Investigation of NO_2 Oxidation Kinetics and Burning Mode for Medium Duty Diesel Particulate: Contrasting O_2 and NO_2 Oxidation

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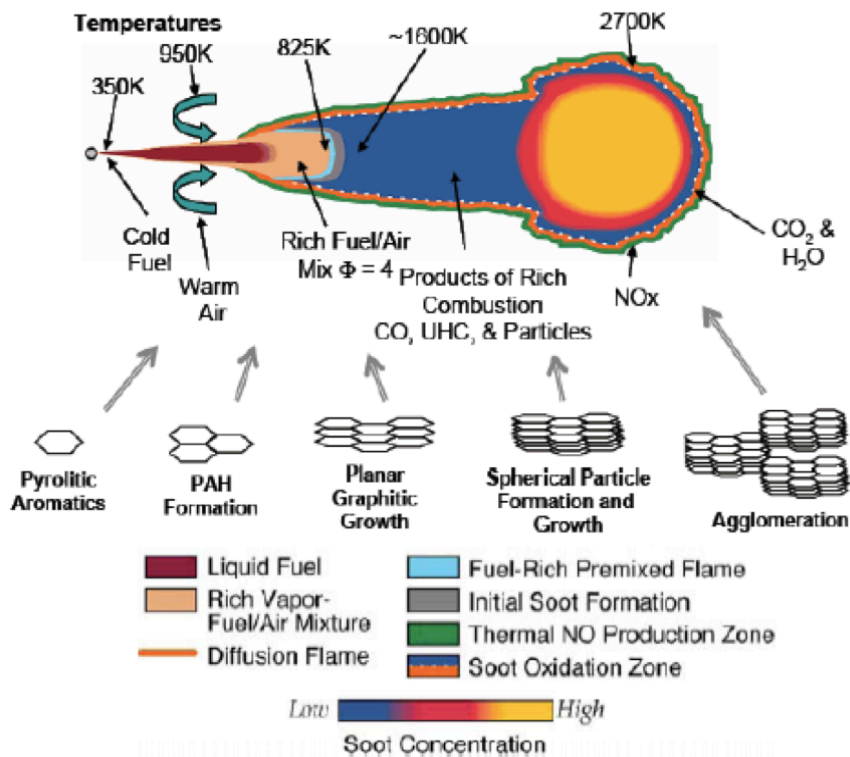
Motivation

- Understanding particulate oxidation kinetics can lessen the fuel penalty, allow greatest possible efficiency advantage for diesels.

- Control of particulate oxidation remains the most challenging issue.

- Too frequent regeneration is inefficient and expensive in fuel.

- Infrequent regeneration can lead to engine inefficiency and/or uncontrolled regeneration events that may damage the catalyst.

- Currently, soot oxidation routines in DPF models treat thermal and catalytic reactions as parameterized global reactions fit to data.
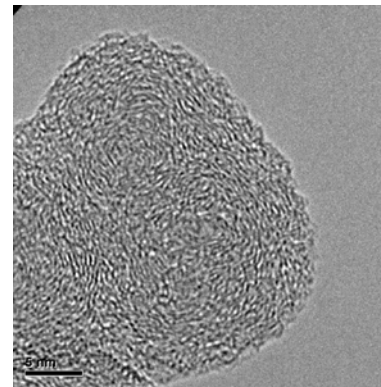
Adapted from http://www.unep.org/tnt-unep/toolkit/Actions/Tool11/Facts.html
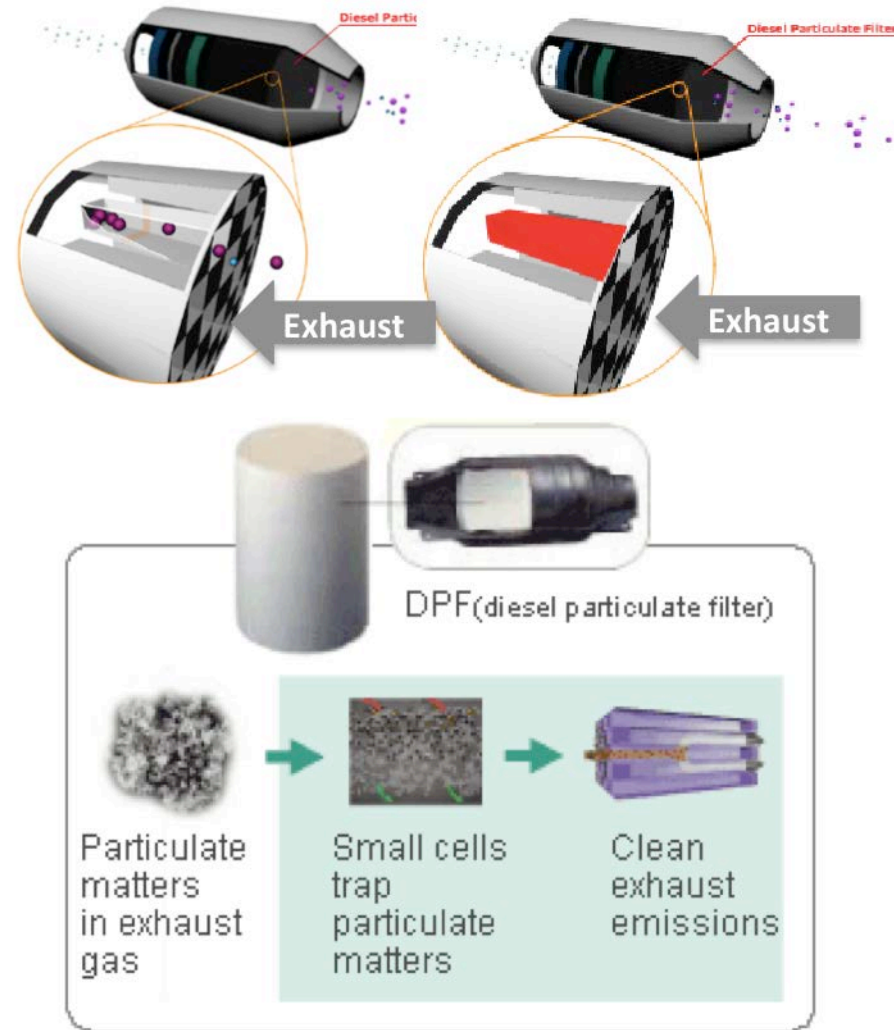
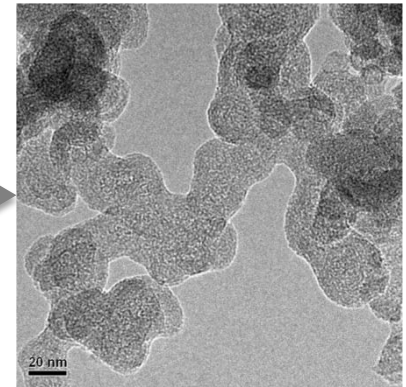# Background: Diesel particulates form from incompletely burned aromatics in fuel-rich regions of the flame

- Graphitic (fixed) carbon backbone with adsorbed (mobile) hydrocarbons.
- Mobile phase is named by how it is removed: SOF vs. VOF.
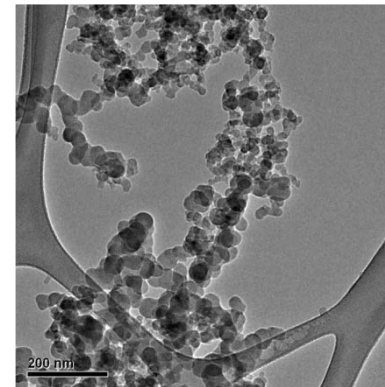- Primary particles form first, function of fuel,T,P, t, and then link together form aggregates and agglomerates.

Dec conceptual model of PM formation, SAE 970973

Primary Particles

Aggregates

Agglomerates

Objectives

- Measure the O_2 and NO_2 oxidation reactivity of a representative range of diesel engine particulates generated under highly controlled conditions

- Correlate reactivity variations with engine parameters and fuel type

- Relate reactivity variations to fundamental differences in particle morphology and chemistry

