



Combustion & Reaction
Characterization Lab

TEXAS A&M
UNIVERSITY

INVESTIGATION OF BURNING MODE FOR DIESEL PARTICULATE OXIDATION: CONTRASTING O₂ & NO₂

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Cambridge Particle Meeting

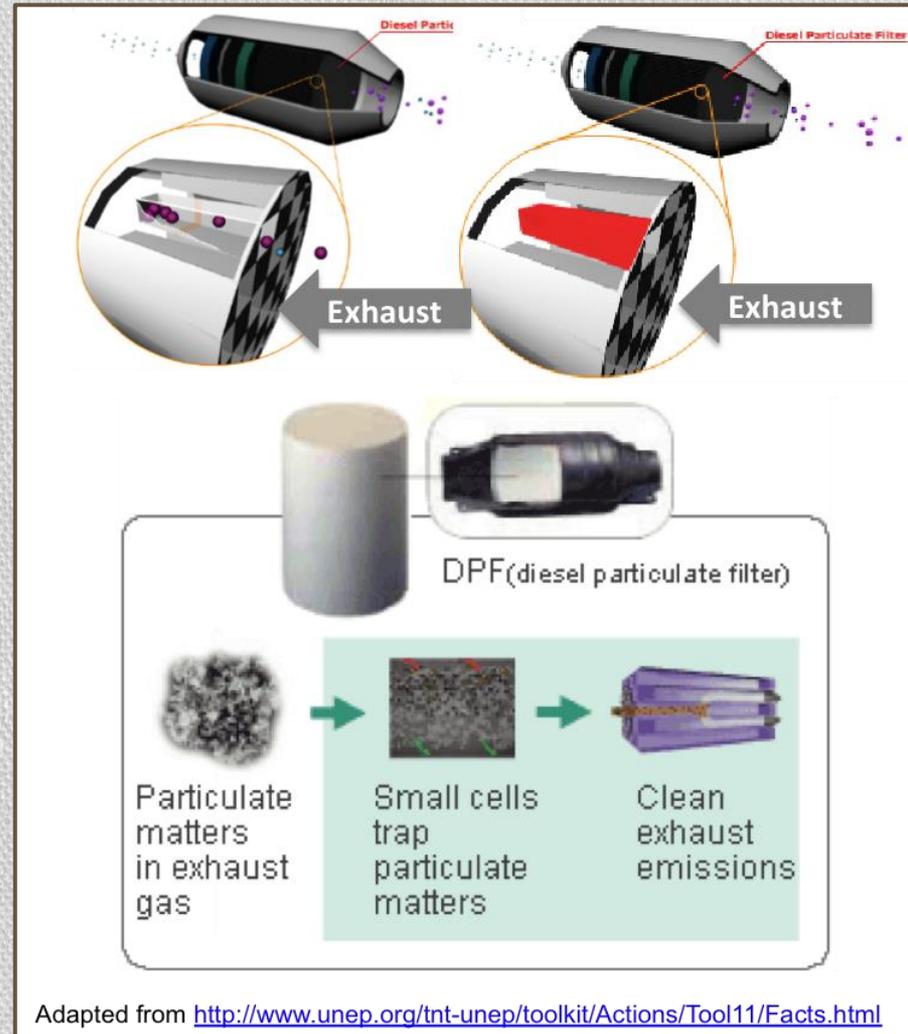
24 May 2013

Funding Source: US Department of Energy Office of Vehicle Technologies

Sponsors: Gurpreet Singh & Ken Howden

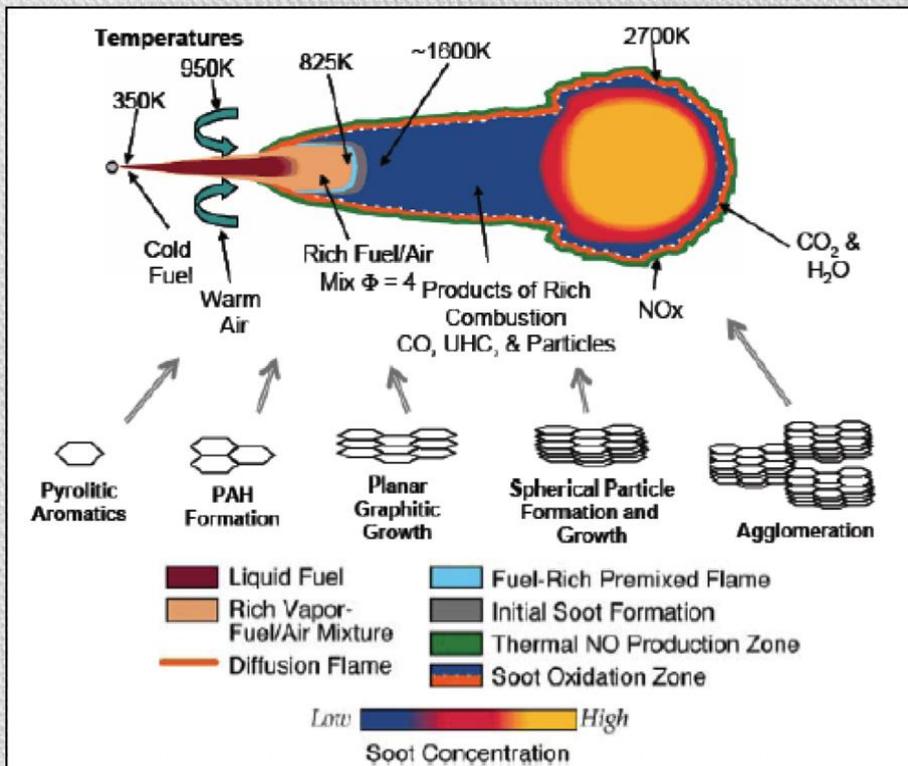
Motivation

- 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.



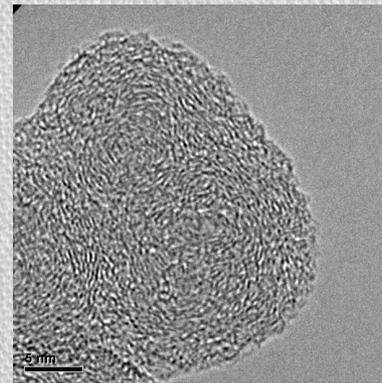
Diesel particulates form from incompletely burned aromatics in fuel-rich regions of the flame

- Primary particles form first, function of fuel, T, P, t, and then link together form aggregates and agglomerates.

