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EMISSIONS FROM ETHANOL – GASOLINE BLENDS: PHYSICAL & CHEMICAL CHARACTERIZATION OF SIDI PARTICULATES

Chethan K. Gaddam, Randy L. Vander Wal

2012 DOE Crosscut Workshop on Lean Emissions Reduction Simulation

April 30th – May 2nd, 2012

University of Michigan – Dearborn

Acknowledgements:
(Project title: **SIDI Fuel Neutral Particulate Study**)

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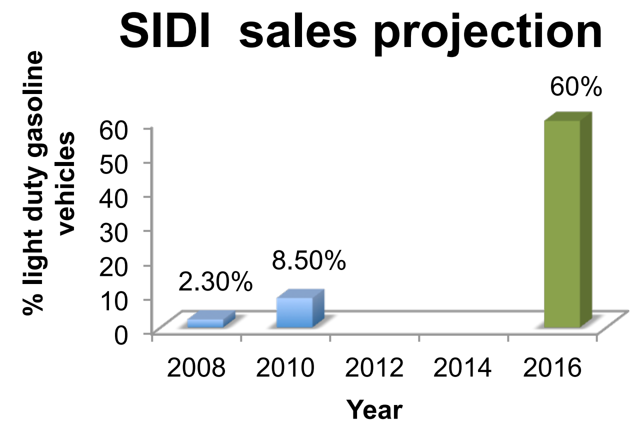
INTRODUCTION

- SIDI engine deployment and particle emissions

fuel efficiency

reduce CO_2 emissions

PN emissions



- Gasoline exhaust particles
  - Health effects – asthma, lung cancer, respiratory & cardiovascular diseases
  - Climate effects – scattering & absorbing light, cloud nuclei

- Blending ethanol with gasoline
  - Octane enhancement
  - EU promotes bio-fuel use (5.75% by 2010 and 10% by 2020)
  - Ethanol trade – increase 25 fold by 2020

J. P. Szybist et al., 2011; D. D. Dutcher et al., 2011; J.M. Storey 2010

Motivation

- OEMs want to anticipate future requirements
  - when filtration is required
  - Nature of regulations (EU, California ?)
- If particulate filtration is required
  - Clues to adaptation of DPF technology
  - Particulate size and shape
- Remove volatile content
- SIDI particle morphology
  - Mathis et al. (2004) – volatility of 20 nm dia. particles
  - Barone et al. (2012) – primary particle & droplet dia.

MOTIVATION

Nanostructure

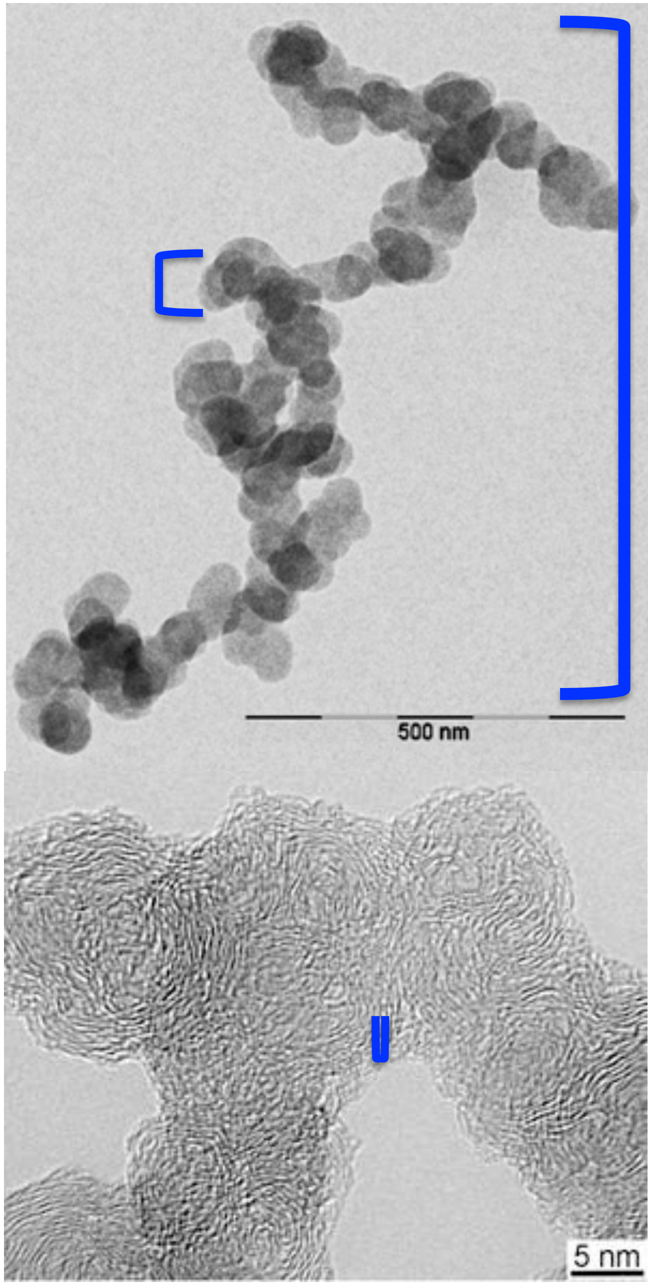
- It will control oxidation characteristics
- Convolved with soot surface chemistry

Aggregate Morphology

- Dictates surface area available for heterogeneous chemistry

Aggregate Size

- Affects light absorption and scattering properties of soot, important for radiative forcing calculations.



Vander Wal et al., 2003, 2004, 2006..

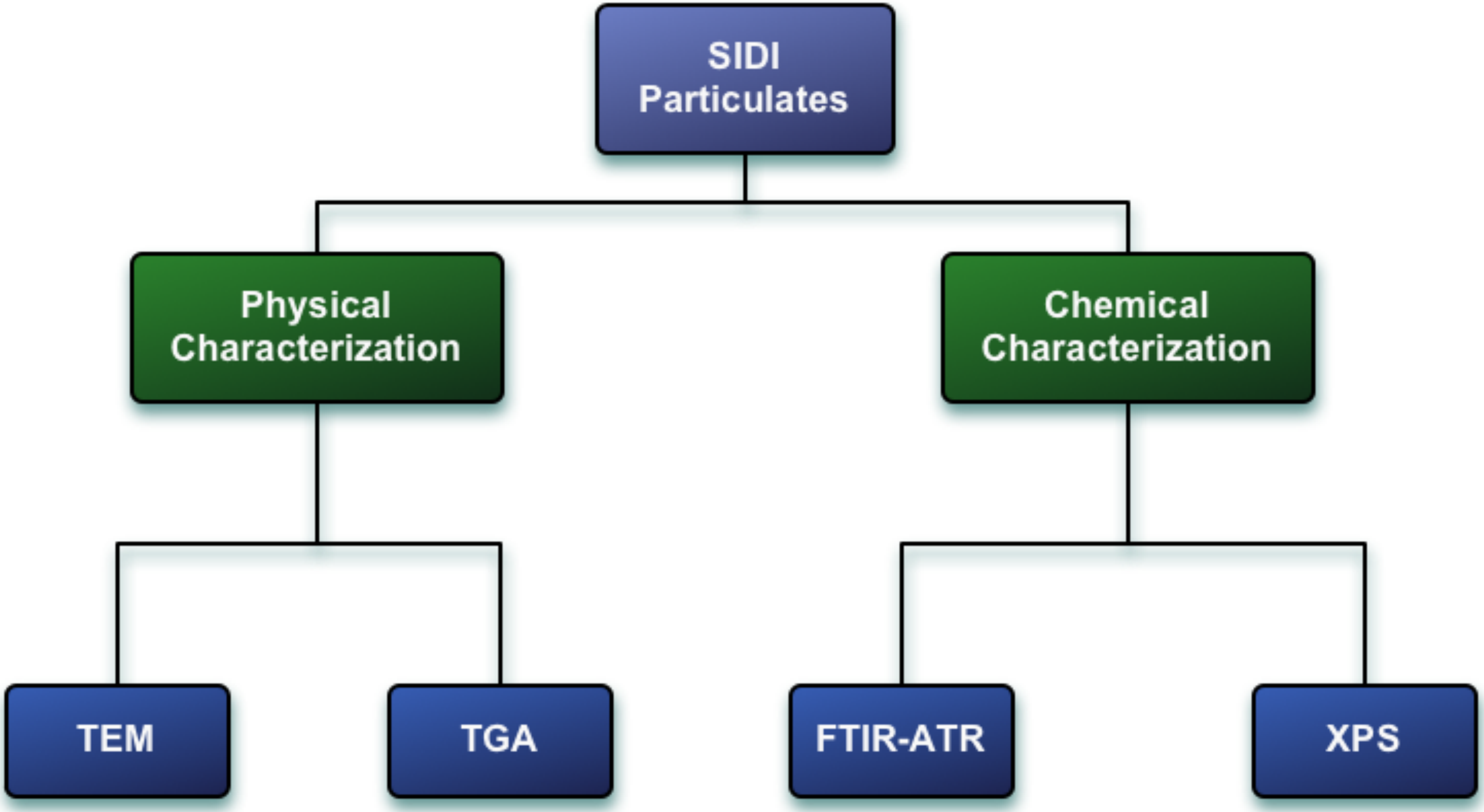
OBJECTIVES

- Systematic characterization of SIDI soot
  - Particle size distribution
  - Soot morphology
  - Nanostructure
  - Oxidative reactivity
  - Chemical composition

