Impact of EGR on Soot Nanostructure and Reactivity

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Background

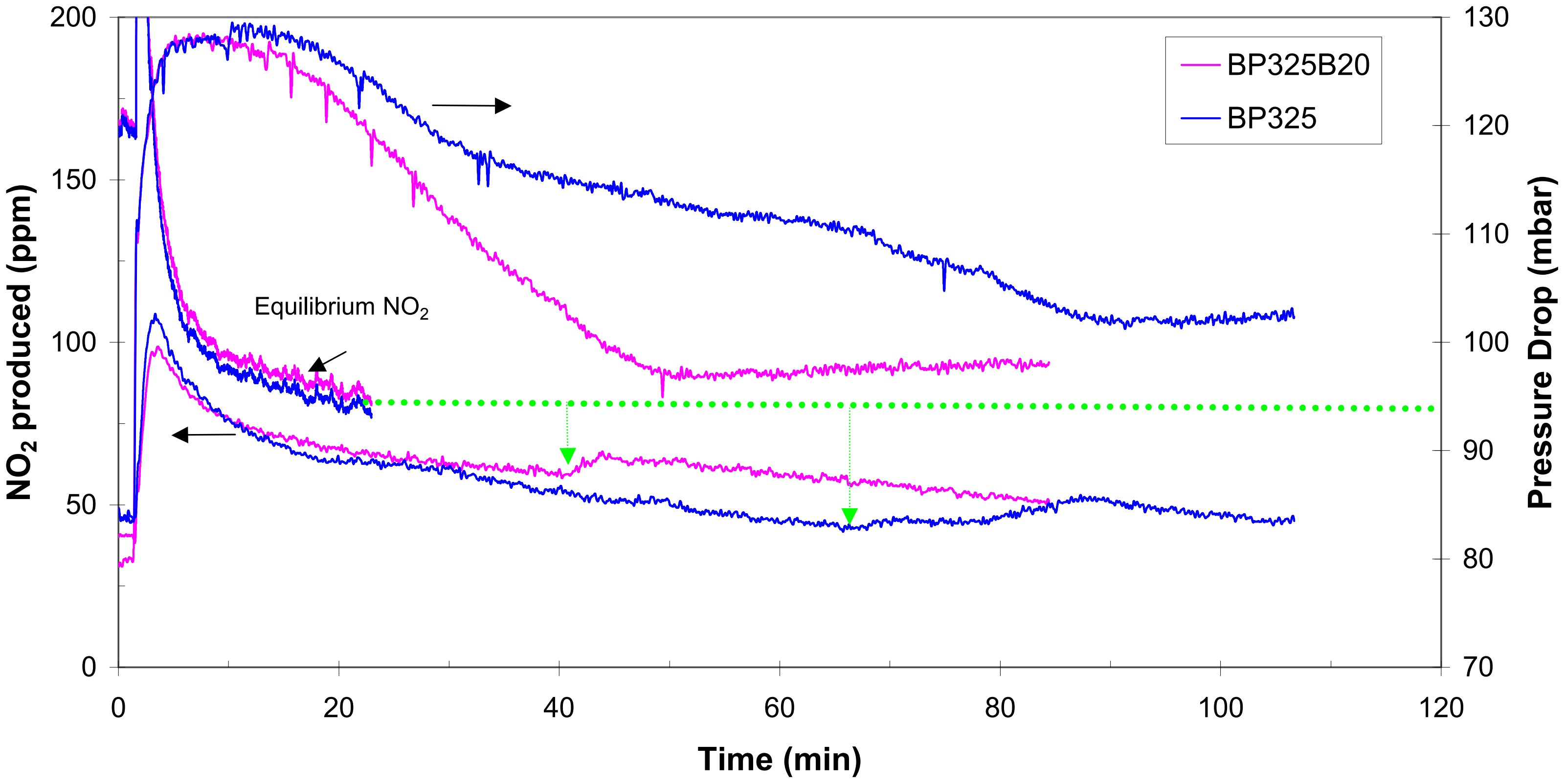
- Vander Wal et al. published in *Combustion & Flame* in 2003 and 2004 papers demonstrating: (1) differences in the structure within soot primary particles with benzene, ethanol and acetylene, and (2) particles with less ordered structure provided higher oxidative reactivity
- Observations of a soot 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 ?
- Extensive observations by Song and Boehman on variations in soot reactivity with alternative fuels leading to significantly different behavior for B100-derived soot, reported at DEER 2005 and published in *Combustion & Flame* 2006

Summary

- Previous observations on impacts of fuel formulation on diesel soot nanostructure and reactivity
  - ➔ Enhanced reactivity of B100 soot arises from surface oxygen functional groups and leads to a unique oxidation process
  - ➔ Diesel soot (from neat F-T diesel) follows a “shrinking core” oxidation process
- How will EGR affect the formation and maturation of diesel soot?
  - ➔ Reduced temperature may affect the pool of soot precursors and alter the transition to an ordered and graphitic structure
  - ➔ Shift in gas composition from EGR (less O_2 and more CO_2) may exert chemical effects on the soot formation process
  - ➔ i.e., three effects may be present – thermal, chemical and dilution

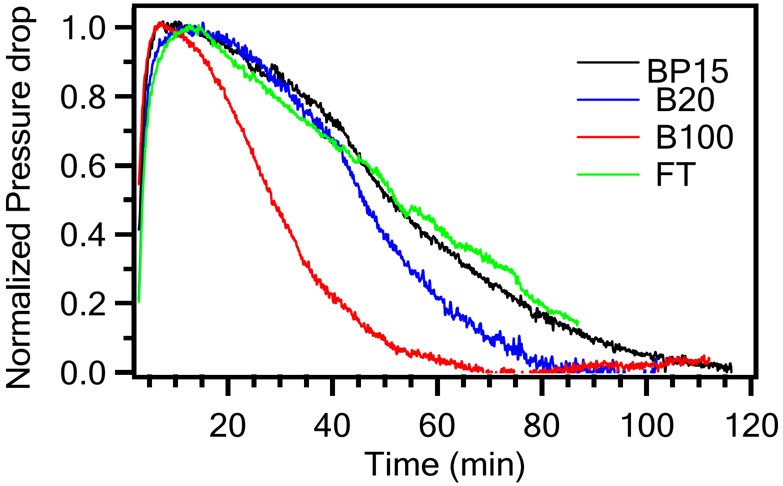
Fuel Composition Effects on Emissions

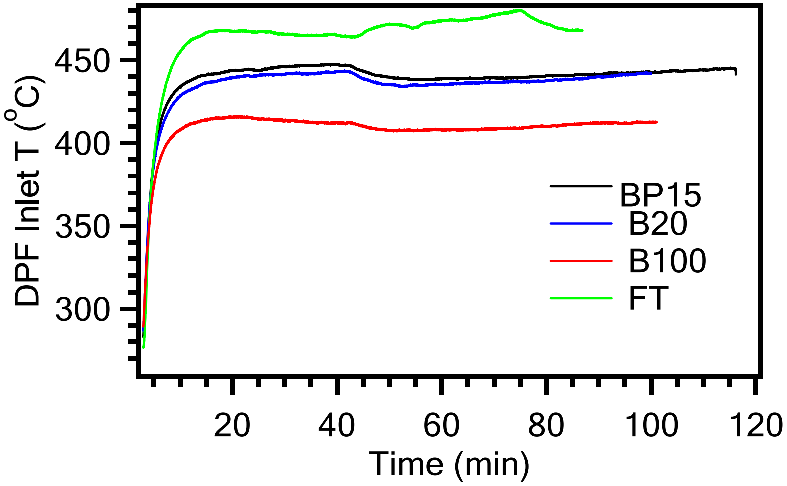
BP-325 and BP-325/B20 Test Fuels in a High Temp Regeneration

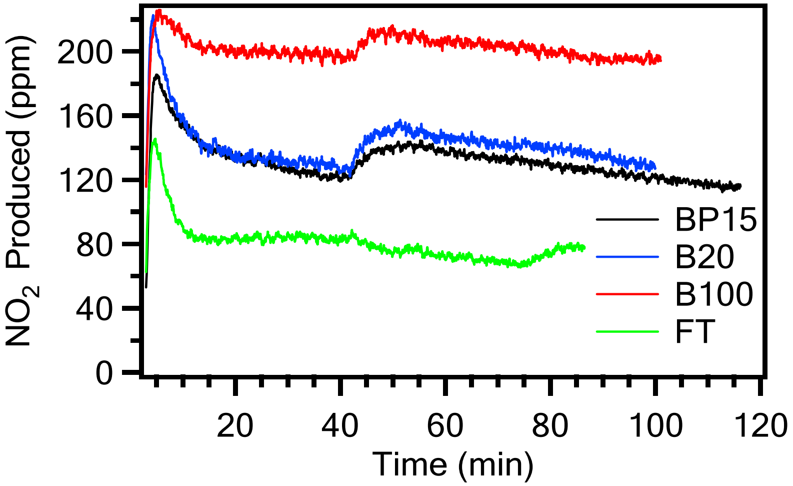


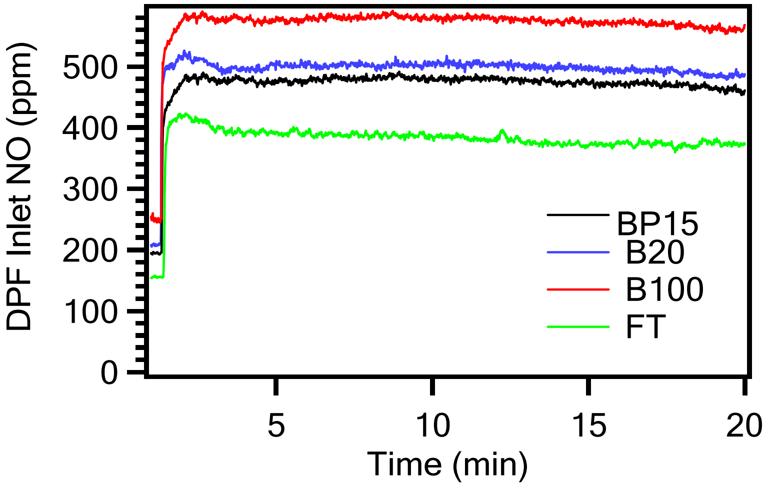
Initial observation of soot reactivity enhancement with biodiesel

