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Thermokinetic Analysis of Ethylene Flame Soot and Diesel Engine Soot

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11th DOE CLEERS Workshop

May 13-15, 2008

Outline

- Soot Reactivity
 - Definition
 - Determining Factors
 - Significance
 - Activities at Penn State
- Experimental
- Thermal & Kinetic Analysis
- Conclusions

Soot Reactivity

Soot oxidative reactivity can be defined as the ease to burn-off Soot at low temperature and/or short time

- ❖ Fuel source
 - Biodiesel soot vs. diesel soot

- ❖ Combustion conditions
 - Low engine load vs. high engine load
 - EGR effects

Soot Reactivity Determining Factors

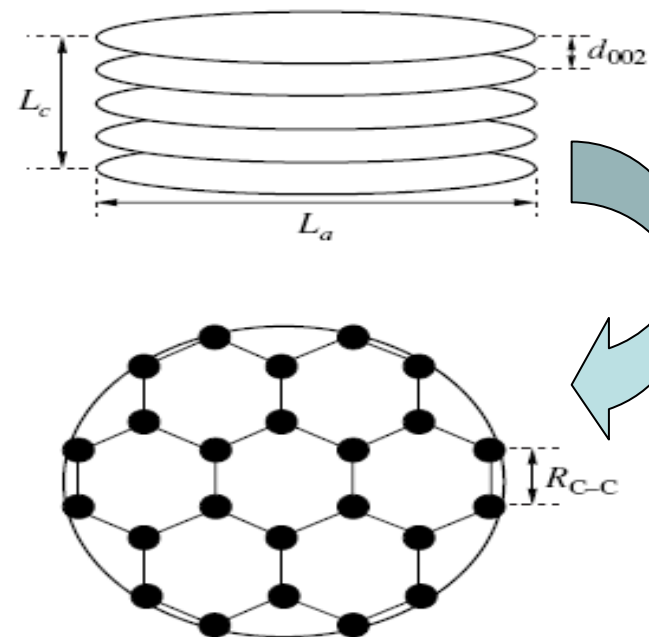
Chemical Properties

- H/C (very low, < 0.1)
- O/C (fuel dependent)
- Impurities (e.g., Ca)
- Catalysts

Physical Properties

- Crystallite Height (L_c)
- Crystallite Width (L_a)
- d -spacing
- tortuosity

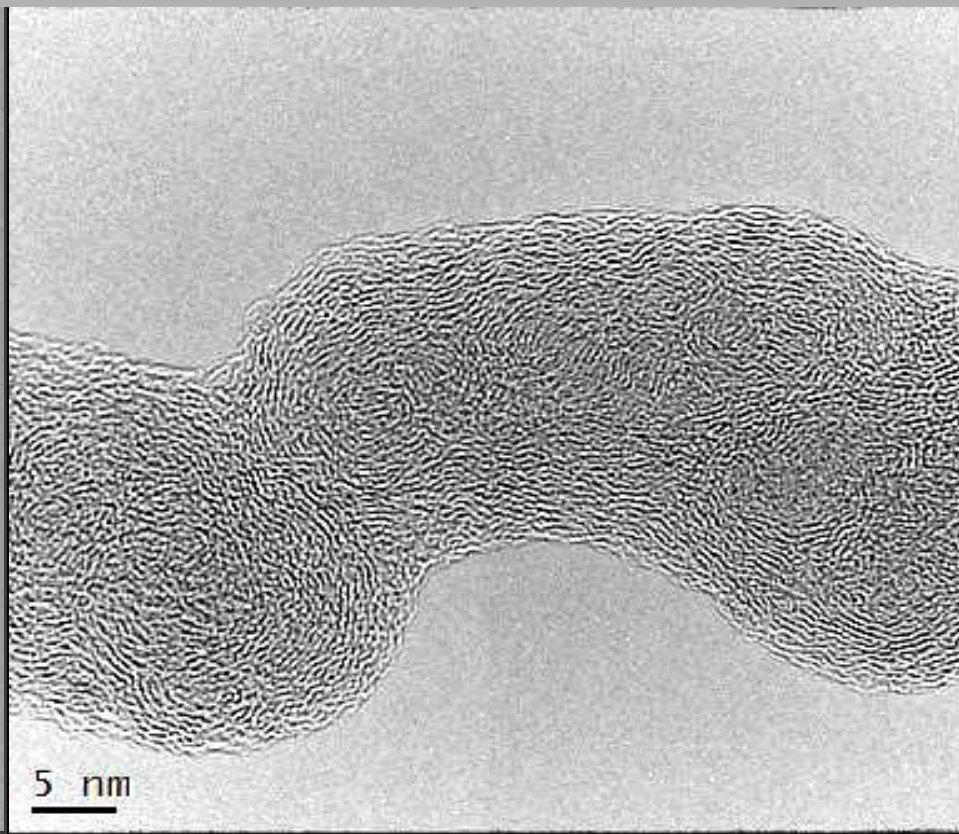
Soot Nanostructure



Soot Morphology and Nanostructure



TEM of diesel soot aggregate composed of many primary particles.



HRTEM of diesel soot primary particles exhibit “*turbostratic*” structure : randomly oriented fringes in the core, long and concentrically arranged fringes at the outermost

Soot Issues and Implications

- Diesel soot is a byproduct carcinogenic carrier results from poor combustion
- Diesel particulate filter (DPF) and exhaust gas recirculation (EGR) to control PM and NOx emissions, respectively.
- EGR suppresses NOx formation but increases PM emissions
 - The DPF physically captures the resulting PM and prevent its release to the atmosphere

PROBLEM:

- Diesel soot requires temperature higher than 500°C to oxidize in air in DPFs
- Diesel exhaust temperature range is 250 – 350°C.