- Develop oxidation kinetic expressions and parameters suitable for DPF modeling and control.
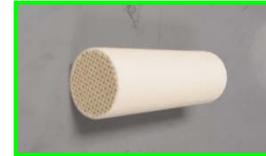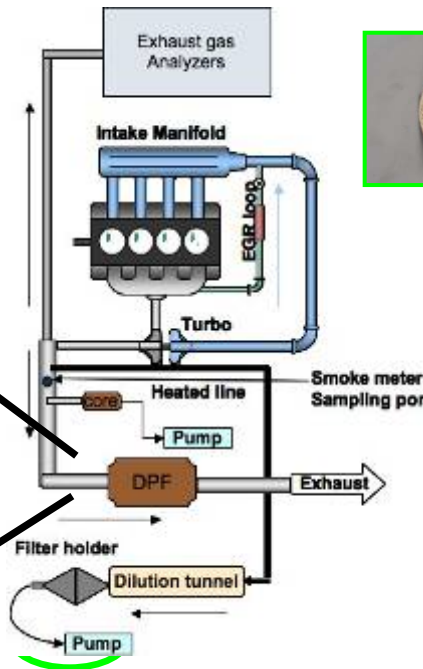
Approach: Measure reactivity, chemical composition, surface area, and microstructure of engine-generated PM samples
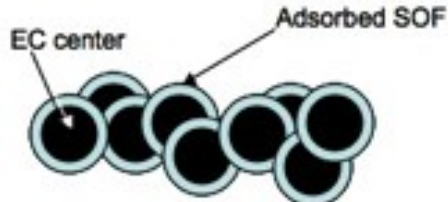
Powder PM samples
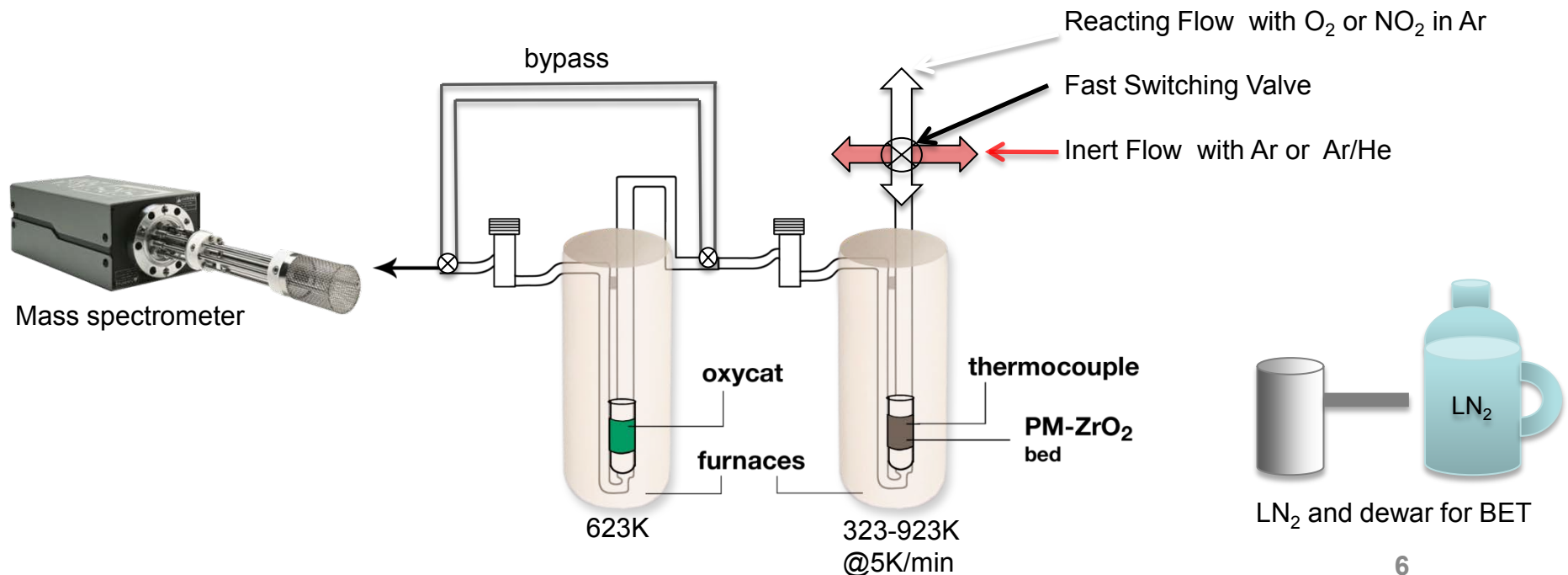
Kinetic Studies, BET

Chemical Analysis

Microscopic Analysis (TEM)

PM generation on Diesel engine dynamometers

Mercedes Benz 1.7L & Cummins ISL engines

Multiple fuel blends (conventional and biodiesel)

Steady operation at different speeds/loads

Highly controlled PM sampling protocols

Oxidation reactivity and surface area measurements utilize a specialized fixed-bed micro-reactor

- ## The micro-reactor operates in multiple modes
  - Temperature programmed desorption (TPD) in Ar removes and measures volatiles
  - Temperature programmed oxidation (TPO) in Ar/O_2 or Ar/NO_2 measures non-isothermal oxidation rates for raw and devolatilized PM
  - Isothermal, pulsed oxidation (IPO) measures oxidation rates for devolatilized PM as a function of temperature, O_2/NO_2 content
  - In situ BET surface area measured by flowing Ar/He uptake at various stages of oxidation without removing the sample

Reacting Flow with O_2 or NO_2 in Ar

Fast Switching Valve

Inert Flow with Ar or Ar/He

bypass

Mass spectrometer

oxycat

furnaces

623K

thermocouple

PM-ZrO_2 bed

323-923K @5K/min

LN_2

LN_2 and dewar for BET

Previously, Temperature Programmed Oxidation Experiments revealed fuel-dependent differences in O_2 oxidation experiments on light-duty PM.
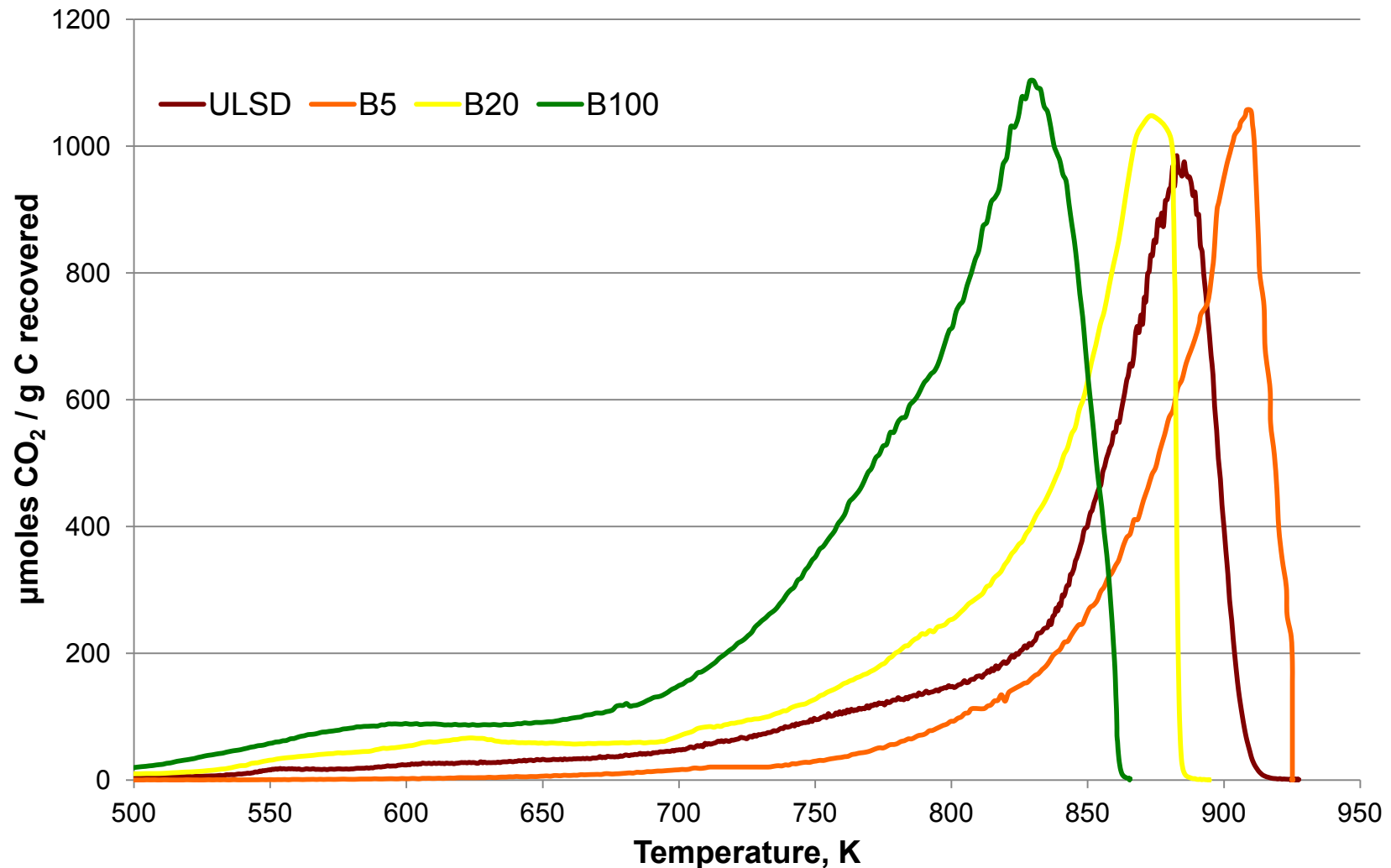
Isothermal, Pulsed Oxidation (IPO) provides fixed carbon oxidation rate measurements at nearly constant particle temperature (T_p)

- Isothermal (<4°C change in temperature)
- Differential (<4% C conversion per pulse)
- Make repeated measurements at different temperatures, different degrees of oxidation (stages of particle burnout)

