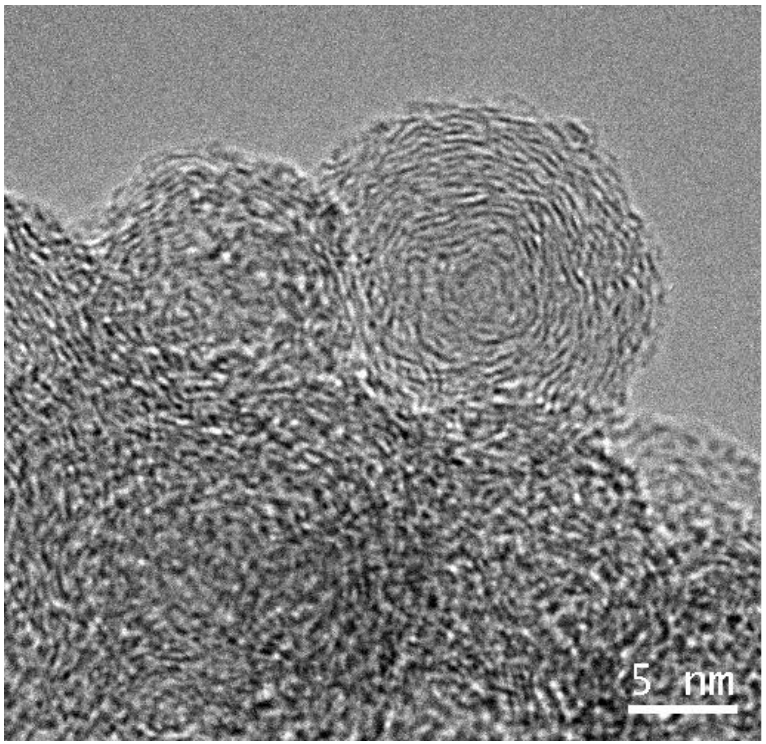




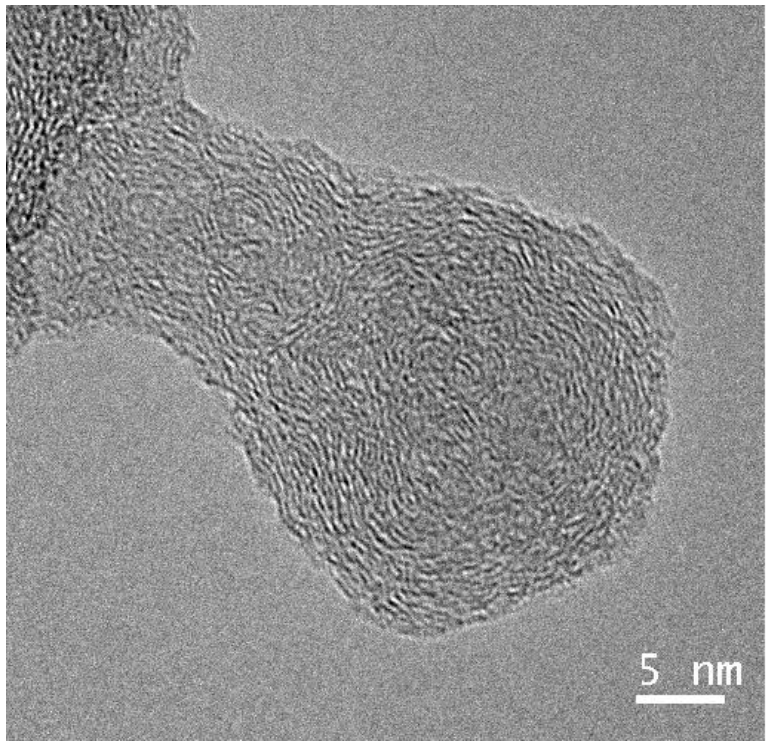




Electron Microscopy of Initial Soot Nanostructure

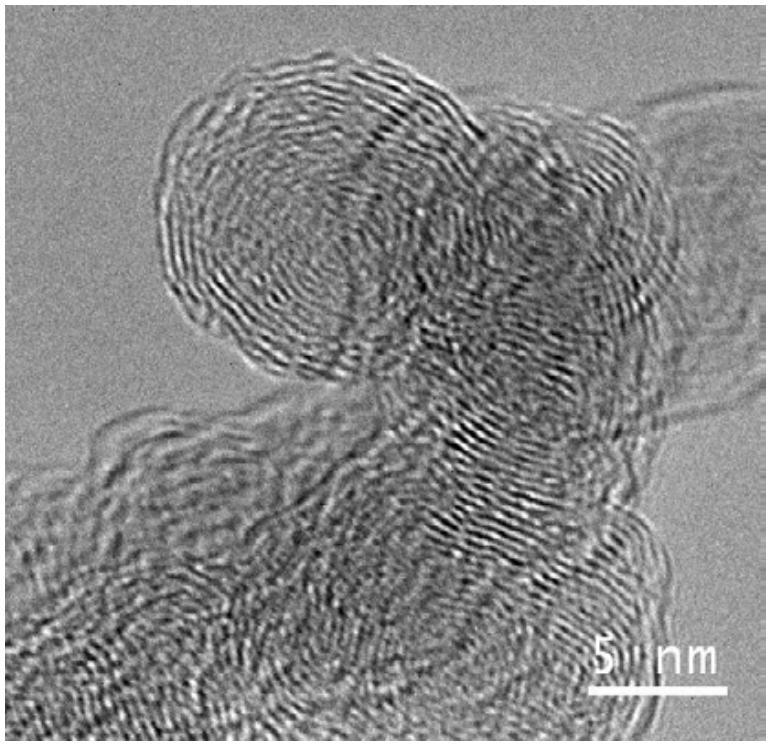


(a) BP15 Derived PM

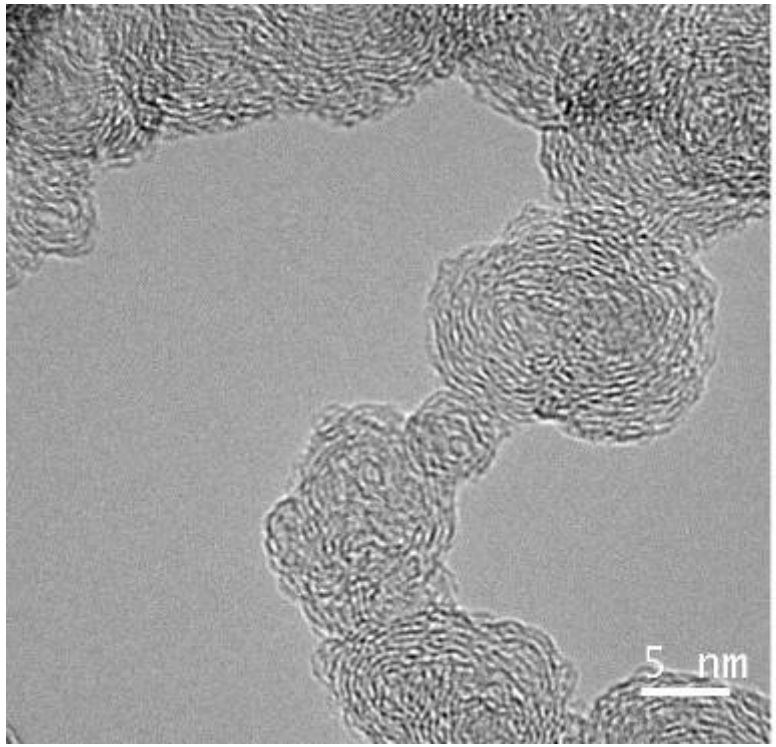


(b) BP15B20 Derived PM

Initial Soot Nanostructure



(c) B100 Derived PM

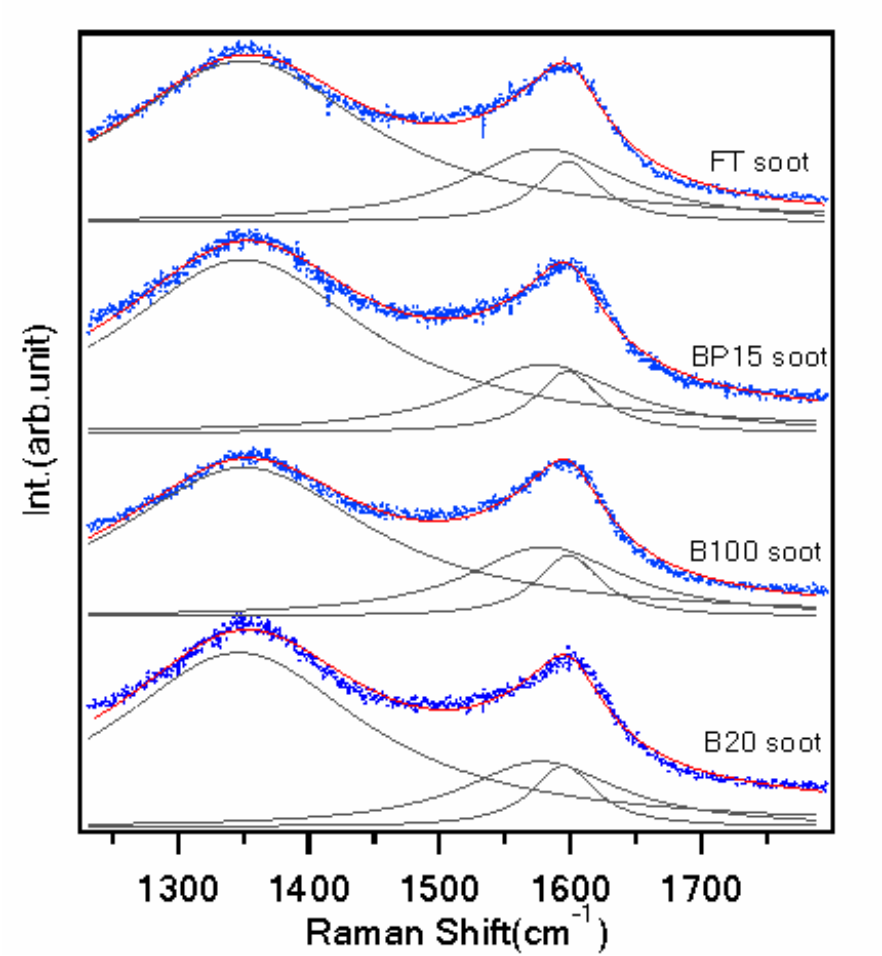


(d) F-T diesel Derived PM

Summary

- **From a comparison of DPF regeneration behavior**
  - ➔ **Enhanced regeneration of B100 in terms of both rate and BET is observed, whether this comes from particulate reactivity or catalyst activity which is sensitive to fuel sulfur**
  - ➔ **This difference in oxidation rate of DPF soot cake is reproduced in mass based rate on TGA as will be shown**