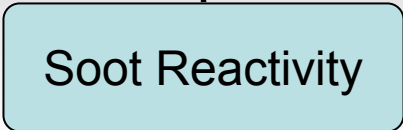
SOLUTIONS:

- Increase engine exhaust temperature (e.g., engine management) → DPF damage
- Enhance soot oxidative reactivity (FBC, nanostructure manipulation).

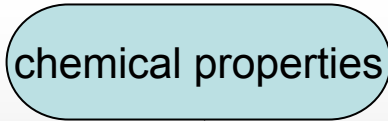
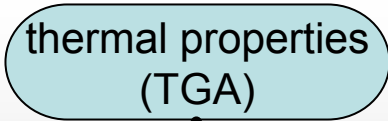
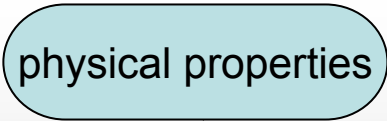
Activities at Penn State



affected by



characterized by



- XRD (quantitative nanostructure)
- Raman (deg. of graphitization)
- TEM (morphology)
- HRTEM (qualitative nanostructure)
- EELS (deg. of graphitization)

- Nonisothermal**
- oxidation
- kinetics

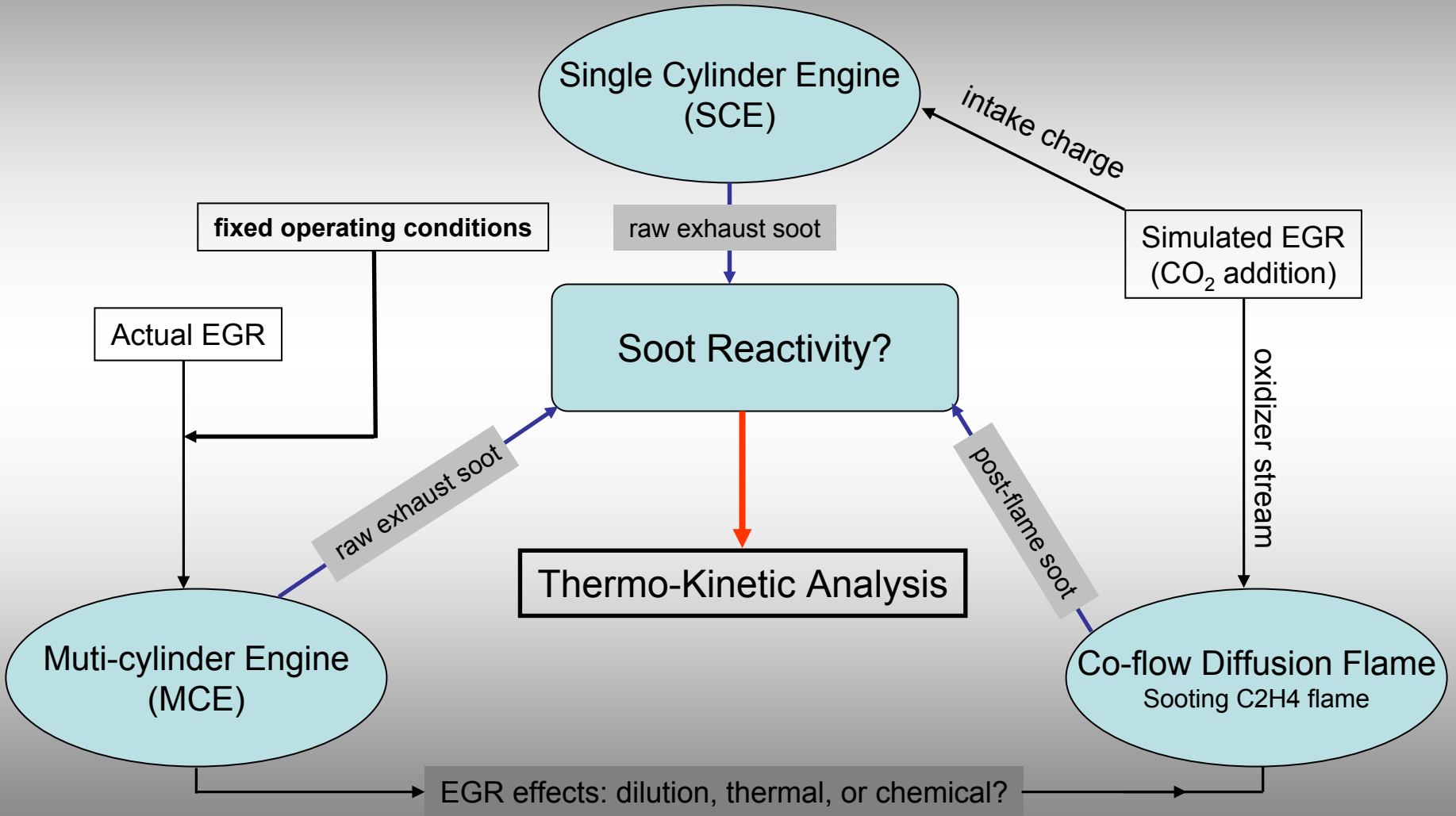
- Isothermal**
- oxidation
- kinetics

- CHNO
- XPS (O/C, impurities)
- EELS (O/C, impurities)
- FTIR (functional groups)
- Chemisorption (active sites)

Activities at Penn State

1. 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 FT diesel) follows a “shrinkage core” oxidation process
2. How will EGR affect the formation, maturation, and oxidation kinetics of diesel soot?
 - Reduced temperature may affect the pool of soot precursors and alter the transition to an ordered and graphitic structure
 - Shift 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