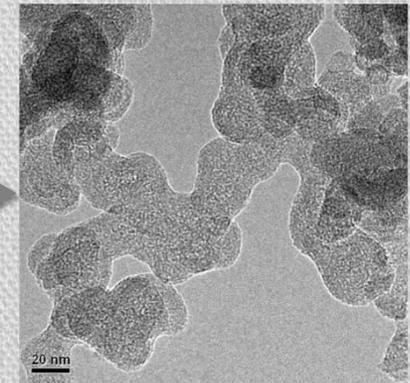


Dec conceptual model of PM formation, SAE 970973

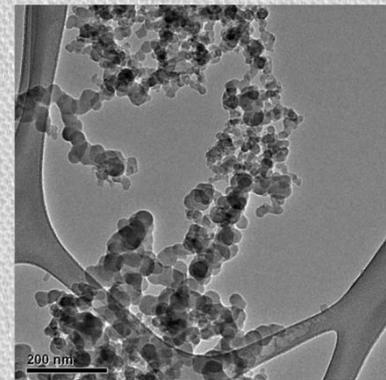
Primary Particles



Aggregates



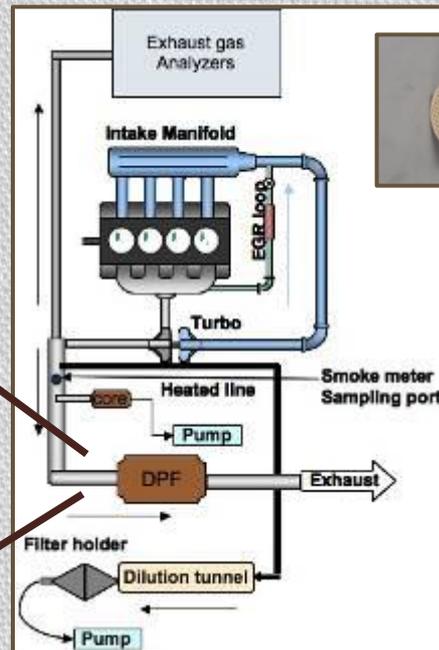
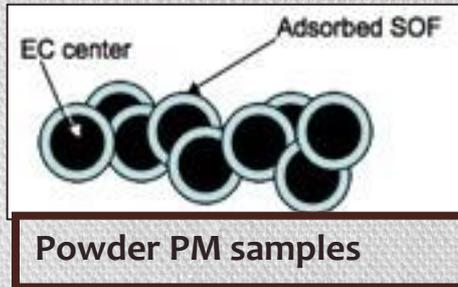
Agglomerates



Objectives

- Measure the O₂ and NO₂ 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.

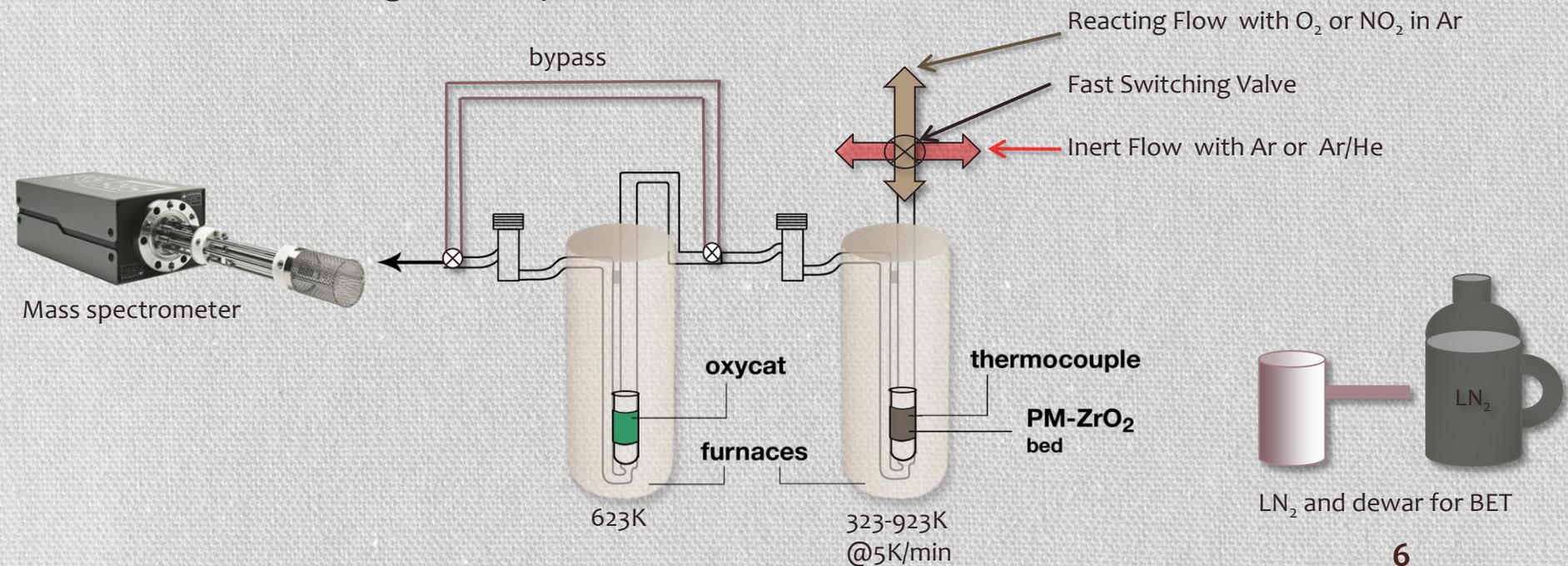
Approach: Measure reactivity, chemical composition, surface area, and microstructure of engine-generated PM samples



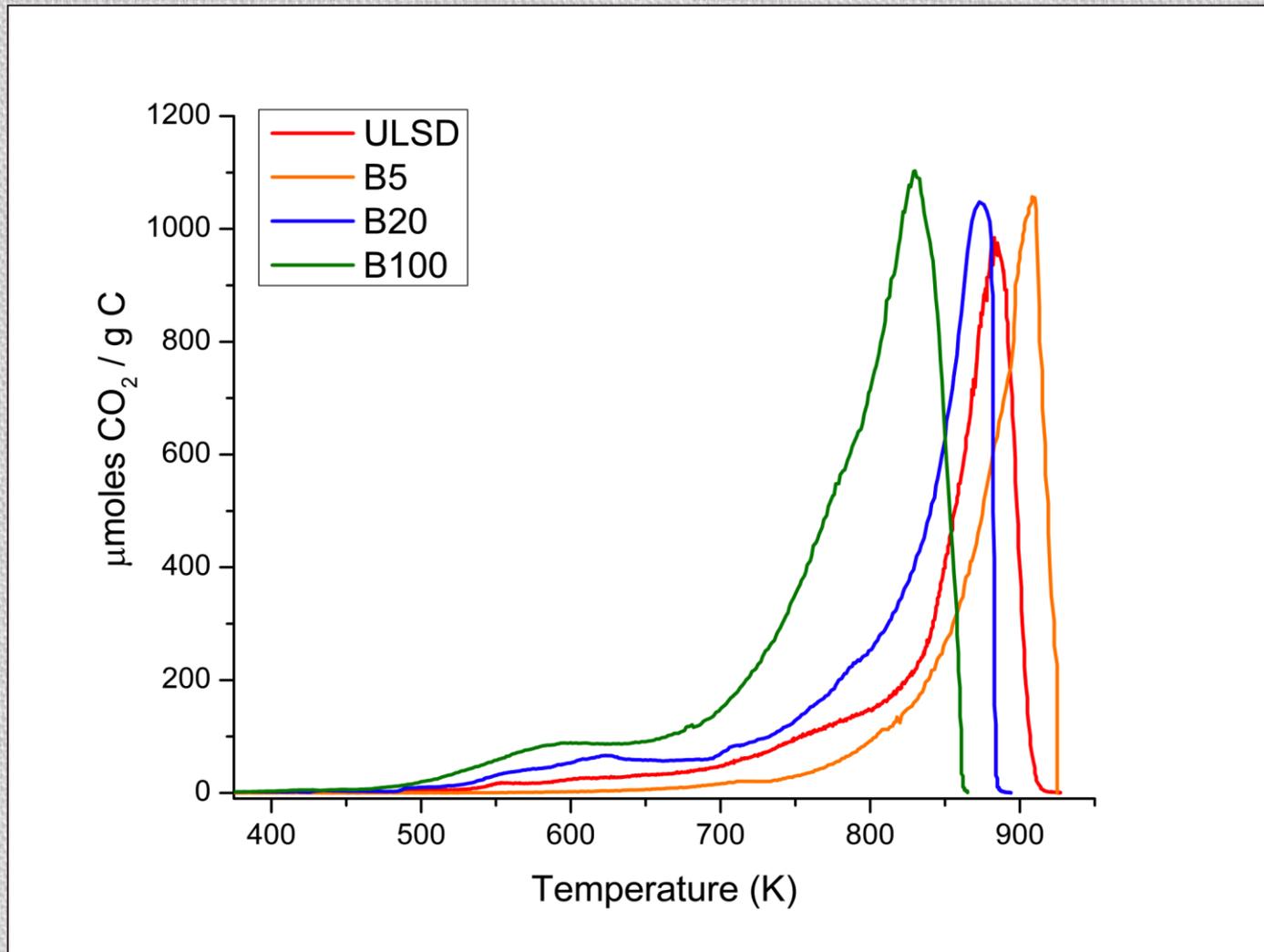
PM generation on Diesel engine dynamometers
Mercedes Benz 1.7L & Cummins ISL engines
Multiple fuel blends (conventional and biodiesel)
Steady operation at different speeds/loads
Highly controlled PM sampling protocols