Raman Analysis of Initial Structure



Id/Ig was extracted from 2 curves deconvoluted after lorentzian curve fitting

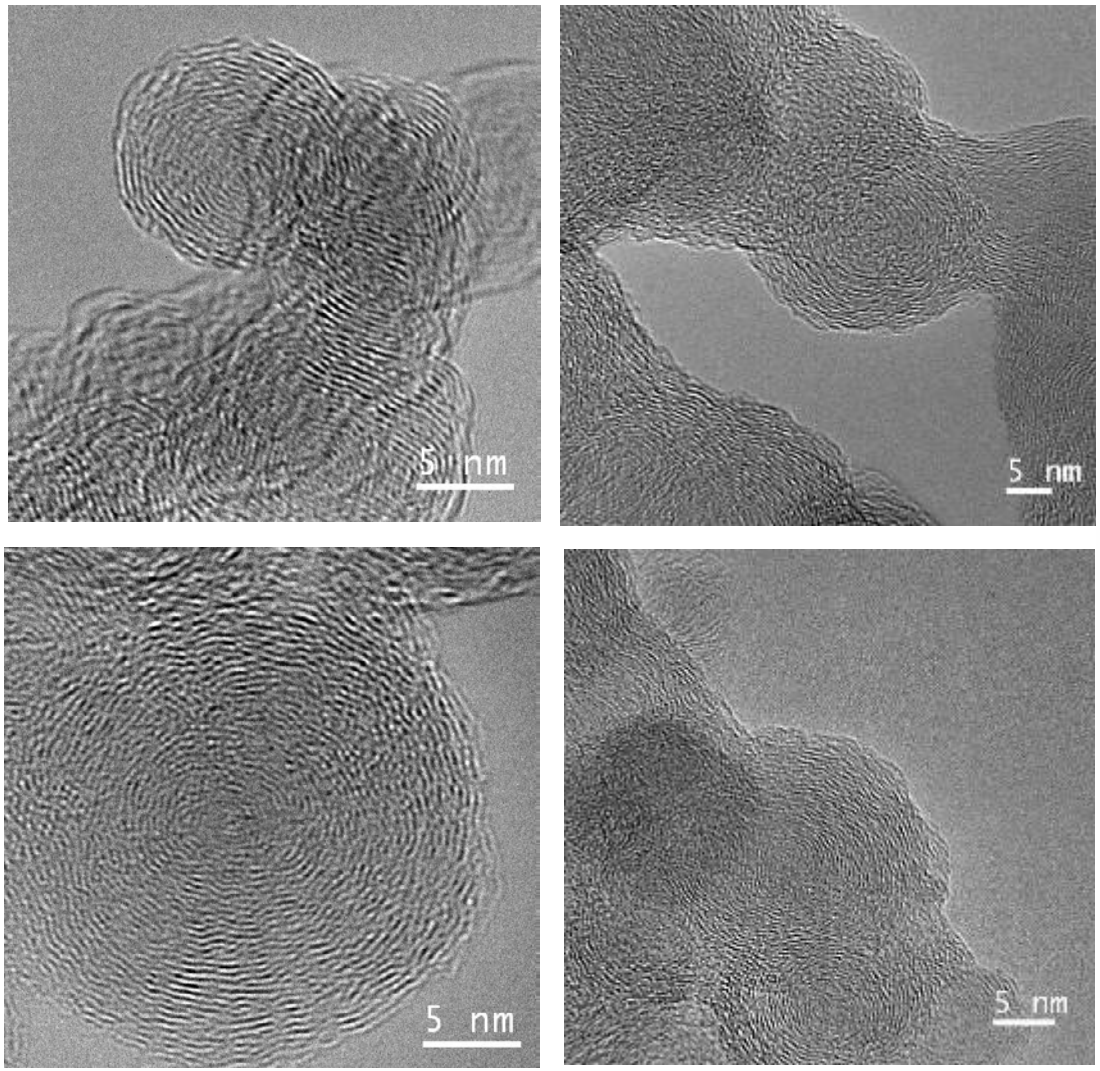
Gra-phitic order	Soot type	D band cm^{-1}	G band cm^{-1}	I_d/I_g*
3	BP15	1354	1598	1.11
4	B20	1354	1598	1.18
1	B100	1354	1598	1.06
2	FT	1354	1598	1.12
	Graphite	1354	1583	0.37

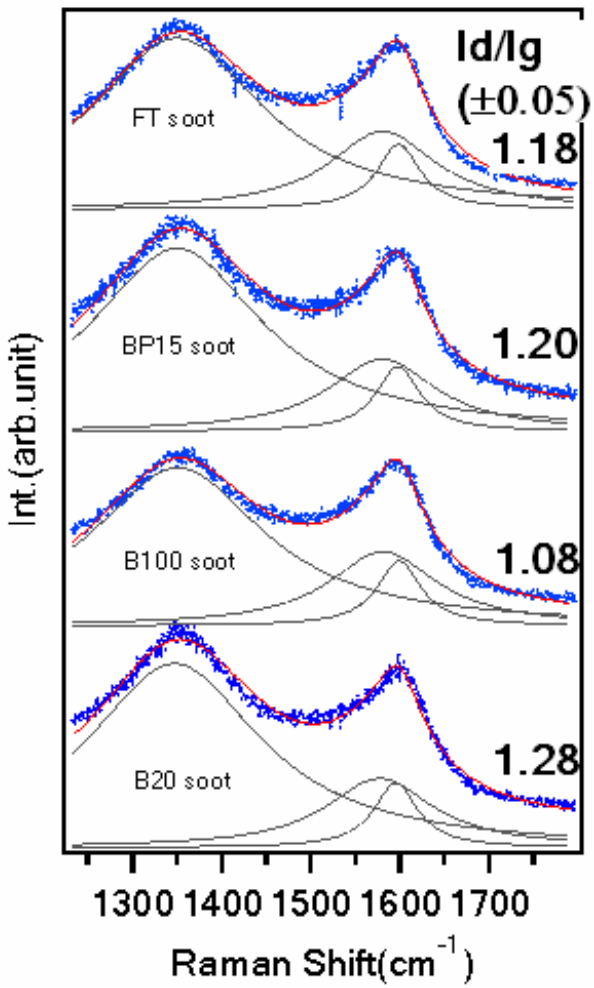
Error bar : ±5% (± 0.05)