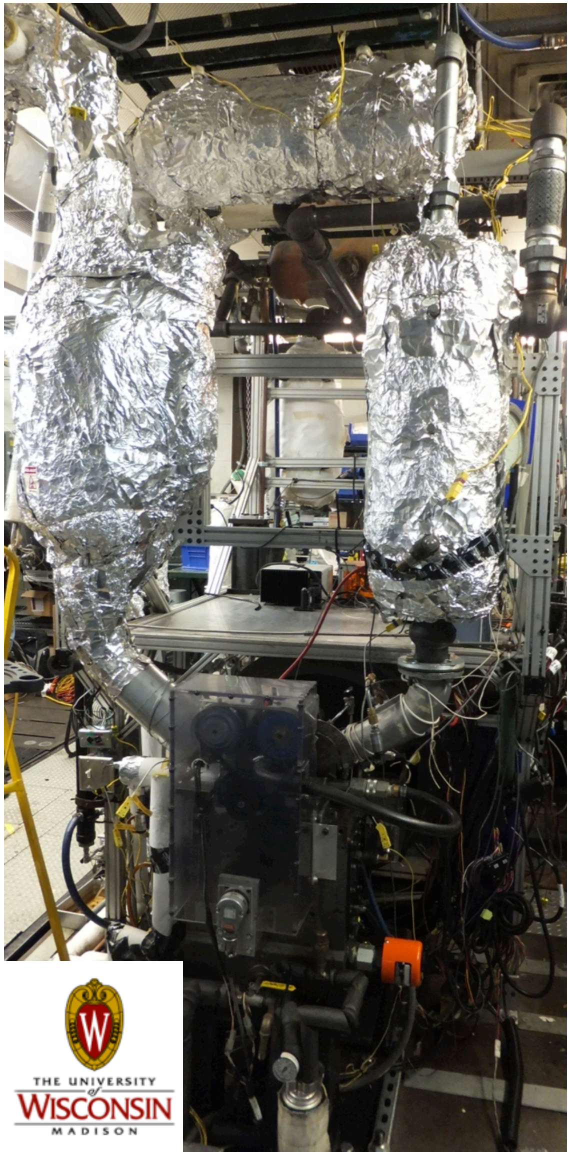
OUTLINE

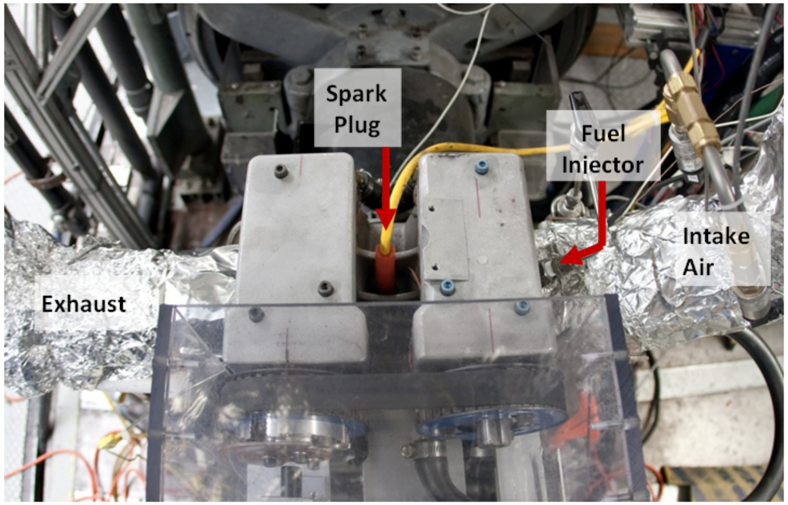
- Introduction
- Objectives
- Approach
- Experimental setup
- Results
- Summary & Implications

APPROACH


SIDI Particulates
Physical Characterization
Chemical Characterization
TEM
TGA
FTIR-ATR
XPS

SIDI Engine



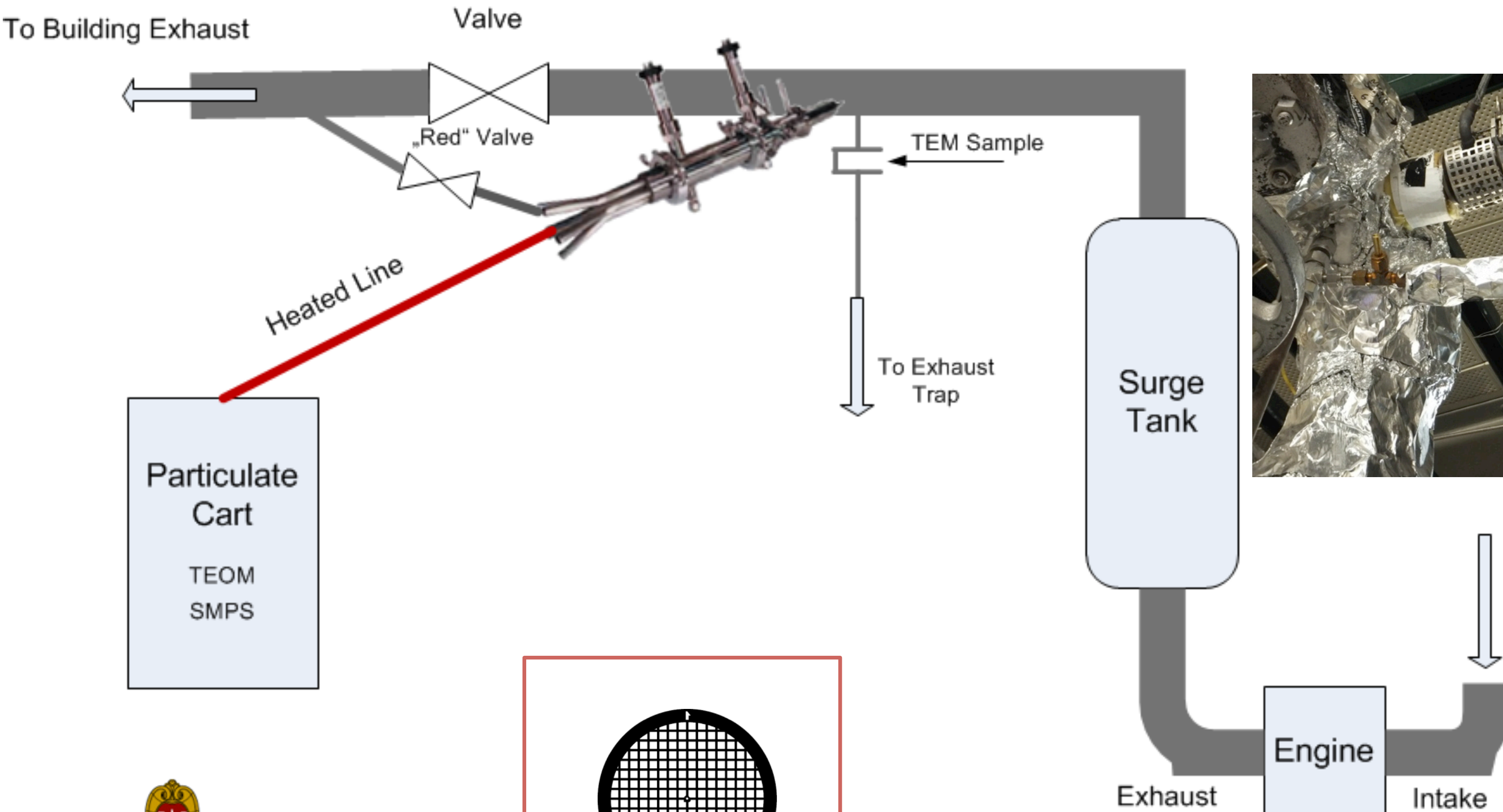


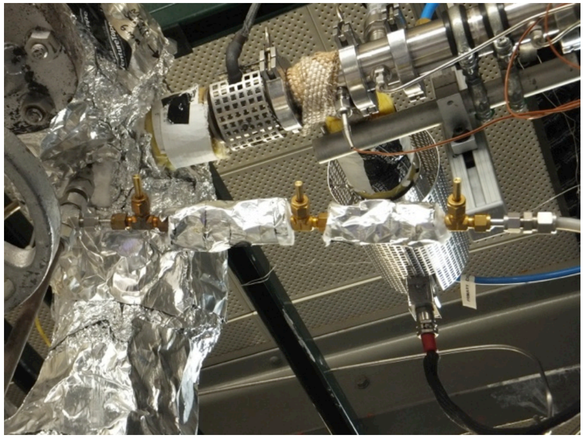
Engine Parameter	Units	Value
Compression Ratio	[-]	11.97
Bore	[mm]	85.96
Stroke	[mm]	94.6
Displacement	[cm^3]	549
Clearance Volume	[cm^3]	50
Connection Rod Length	[mm]	152.4