505°C Pulsed Oxidation of ULSD PM in 10% O_2
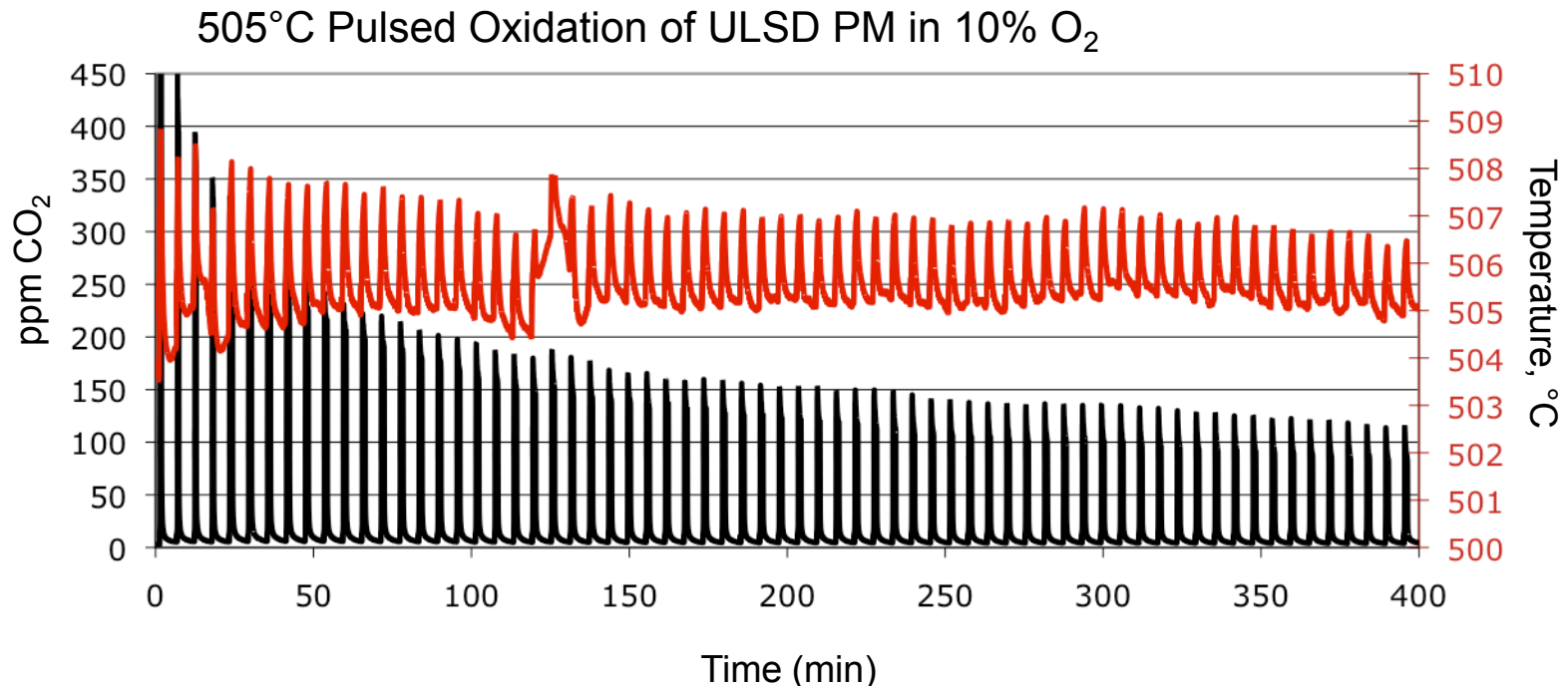
Observed oxidation rates reveal fuel-dependency

Reaction rate, $r = -d(M_C/M_{C,o})/dt$, which we can measure experimentally.

Calculate $-k$ from the slope of $\ln(M_C/M_{C,o})$ vs time plot. Plot k vs $1/T$ for to find E_A.

Temperature range of activity defined by TPOs:
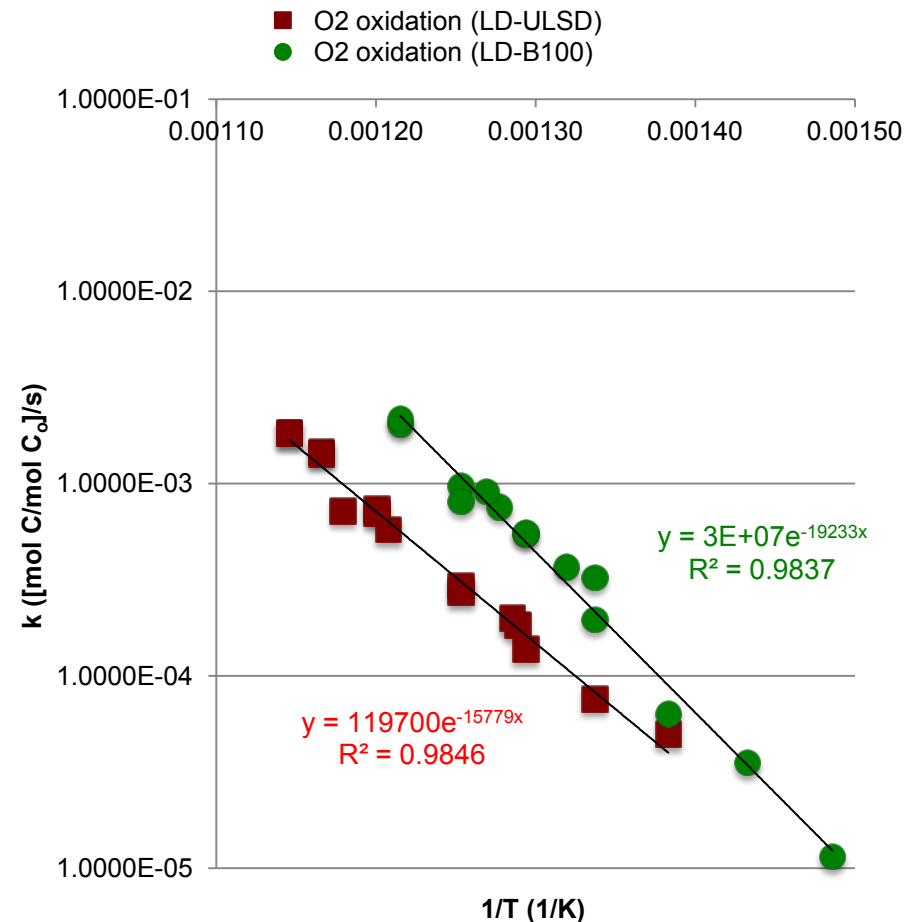ULSD: 723-923 K (E_A = 129 ± 7 kJ/mol)
B100: 673-823 K (E_A = 160 ± 3 kJ/mol)

Why are they different?
   Normalize data:
   -To initial sample size to remove differences caused by sample size.
         -Heterogeneous system – consider Surface area evolution with burnout ?

■ O2 oxidation (LD-ULSD)
● O2 oxidation (LD-B100)

$y = 3E+07e^{-19233x}$
$R^2 = 0.9837$

$y = 119700e^{-15779x}$
$R^2 = 0.9846$

k ([mol C/mol C_o]/s)

1/T (1/K)

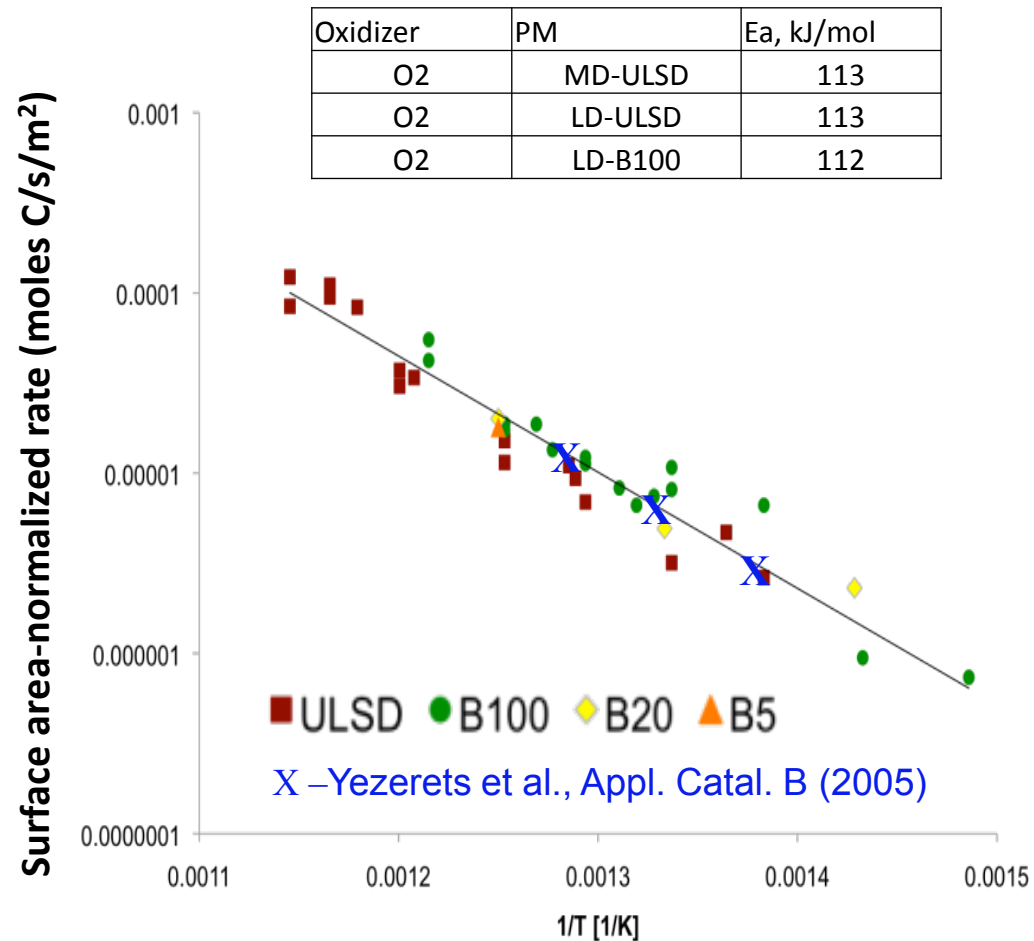| Oxidizer	PM	Ea/R	Ea, kJ/mol
O2	LD-B100	19233	160
O2	LD-ULSD	15779	129

In-situ BET measurements made in combination with IPO reveal how fixed carbon surface area evolves with degree of particle oxidation

- Different fuel blends exhibit different trends within a single engine type.