Experimental Approach

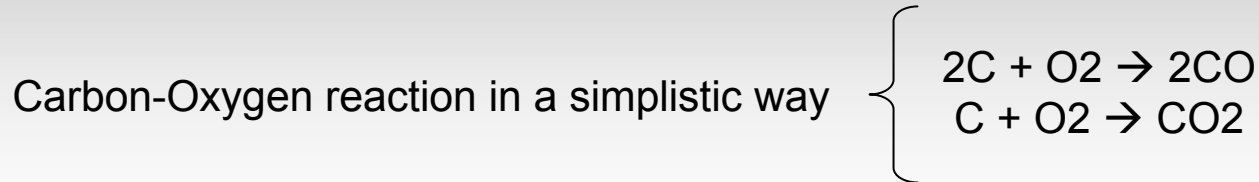


Experimental Techniques

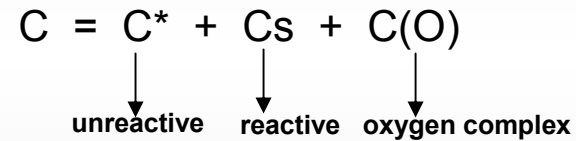
- ❖ Thermogravimetric Analysis (TGA) Instrument
 - ❑ Reactivity Measurements
 - ✓ Isothermal in Air @ 450 °C
 - ✓ Oxygen chemisorption → active sites
 - ❑ Kinetic Analysis
 - ✓ Non-isothermal in Air, heating rates (β) of 1.5, 3, 5, and 7 °C/min
 - Compared to Isothermal
 - fast
 - allows for multiple runs / day (repeatability check)
 - less expensive
 - yet, less accurate
 - ❑ All soot samples were heat-treated in N₂ to remove the volatile fraction
- ❖ Supportive Techniques
 - ❖ X-Ray Diffraction (crystallite width → active sites)
 - ❖ HRTEM (burning mode)

Soot Active Sites

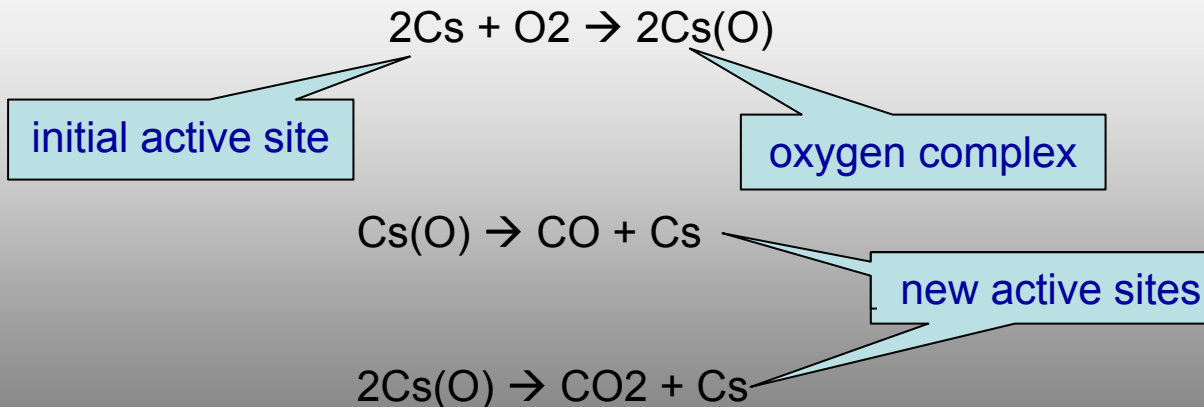
Active Sites are defined as the carbon atoms which have high affinity to *chemisorb* and *react* with oxygen → analogous to catalyst