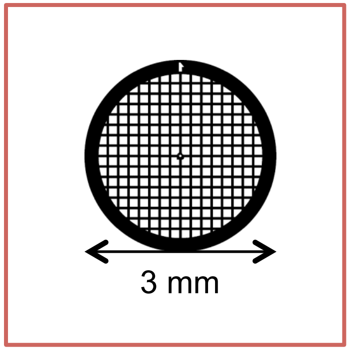
Gasoline direct injected Ricardo Hydra

- Single cylinder research engine
- Four-stroke engine

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

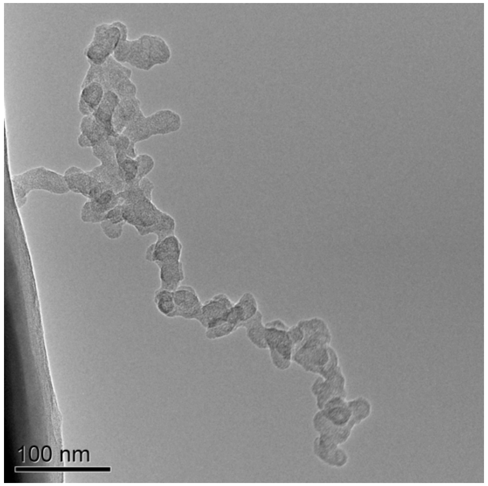
Engine Operating Conditions

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

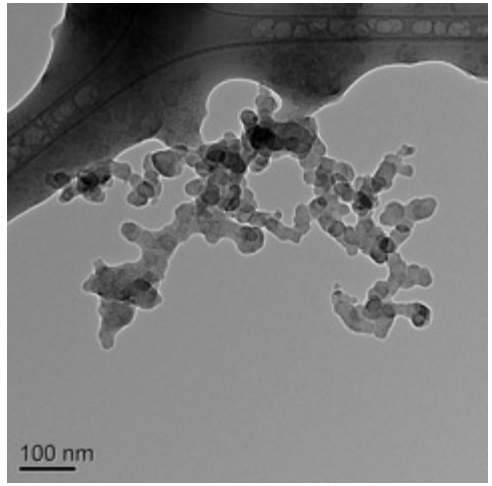
Results

Physical Characterization

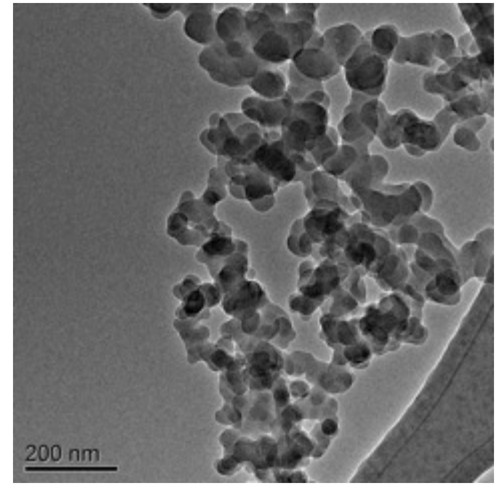
Aggregate Morphology



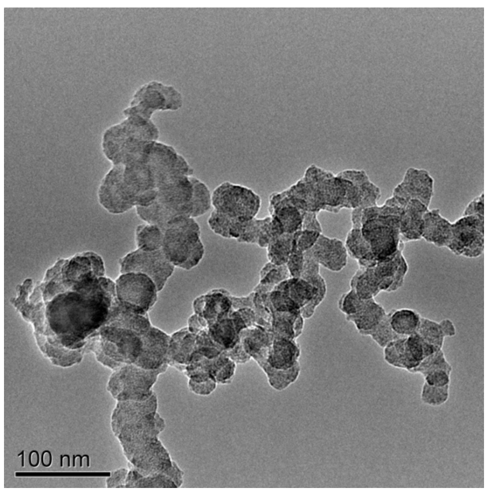
EEE – EOI 280



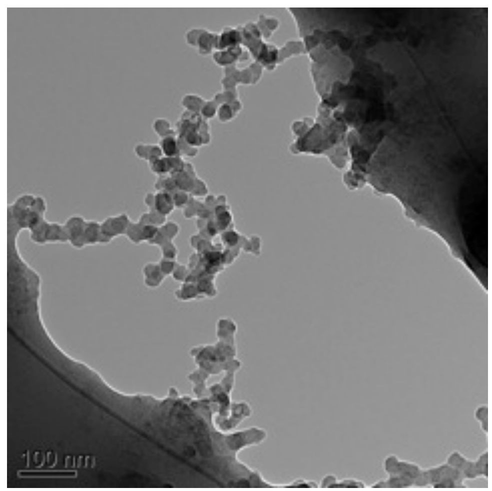
E20 – EOI 280



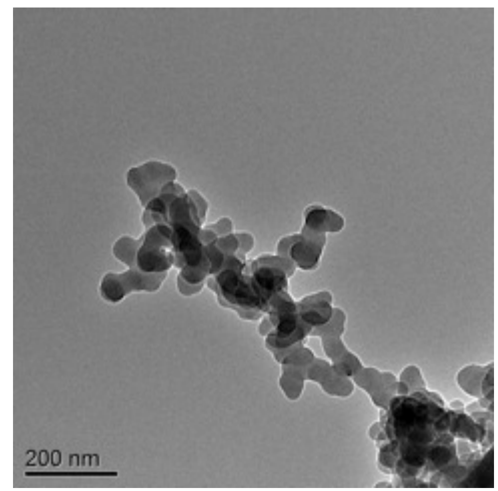
E85 – EOI 280



EEE – Lean



E20 – Lean

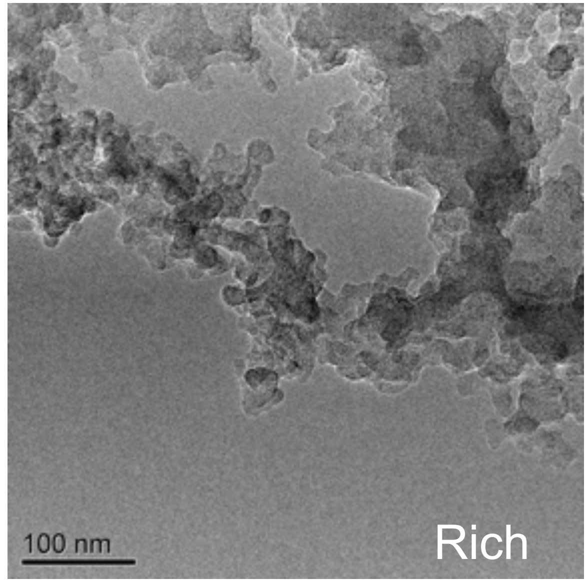


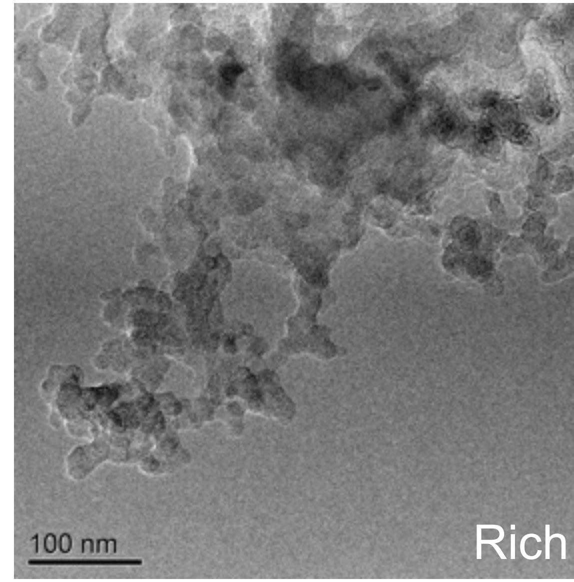
E85 – Lean

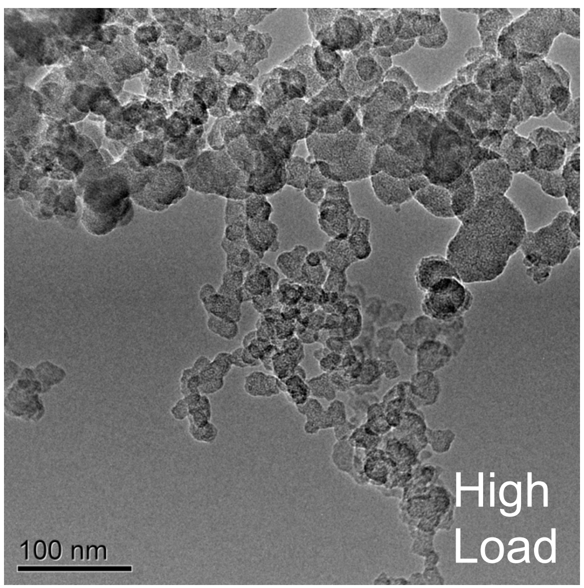
- EEE and E20 – open, branched
- E85 – dense, compact
- Growth after aggregation for E85