- Provides basis for modeling reaction front geometry

- For O_2 oxidation, reaction does not follow a shrinking core model, surface area evolution implies a more complex (possibly fractal) surface


LD-fixed carbon oxidation in 10% O_2
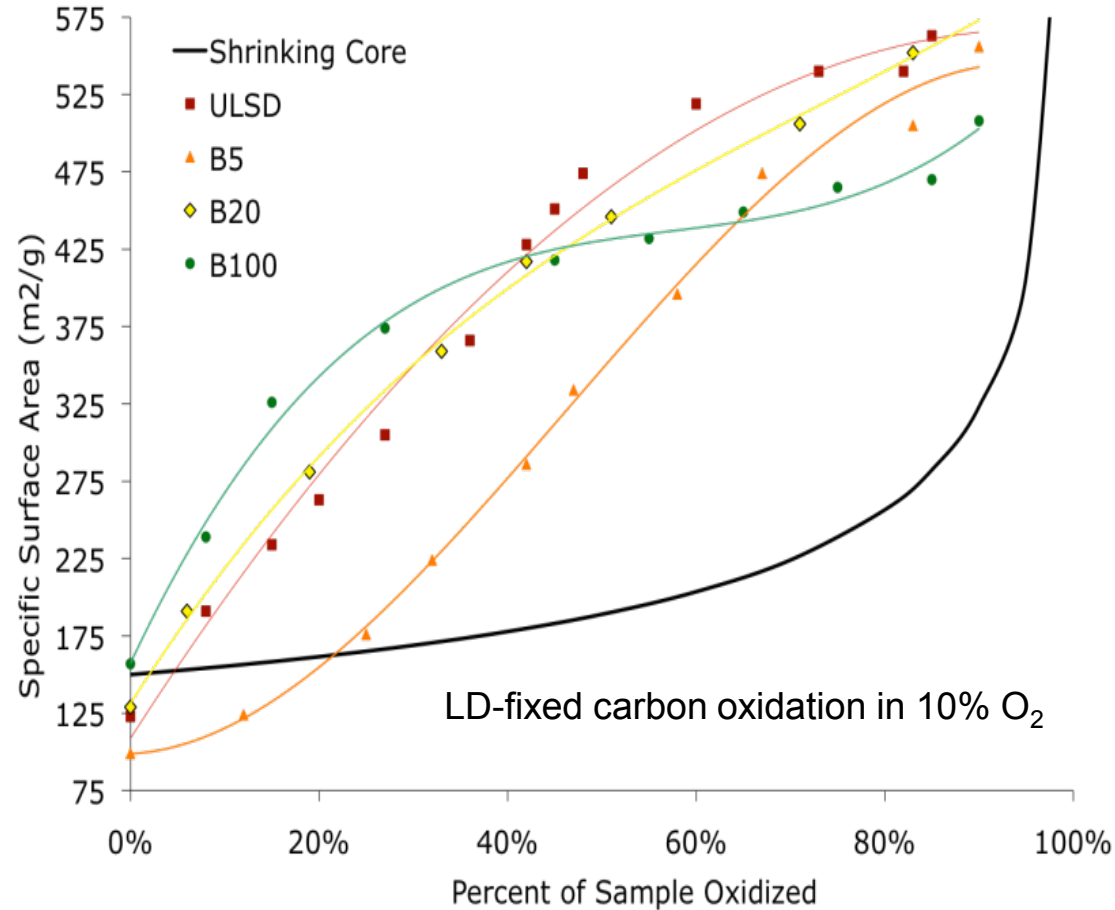
Global Arrhenius kinetics for O_2 oxidation are extracted from the combined IPO oxidation rate and BET measurements

- O_2 oxidation rates normalized to surface area exhibit consistent trend for different fuel blends, different degrees of oxidation

- Our observations also match measured trend of Yezerets et al (2005) for different PM

- $E_A \approx 113\pm6$ kJ/mole

- Value of E_A consistent with Zone II burning ('pore' diffusion controlled)

- Rates within range reported for coal chars (e.g., Essenhigh, R., *Fundamentals of Coal Combustion*, in *Chemistry of Coal Utilization*, 1981)
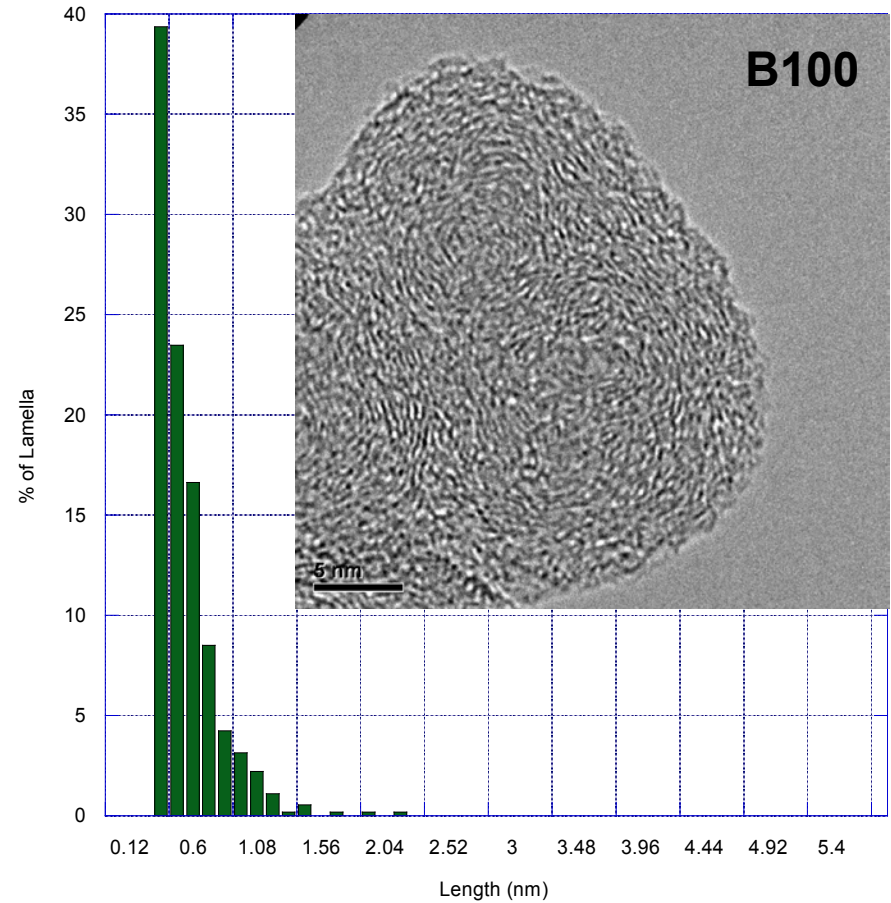
Oxidizer	PM	Ea, kJ/mol
O2	MD-ULSD	113
O2	LD-ULSD	113
O2	LD-B100	112

X −Yezerets et al., Appl. Catal. B (2005)

Lamella statistics from HR-TEM analysis seem to correlate with fuel-related differences
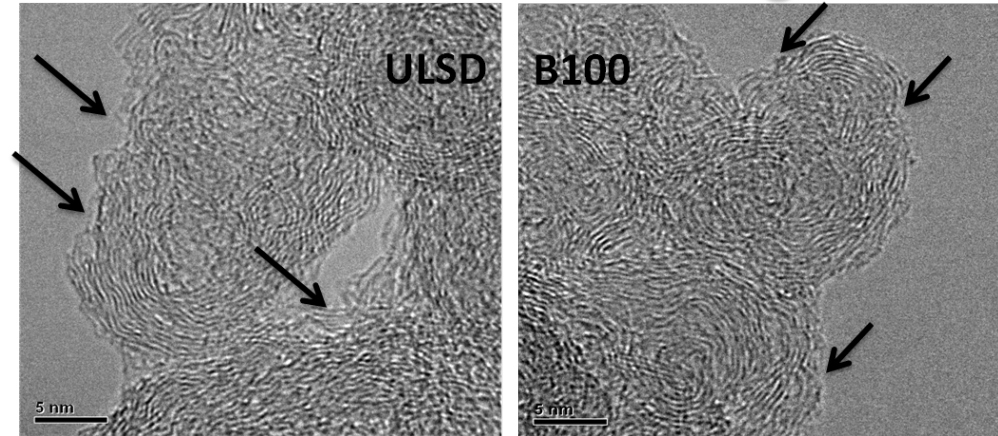
ULSD Nascent Lengths
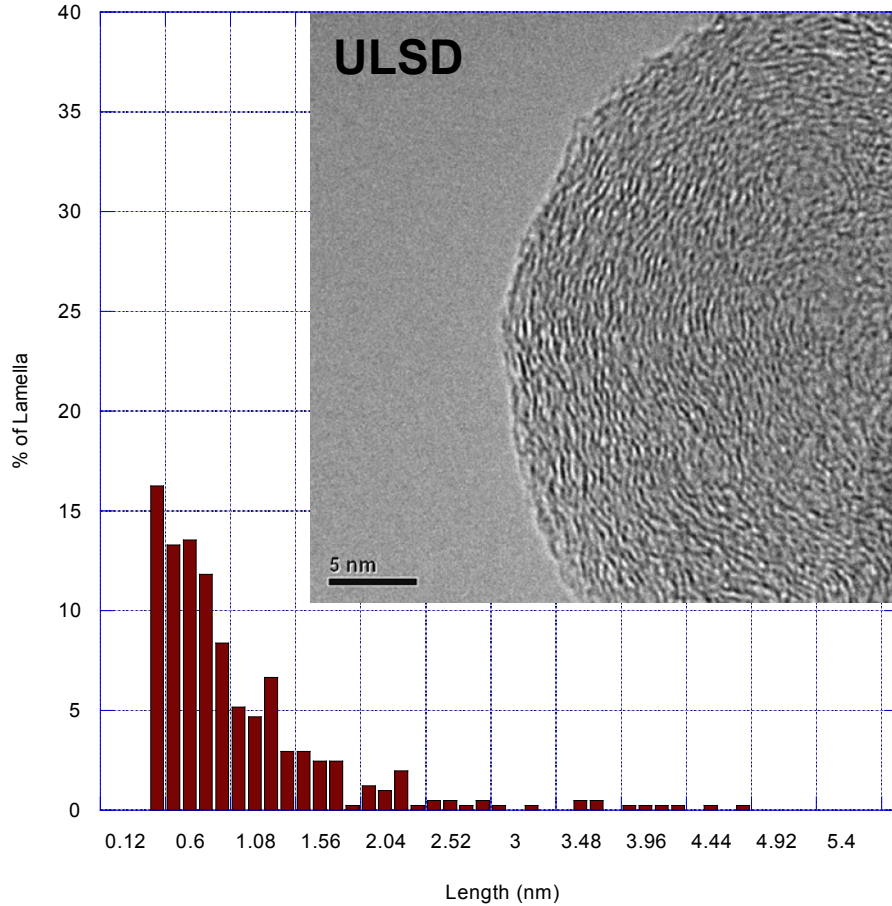
B100 Nascent Lengths

Lamella and primary particle diameter analysis at 50% O₂ oxidized seem to indicate LD PM are becoming more similar with burnout.