Nature of carbon sites

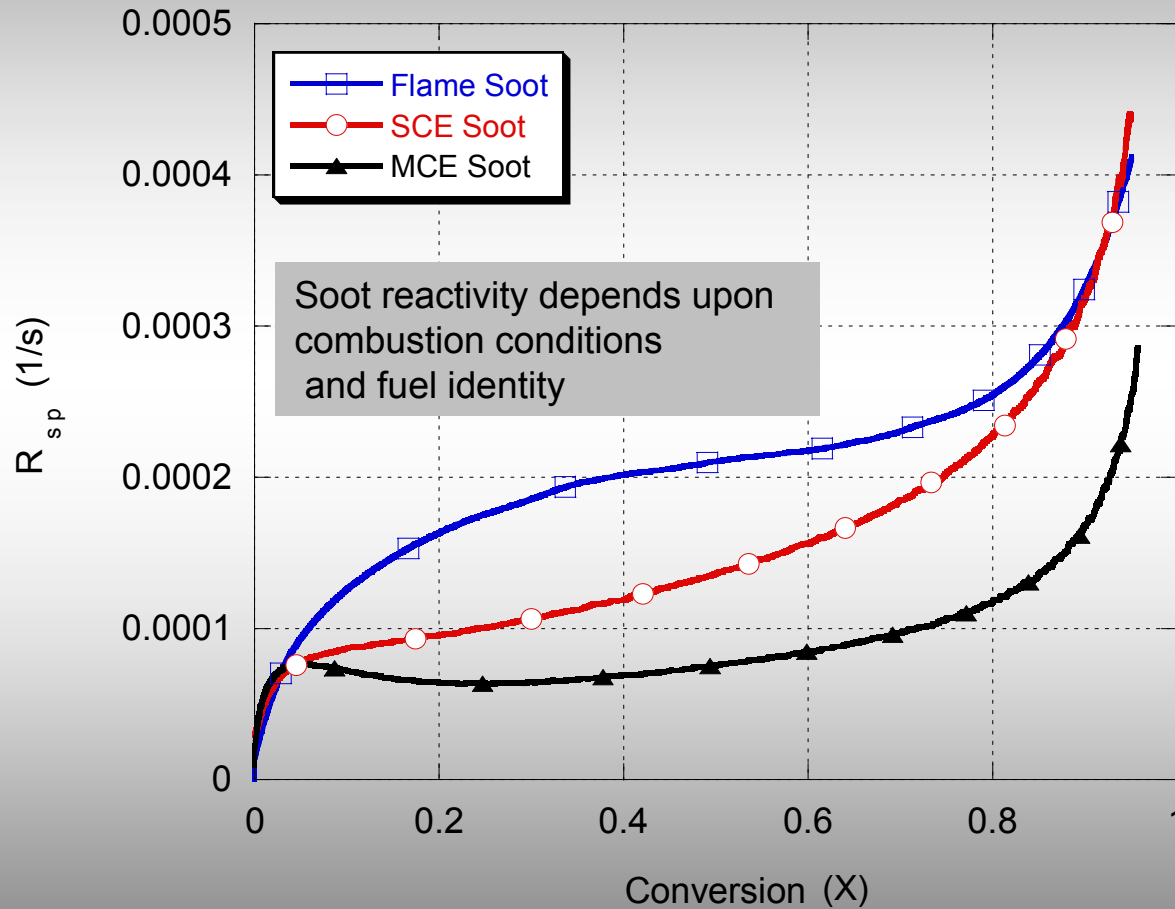


Elementary reactions



Baseline Soot

Isothermal TGA in air @ 450 °C



Soot reactivity depends upon combustion conditions and fuel identity

Reactivity increases with X

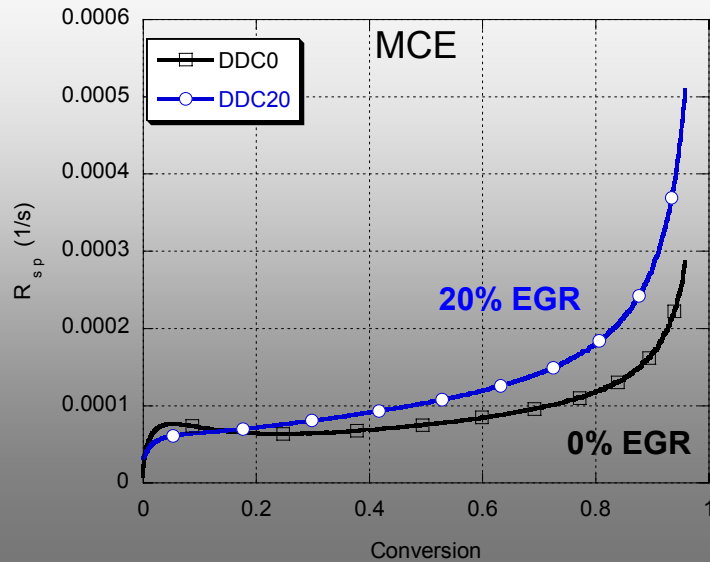
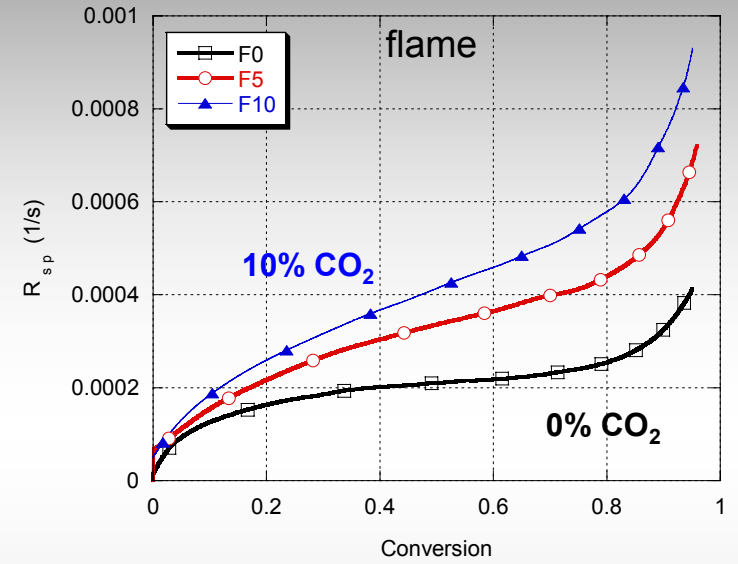
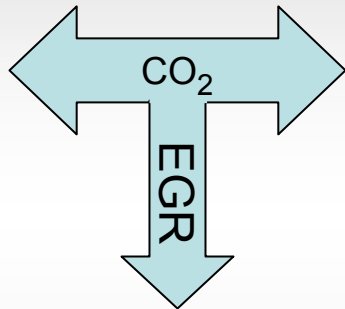
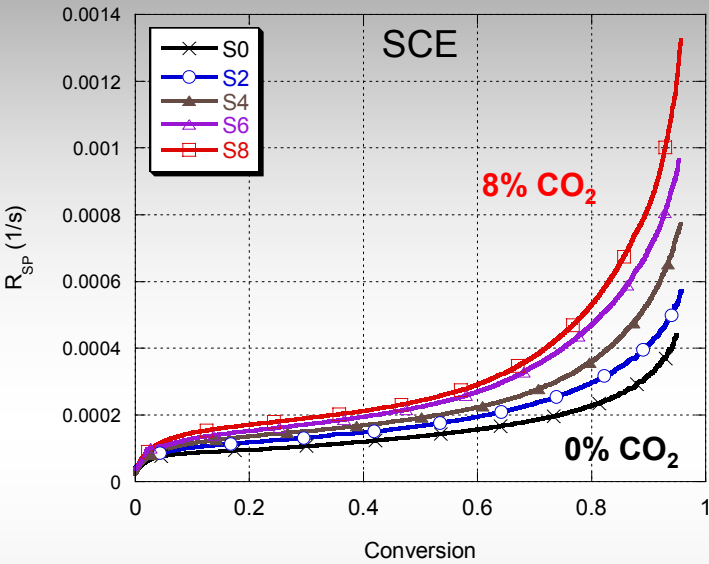


Active sites are renewable

Specific rate vs. conversion profiles of flame and diesel engines soot.