High Temperature Regeneration (from 280 to 450 °C)





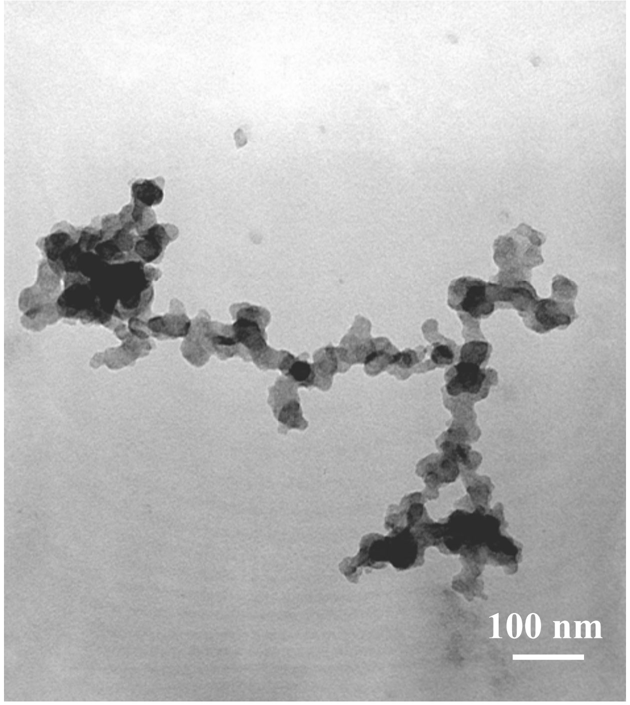




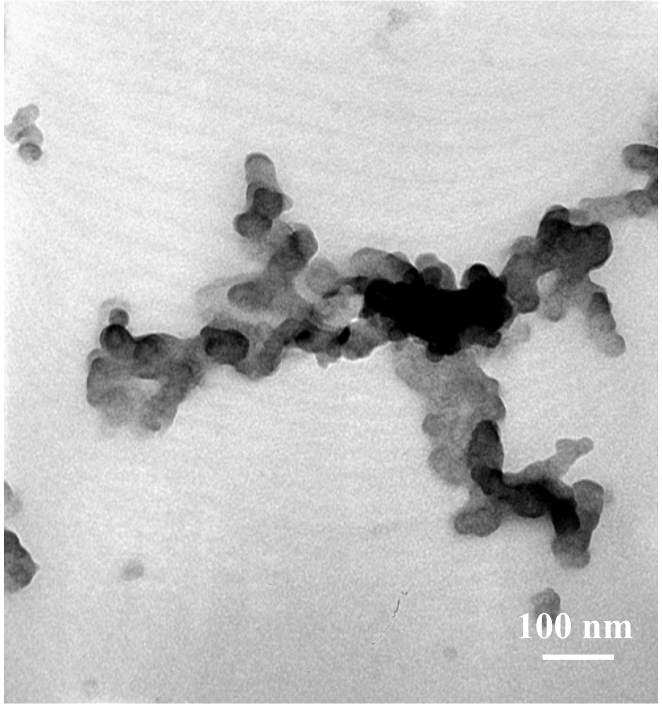
Follow-up observations with neat biodiesel and F-T

Variation in Heavy Hydrocarbon Fraction

Soot Morphology



(c) BP15 Derived PM

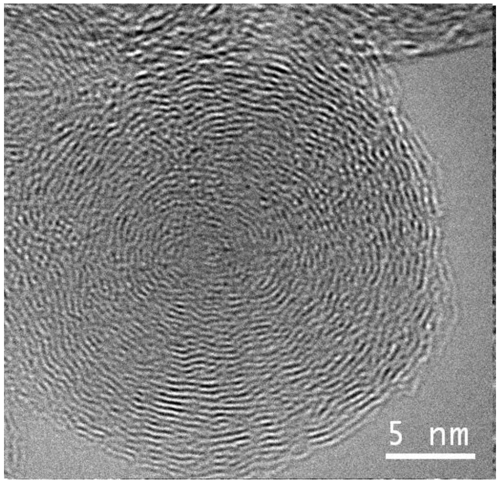


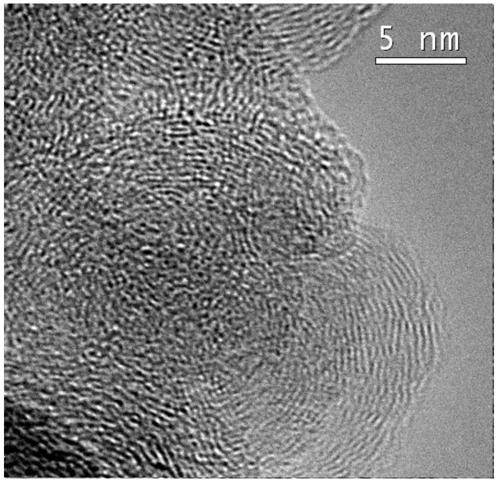
(d) BP15B20 Derived PM

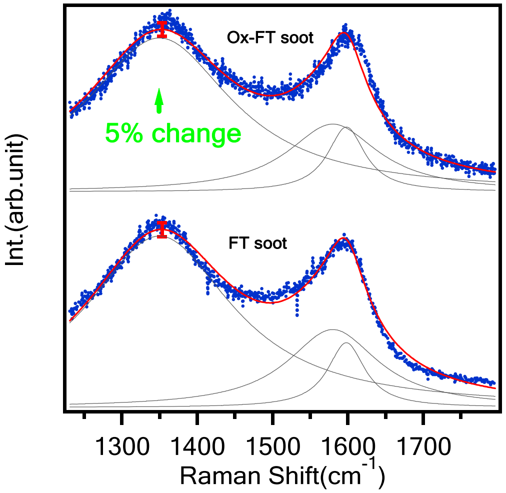
Structural Change During Early Stage of Oxidation (30min)

Initial **Oxidized**

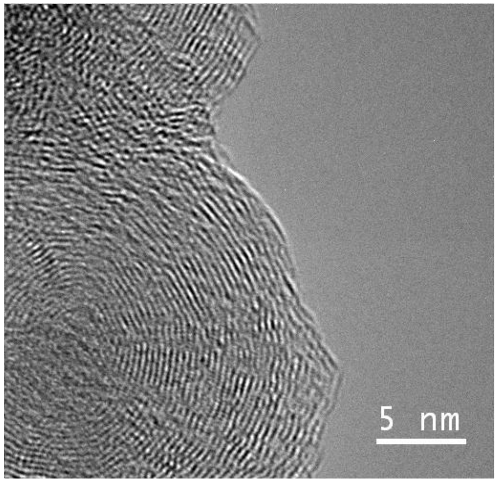
FT

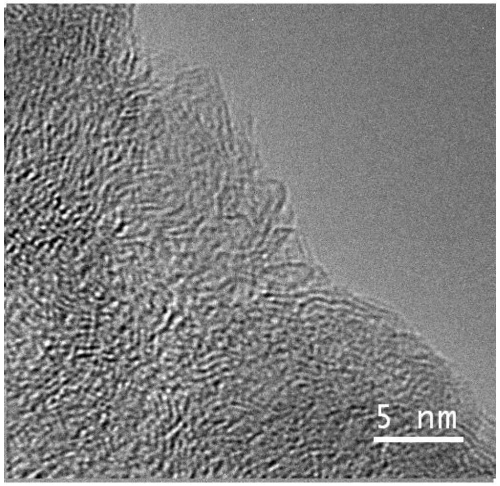


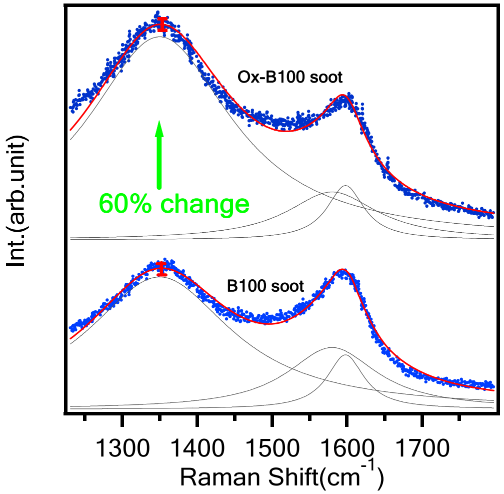




B100







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

Approach for Examination of the Impact of EGR

- Examined the impact of EGR and “simulated EGR” in three different experimental systems
  - Co-flow laminar ethylene diffusion flame (a Santoro burner)
  - Yanmar LA70 5.8 hp DI naturally aspirated diesel engine
  - DDC/VM Motori 2.5L, 4 cyl, 16 valve, common rail diesel engine (referred to here as “DDC” engine)
- Focus in this presentation is on the 2.5L engine results
  - Impact of simulated EGR (dry CO_2 injection in the intake)
  - Impact of 20% EGR
  - Examined soot structure, reactivity and oxidation kinetics