- Analysis of 50% burnout shows 'divot' formation on the surface. Suggest some type of internal surface formation

- In agreement with surface area trends becoming similar ~50% burnout.

- Possible diffusion paths opening at external surface and leading inward
  - Working to develop a geometrical explanation of surface area behavior


- Average primary particle sizes
  - ULSD: 33 nm nascent → 31 nm partially oxidized
  - B100: 31 nm nascent → 29 nm partially oxidized

- Lamella lengths become similar with oxidation
  - ULSD: 0.84 nm nascent → 0.22 nm partially oxidized
  - B100: 0.52 nm nascent → 0.19 nm partially oxidized

Comparison of ULSD TPOs: NO_2, O_2, $NO_2 + O_2$
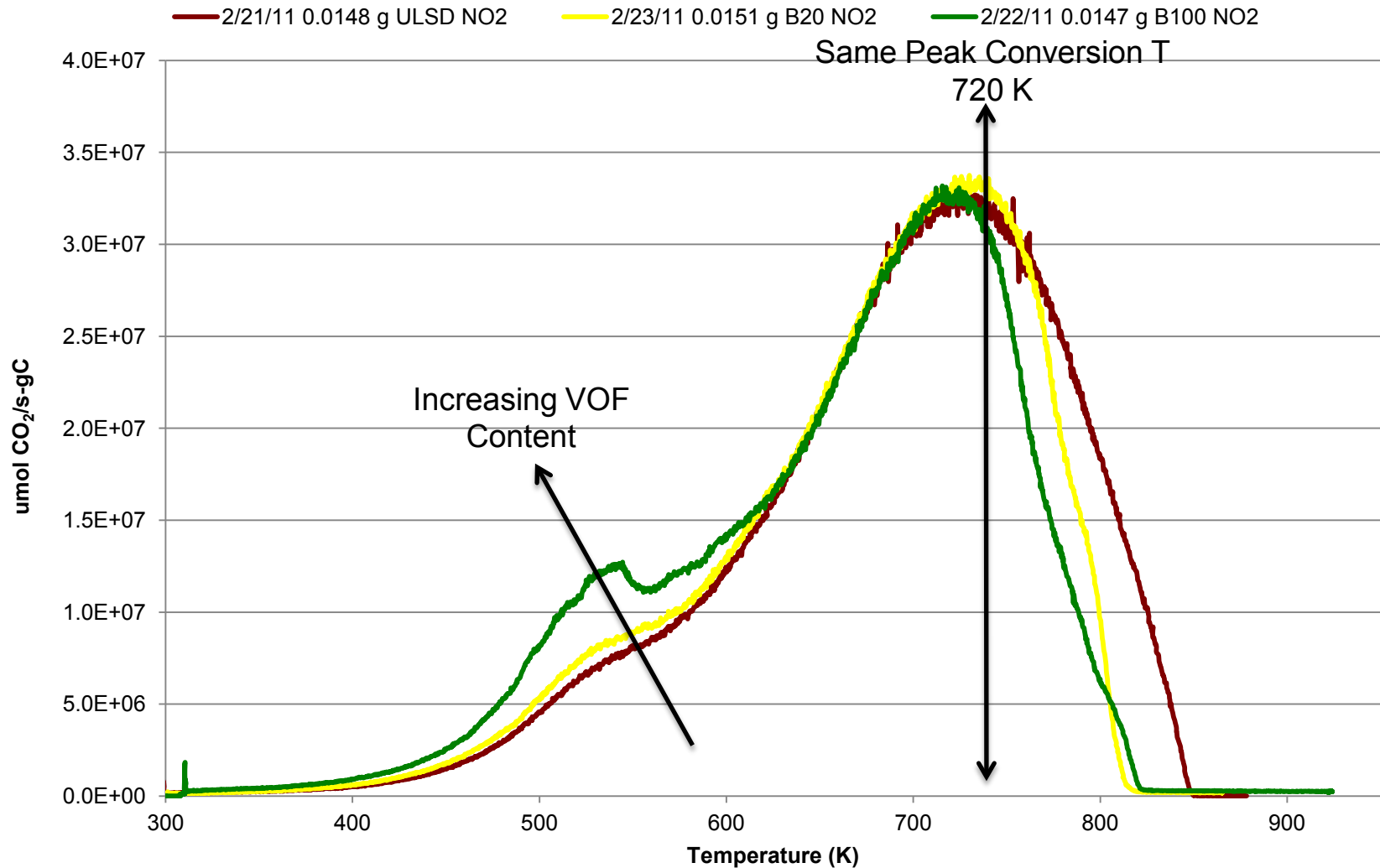
- 1% NO_2 TPO exhibits low temperature activity, usually associated with passive regeneration

- 500ppm NO_2 combined with 10% O_2 show little improvement at lower temperatures, O_2 oxidation dominates (non-catalyzed)
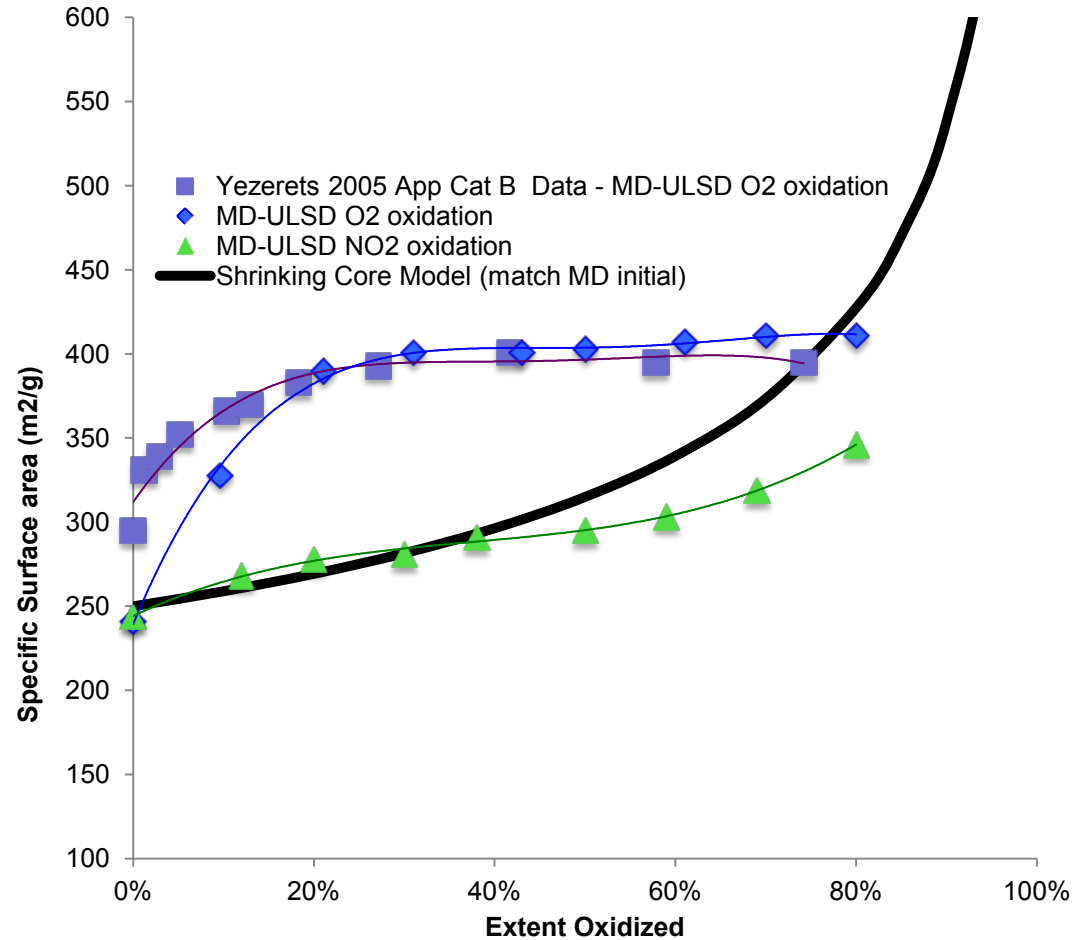
ULSD Oxidizer Comparison
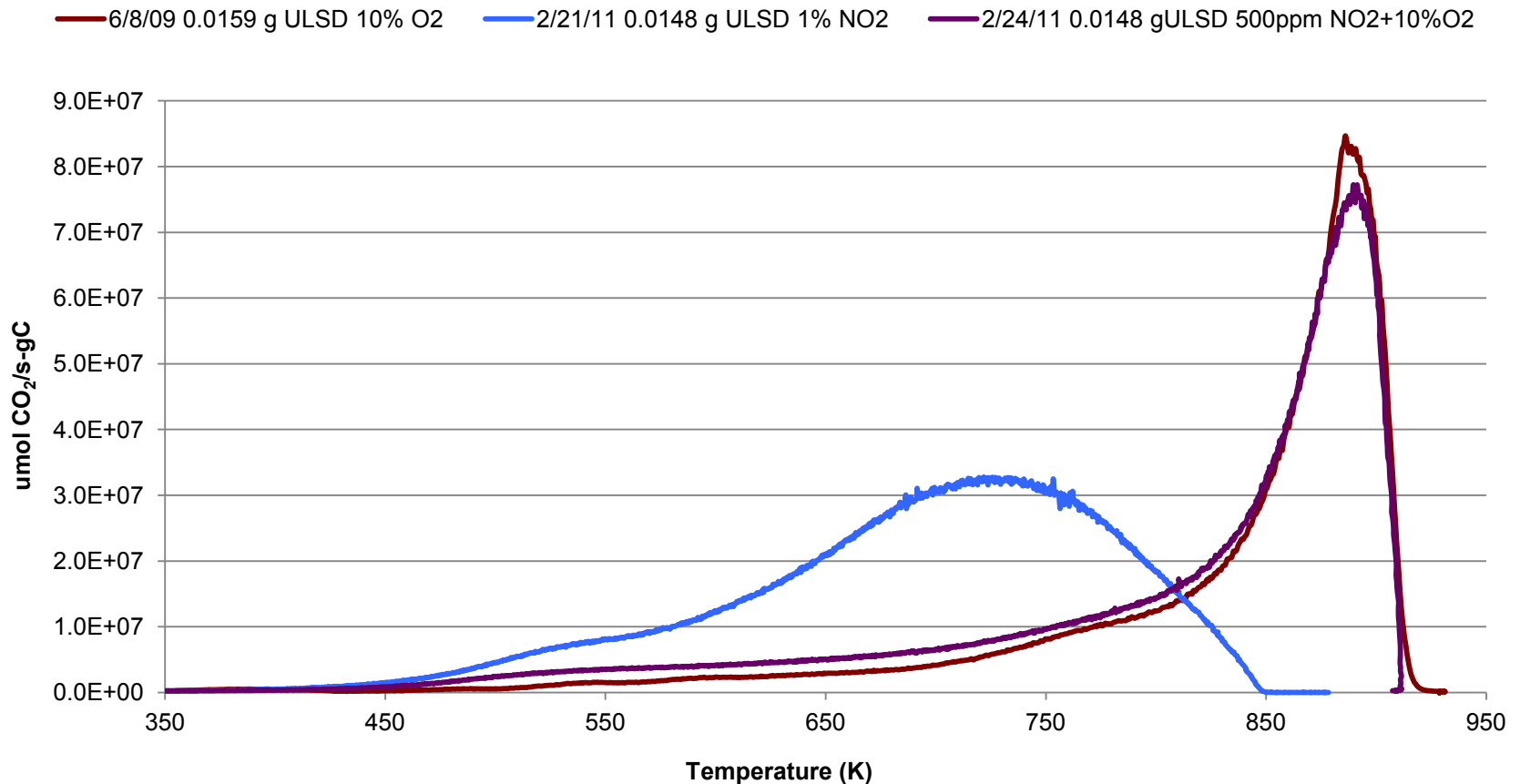
In contrast to O$_2$ TPOs, NO$_2$ TPOs show no fuel dependent behavior