Raman Analysis of Initial Structure

(a) B100

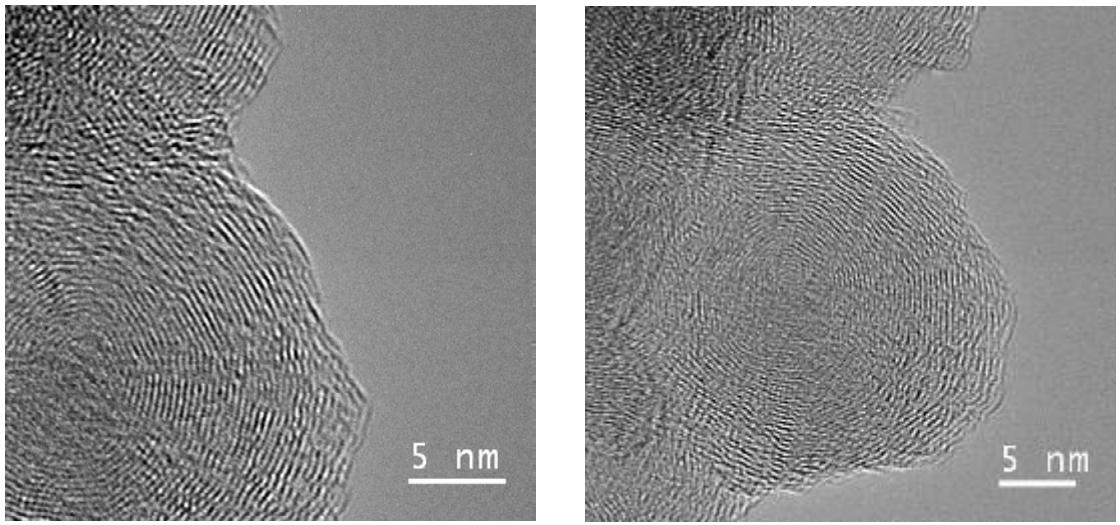
(b) FT



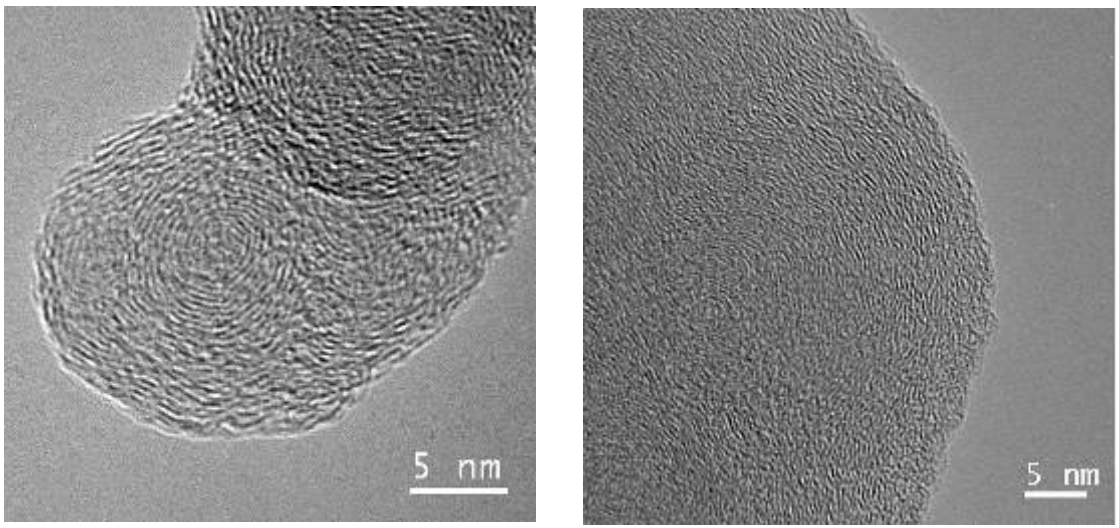


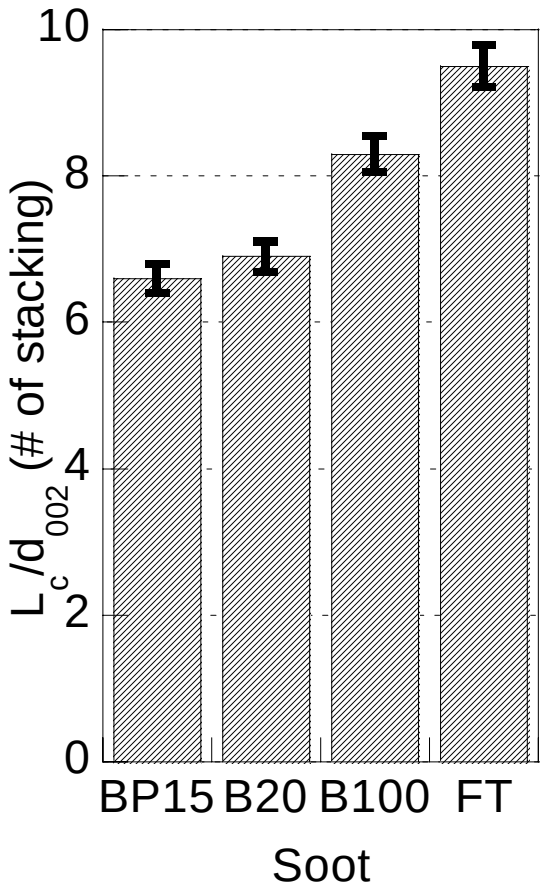
XRD Analysis of Initial Structure

(c) BP15



(d) B20



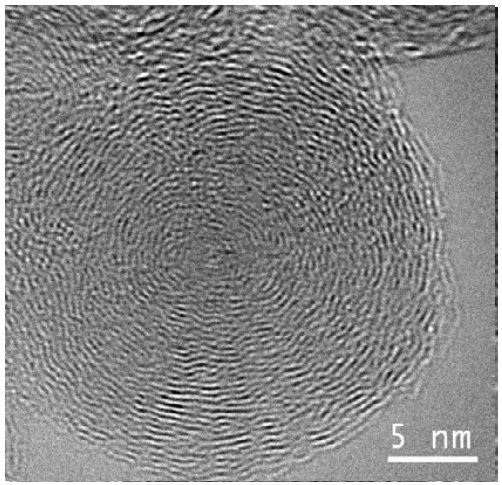


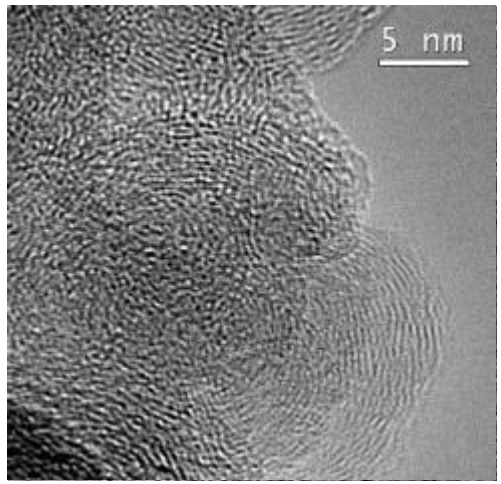
Structural Change During Early Stage of Oxidation (30min)