Impact of EGR on Soot Oxidation Rate

2.5L VM Motori/DDC Turbodiesel, 1600 rpm, 60 lb-ft

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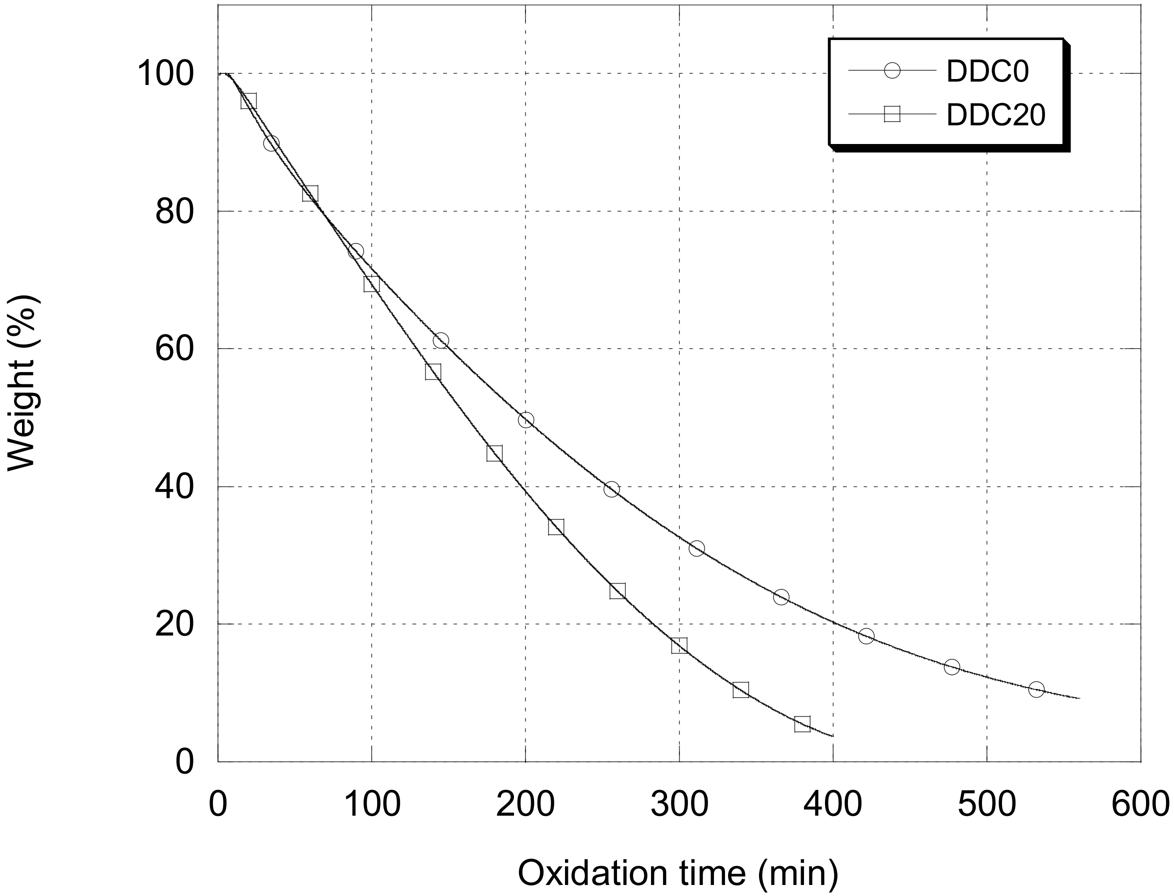
2.5L VM Motori/DDC Turbodiesel, 1600 rpm, 60 lb-ft

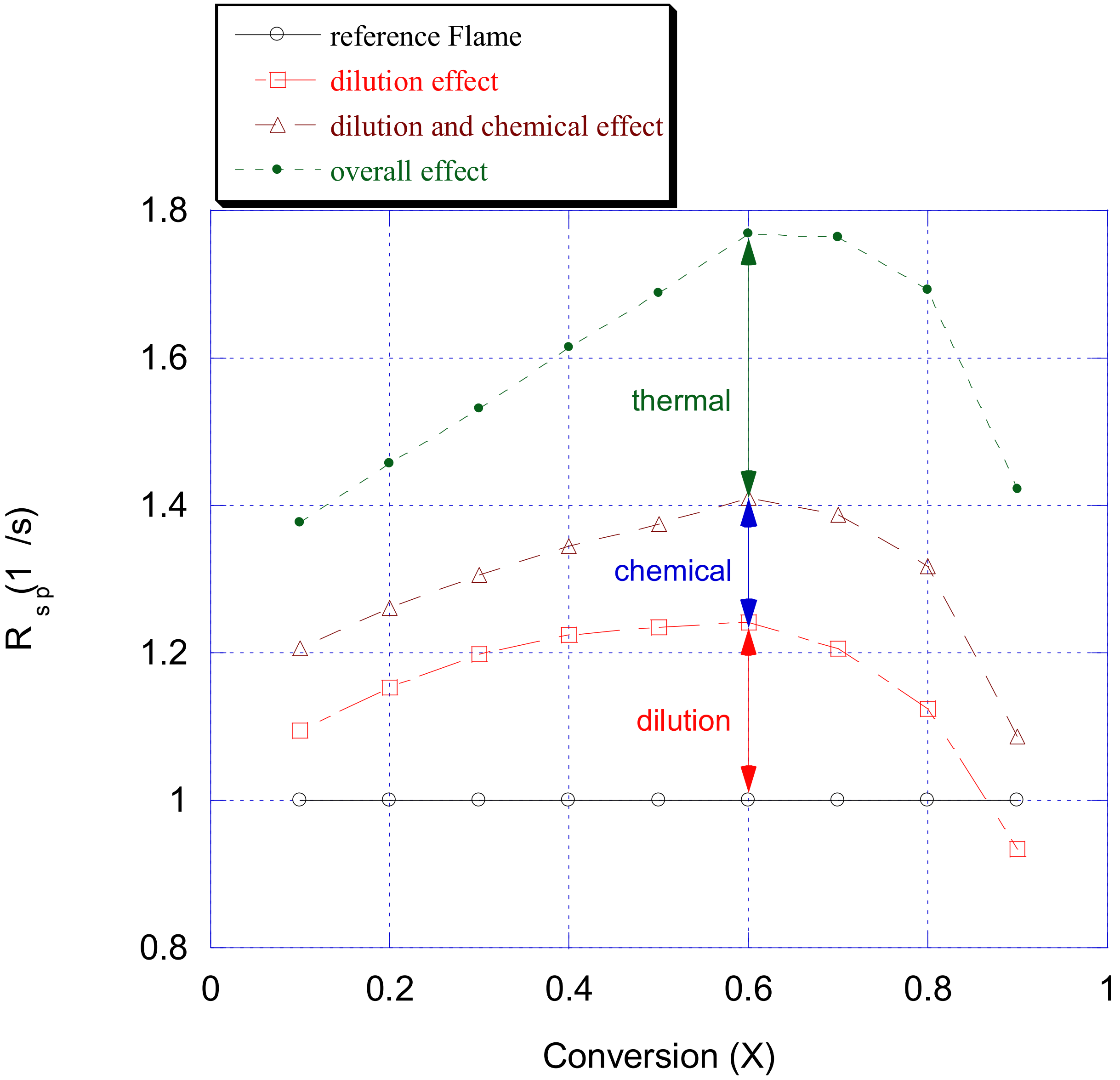


Changes in Active Surface Area with “EGR”

Soot Symbol	Soot Origin	Amount of Chemisorbed Oxygen	
		Oxygen Uptake (g_{oxygen} / g_{soot})	ASA_i (m^2 / g)
F0	Diffusion flame (0% CO2)	0.00704	22.0
F15	Diffusion flame (15% CO2)	0.0144	45.0
S0	Yanmar engine (0% CO2)	0.00544	17.0
S8	Yanmar engine (8% CO2)	0.01056	33.0
DDC0	DDC engine (0% EGR)	0.00352	11.0
DDC20	DDC engine (20% EGR)	0.00832	26.0