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/O₂ or Ar/NO₂ 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, O₂/NO₂ content
 - In situ BET surface area measured by flowing Ar/He uptake at various stages of oxidation without removing the sample

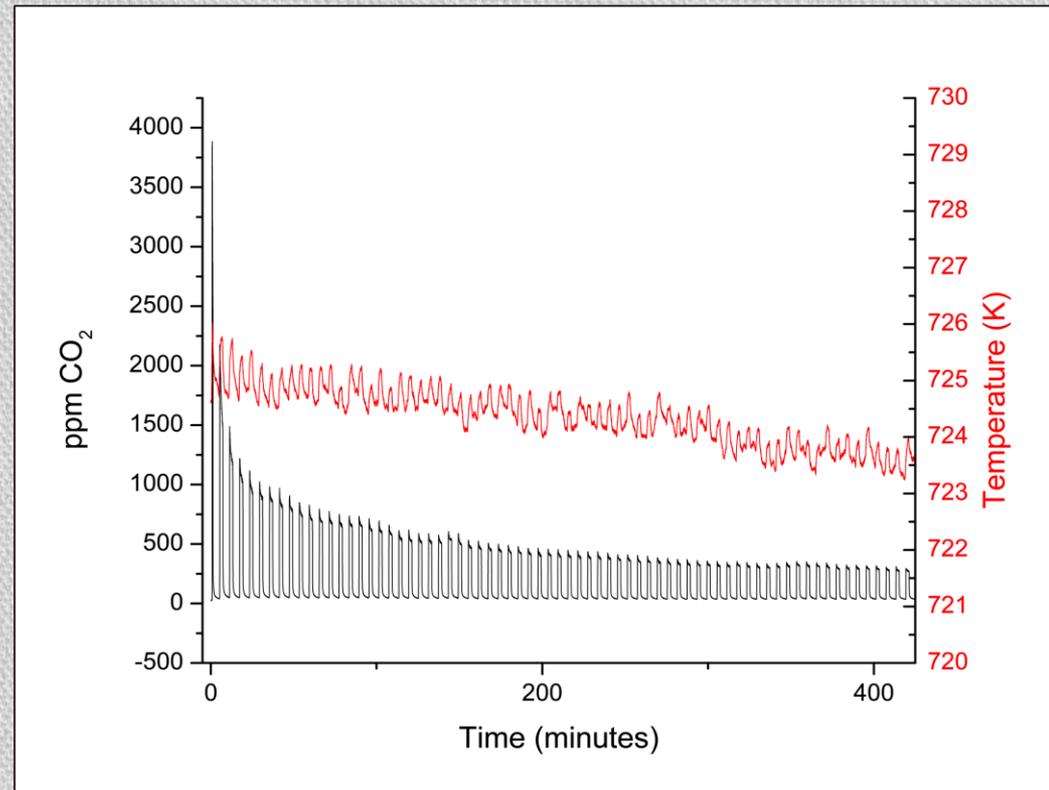


Previously, Temperature Programmed Oxidation Experiments revealed fuel-dependent differences in O_2 oxidation experiments on light-duty PM.



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)
- Technique from Yezerets, et. al



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 ($E_A = 129 \pm 7$ kJ/mol)

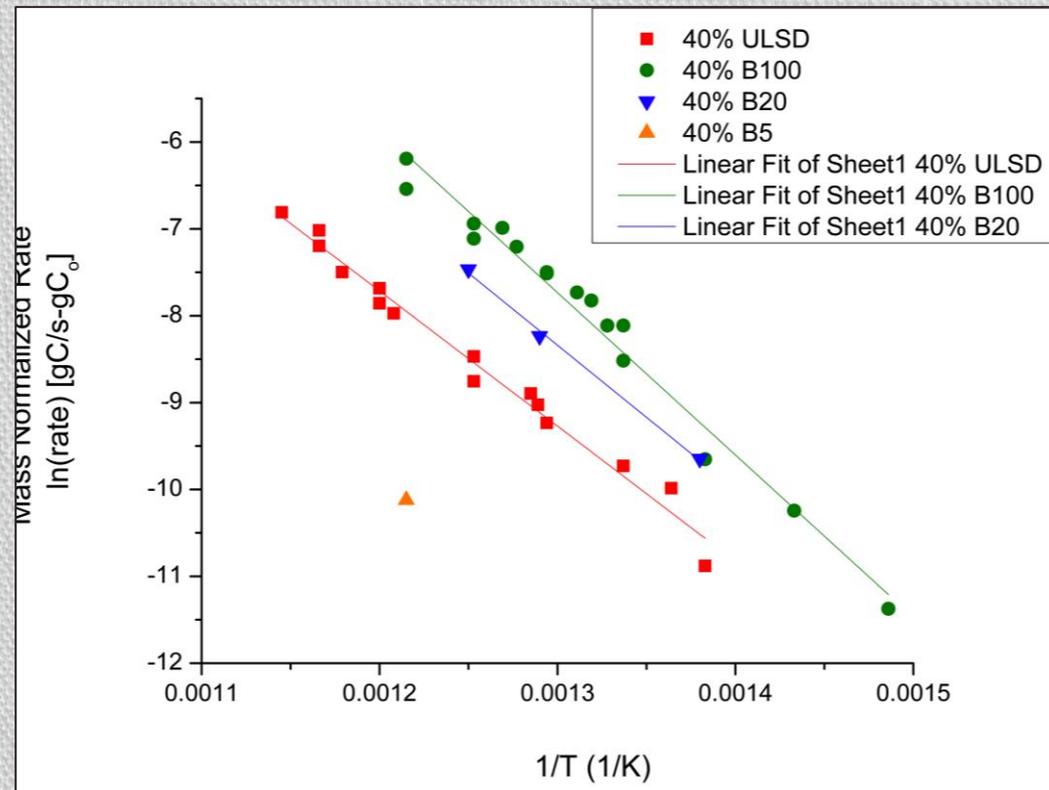
B100: 673-823 K ($E_A = 160 \pm 3$ kJ/mol)

Why are they different?

Normalize data:

-To initial sample size to remove differences caused by sample size.