1% NO2 TPOs on LD PM

BET measurements reveals oxidizer-dependent surface area evolution with degree of particle oxidation for MD-PM

- Engine size impacts surface area trend/limit
  - O_2 oxidation surface area profile is different for LD and MD PM
  - Current MD-PM is consistent with data from Yezerets, 2005.
- Though the O_2 oxidation reaction does not follow a shrinking core type burnout, the NO_2 oxidation fits the trend.
- BET with NO_2 data for biofuel blends needs to be collected.

Chart legend:
- Yezerets 2005 App Cat B Data - MD-ULSD O2 oxidation
- MD-ULSD O2 oxidation
- MD-ULSD NO2 oxidation
- Shrinking Core Model (match MD initial)

Y-axis: Specific Surface area (m2/g)
X-axis: Extent Oxidized

NO$_2$ Oxidation activation energy is still very different from O$_2$ oxidation, even after surface area normalization.

- Calculate a much smaller activation energy from NO$_2$ IPO data, (left) indicates possible diffusion limitation
- NO$_2$ oxidation surface area increases much more than for O$_2$, however instantaneous surface area normalization is not enough to match the measured O$_2$ reaction kinetics (right)
- Still need to collect data on biofuel blends.

| Oxidizer	PM	Ea/R	Ea, kJ/mol
O2	ALL	13625	113
NO2	MD-ULSD	1793	15
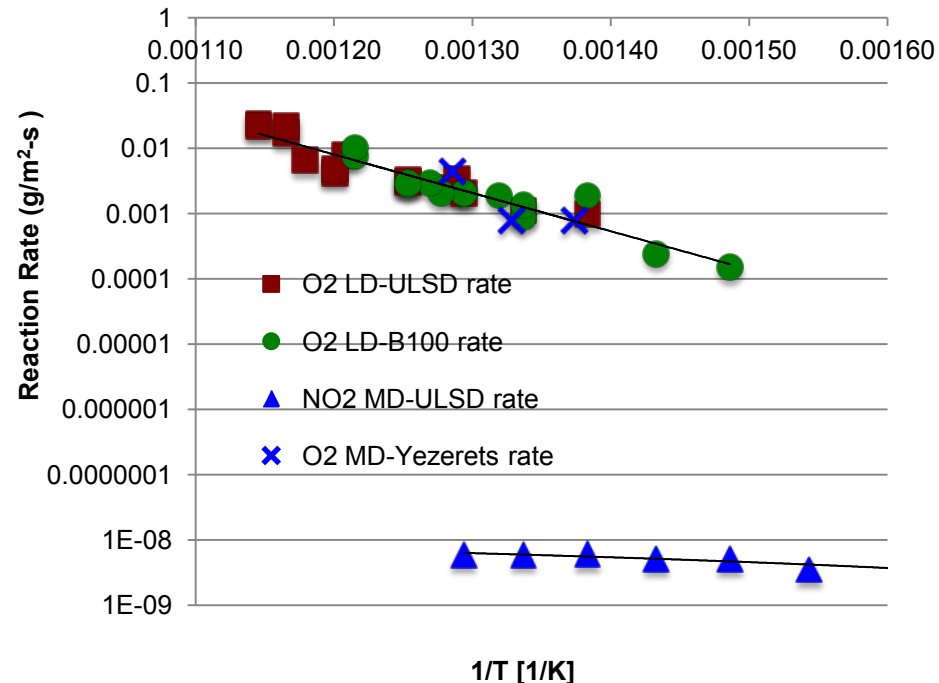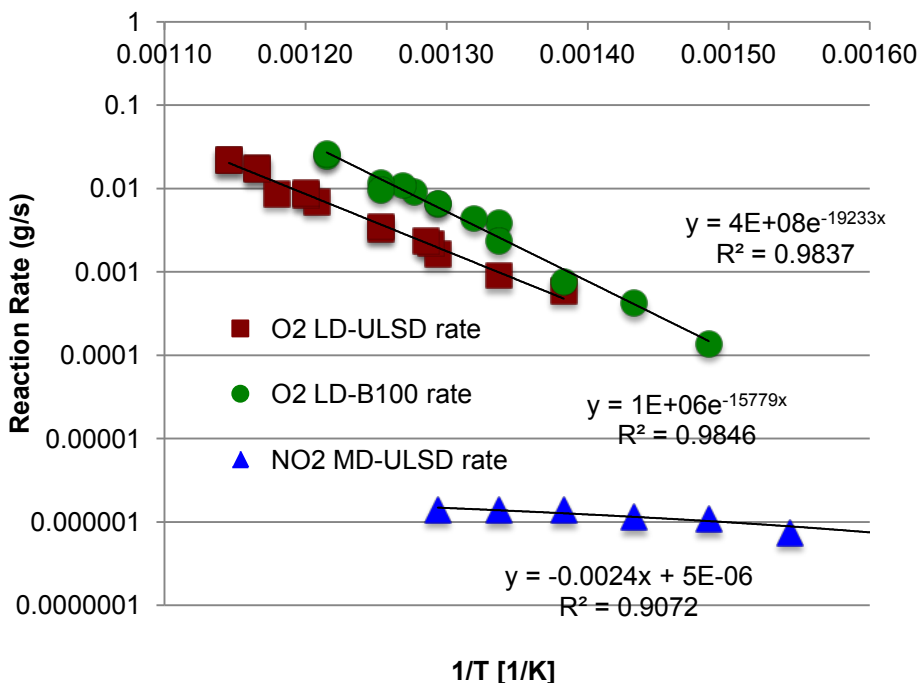
Experimental data matches the shrinking sphere prediction