- Deconvoluting the competing effects of “EGR” by combination of CO_2 and Ar addition to an ethylene diffusion flame
  - Thermal
  - Dilution
  - Chemical
- Relative impact on oxidative reactivity

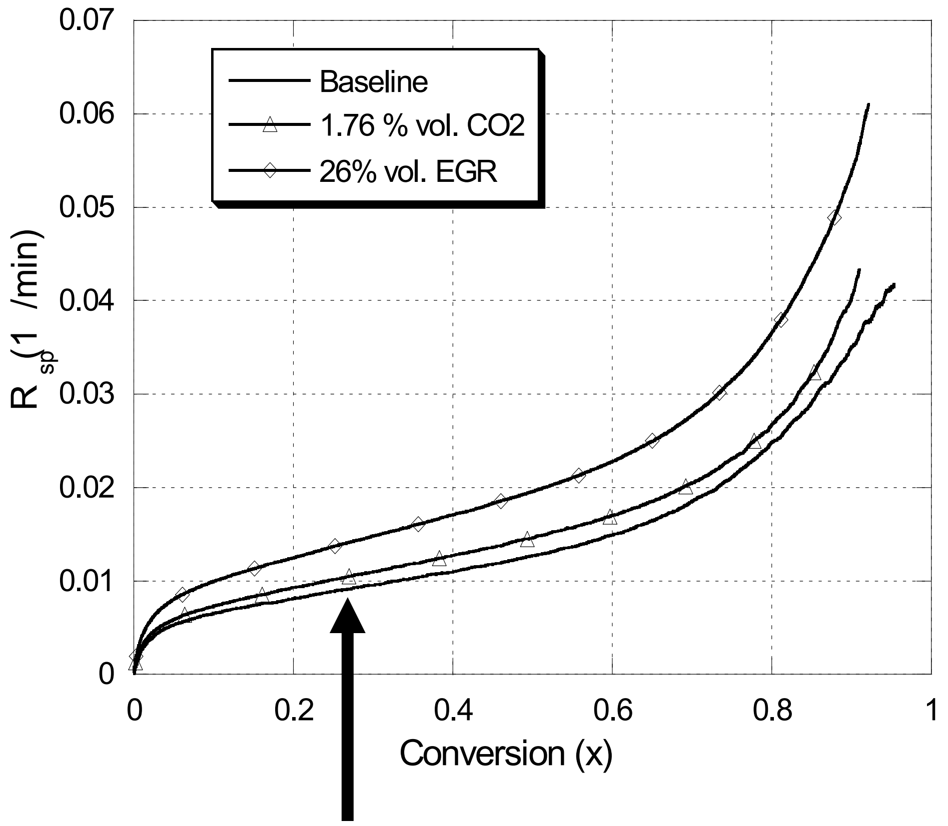
thermal > dilution >> chemical



Chemical Impact on Soot Oxidation Rate

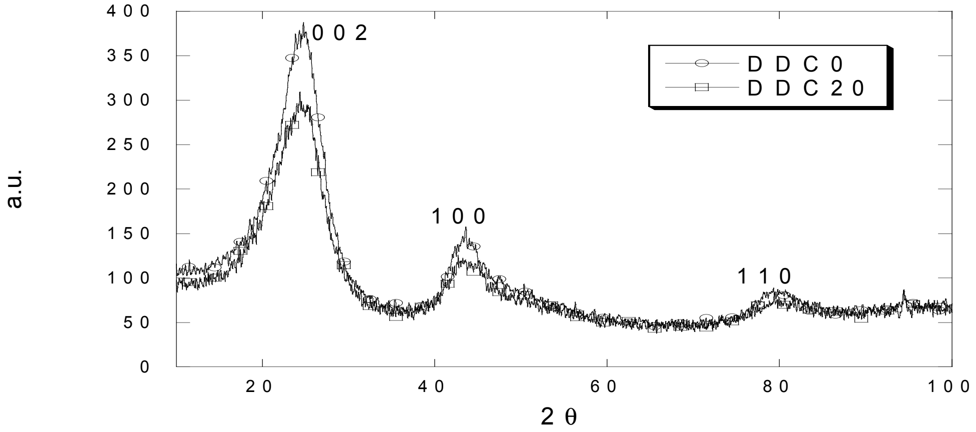
Comparing 1.76% CO_2 Addition vs. 26% EGR

Engine Speed	**1500 rpm**	
Engine Torque	**50 lb-ft.**	
Start of Pilot Injection (ºBTDC)	**31**	
Start of Main Injection(ºBTDC)	**-3**	
Intake Gas Temperature (ºC)	**0% EGR**	**38**
	CO_2 Addition	**36**
	EGR	**78**
Exhaust Temperature (ºC)	**0% EGR**	**215**
	CO_2 Addition	**212**
	EGR	**241**



Chemical effect (from CO_2) is small, confirming the flame results

XRD spectra

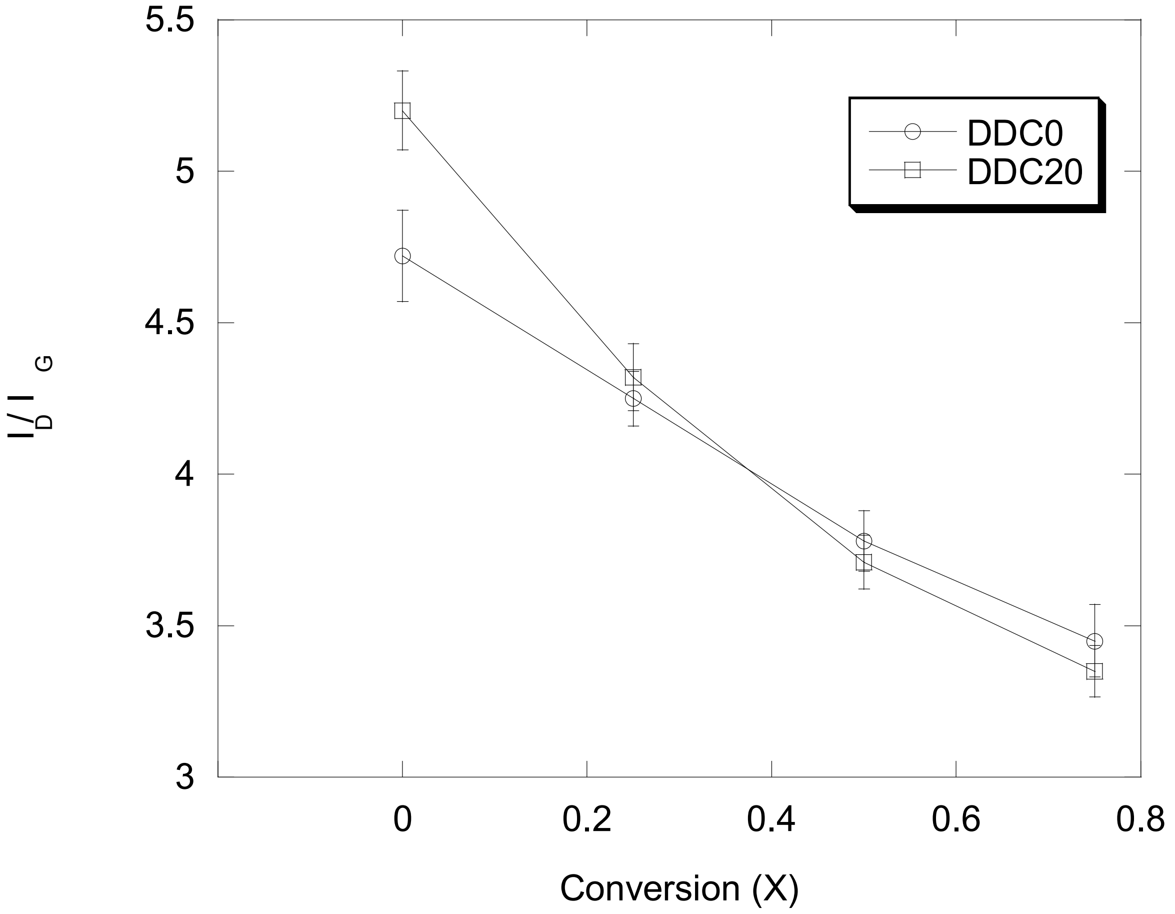


Structural characteristics from the XRD spectra

Soot Symbol	Soot Origin	d_{002} (nm)	L_c (nm)	L_a (nm)	k (layers)	*R*
F0	**Diffusion flame (0% CO_2)**	**0.356**	**1.321**	**2.587**	**~ 5**	**4.01**
F15	**Diffusion flame (15% CO_2)**	**0.358**	**1.183**	**2.049**	**~ 4**	**3.01**
Y0	**Yanmar engine (0% CO_2)**	**0.355**	**1.237**	**3.030**	**~ 5**	**4.68**
Y8	**Yanmar engine (8% CO_2)**	**0.357**	**1.213**	**2.477**	**~ 4**	**4.22**
DDC0	**DDC engine (0% EGR)**	**0.349**	**1.345**	**2.919**	**~ 5**	**4.56**
DDC20	**DDC engine (20% EGR)**	**0.351**	**1.207**	**2.526**	**~ 4**	**3.97**