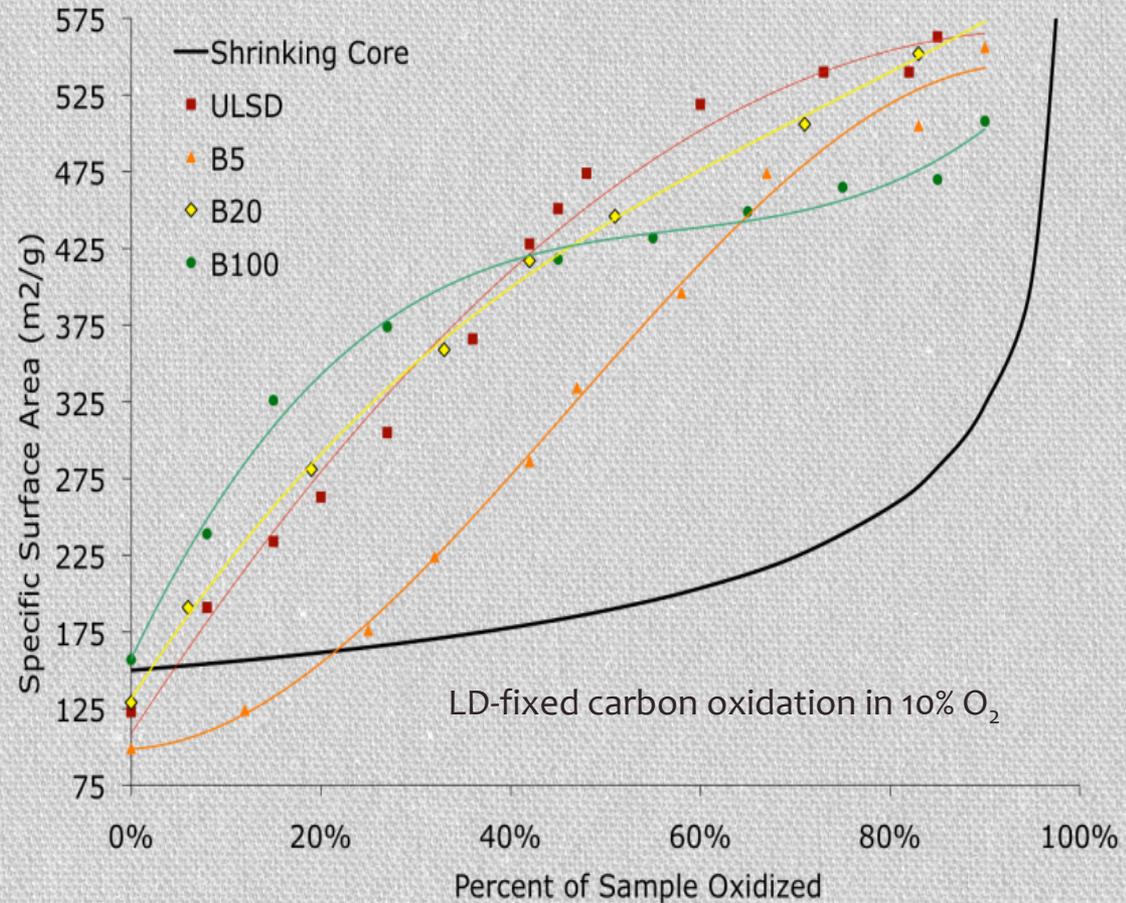
-Heterogeneous system – consider Surface area evolution with burnout ?



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

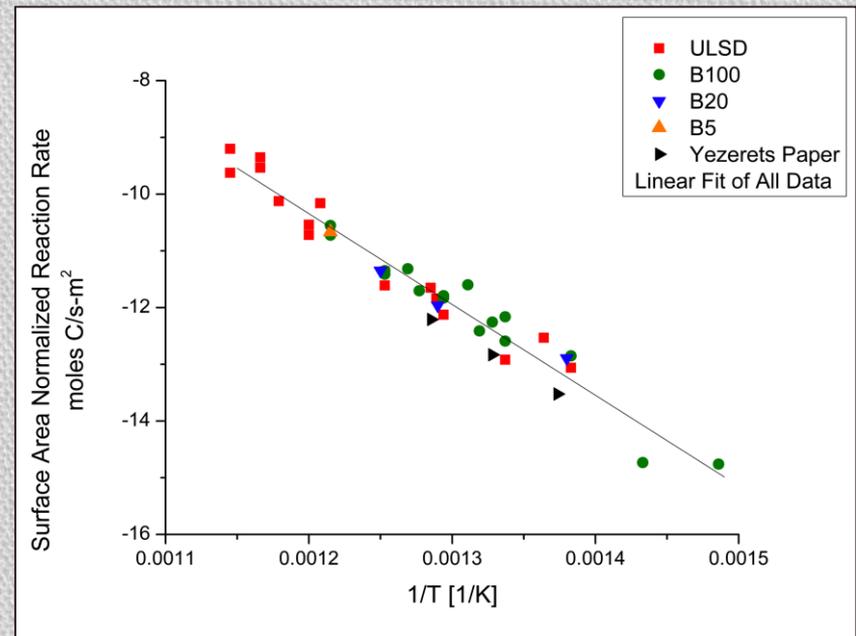
- Different fuel blends exhibit different trends within a single engine type.
- Provides basis for modeling reaction front geometry
- For O_2 oxidation, reaction does not follow a shrinking core model, surface area evolution implies a more complex (possibly fractal) surface



Global Arrhenius kinetics for O₂ oxidation are extracted from the combined IPO oxidation rate and BET measurements

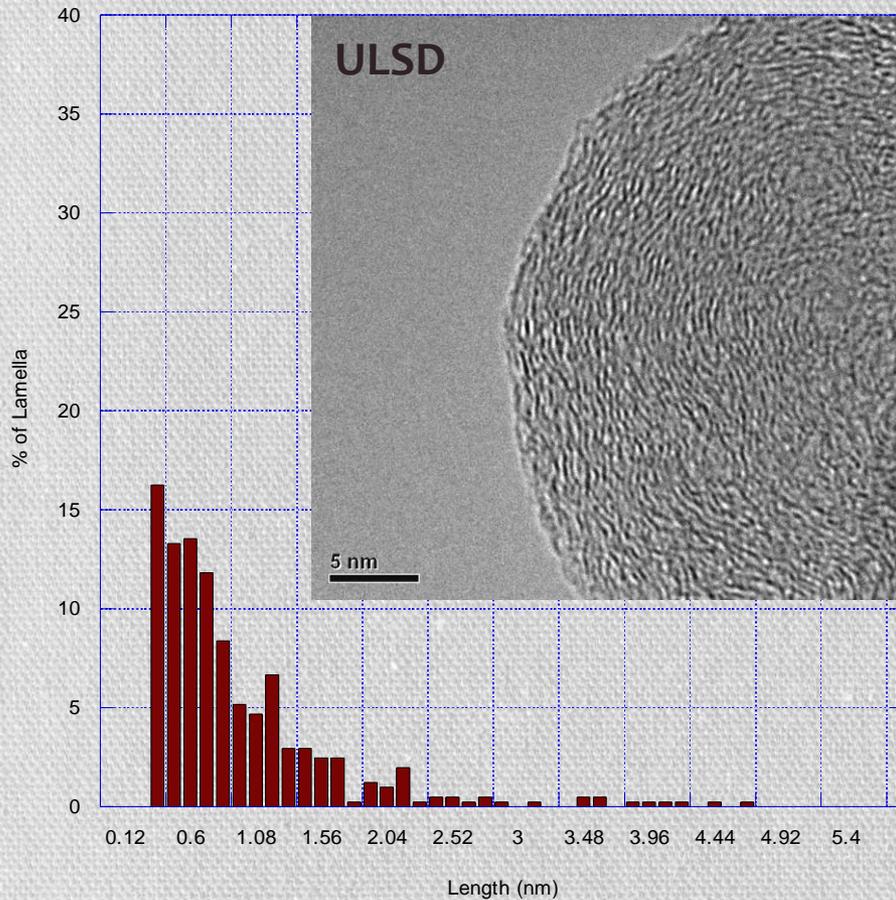
- O₂ oxidation rates normalized to surface area exhibit consistent trend for different fuel blends, different degrees of oxidation
- Our observations also match measured trend of Yezerets et al (2005) for different PM
- $E_A \approx 113 \pm 6$ kJ/mole
- Value of E_A consistent with Zone II burning ('pore' 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