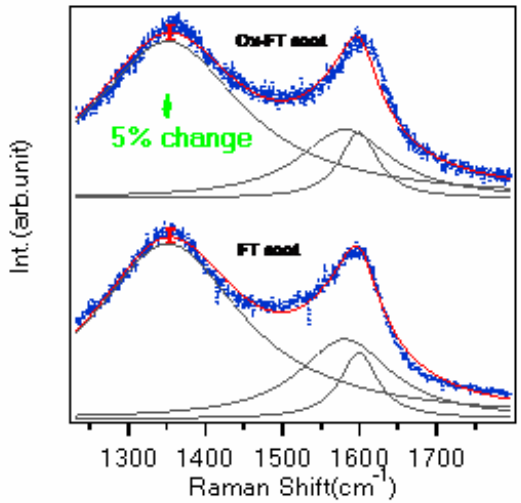
Initial

Oxidized

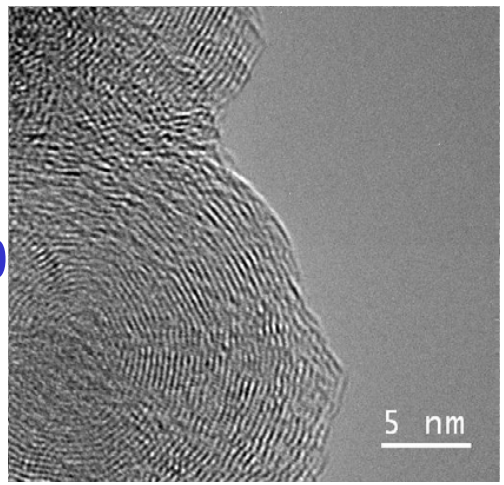
FT

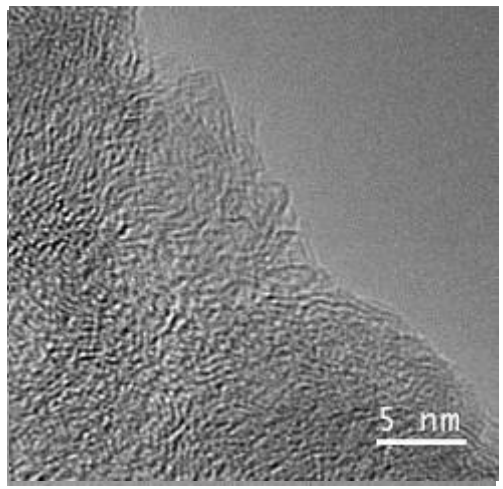


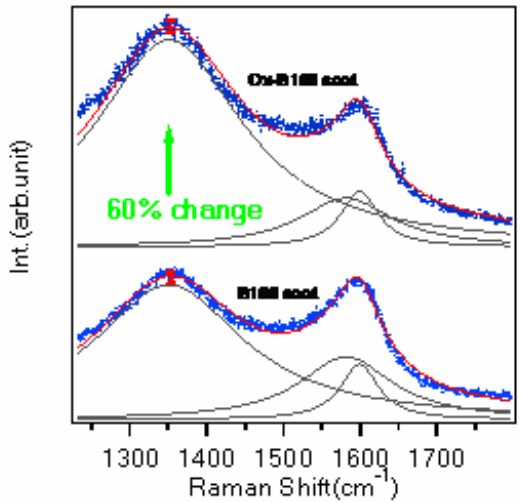




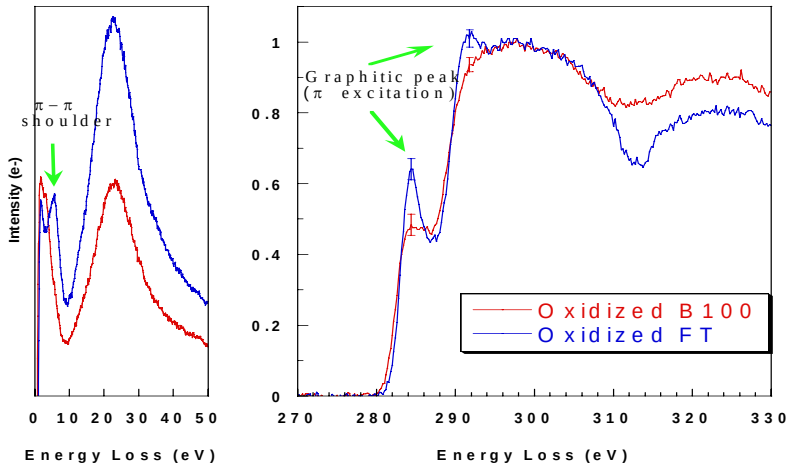
B100



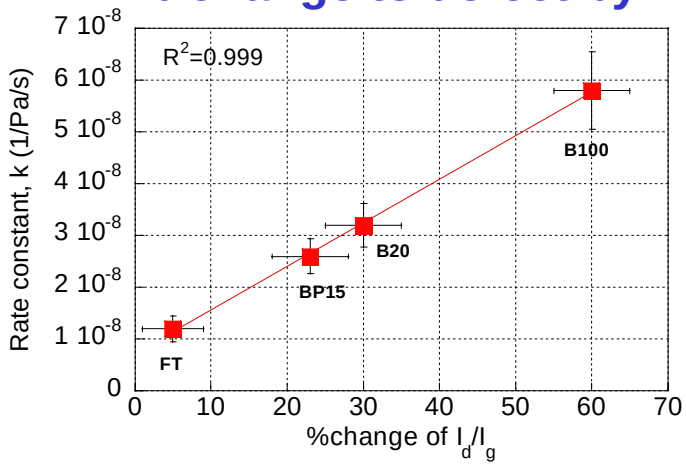




Electron Energy Loss Spectra



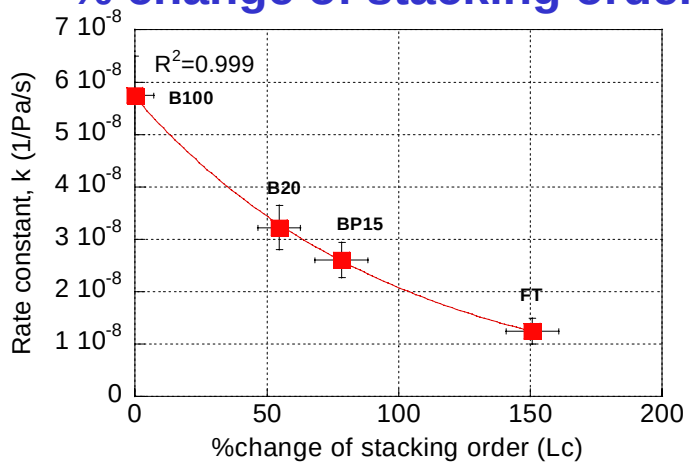
% change to defect by Raman



% change of I_π/I_σ ratio by EELS

Soots	Before	After	%Change
FT	0.642	0.610 (±0.03)	-2
B100	0.650	0.489 (±0.03)	-26

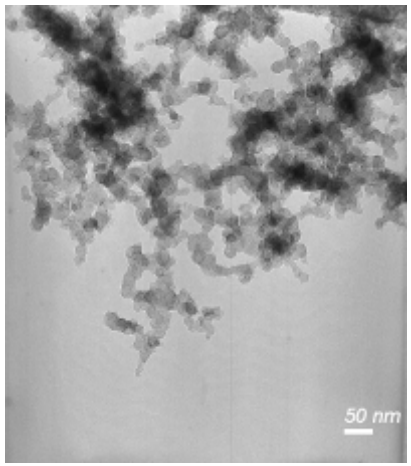
% change of stacking order by XRD

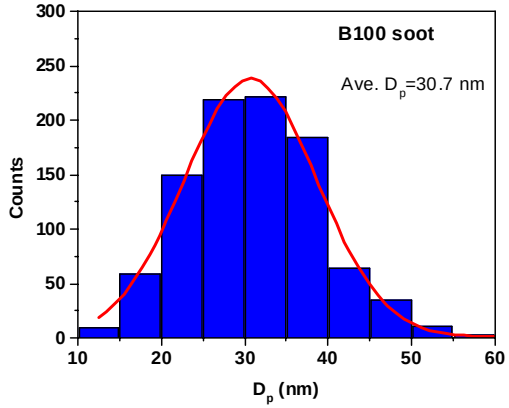


Surface Area Based Oxidation Rate

B100

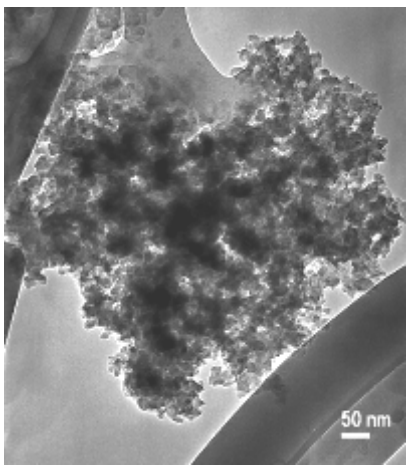
Initial

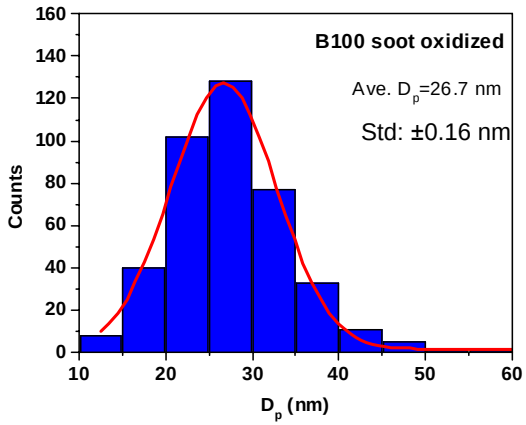




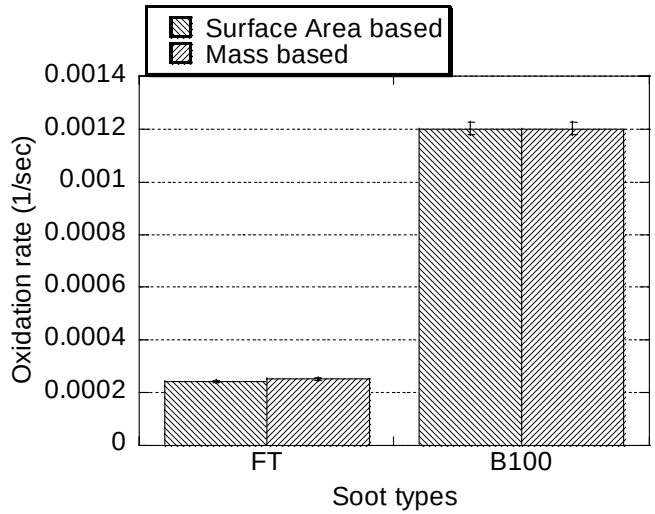
-4.0 nm

Oxidized



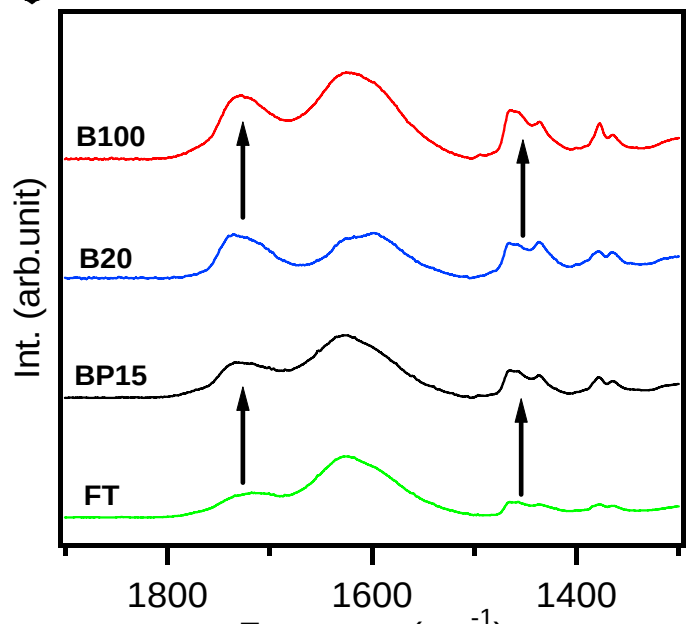


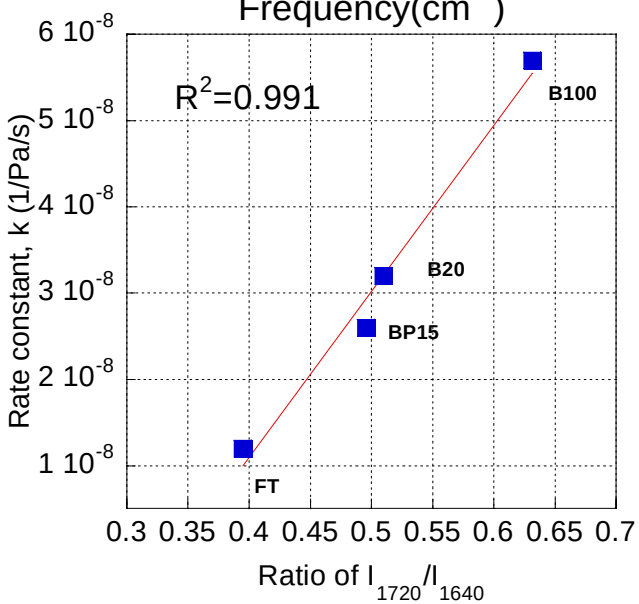
Comparison of surface area and mass based oxidation rate



Remaining Question : Under surface burning, why did B100 soot undergo severe structural change even though its initial nanostructure was the same as for FT soot ?