Impact of Oxidizer Diluents

Isothermal TGA in air @ 450 °C.



soot reactivity augmented by diluents addition

reactivity increases in the same manner

Characterization of *Initial* Active Sites

$$C = C^* + (C_s) + C(O)$$

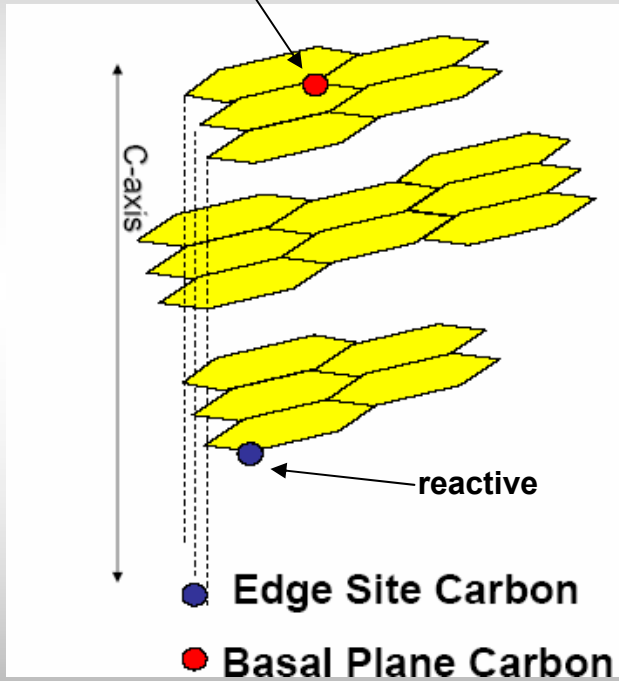
Soot Symbol	Soot Origin	Amount of Chemisorbed Oxygen	
		Oxygen Uptake (g _{oxygen} / g _{soot})	ASA _i (m ² / g)
F0	Diffusion flame (0% CO₂)	0.00704	22.0
F15	Diffusion flame (15% CO₂)	0.0144	45.0
SCE0	SCE (0% CO₂)	0.00544	17.0
SCE8	SCE (8% CO₂)	0.01056	33.0
MCE0	MCE (0% EGR)	0.00352	11.0
MCE20	MCE (20% EGR)	0.00832	26.0

To retain the initial nanostructure of the soot, no heat-treatment was applied to remove the oxygen complexes C(O) from soot surfaces

Nanostructural Analysis

The Edge Site Carbon

Reactivity of edge site carbon is much higher than that of basal plane carbon: $C_e/C_b \propto ASA_i \propto (1/L_a)$



Vander Wal, 2004

Soot Symbol	Soot Origin	L_a (nm)	C_e/C_b	ASA_i (m^2/g)
F0	Diffusion flame (0% CO ₂)	2.587	0.184	22.0
F15	Diffusion flame (15% CO ₂)	2.049	0.218	45.0
SCE0	SCE (0% CO ₂)	3.030	0.165	17.0
SCE8	SCE (8% CO ₂)	2.477	0.190	33.0
MCE0	MCE (0% EGR)	2.919	0.169	11.0
MCE20	MCE (20% EGR)	2.526	0.188	26.0

L_a from XRD

C_e/C_b was determined in accordance to a theoretical assessment performed by Belenkov [Belenkov, 2000]

Soot Oxidation Kinetics

How do EGR and CO₂ change soot oxidation kinetics?

- Determination of the kinetic parameters of soot oxidation of diverse soot samples: Activation Energy (E_a), Pre-exponential Factor (A), reaction order *w.r.t.* soot (n)

APPROACH

- The analysis is based on multiple nonisothermal TGA experiments
- Determine (E_a) without knowledge about the reaction model *a priori*
- Estimate (A) by using the compensation effect correlation
- Estimate (n) by assuming an appropriate reaction model
- Develop a simplified model that describes the oxidation process

Soot Oxidation Kinetics

1. Activation Energy

Theoretical Background

- A *model-free* isoconversional method from nonisothermal data was used
- Basis: Kissinger, Akahira, and Sunose (KAS)

$$\ln \frac{\beta}{T^2} = \ln \left[\frac{AE}{Rg(X)} \right] - \frac{E}{RT}$$

T: T (X, β)