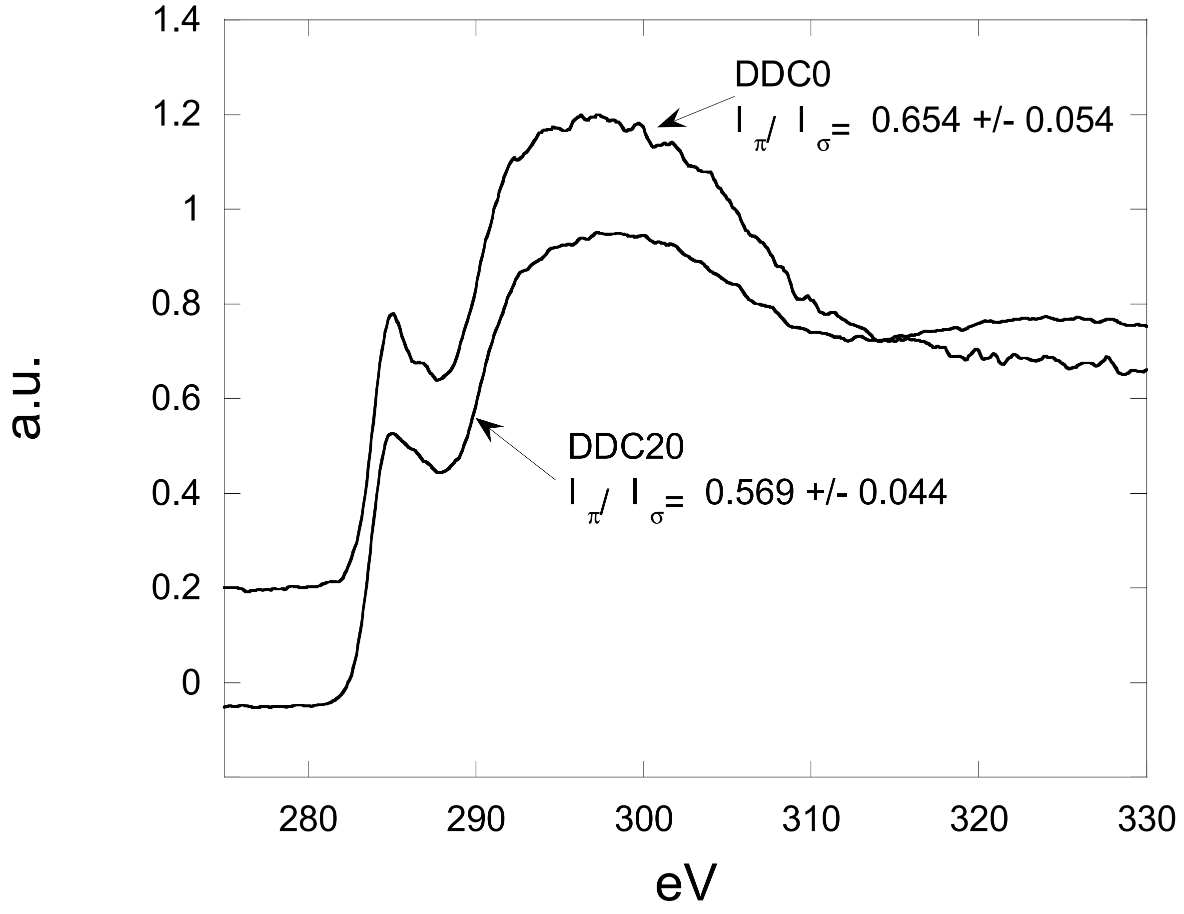
Indicates more edge sites which means higher reactivity ↑

2.5L VM Motori/DDC Turbodiesel, 1600 rpm, 60 lb-ft



No clear trend with extent of oxidation

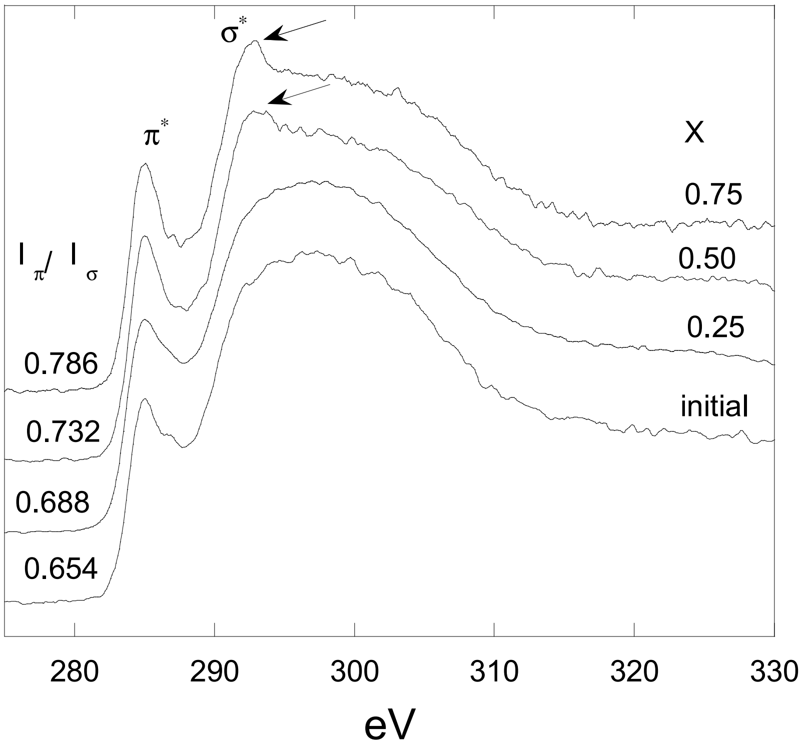
2.5L VM Motori/DDC Turbodiesel, 1600 rpm, 60 lb-ft



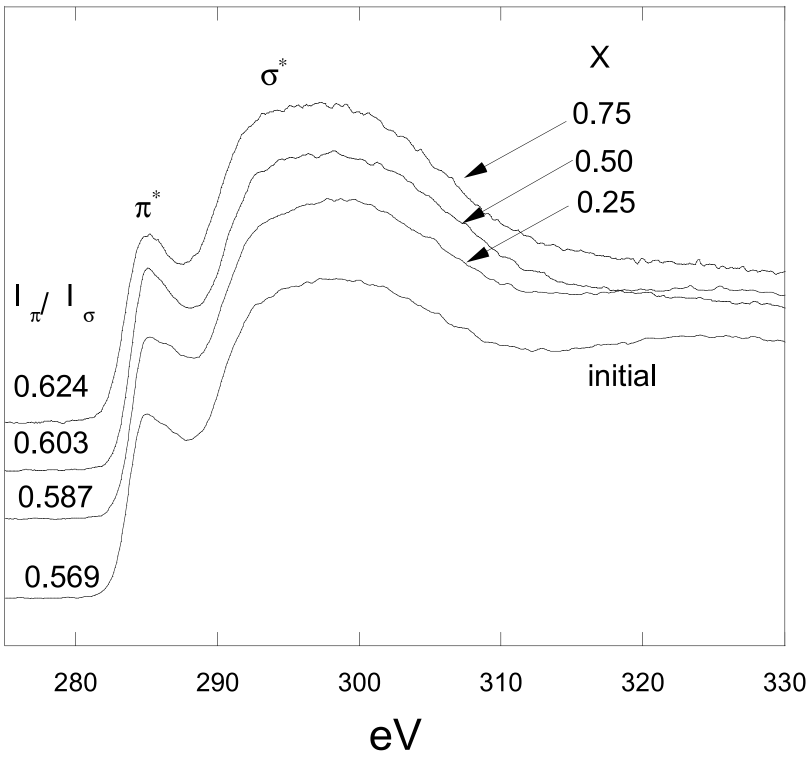
Initial difference in the π peak indicates greater disorder in the EGR soot