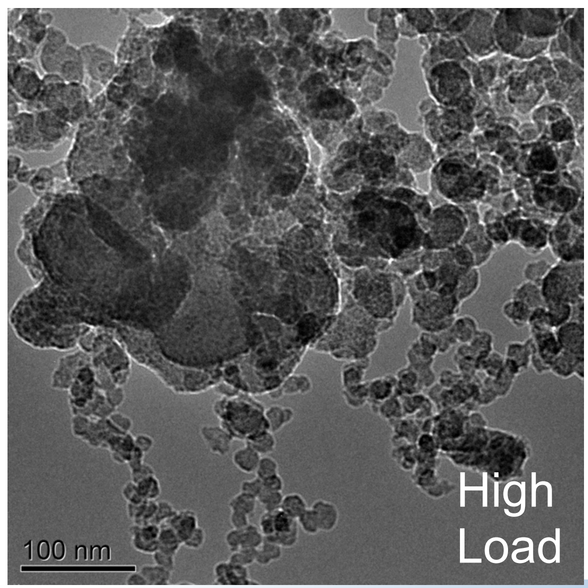
AGGREGATE MORPHOLOGY

- Denser, compact
  - nucleation density
  - rate of concurrent/ subsequent surface mass growth



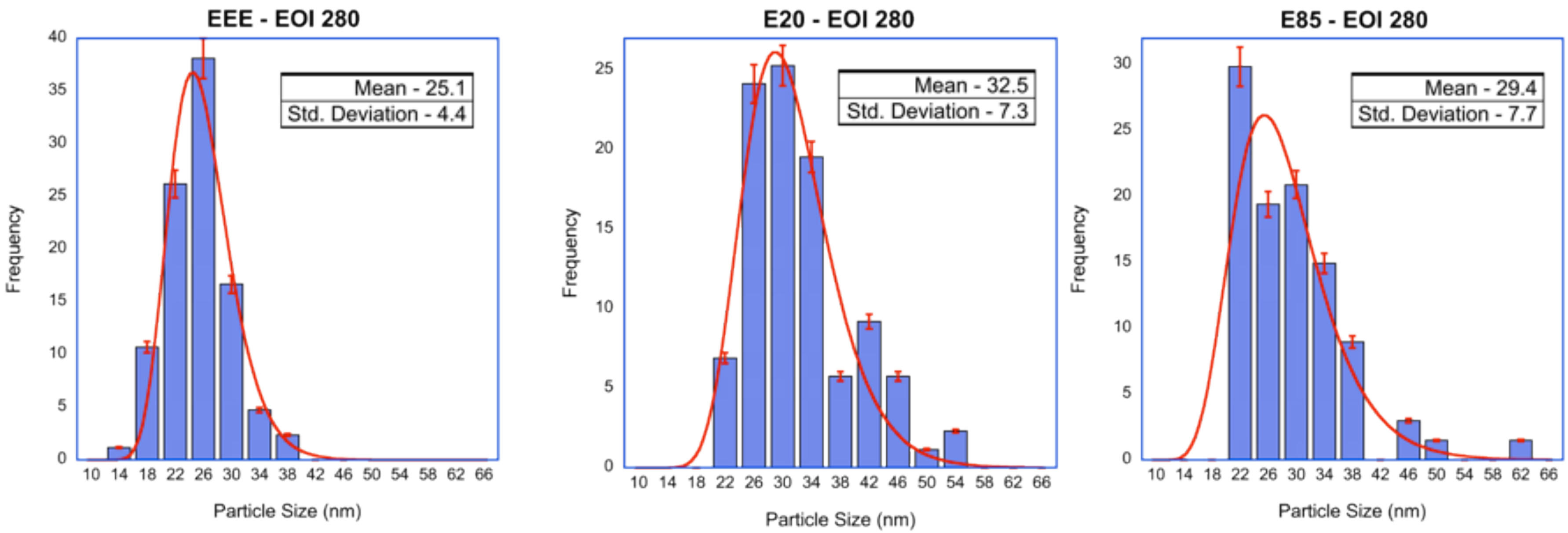






- Significant variation in primary particle size within aggregate

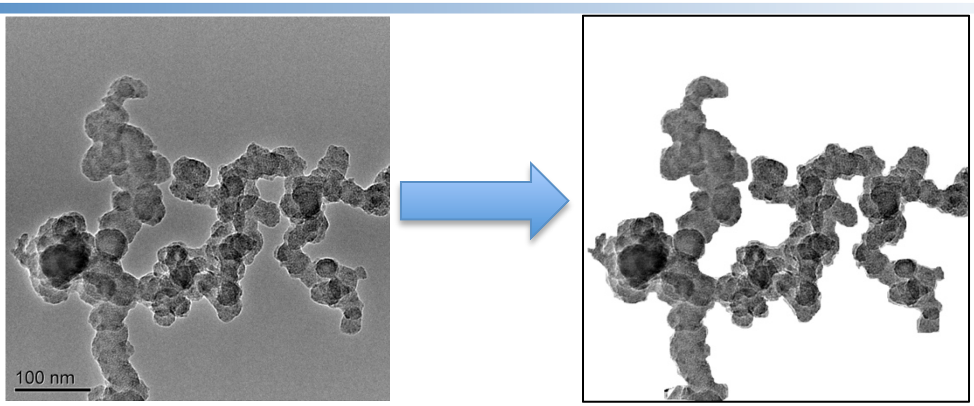
Primary Particle Size Distributions



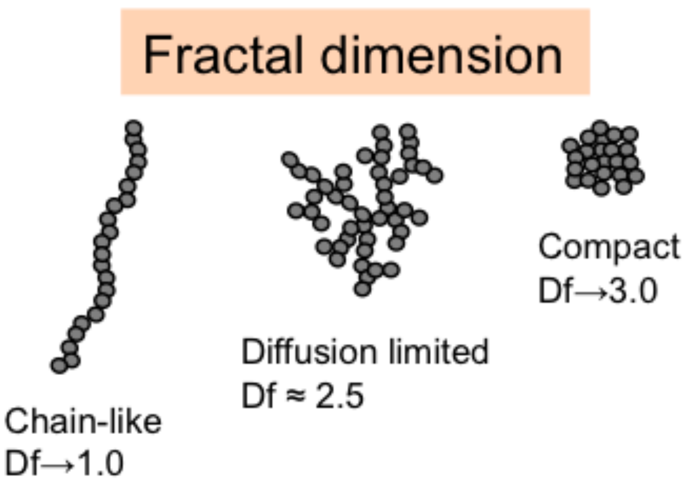
- Mean particle size ~14 – 51 nm
  - Diesel soot ~19 – 35 nm
- Primary particle size
  - Strong variation with fuel blend

Lee et al., 2002; Wentzel et al., 2003; Park et al., 2004;
Zhu et al., 2005; Neer and Koylu, 2006; Barone et al., 2011

Fractal Dimension



Engine Parameter	Fractal Dimension
Late EOI	2.20
Rich	2.37
EOI 280	1.69
Lean	1.86
Heavy Load	2.06

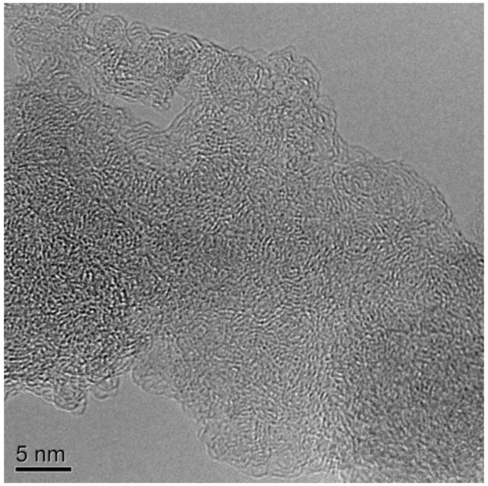


- Aggregate – fractal like structures
- Irregularity – fractal dimension, D_f,
- Power law relationship $n_{po} = K_f \left(\frac{d_g}{d_{po}}\right)^{D_f}$

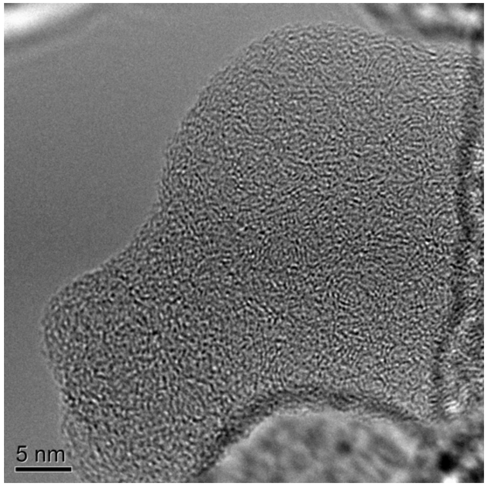
M. Lapuerta et al., *J. Colloid and Interface Science*, July 2006.