Oxygen Functionality of Initial Soot Samples





IR spectra band assignment

Range (cm^{-1})	Chemical group
1700	Lactone, Carboxyl (bonded to two O or OH atoms)
1600 Under controversy	Aromatic C=C stretch C=O conjugated with aromatic
1450	Aliphatic C-H
1400	Sulfate
1250	Ether, Phenol
Below 1200	Electronic Noise due to high absorption of Kbr

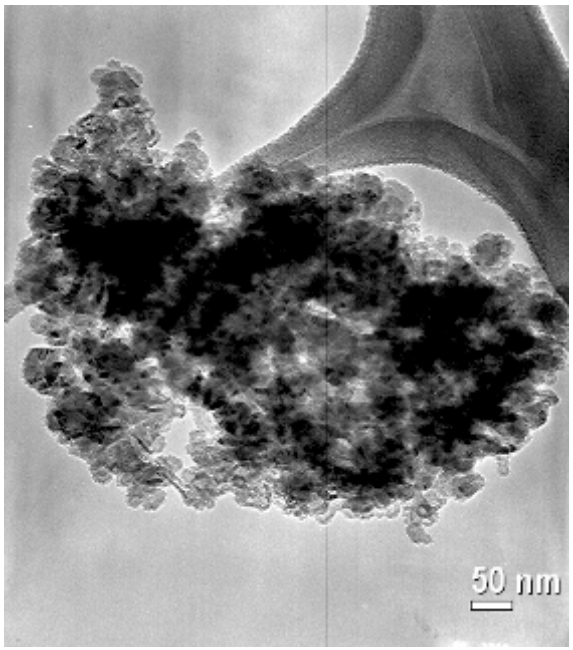
From Fanning, Boehm, Smith

Summary

- **From a comparison of particulate reactivity:**
  - ➔ **There is no definitive impact of initial nanostructure on oxidation rate**
  - ➔ **Under surface burning dominance during the early stage oxidation, the degree of internal structural change exerts a strong influence on the oxidation rate**
  - ➔ **The relative amount of initial oxygen groups is an important factor governing the soot oxidation rate**