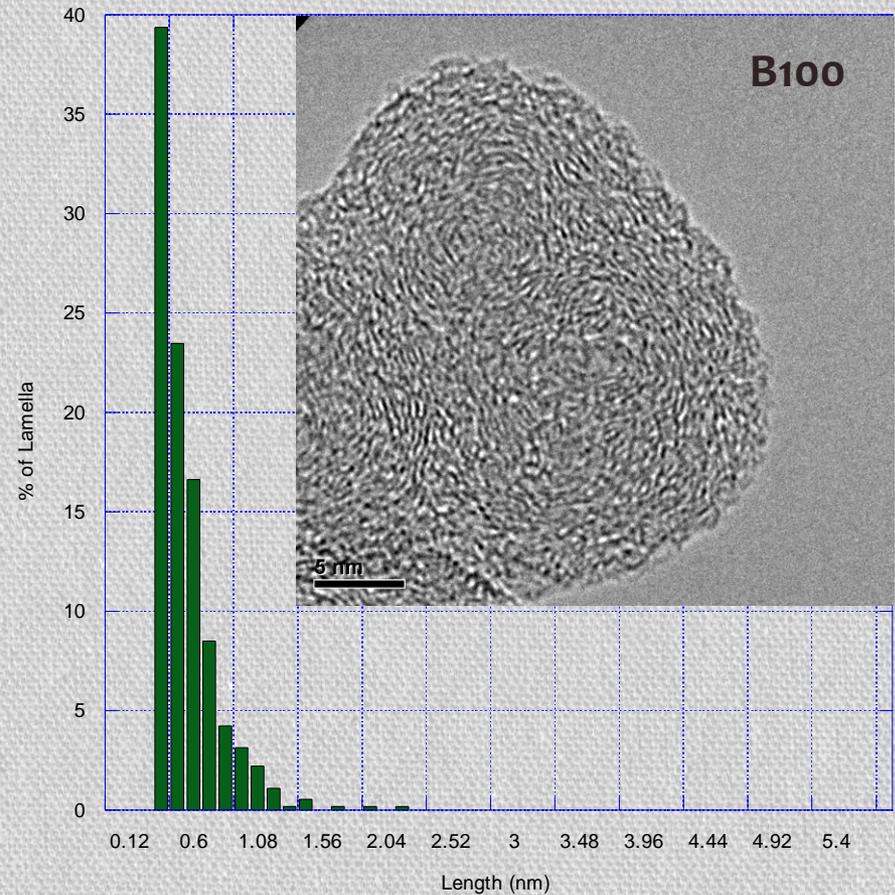


Lamella statistics from HR-TEM analysis seem to correlate with fuel-related differences

ULSD Nascent Lengths

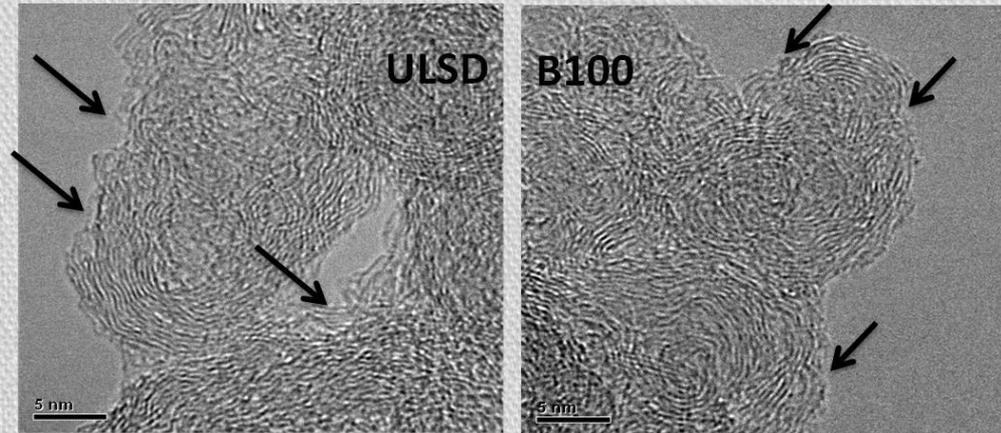


B100 Nascent Lengths



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



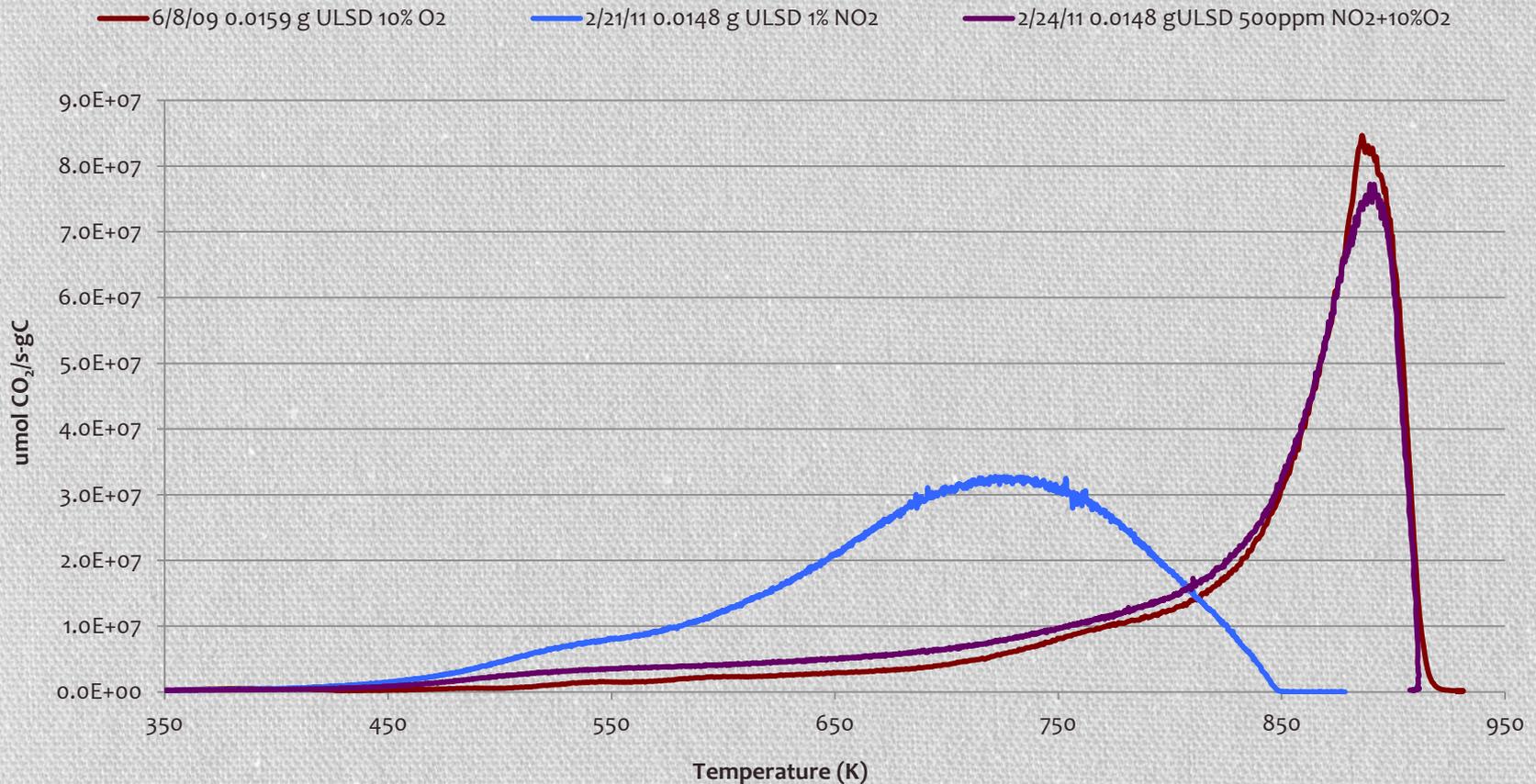
- Average primary particle sizes
 - ULSD: 33 nm nascent → 31 nm partially oxidized
 - B100: 31 nm nascent → 29 nm partially oxidized
- Lamella lengths become similar with oxidation
 - ULSD: 0.84 nm nascent → 0.22 nm partially oxidized
 - B100: 0.52 nm nascent → 0.19 nm partially oxidized