NANOSTRUCTURE

EEE

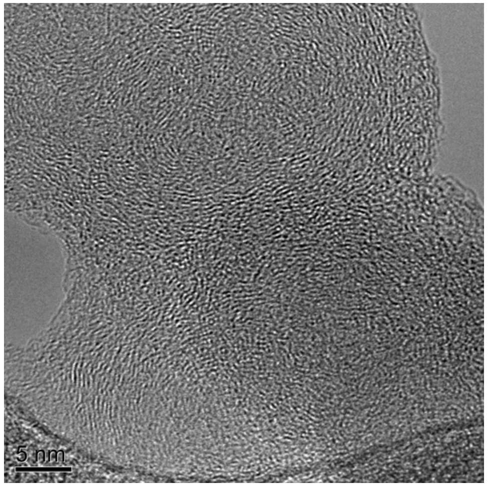


Late EOI
Highly curved, amorphous

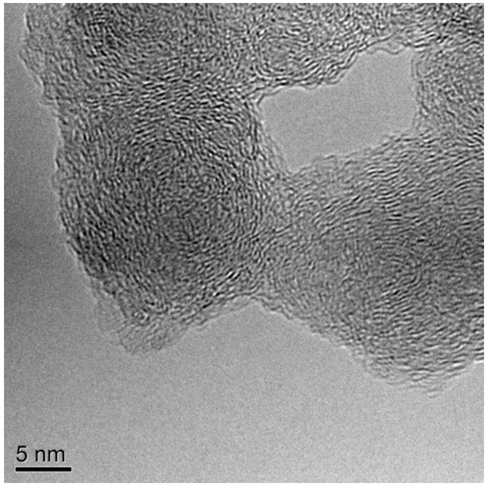


Rich
Amorphous

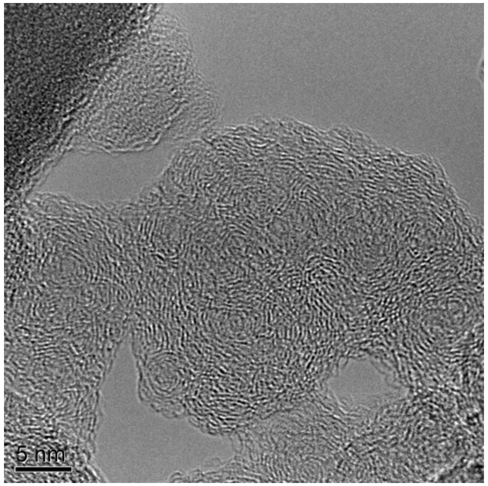
- Nanostructure – graphene layer plane dimensions, their tortuosity and relative orientation
- Nanostructure was generally amorphous or lacked significant order



EOI 280
Better order with short but recognizable lamella

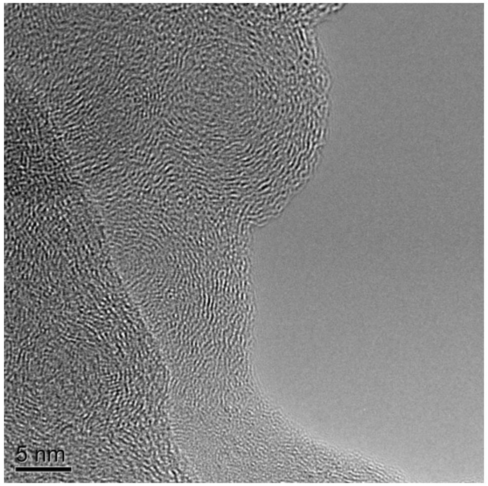


Lean
Disorganized, but not chaotic

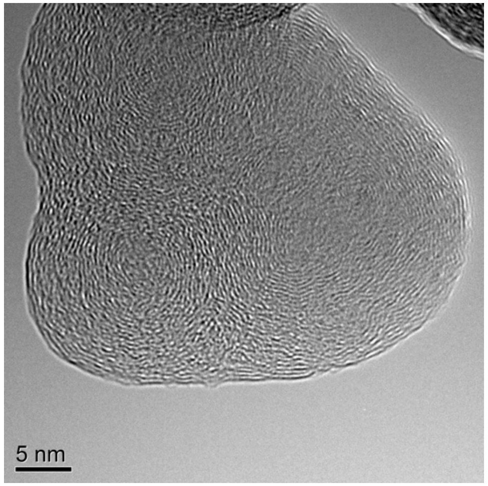


Heavy Load
Recognizable nanostructure

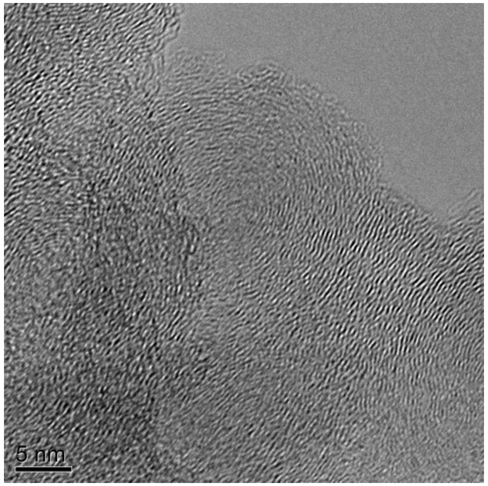
NANOSTRUCTURE E20



E20 – EOI 280



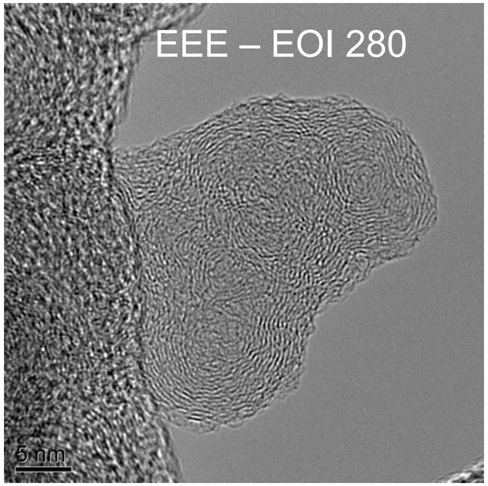
E20 – MBT -15

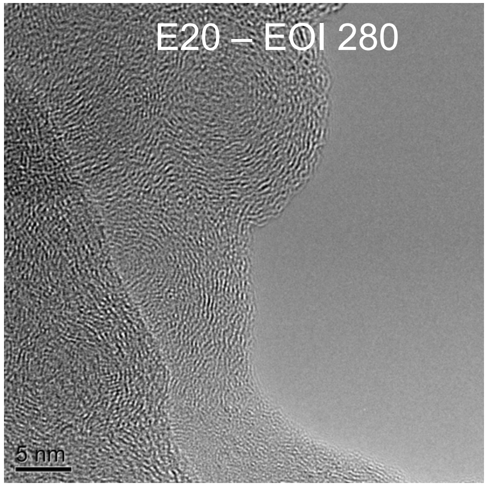


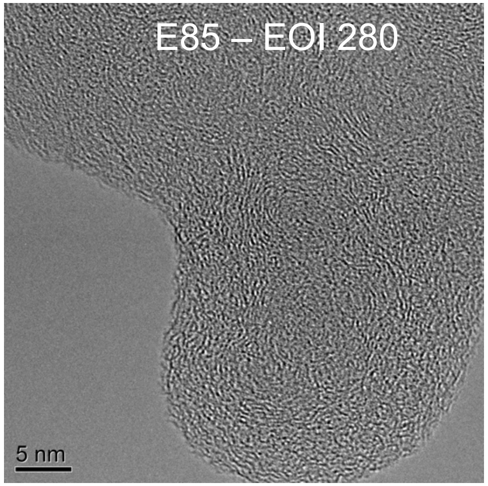
E20 – Lean

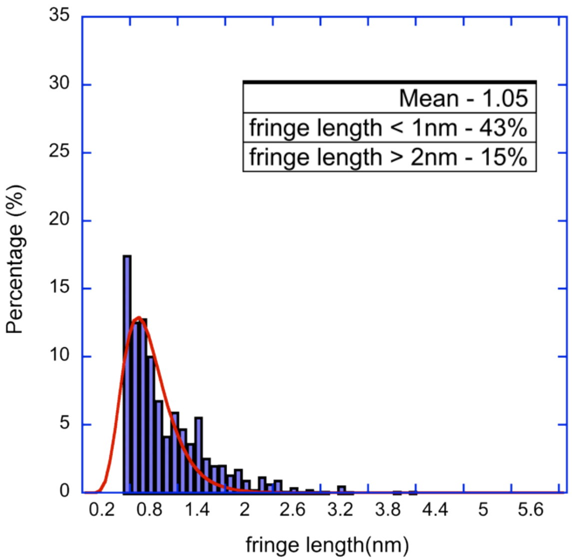
- Nanostructure is mostly amorphous & non-structured
- Across test conditions for given fuel, nanostructure largely unvarying, *with one exception*