Low activation energy and the shape of the specific surface area evolution indicated that the reaction may be progressing only on the exterior surface of the particulate.
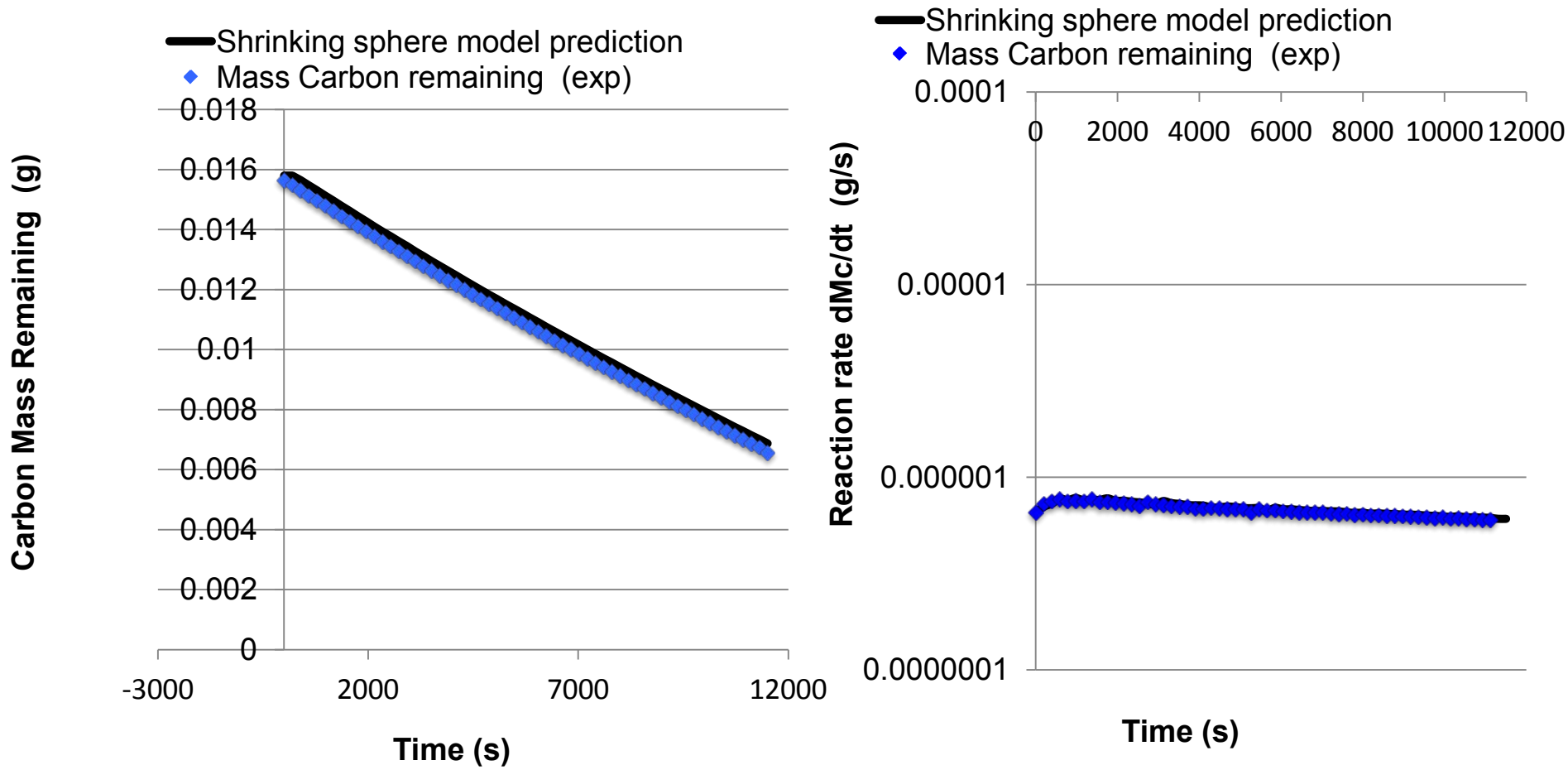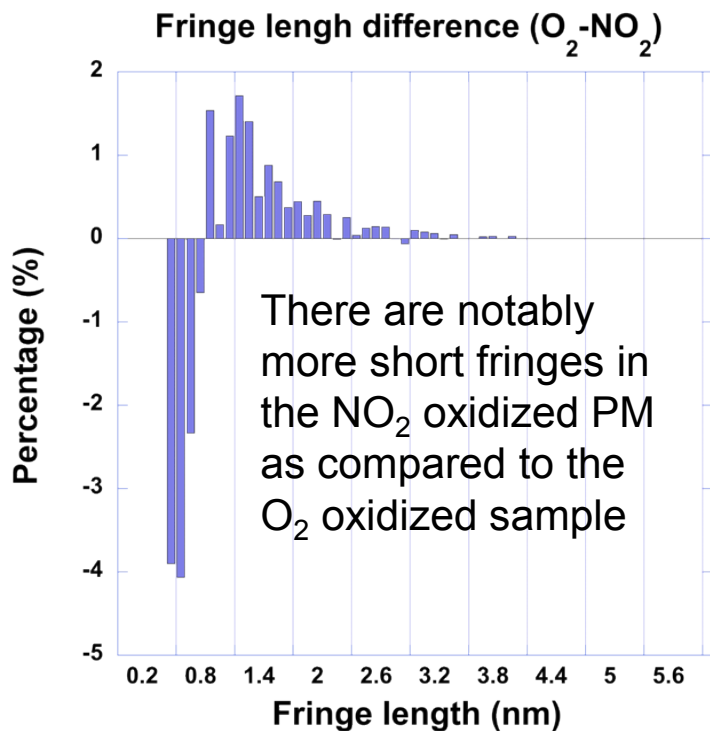
Comparison of HR-TEM for nascent MD-ULSD PM and 50% oxidized samples highlights differences in particle evolution
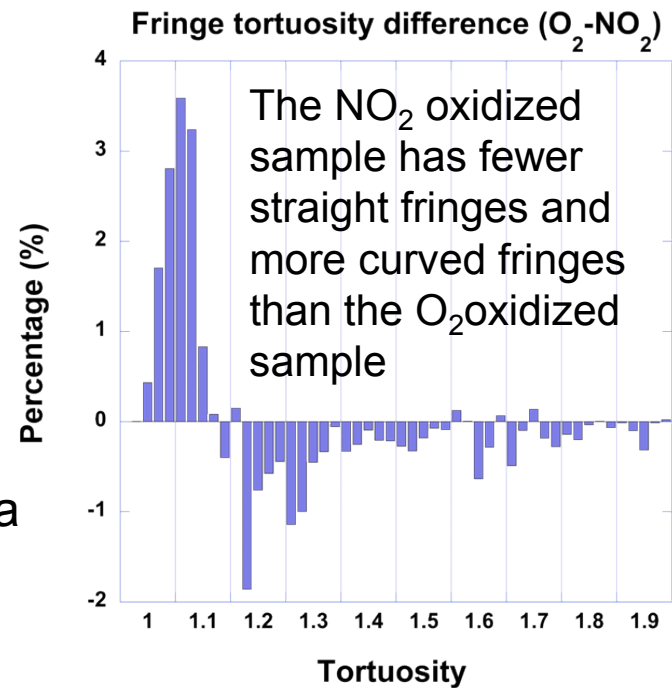

Nascent MD-ULSD

50% O_2 oxidized MD-ULSD

50% NO_2 oxidized MD-ULSD
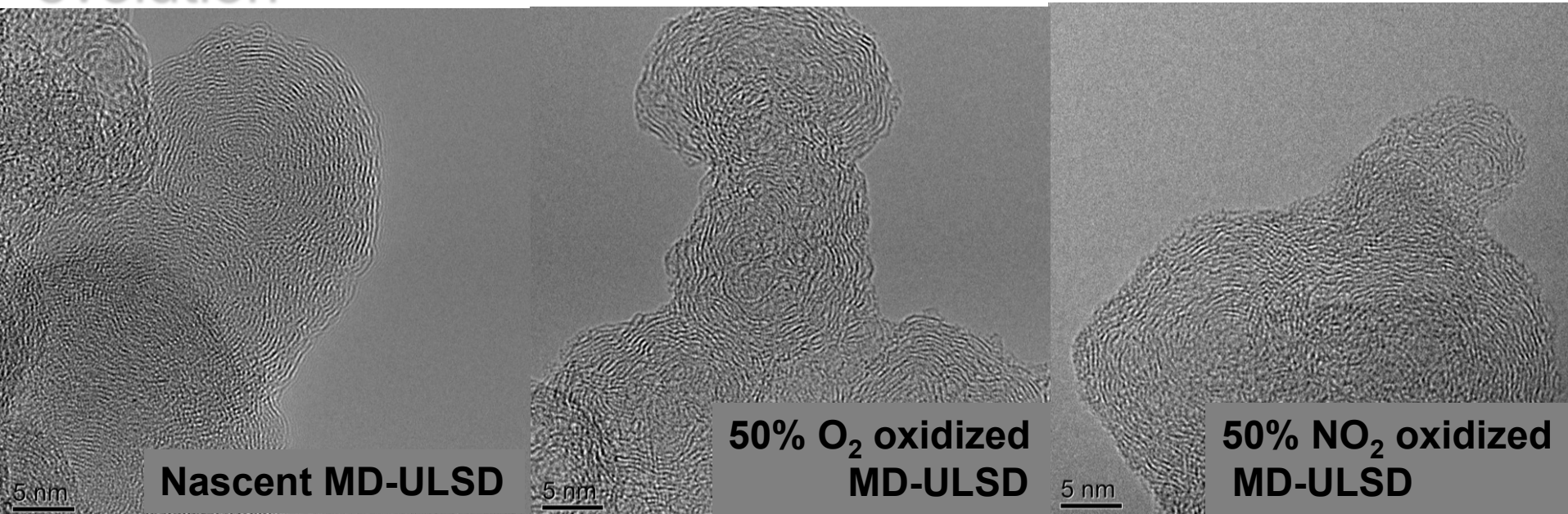
O_2 oxidation of MD-ULSD develops 'divots' related to the increasing porosity/surface area seen with extent oxidation, similar to LD-PM. Divots indicate preferential reactivity.

NO_2 oxidation shows a difference in the outermost layer of the particulate. The crumbling is indicative that NO_2 reacts upon contact and breaks up the outer surface of the particulate, indiscriminately.