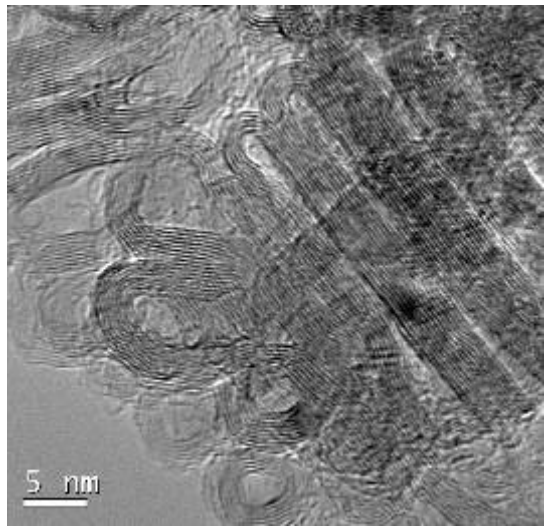
B100 Soot

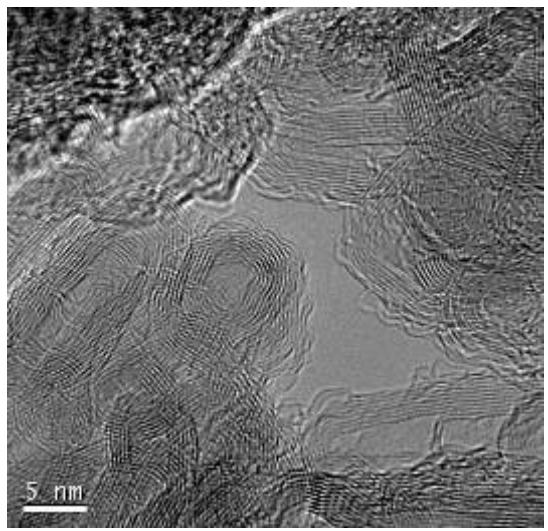
105k x



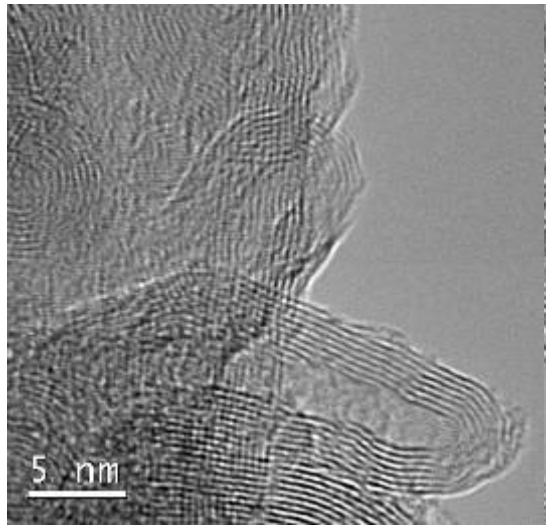
75% burn off, 50 min

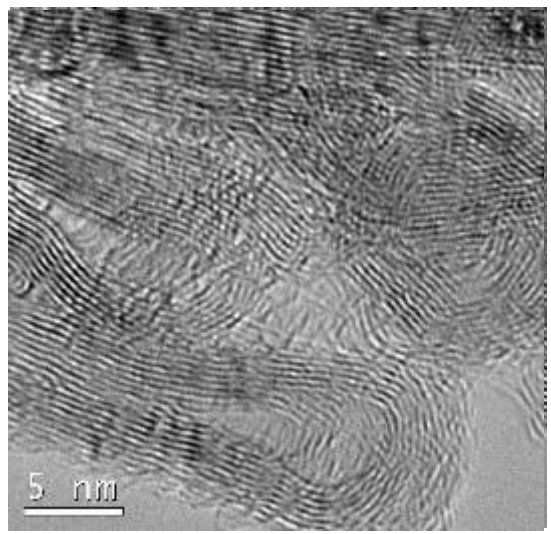
500k x





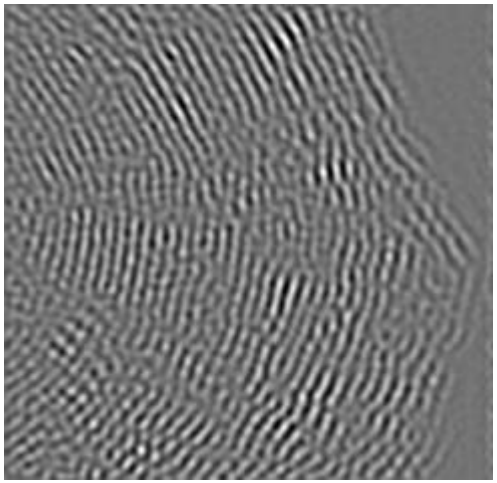
800k x

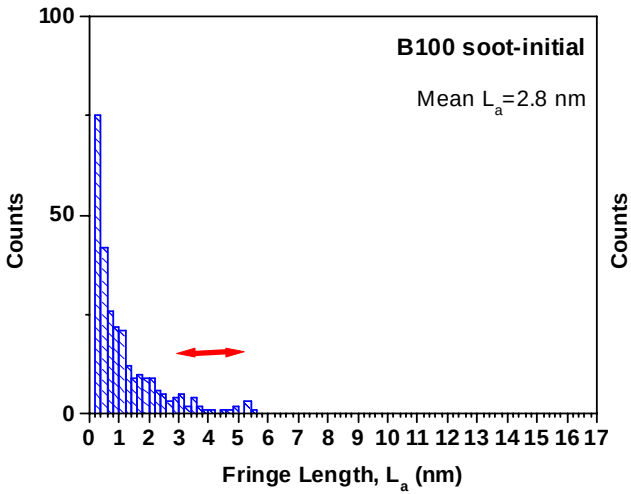




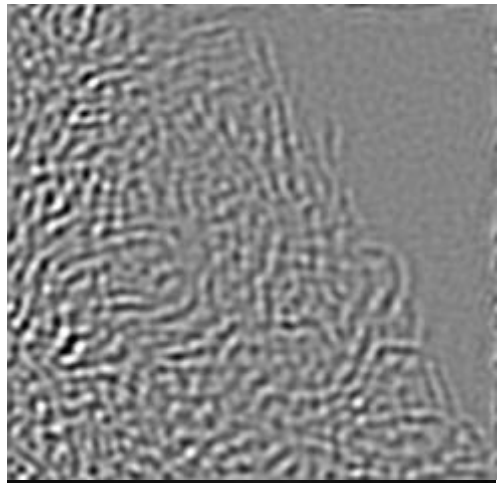
Fringe Length Analysis - B100 Soot

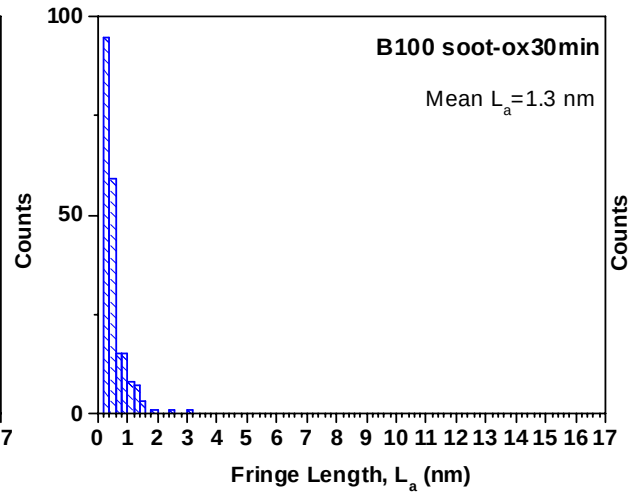
Initial