Comparison of ULSD TPOs: NO_2 , O_2 , $\text{NO}_2 +$

O_2

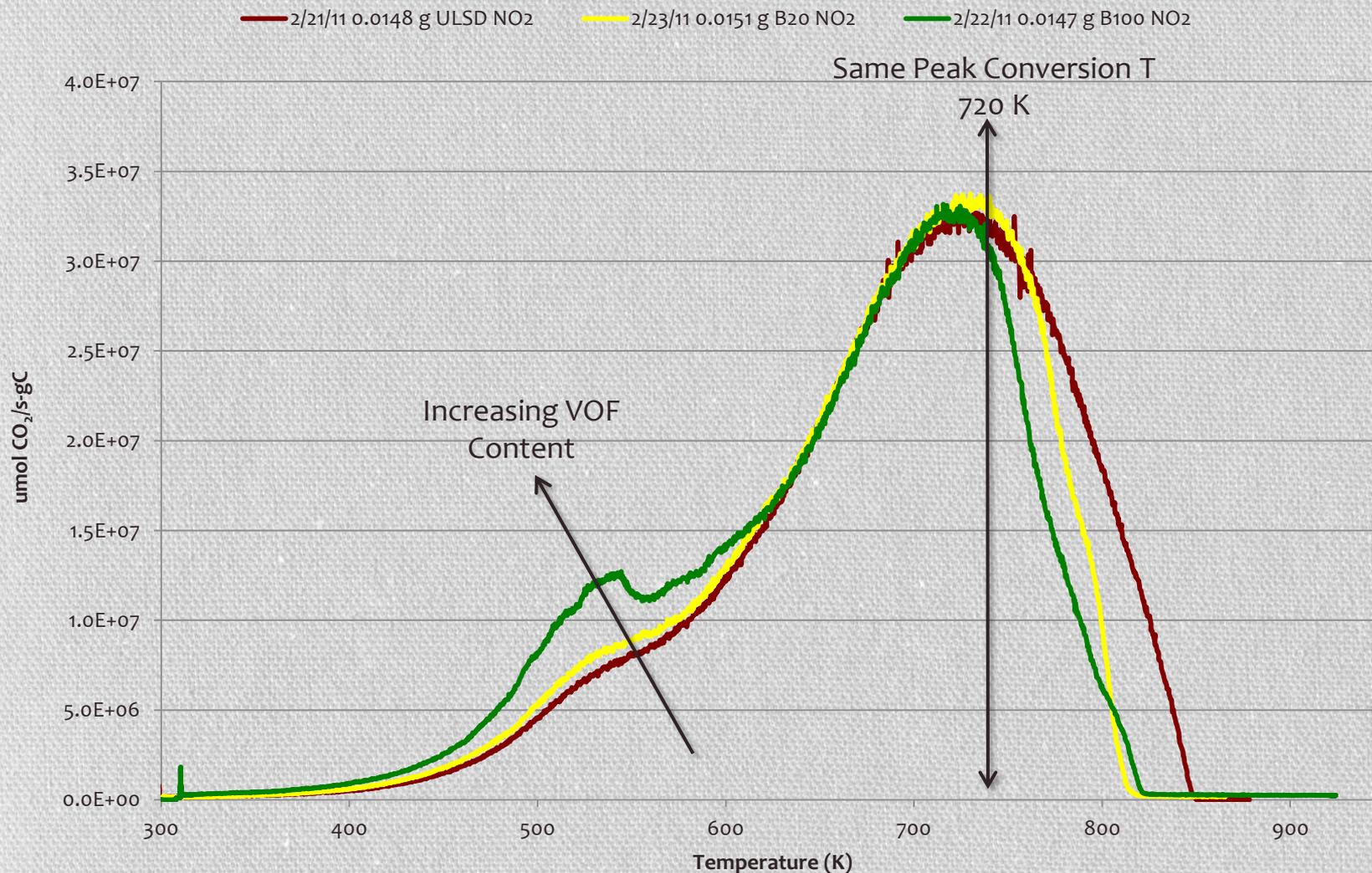
- 1% NO_2 TPO exhibits low temperature activity, usually associated with passive regeneration
- 500ppm NO_2 combined with 10% O_2 show little improvement at lower temperatures, O_2 oxidation dominates (non-catalyzed)

ULSD Oxidizer Comparison



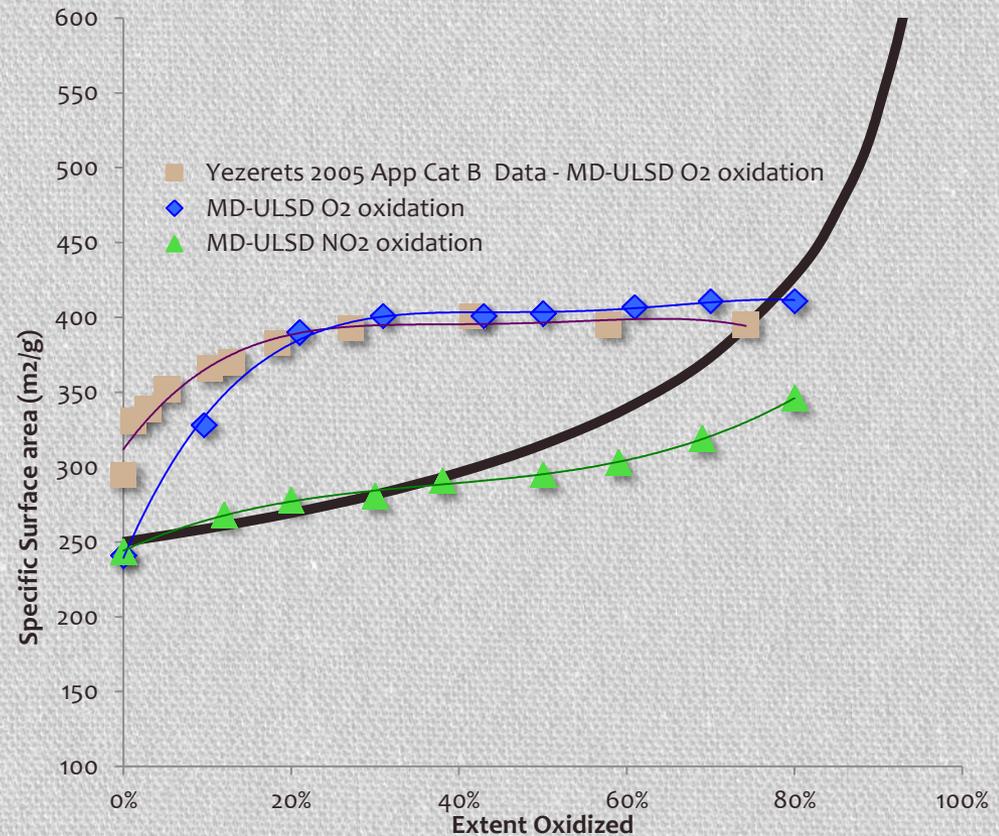
In contrast to O₂ TPOs, NO₂ TPOs show no fuel dependent behavior