EELS Analysis of Oxidized Soot Structure

2.5L VM Motori/DDC Turbodiesel, 1600 rpm, 60 lb-ft



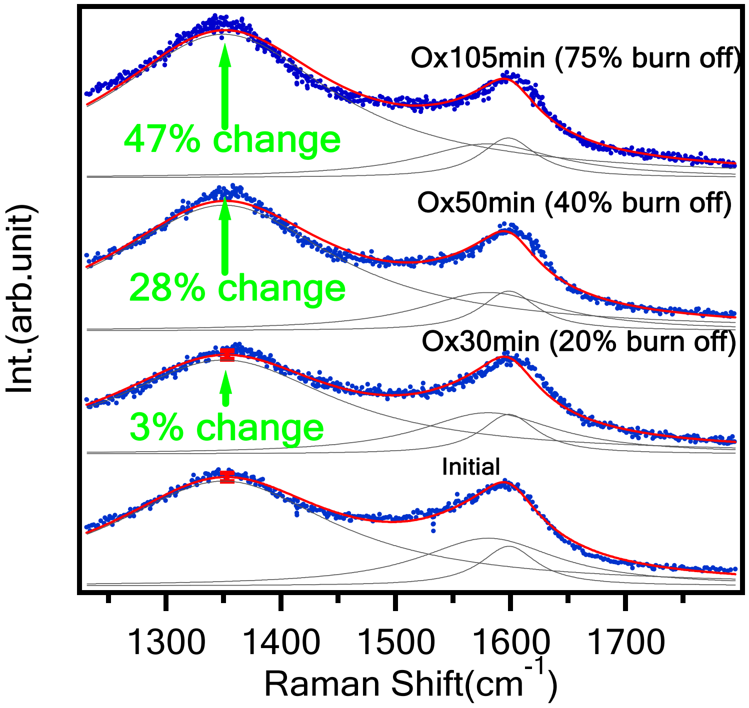
0% EGR

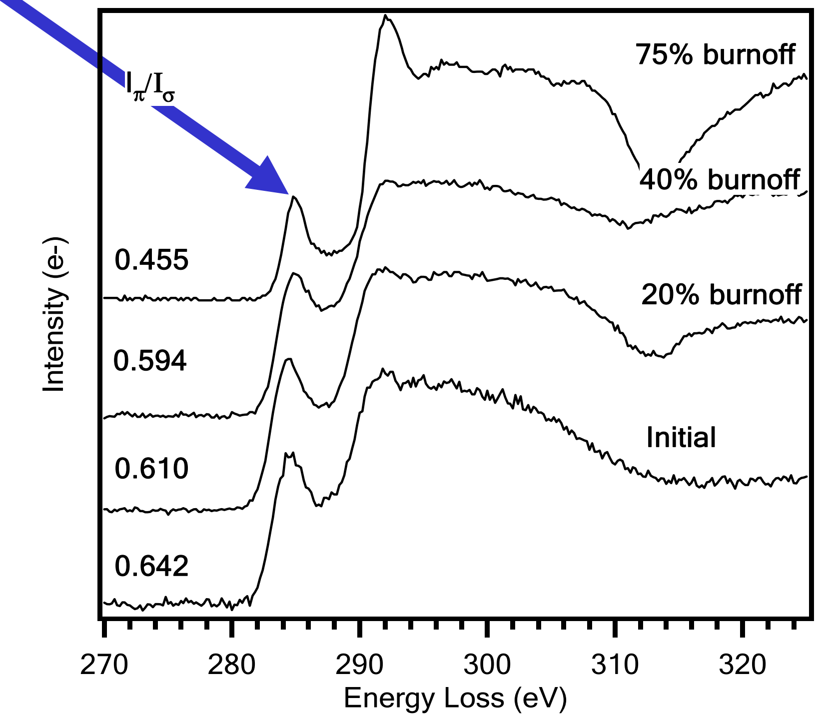


20% EGR

Presence of σ* peak in 0% EGR soot indicates graphitization of the 0% EGR soot during oxidation

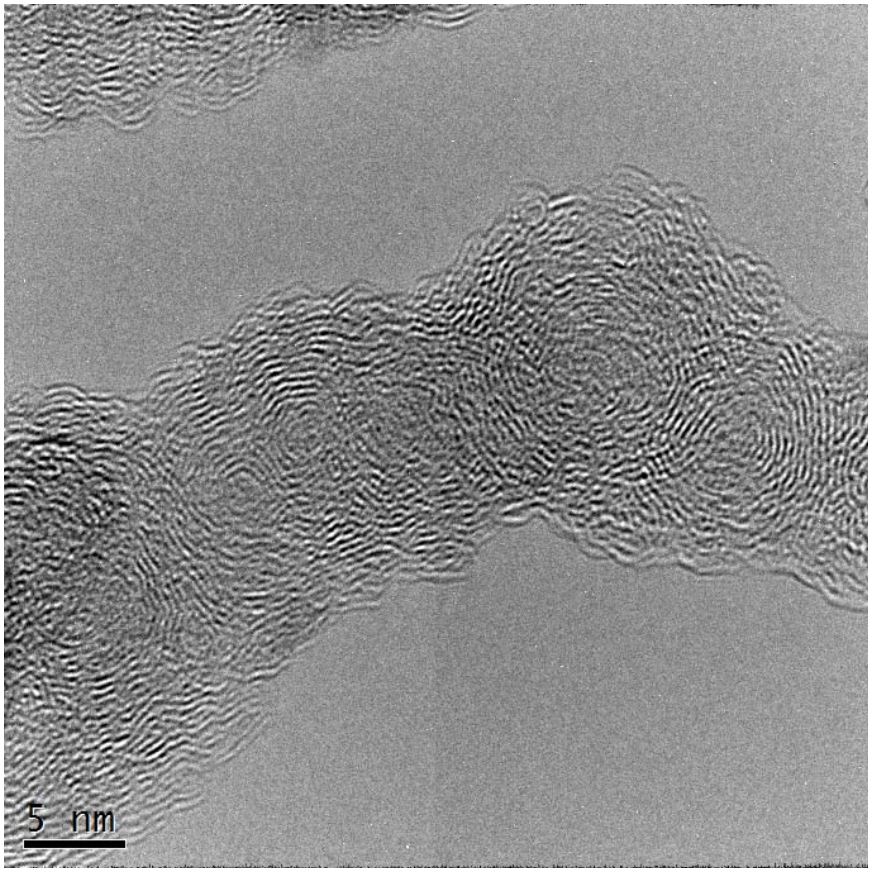
Gradual increase in D band and decrease in relative ratio of graphitic peak suggesting a tendency toward disordered state



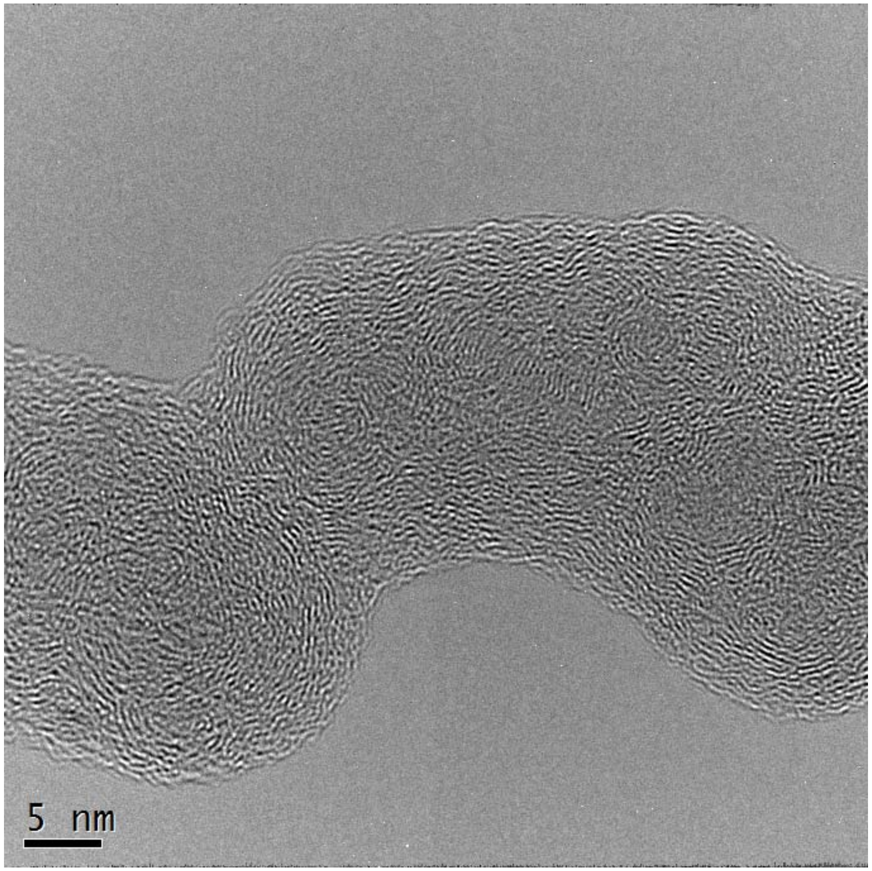


From previous analyses of FT100 soot (DEER 2005)