X: conversion

β : heating rate

g(X): reaction model

Conversion model functions $g(X)$ for solid state reactions

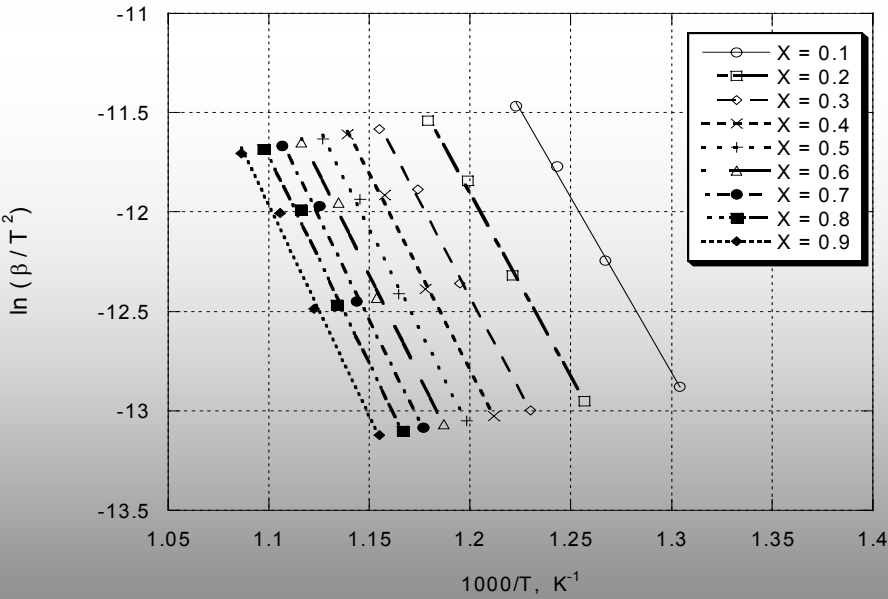
No.	Reaction model	Symbol	$g(\alpha)$
1	Nucleation and growth (Avrami–Erofeev equation)	$A_{1.5}$	$(-\ln(1-\alpha))^{1/1.5}$
2	Nucleation and growth (Avrami–Erofeev equation)	A_2	$(-\ln(1-\alpha))^{1/2}$
3	Nucleation and growth (Avrami–Erofeev equation)	A_3	$(-\ln(1-\alpha))^{1/3}$
4	Nucleation and growth (Avrami–Erofeev equation)	A_4	$(-\ln(1-\alpha))^{1/4}$
5	Phase boundary controlled reaction (contracting linear)	P_1	α
6	Phase boundary controlled reaction (contracting area)	P_2	$(1 - (1 - \alpha)^{1/2})$
7	Phase boundary controlled reaction (contracting volume)	P_3	$(1 - (1 - \alpha)^{1/3})$
8	One dimensional diffusion	D_1	α^2
9	Two dimensional diffusion	D_2	$(1 - \alpha) \ln(1 - \alpha) + \alpha$
10	Three dimensional diffusion	D_3	$(1 - (1 - \alpha)^{1/3})^2$
11	Ginstling–Brounshtein equation	D_4	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3}$
12	Chemical reaction (first order)	R_1, A_1	$(-\ln(1 - \alpha))$
13	Chemical reaction (second order)	R_2	$(1 - \alpha)^{-1} - 1$
14	Power law I	L_1	$\alpha^{1/4}$
15	Power law II	L_2	$\alpha^{1/3}$
16	Power law III	L_3	$\alpha^{1/2}$
17	Power law IV	L_4	$\alpha^{3/2}$
18	Zhuravlev equation	D_5	$[(1 - \alpha)^{-1/3} - 1]^2$

Soot Oxidation Kinetics

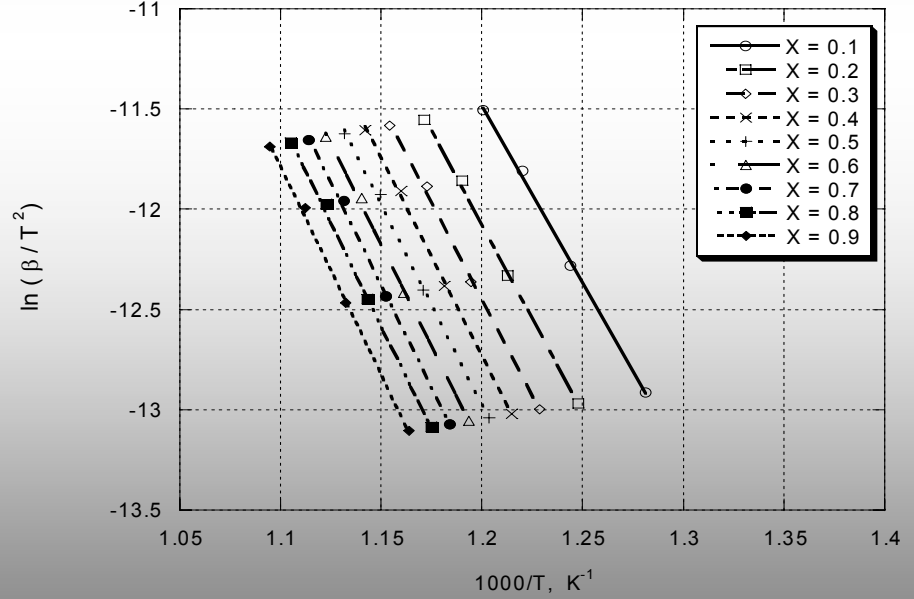
1. Activation Energy

Isoconversional plots at various degrees of conversions

$$\ln \frac{\beta}{T^2} = \ln \left[\frac{AE}{Rg(X)} \right] - \frac{E}{RT} \quad T: T(X, \beta)$$