1% NO₂ TPOs on LD PM



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

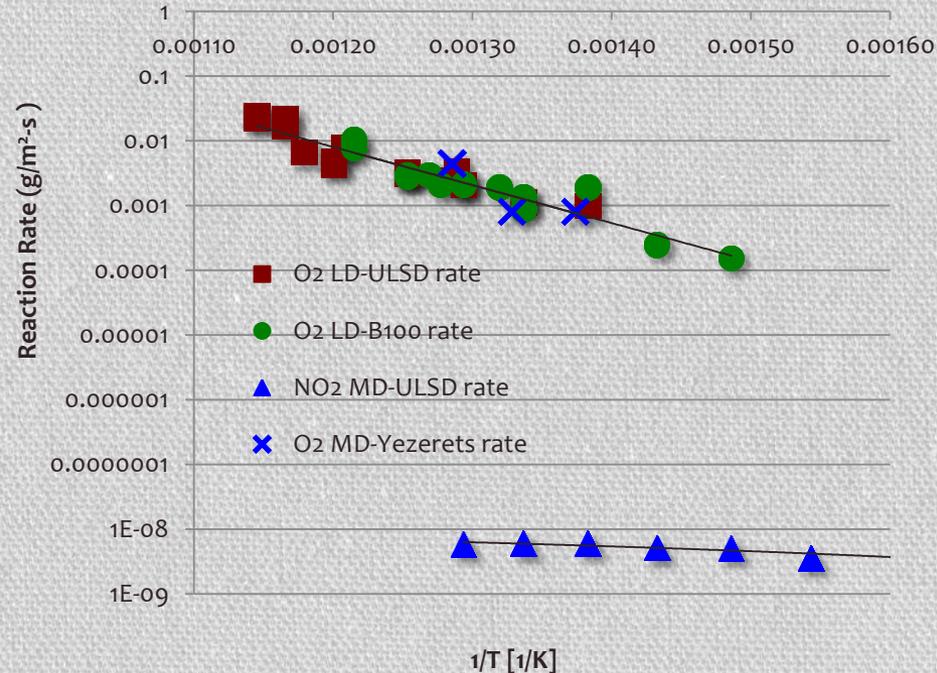
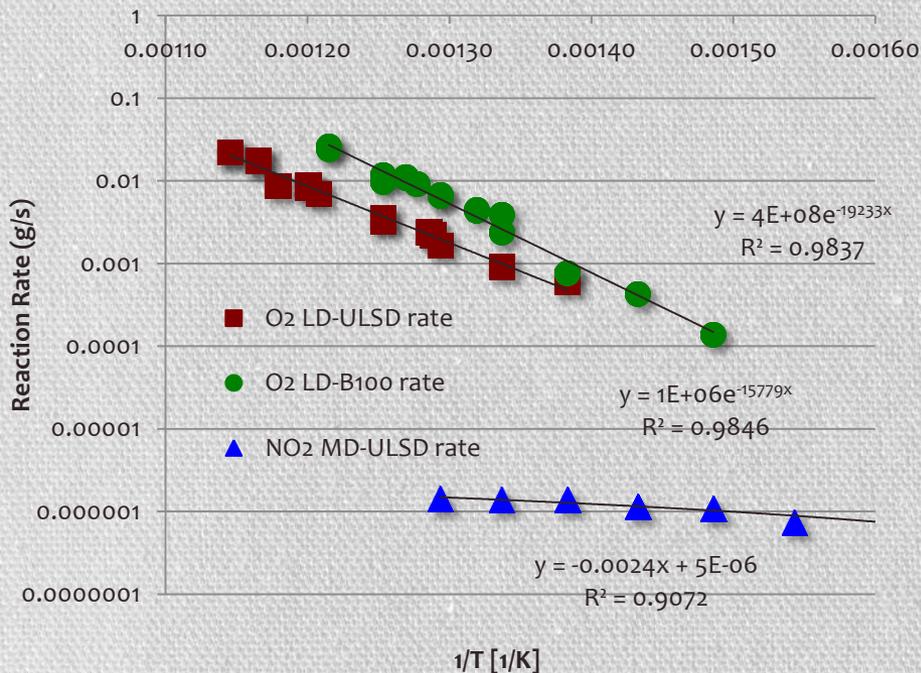
- Engine size impacts surface area trend/limit
 - O₂ oxidation surface area profile is different for LD and MD PM
 - Current MD-PM is consistent with data from Yezerets, 2005.
- Though the O₂ oxidation reaction does not follow a shrinking core type burnout, the NO₂ oxidation fits the trend.
- BET with NO₂ data for biofuel blends needs to be collected.



NO₂ Oxidation activation energy is still very different from O₂ oxidation, even after surface area normalization.

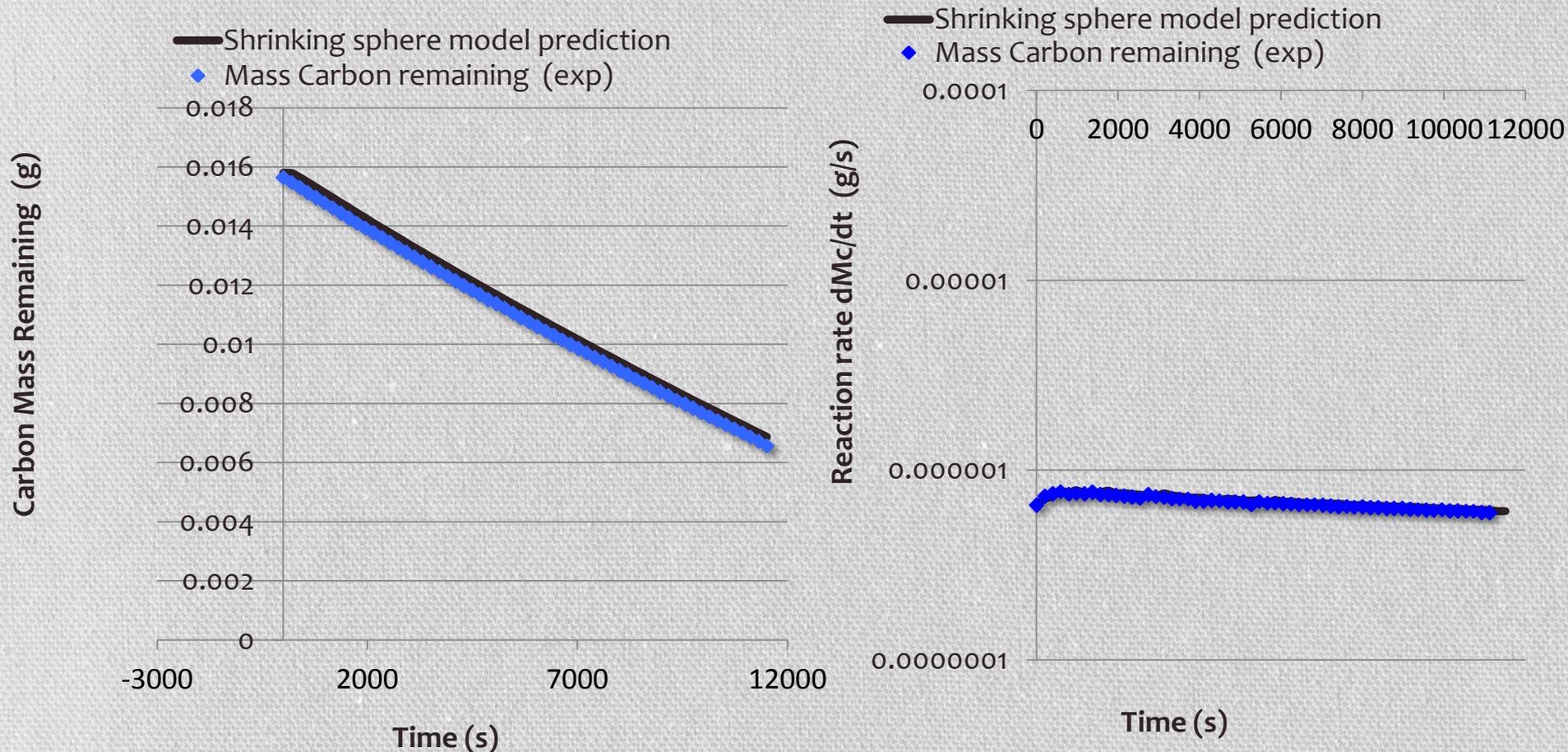
- Calculate a much smaller activation energy from NO₂ IPO data, (left) indicates possible diffusion limitation
- NO₂ oxidation surface area increases much more than for O₂, however instantaneous surface area normalization is not enough to match the measured O₂ reaction kinetics (right)
- Still need to collect data on biofuel blends.