Electron Microscopy of Initial Soot Nanostructure

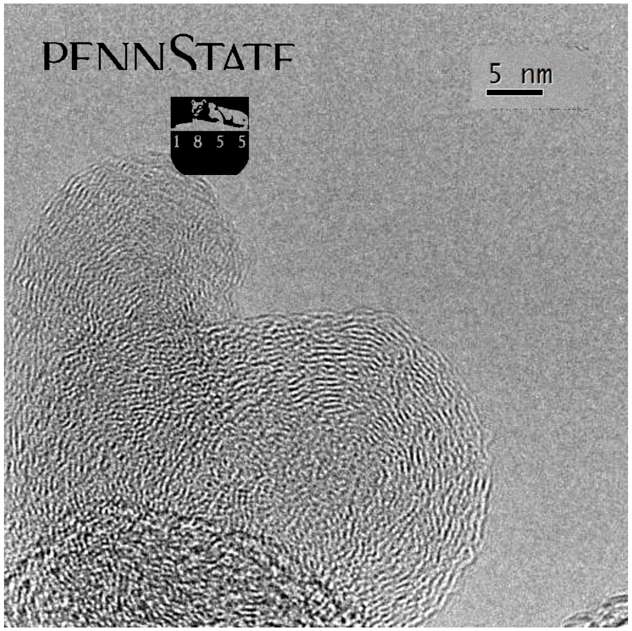


(a) BP15 Derived Soot
(Yanmar Engine)
without CO2

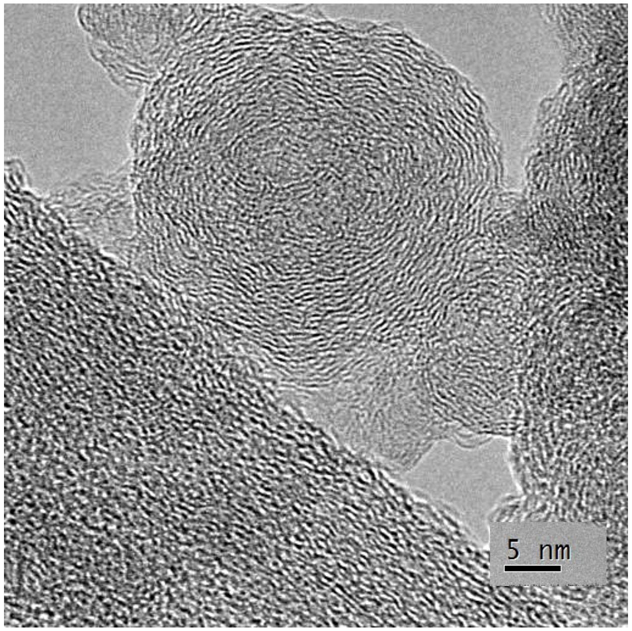


(b) BP15 Derived Soot
(Yanmar Engine)
with CO2

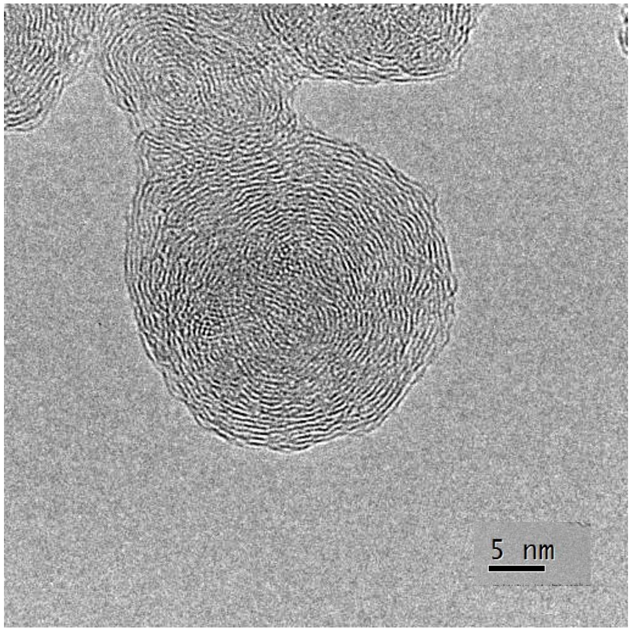
Electron microscopy of DDC soot nanostructure as a function of burn off