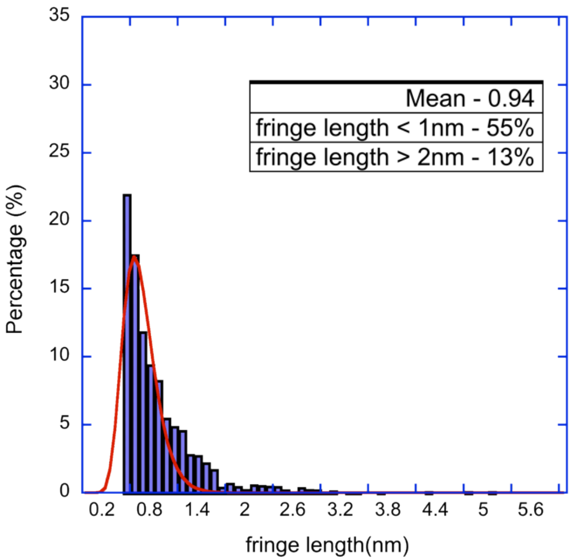
EOI 280 CONDITION

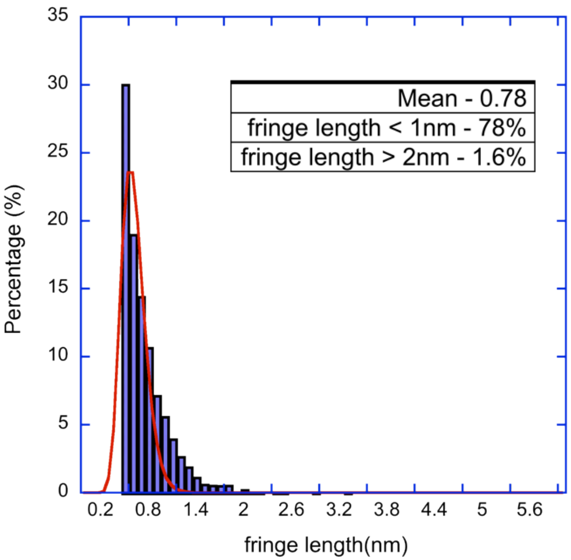






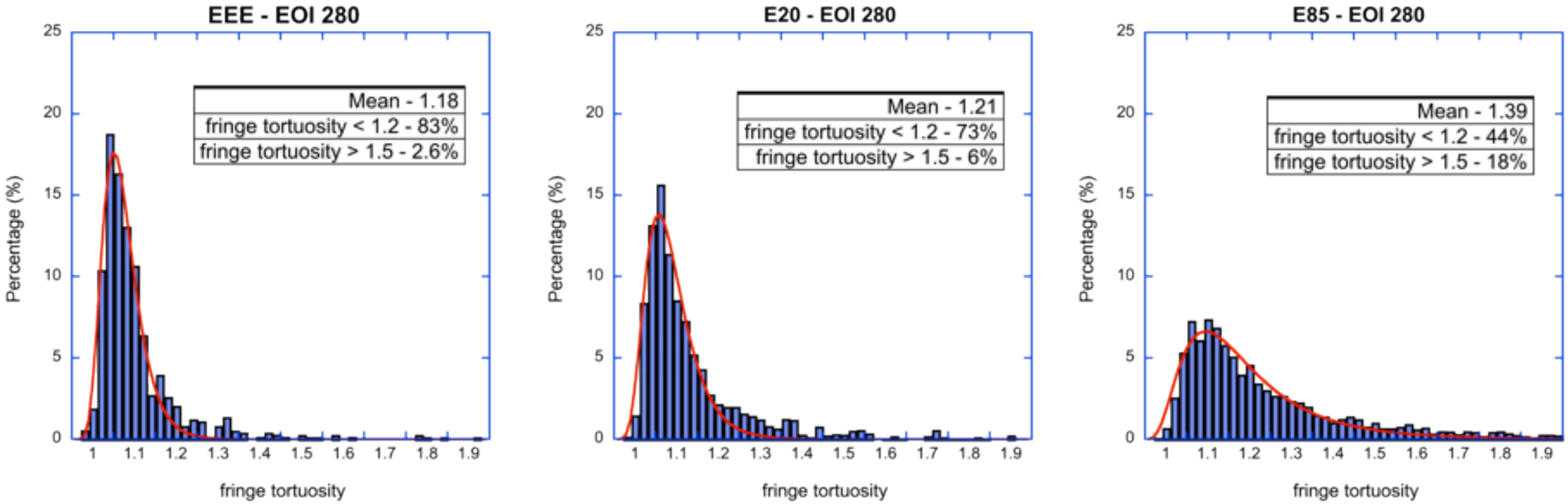






Vander Wal et al., 2003; Kuen et al., 2011

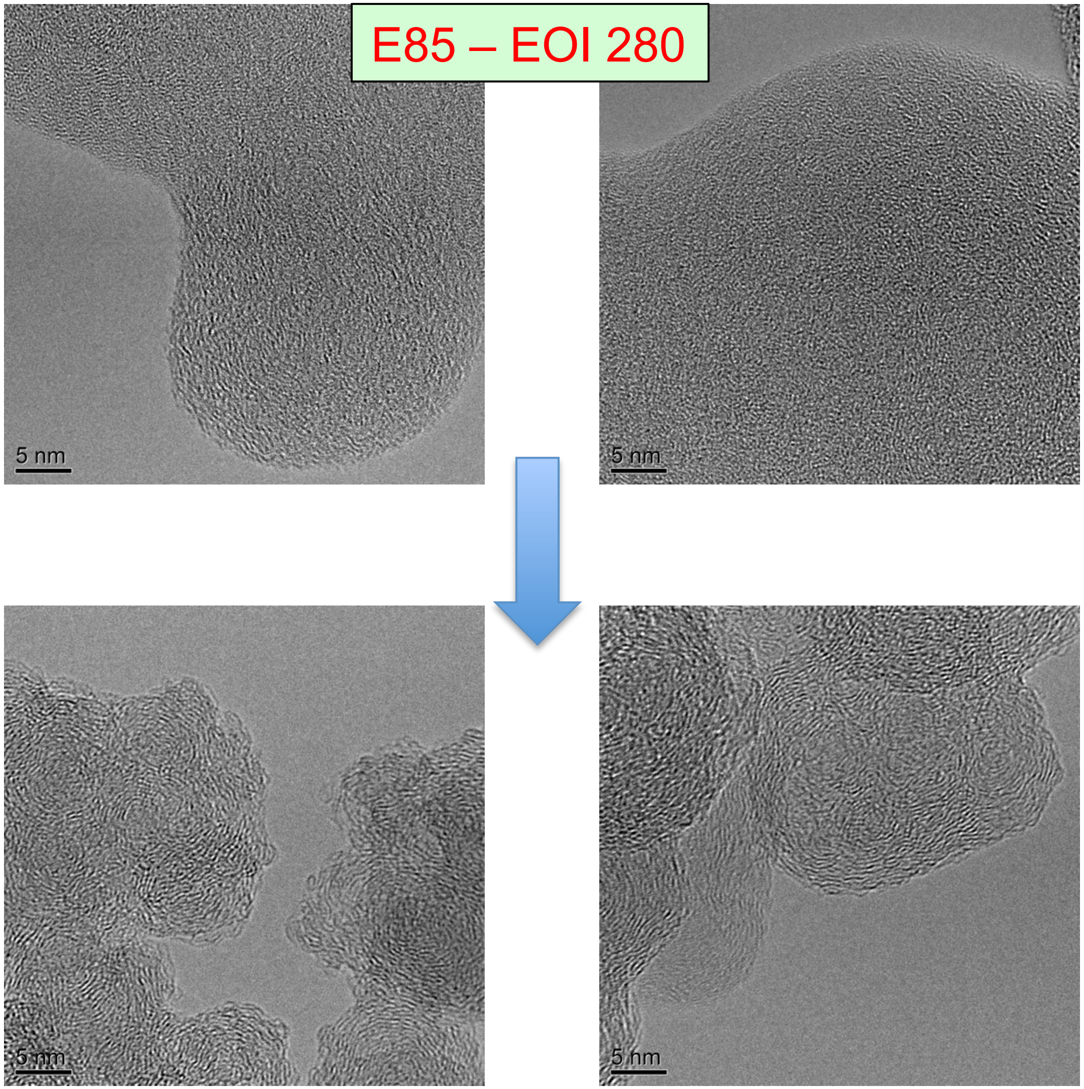
EOI 280 Condition



- Strong variation as evidenced by tortuosity distributions
- E85: More tortuosity – indicative of high curvature
- Implications of fuel oxygen content:
    - a) soot forming processes might be delayed
    - b) chemistry of soot formation is altered
    - c) overall soot production is lessened