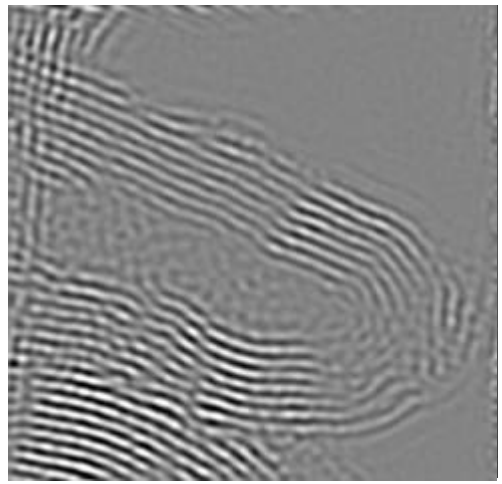


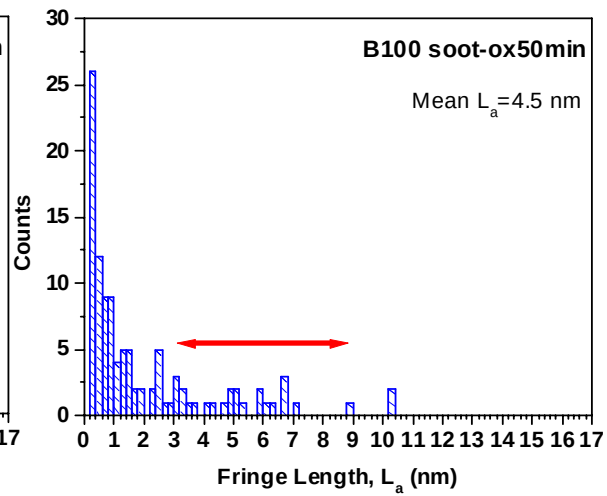
40% burnoff



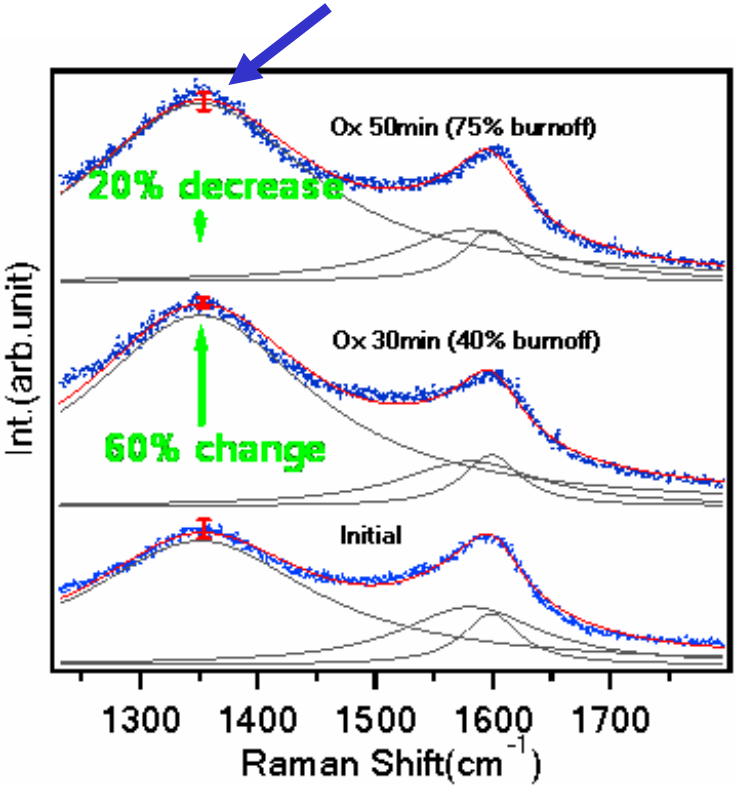


75% burnoff

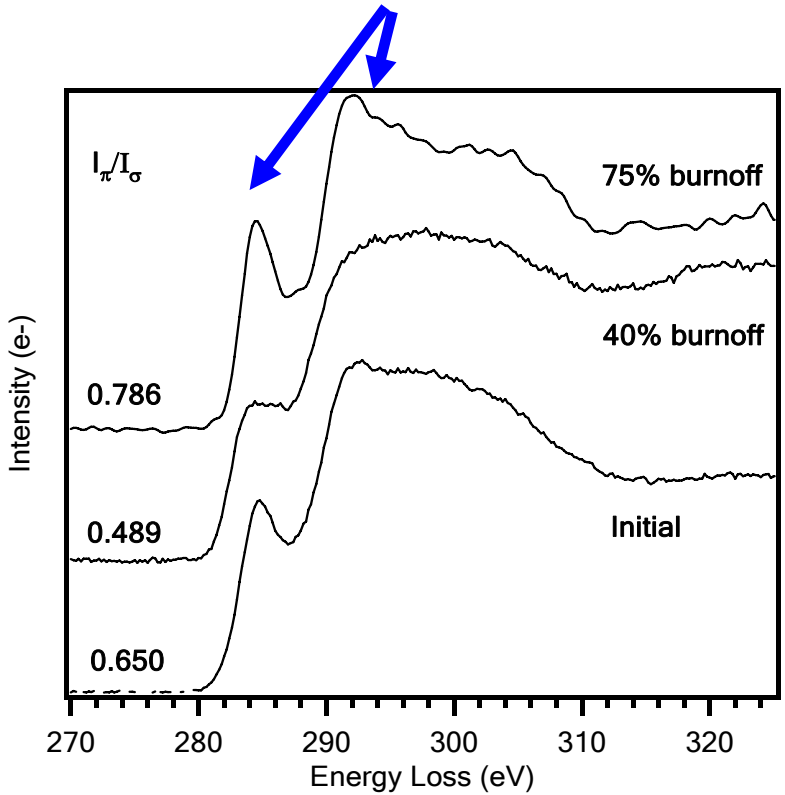




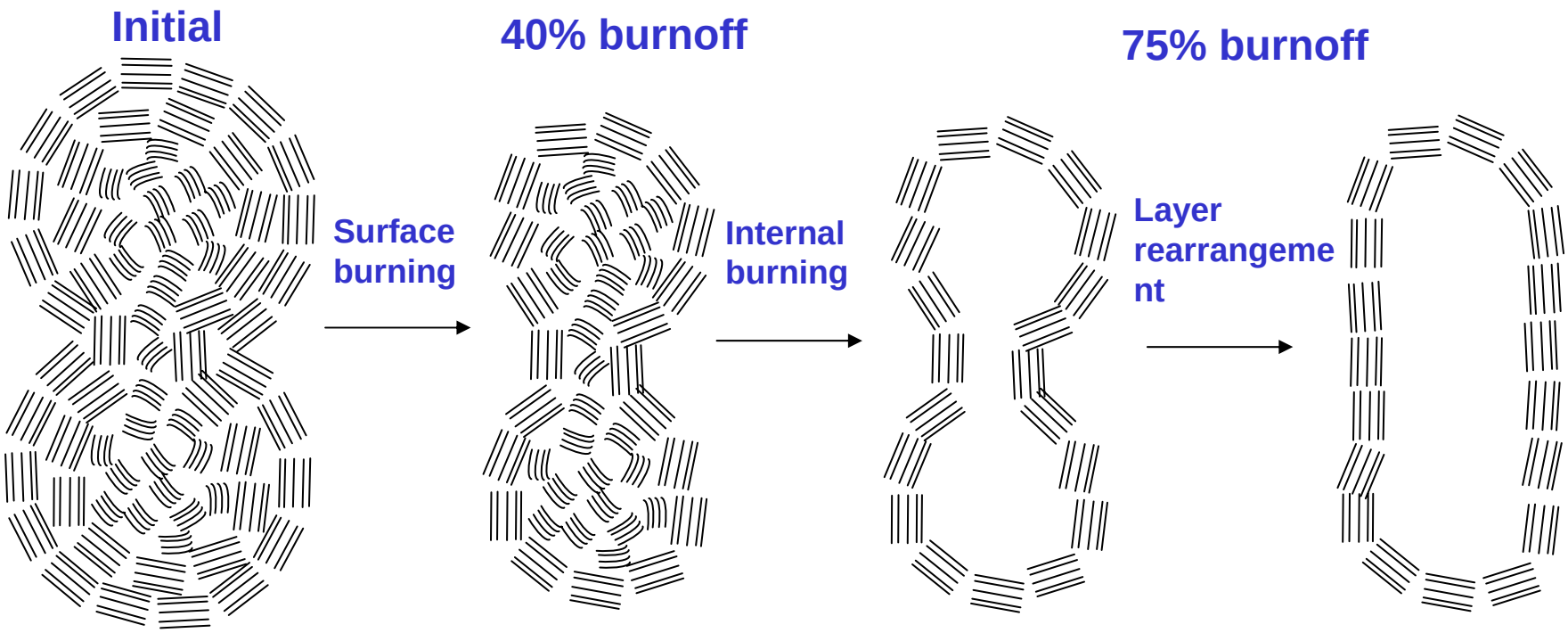
Decrease in D band



Prominent graphitic peak



Oxidation Progression Model for B100 Soot



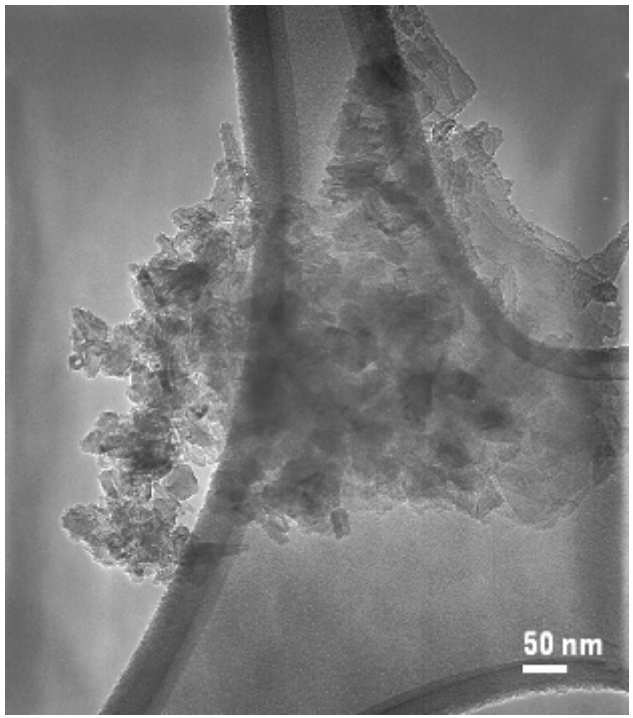
For simplicity, ignore crosslinking in this shell-core structure