Fringe difference analysis (O$_2$ – NO$_2$)

Fringe lengh difference (O$_2$-NO$_2$)

There are notably more short fringes in the NO$_2$ oxidized PM as compared to the O$_2$ oxidized sample

Tortuosity is the ratio of the curvature to the straight line distance (=1 for a straight line)

Fringe tortuosity difference (O$_2$-NO$_2$)

The NO$_2$ oxidized sample has fewer straight fringes and more curved fringes than the O$_2$oxidized sample

The difference plots of fringe length and tortuosity paint a consistent picture of lower reactivity for O$_2$ whereby it preferentially attacks highly curved lamella (which are more reactive due to bond strain) and short lamella (which have a higher proportion of more reactive edge sites). By contrast NO$_2$ reacts indiscriminately.

# Summary of observations to date for diesel PM

- Fuel source impacts particulate properties.
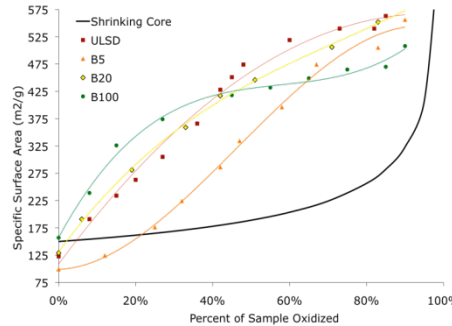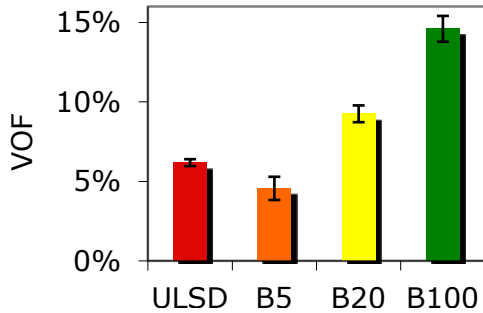
- Rate of oxidation of the fixed carbon component of diesel PM by O_2 is directly dependent on available surface area.

- Oxidation of diesel PM by NO_2 appears to be very different from oxidation by O_2.
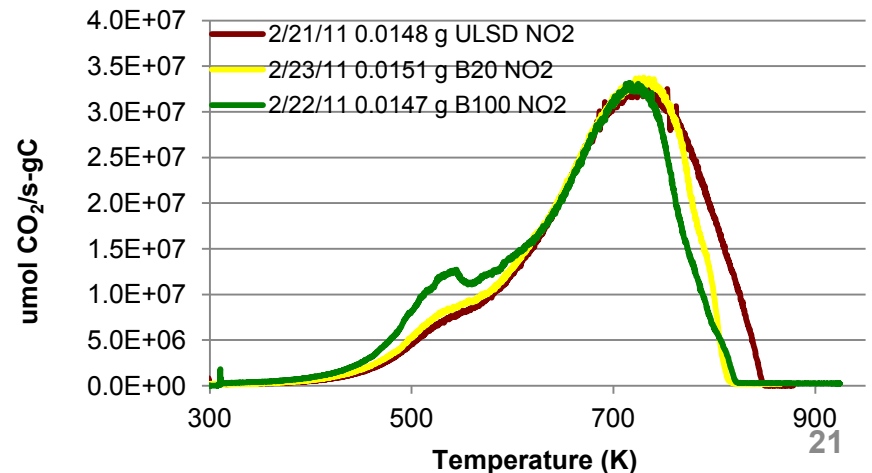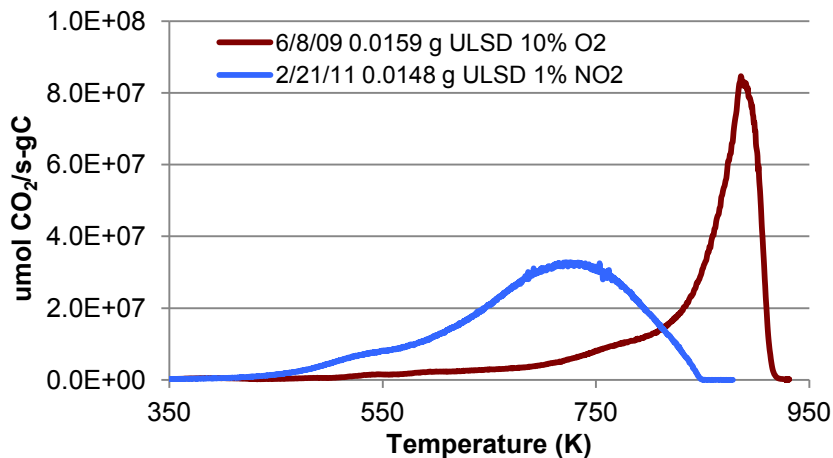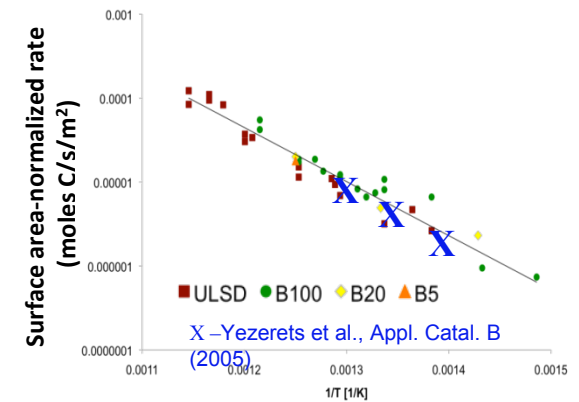
- Surface area evolves differently on PM from different engine types and with burnout depending on oxidizer.

- NO_2 Oxidation rate is consisent with the shrinking sphere prediction.

- Models used for DPF simulation and/or control need to account for biodiesel blending and prior oxidation history (i.e., PM hysteresis) for predicting regeneration rate.

- Different kinetic models will be needed to account for the effects of O_2 and NO_2 in the exhaust on DPF regeneration.

- Further investigation into NO_2 oxidation is necessary.

- Goal is to define key differences, to keep PM oxidation model as simple as possible.
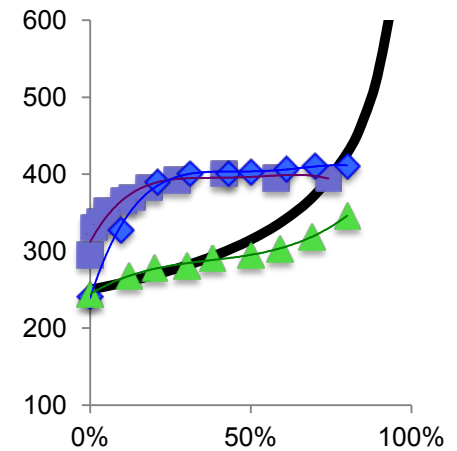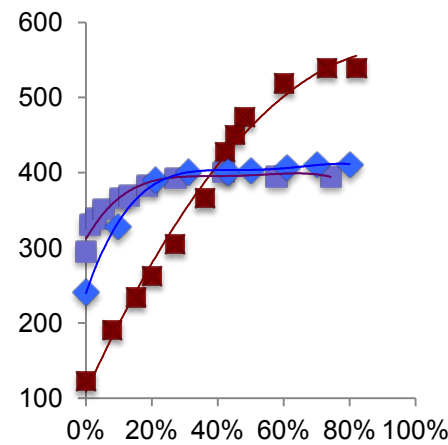
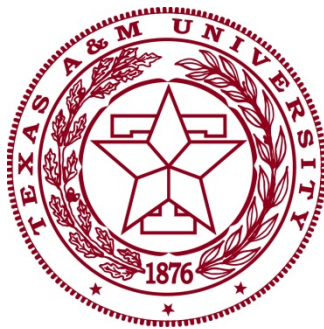# Thank you!

Thank you for your attention!

Questions?

Bonus Slides

Particulate formation occurs in three steps moderated by in- cylinder Temperature and Pressure

- Nucleation
  - Short time scale
 - Very fast, small fraction of mass formed
- Surface Growth & Coalescence
  - Responsible for mass increase & surface area
  - Coalescence reduces total surface area for constant mass
  - Growth increases total mass and surface area
  - Hydrocarbon growth species react heterogeneously on soot surface
  - Particles are made up of equidistant hexagonal graphitic crystallites bent around a sphere.
- Agglomeration
  - Chain formation – particles no longer coalesce, but stick together
- **Particulate formation = f(time, temperature and pressure)**

Graphic from Tree, et al. *Progress in Energy and Combustion Science* 2006, 33
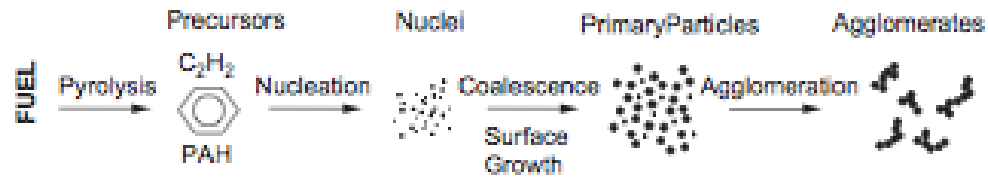
PM data compares wel with coal literature and previous PM studies

Plot compiled by Smith & Essenhigh, compares coal reactivity over many experiments.

PM data fits well with previously reported reactivity data for coal.

Data from Yezerets, et al corrected for surface area is in line with PM data from this study.

● B100 PM   ■ ULSD PM   ▲ Yezerets PM

$$R_i = 305 \exp \frac{-43{,}000}{RT}$$

$R(A) = (Mc/TSA)$, g/cm^2-s

Rate of reaction per unit of internal surface, R_i (g/cm^2−s)

Temperature, T (°C)

Temperature, $\frac{10^4}{T}$ (K^{-1})