Partial Oxidation

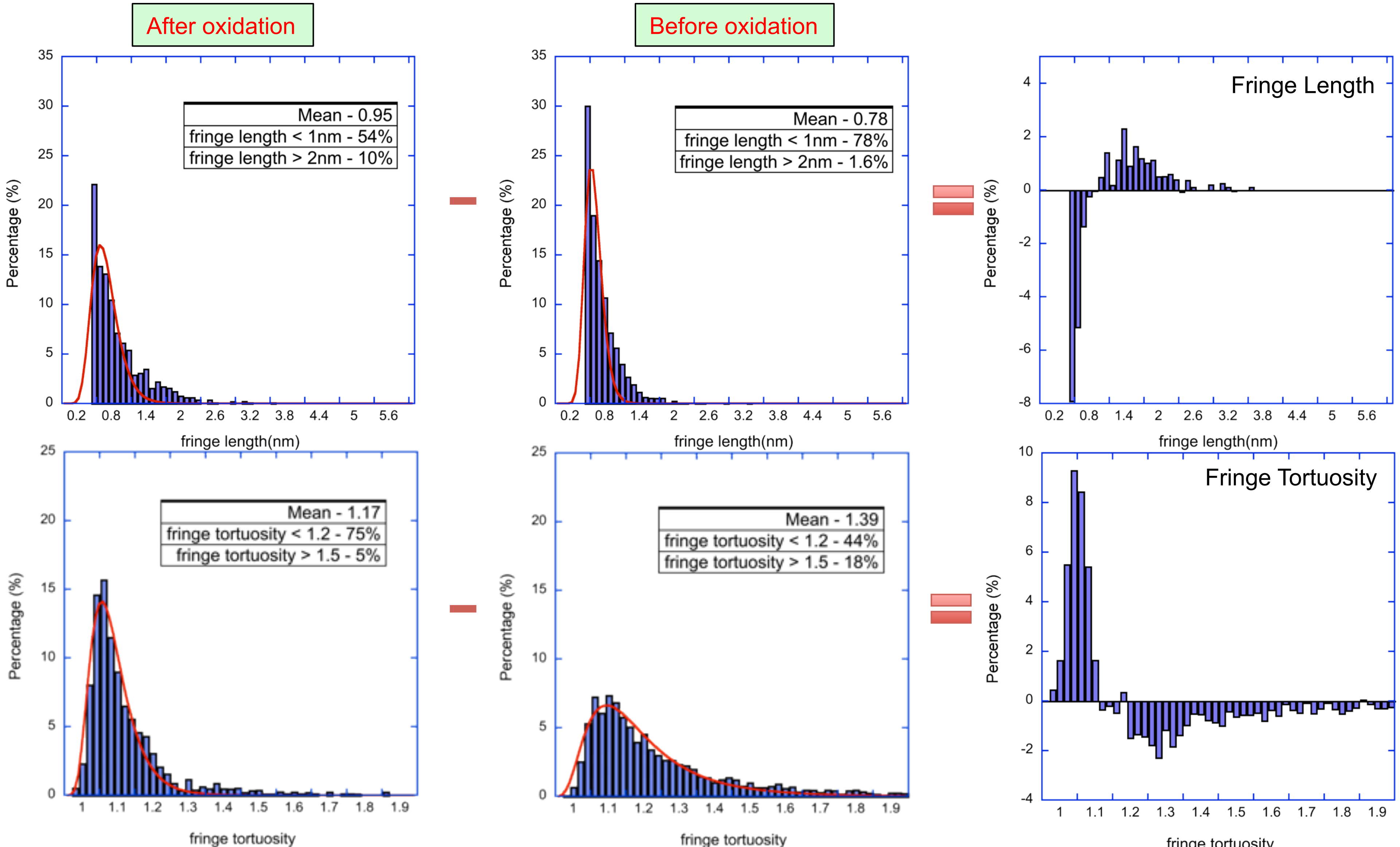
E85 – EOI 280



E85 – EOI 280 – after oxidation at 550 ^{0}C

- **First [known] observation for soot oxidation from a Gasoline engine**
- Evidence of oxidation – induced structural change
- HRTEM and fringe analysis repeated after partial oxidation of EOI 280 sample (E85 fuel)

COMPARATIVE FRINGE ANALYSIS

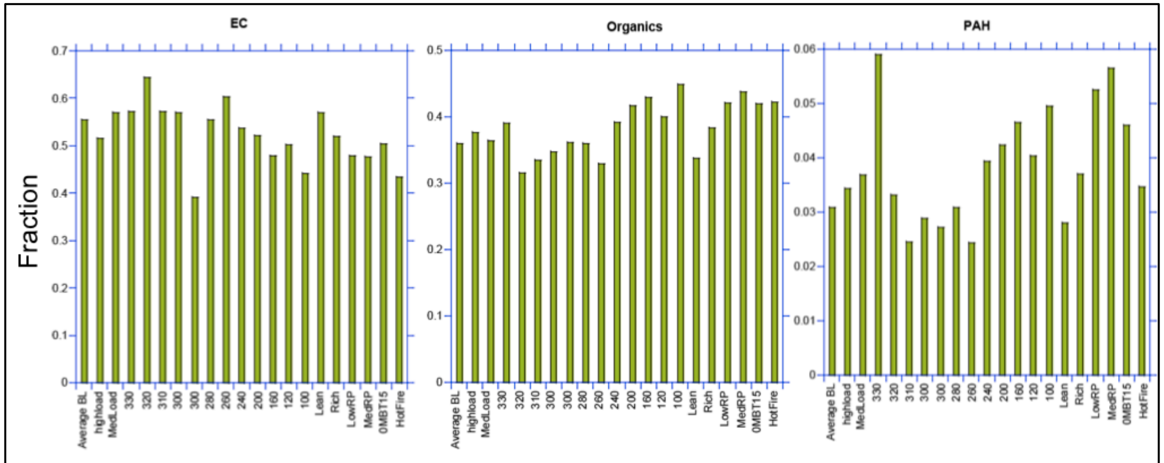


- Distinct change in nanostructure during oxidation
- Lamella become more longer, flattened

Results

Chemical Characterization

MOTIVATION



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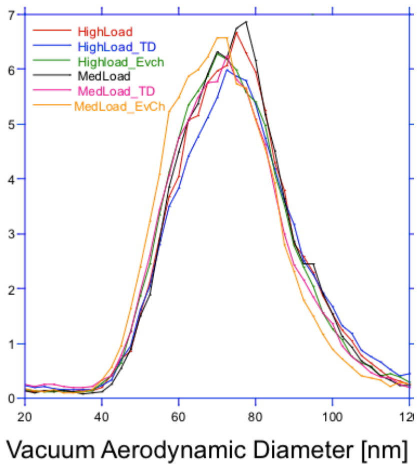
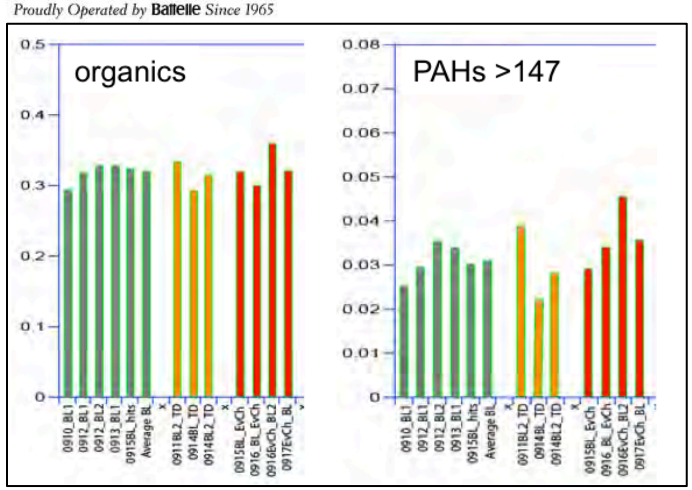
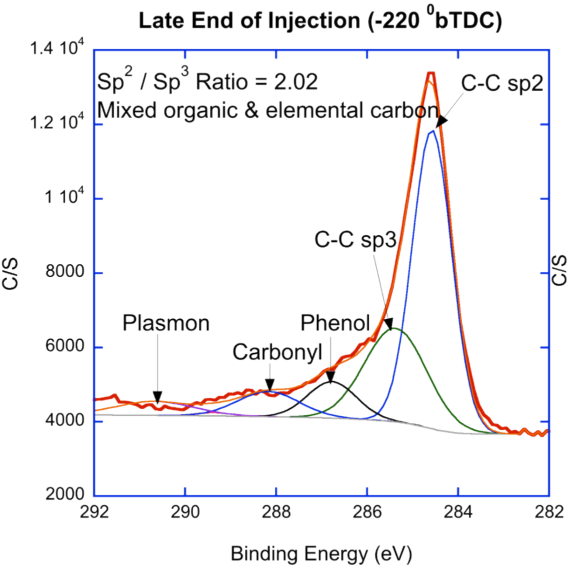
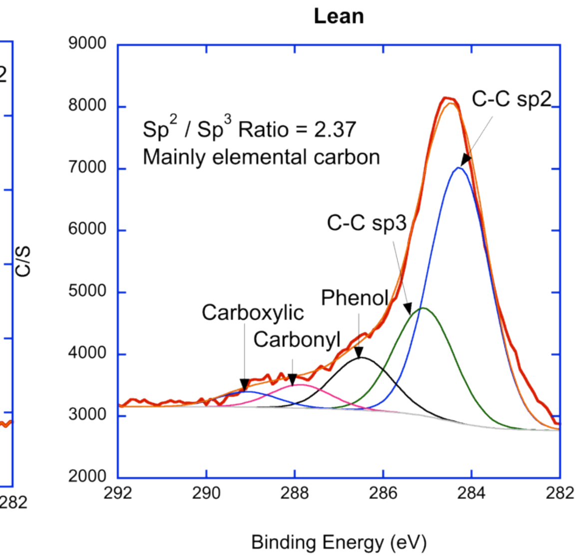