Once micro pore is fully penetrated, central hollow

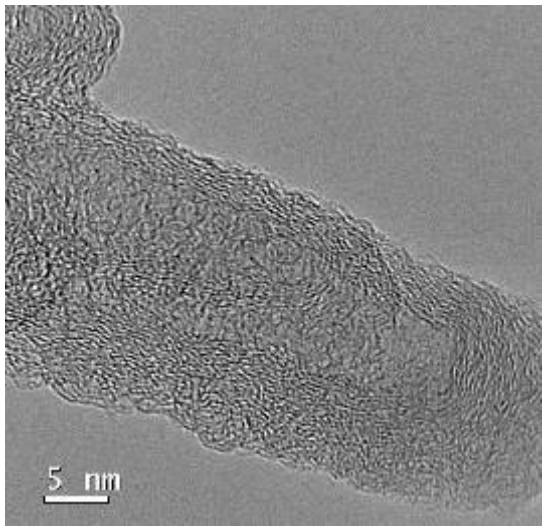
Further coalescence, due to physical factor such as increase in layer mobility and minimizing a strain energy

FT Soot

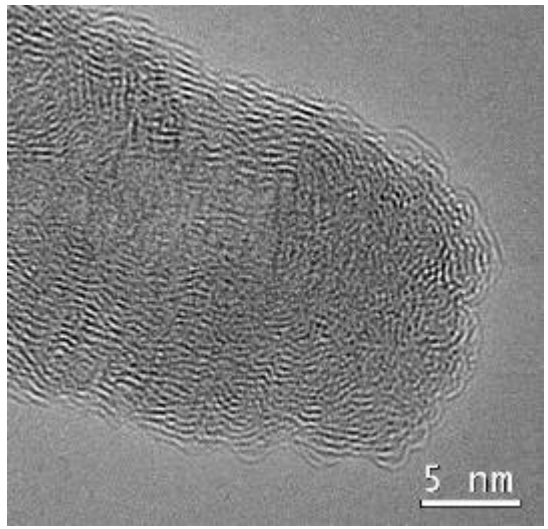
105k x

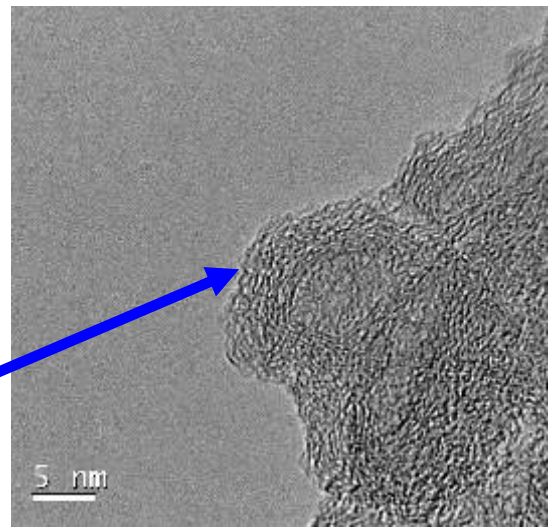


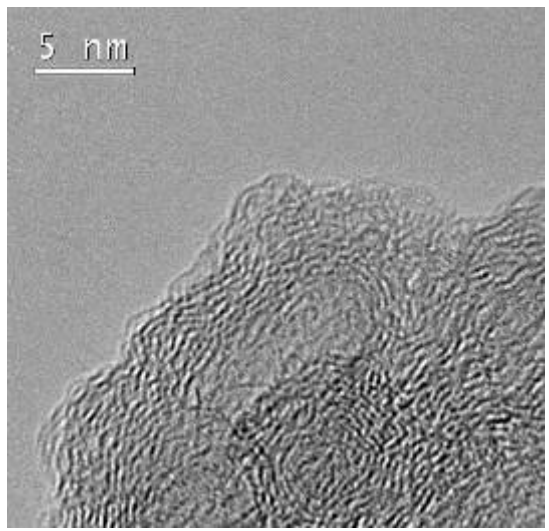
500k x



800k x





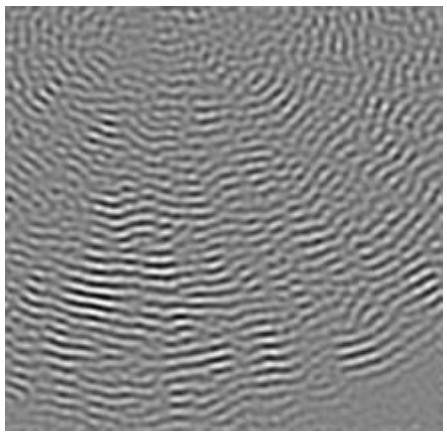


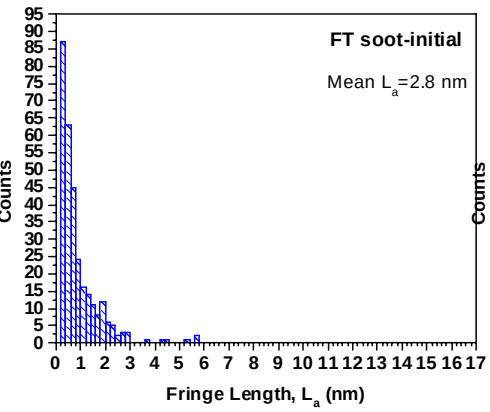
75% burn off, 105 min

Still wavy and much shorter layer than B100

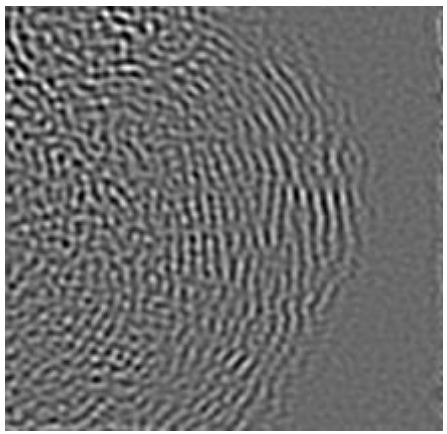
Fringe Length Analysis - FT100 Soot

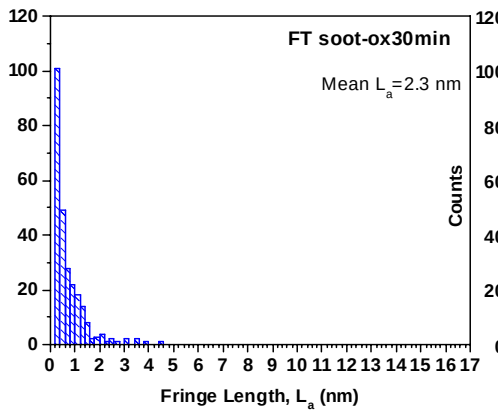
Initial



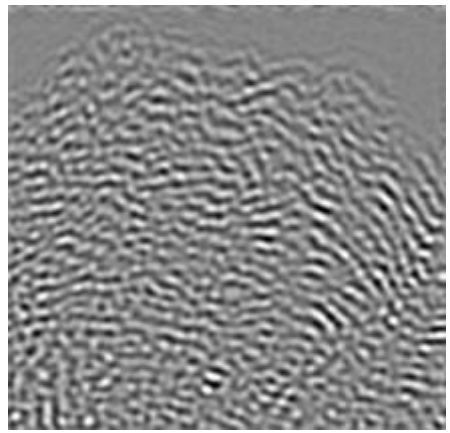


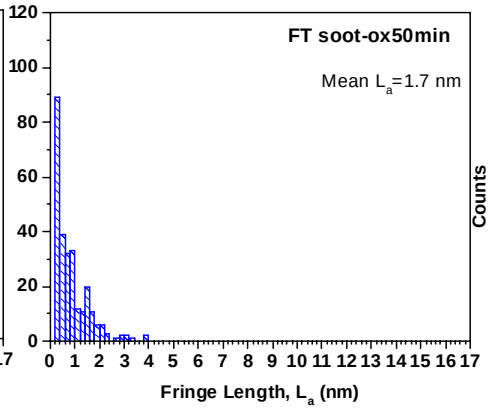
20% burnoff



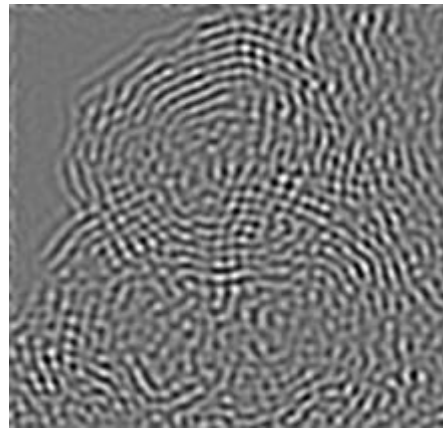


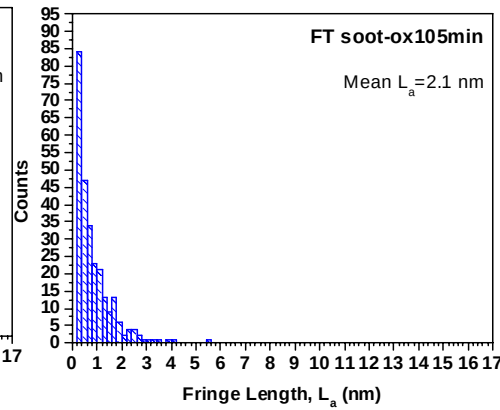
40% burnoff



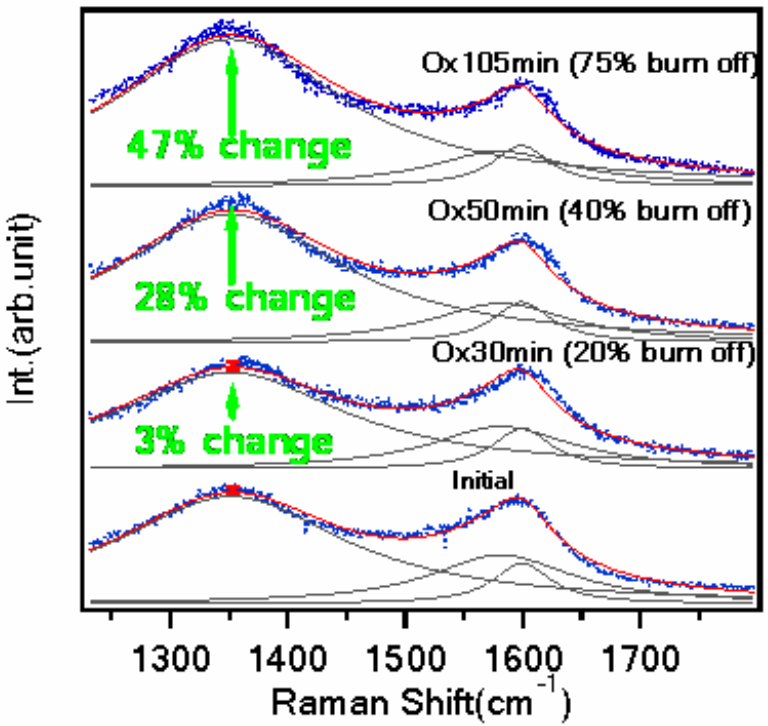


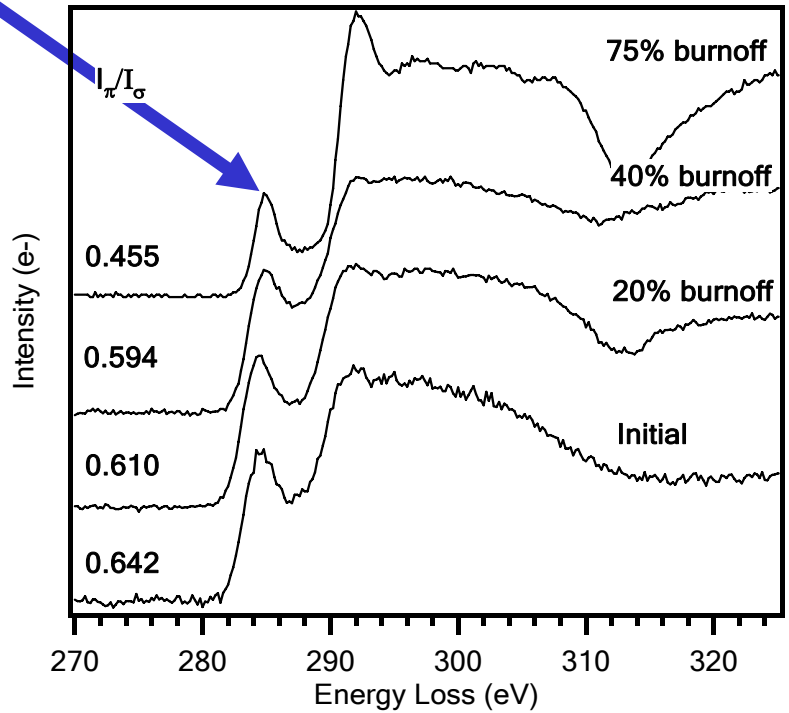
75% burnoff



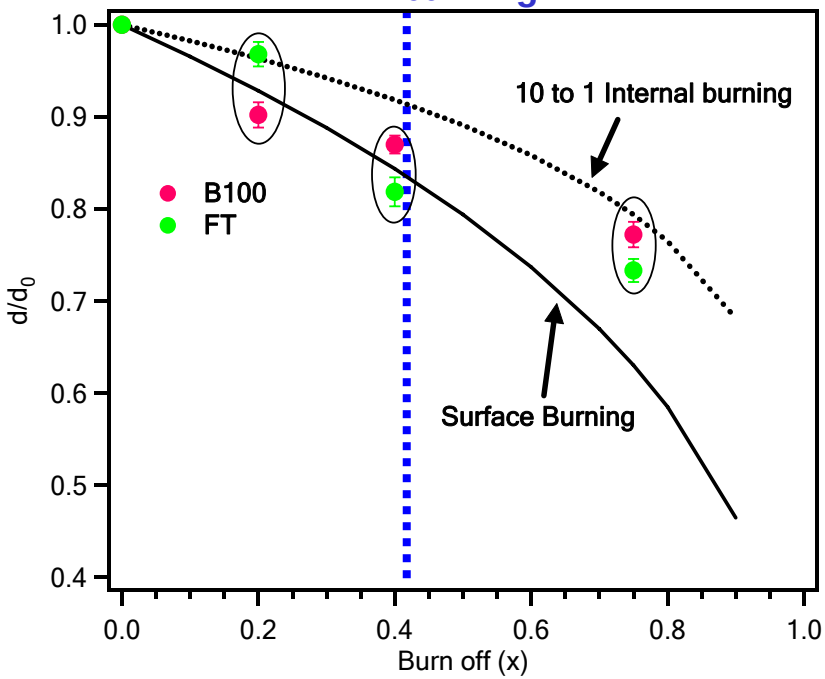


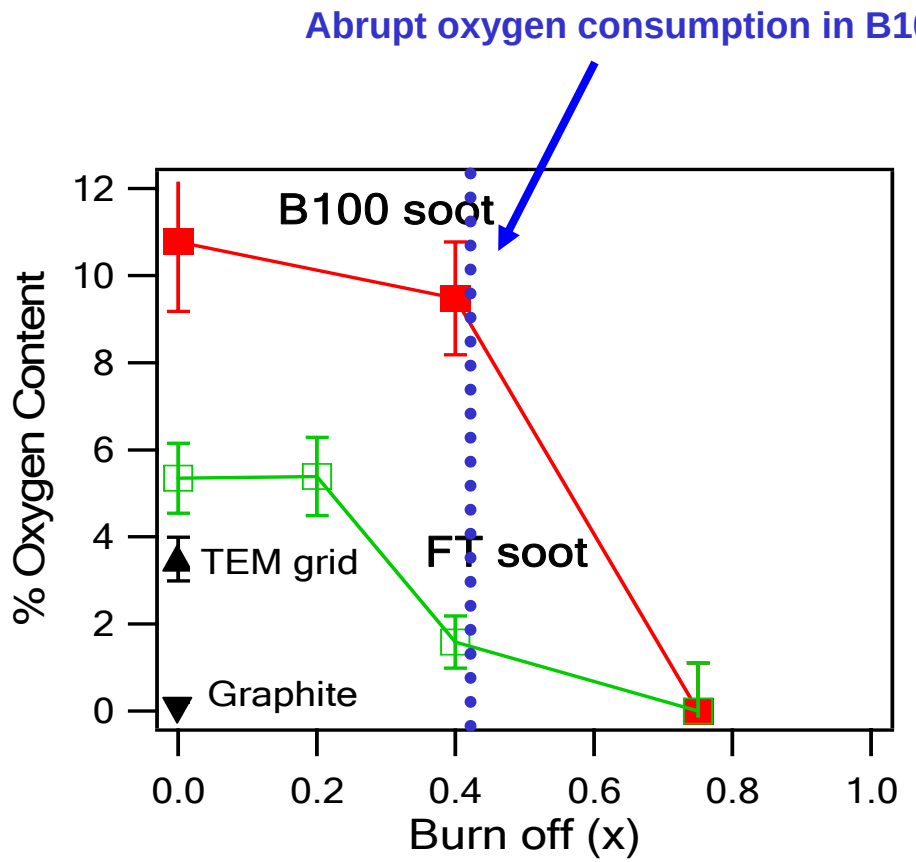
Gradual increase in D band and decrease in relative ratio of graphitic peak suggesting a tendency toward disordered state





Comparison of Burning Regime





Summary

- **B100 soot results in capsule type oxidation through internal burning, leading to a more ordered layer arrangement**
- **FT100 soot undergoes surface burning and less layer rearrangement than B100 soot, even at 75% burn off**
- **Early dramatic changes in inner structure and subsequent hollowing out of primary particles is a crucial factor in enhancing oxidation**
- **Surface reactivity involved in the early stage oxidation also seems to be responsible for a layer arrangement at later stage**

Conclusions

- **Generalized Transition from surface burning to internal burning/layer rearrangement at later stage of oxidation**
- **Enhancement of oxidation and its unique process with B100 soot**
- **Importance of surface oxygen groups for a faster oxidation and layer arrangement**

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