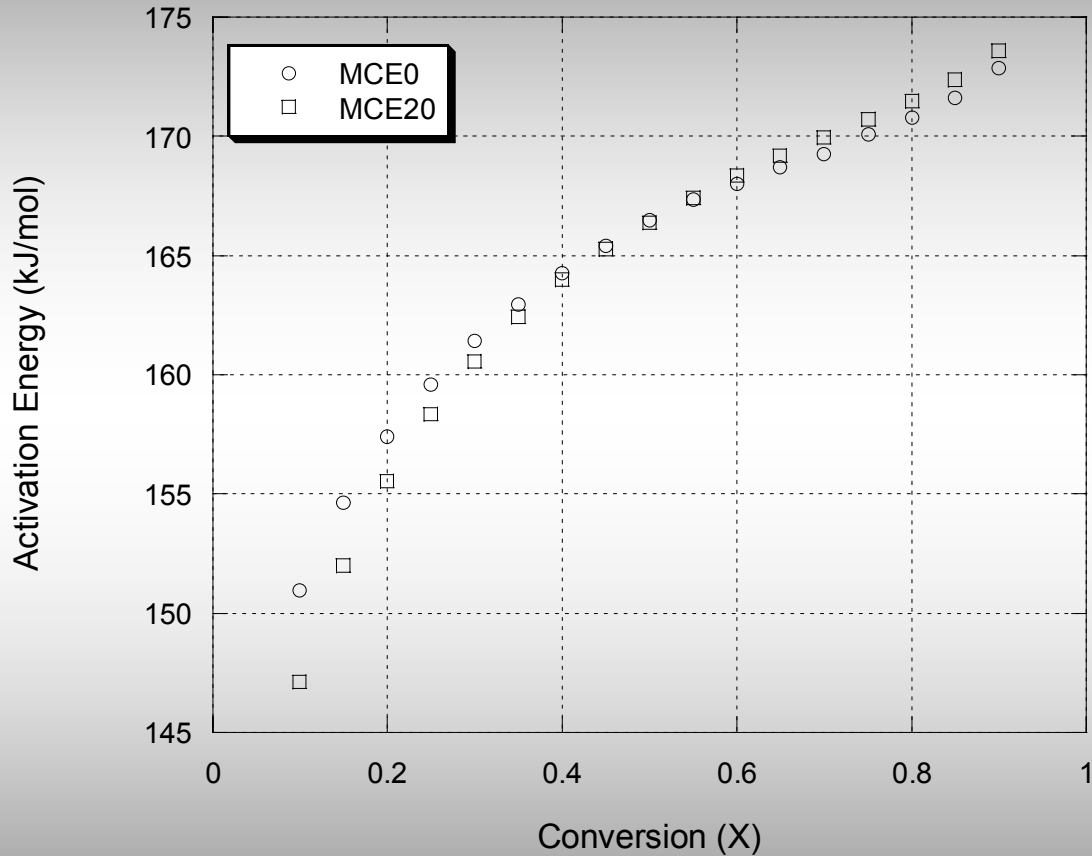


MCE0



MCE20

Model free Ea vs. X



- Ea increases with X
- Ea is not affected by soot formation condition
- Ea averaged values are identical for both cases ~ 165 kJ/mol

Soot Oxidation Kinetics

2. Pre-exponential factor

$$\ln \frac{\beta}{T^2} = \ln \left[\frac{AE}{Rg(X)} \right] - \frac{E}{RT}$$

Which g (x)??

Compensation effect relationship

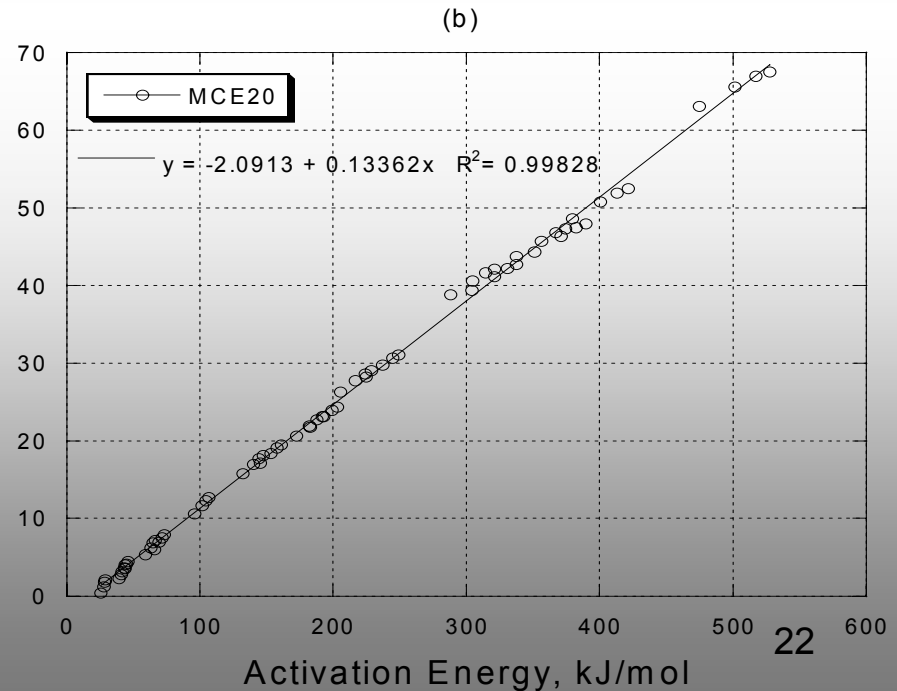
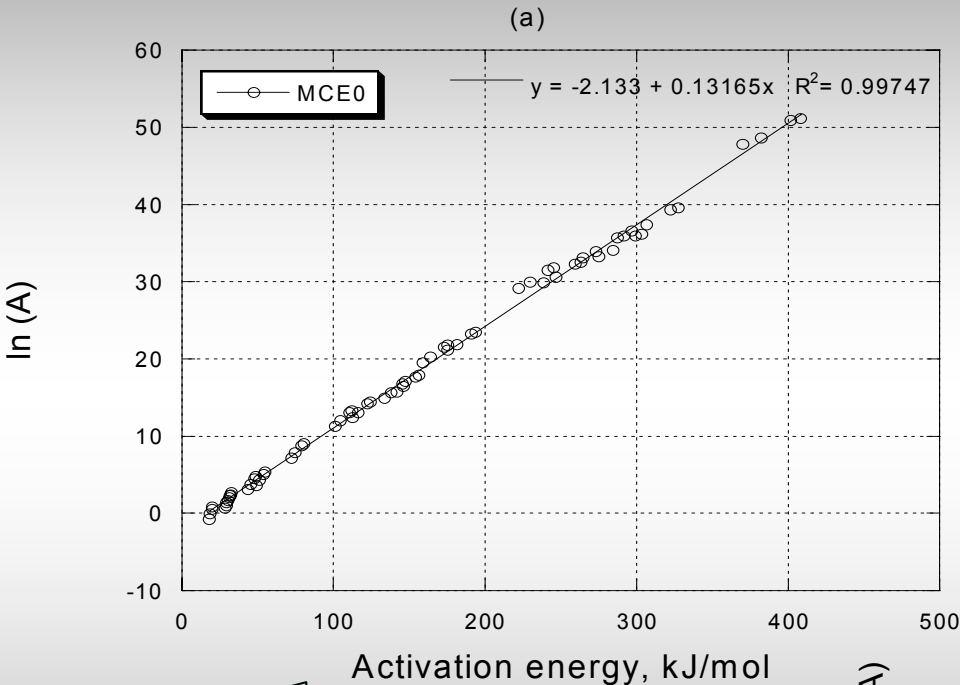
$$\ln(A_j) = a + bE_j$$