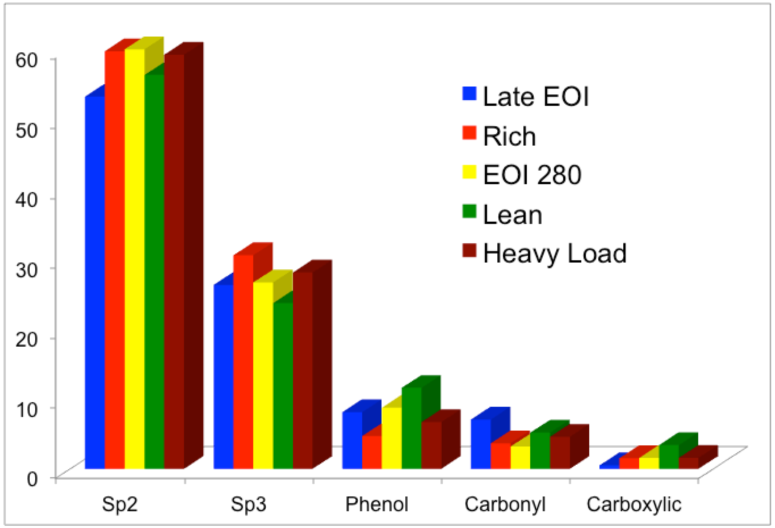
- SPLAT II – significant organic content (40%)
- Two VPR methods
  - Thermodenuder & Evaporative chamber
  - No difference
- Spectroscopy Tech.
  - XPS (Surface..)
  - FTIR-ATR (Bulk..)

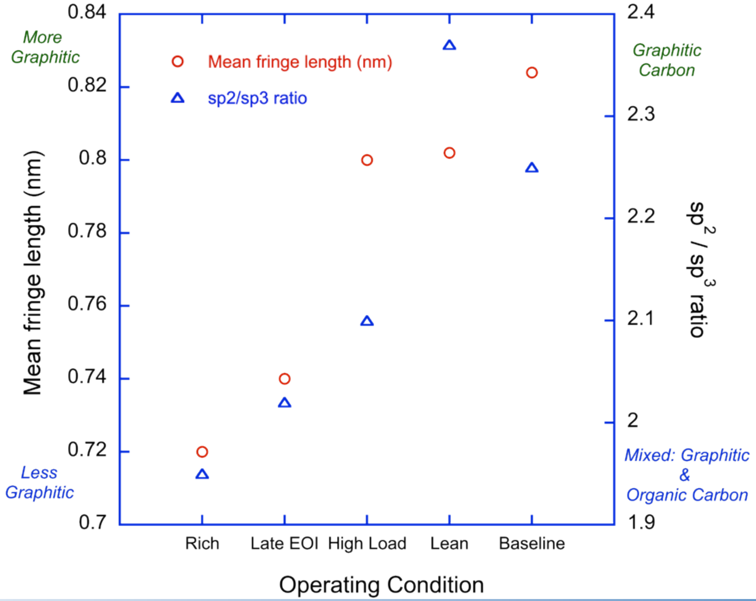
XPS



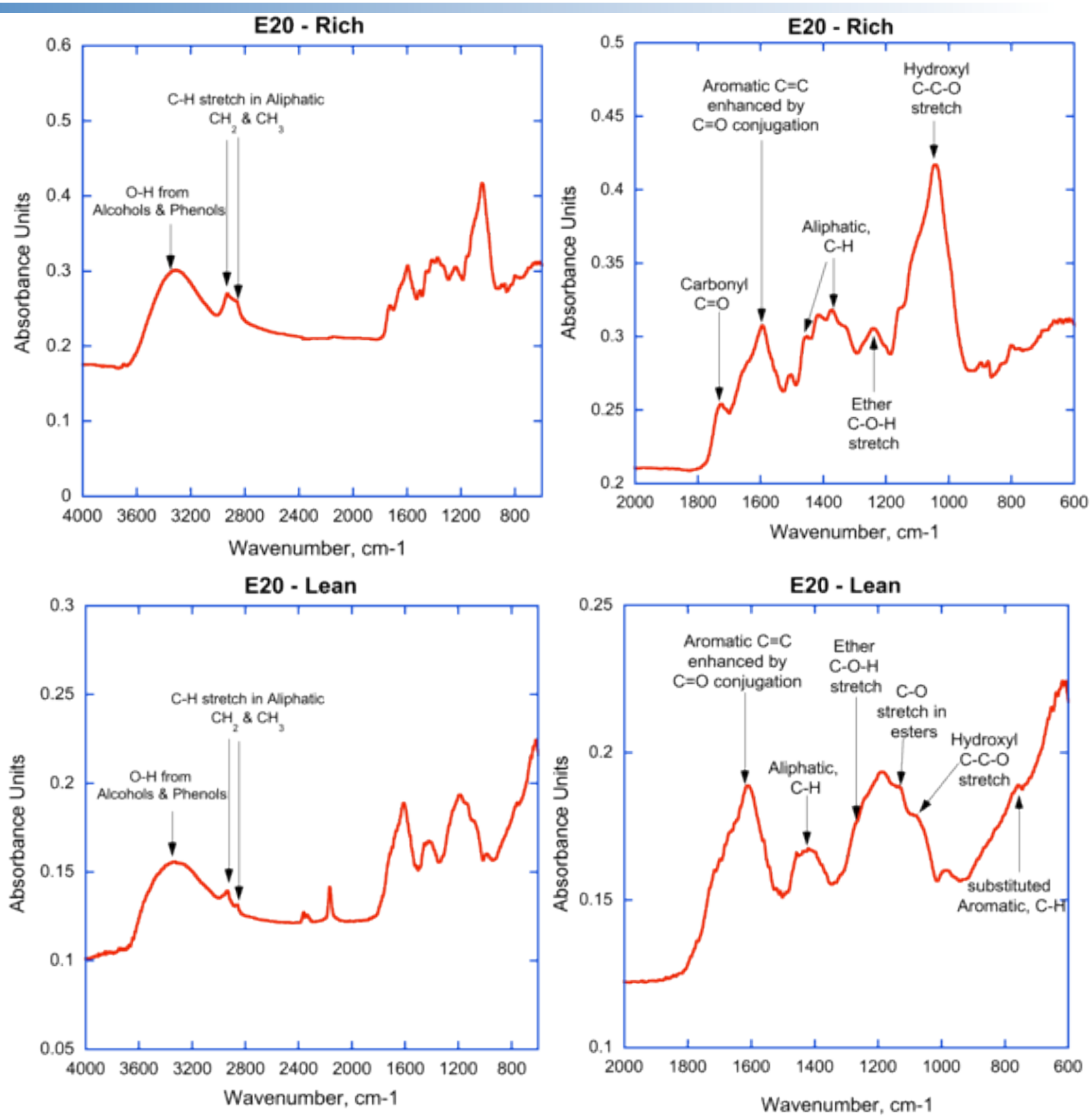


- Substantial organic content
- Consistent with TEM results





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

Summary & Implications

- Primary Particle Analyses
  - Variation of primary particle size as a function of condition, fuel
- Aggregate Morphology
  - Fuel rich conditions: aggregates that are more compact
  - E85: high fusion between particles
- HRTEM & Fringe Analyses
  - General lack of structure, across range of conditions & fuel blends
- Partial Oxidation
  - Distinct change in nanostructure during oxidation
  - Lamella become more longer, flatter
- FTIR – ATR Analyses
  - Indicates significant matrix-distributed organic content
  - Fuel rich conditions led to soots with higher organic content

ACKNOWLEDGEMENTS

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Mark Stewart, Alla Zelenyuk, Andrea Strzelec, Paul Reitz

THE UNIVERSITY of WISCONSIN MADISON

Dr. David Foster, Dr. David Rothamer, Mitchell Hageman, Axel Maier

GM

Kushal Narayanaswamy, Arun Solomon, Paul Najt

MRI Materials Research Institute

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

PENNSTATE 1855

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

Thank You