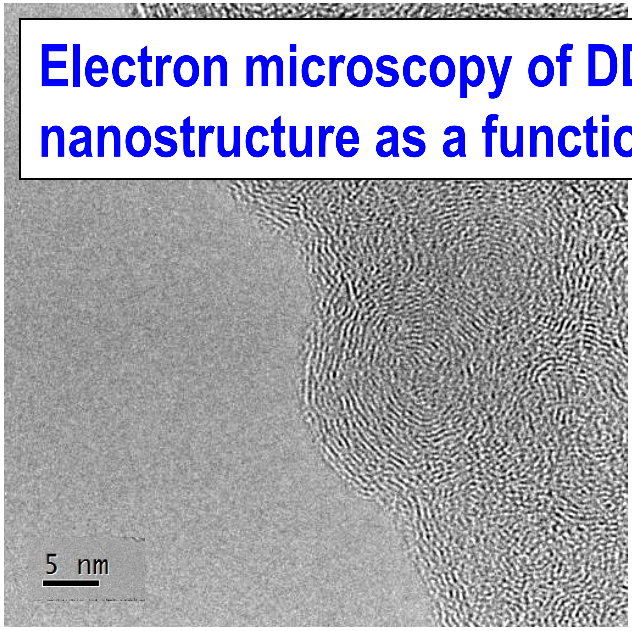
0%EGR – 0BO



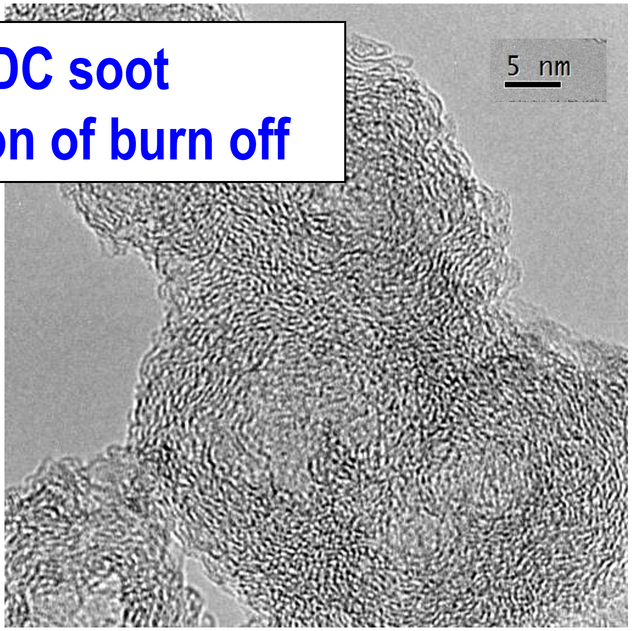
0%EGR-25BO



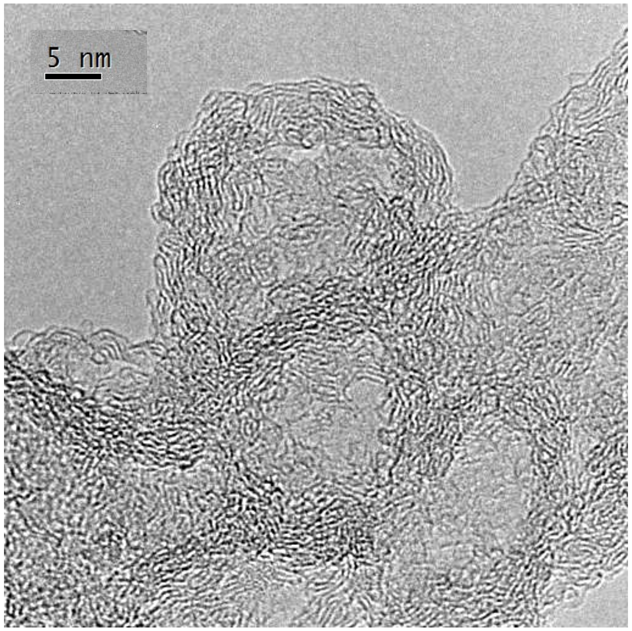
0%EGR-75BO



20%EGR – 0BO



20%EGR – 25BO



20%EGR – 75BO

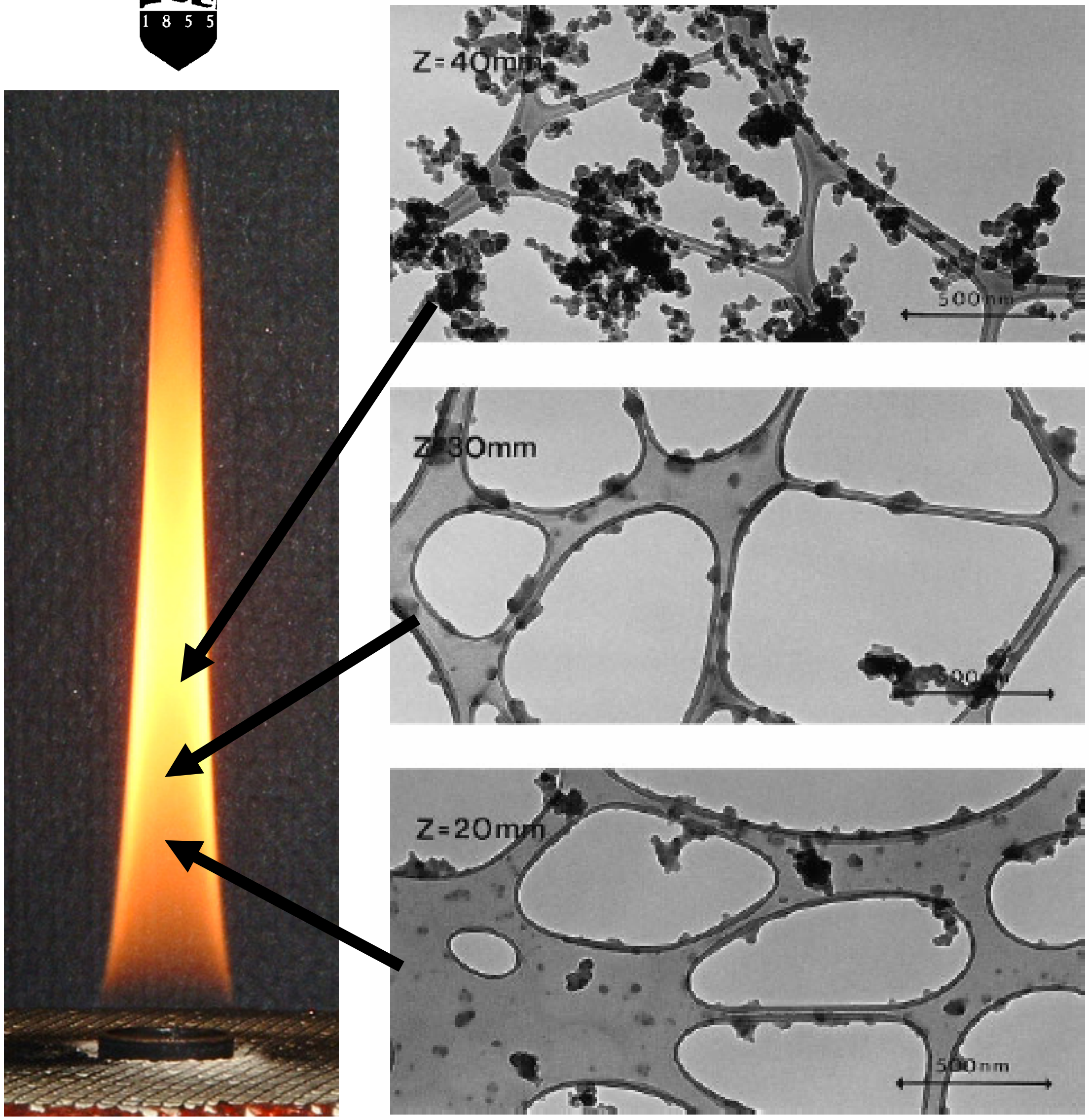
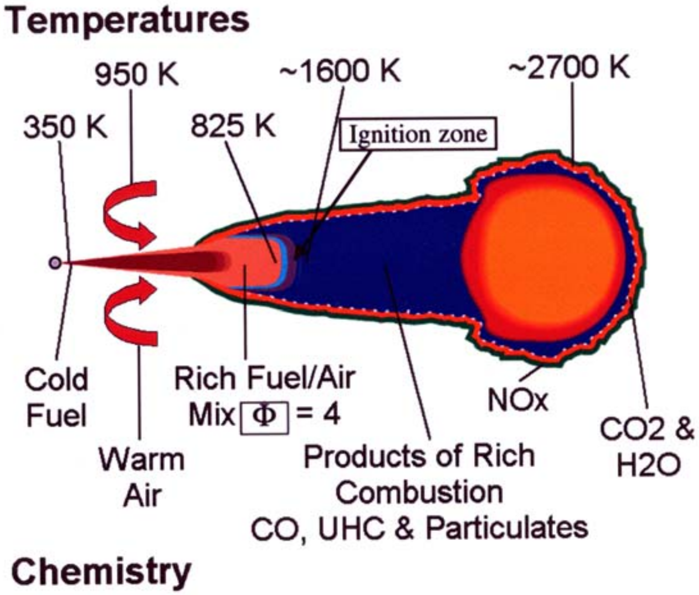
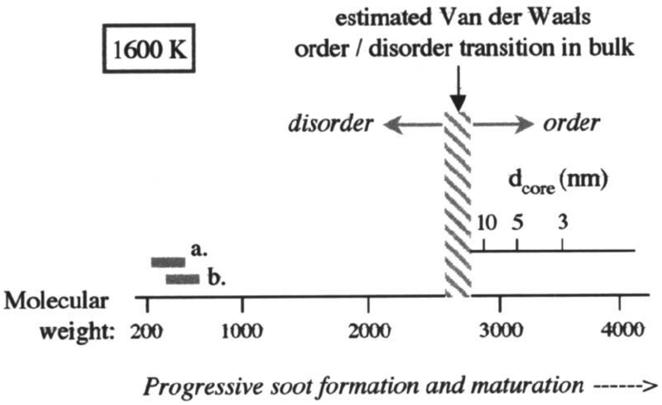


Fig. 1. Micrographs of particulate material captured on lacy carbon grids sampled from the centerline of the ethene diffusion flame. The transition from precursor particles to soot aggregates occurs between $Z = 30$ and 40 mm.

R. A. Dobbins



C. K. Westbrook



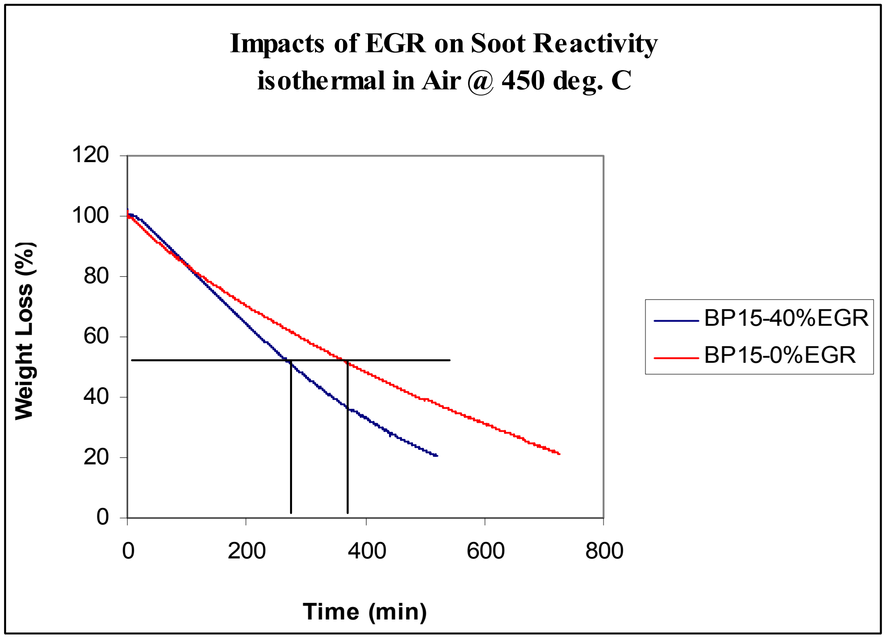
R.H. Hurt

Conclusions

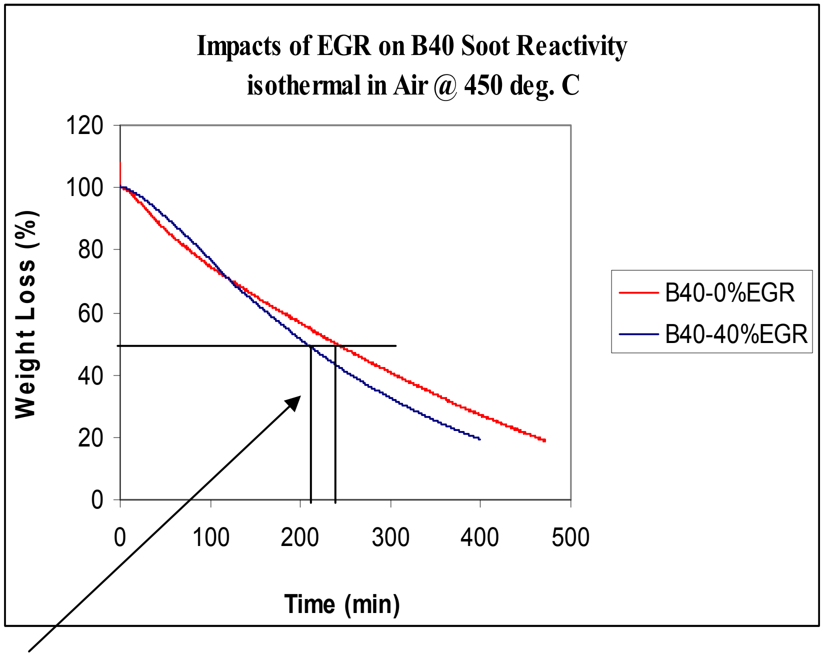
- EGR yields a less ordered initial soot nanostructure and enhanced reactivity due to a greater population of active sites for oxygen chemisoprtion
- The effect of EGR and simulated EGR is consistent between soot samples from ethylene diffusion flames and various diesel engines
- Raman spectroscopy alone may not be sufficient to clearly identify trends in soot structure as a function of extent of oxidation, but a combination of XRD, Raman and EELS can provide a detailed picture of variations in soot nanostructure
- (Not shown here but presented at the Fall 2006 Biodiesel Technical Workshop) The effects of EGR and Biodiesel on soot reactivity are additive! Both enhance reactivity

Impact of EGR on Diesel Soot Reactivity

▪Low Load Condition (Indicated Pilot SOI: 25° BTDC, Indicated Main SOI: -2° BTDC)



Impacts of EGR on Soot Reactivity
isothermal in Air @ 450 deg. C



Impacts of EGR on B40 Soot Reactivity
isothermal in Air @ 450 deg. C

Shortest time to reach 50% burnoff for B40+EGR

B40 and EGR Combined to Enhance of Soot Reactivity: B40+EGR > BP15+EGR ~ B40 > BP15

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-
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