Oxidizer	PM	Ea/R	Ea, kJ/mol
O ₂	ALL	13625	113
NO ₂	MD-ULSD	1793	15

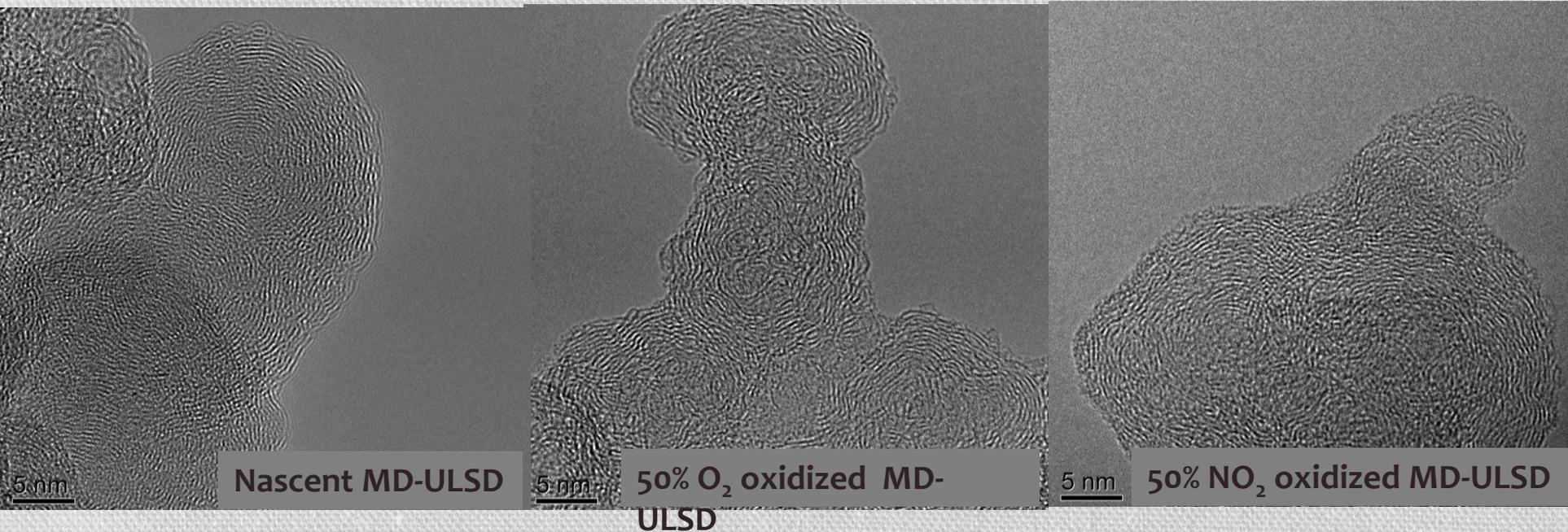


Experimental data matches the shrinking sphere prediction

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



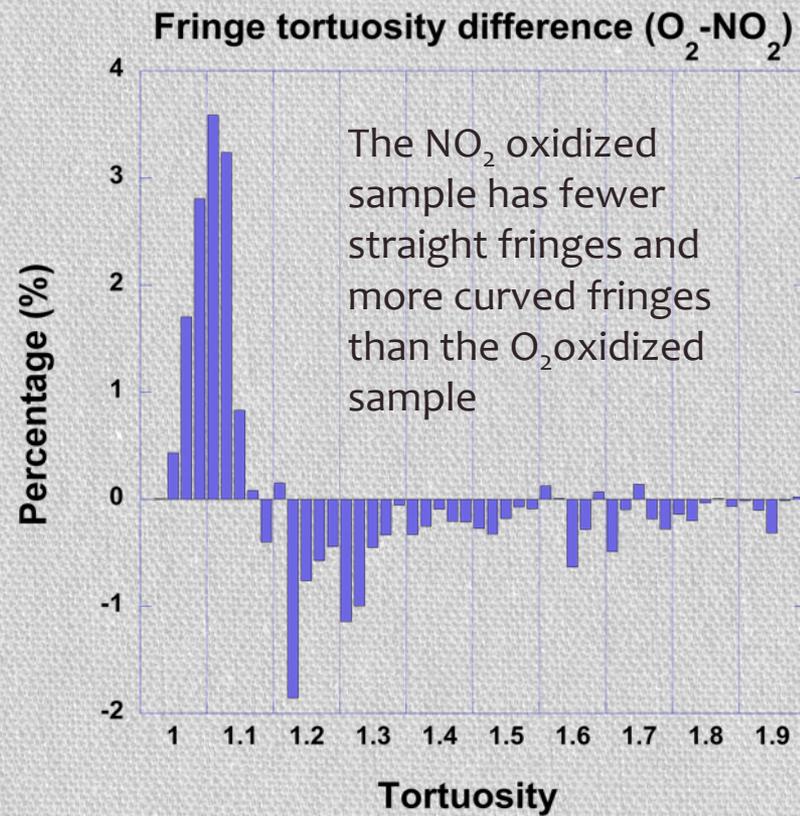
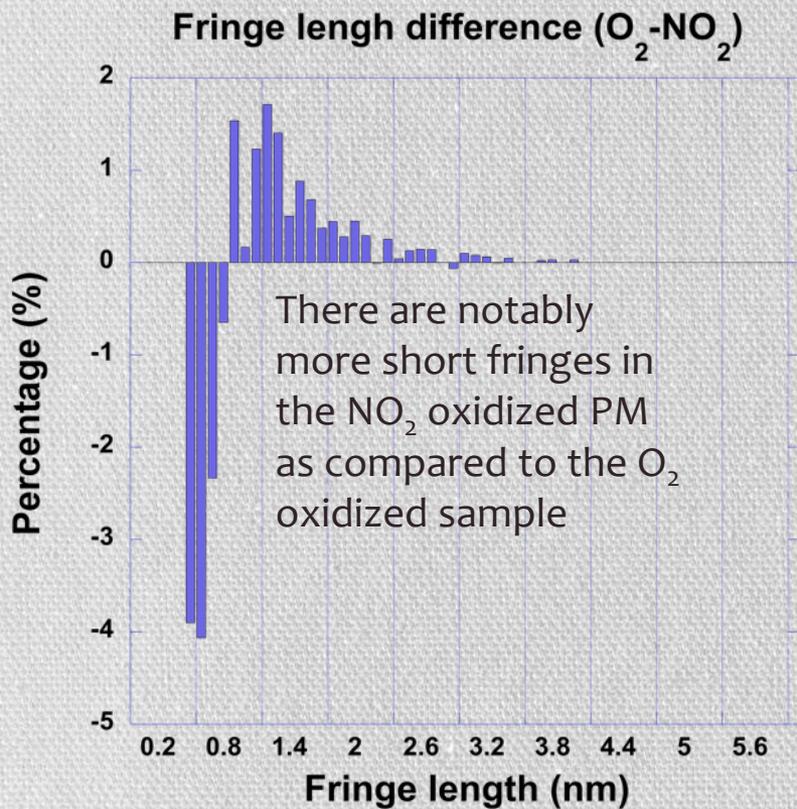
O₂ oxidation of MD-ULSD develops 'divots' related to the increasing porosity/surface area seen with extent oxidation, similar to LD-PM. Divots indicate preferential reactivity.

NO₂ oxidation shows a difference in the outermost layer of the particulate. The crumbling is indicative that NO₂ reacts upon contact and breaks up the outer surface of the particulate, indiscriminately.

Fringe difference analysis ($O_2 - NO_2$)

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.

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



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 consistent 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!



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Questions?

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