Linear relationship of the compensation effect for (a) MCE0 soot and (b) MCE20 soot.

$$\ln(A_j) = a + bE_j$$

a and *b* are the intercept and slope, respectively.

(A) can be unambiguously estimated using previously estimated model-free *E_a*



β : heating rate
 g(X): reaction model

Soot Oxidation Kinetics

3. Reaction order w.r.t. soot

Non-isothermal oxidation can be expressed as

$$\frac{dX}{dt} = \left(\frac{A}{\beta}\right) \exp\left(\frac{-E_a}{RT}\right) f(X)$$

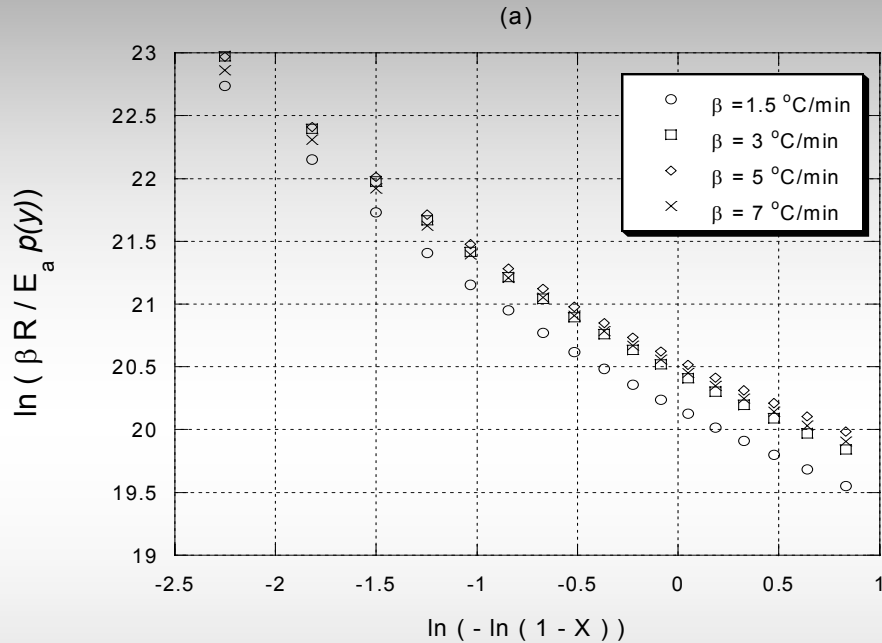
Integrating this equation and assuming a proper model to describe soot oxidation:

$$g(X) = [-\ln(1 - X)]^{\frac{1}{n}}$$

yield

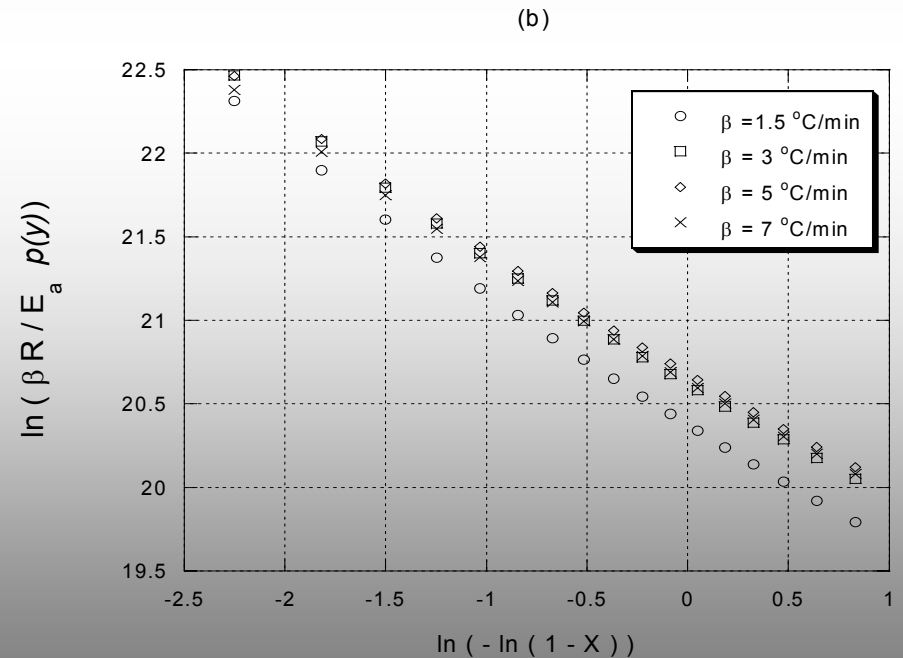
$$\ln\left(\frac{\beta R}{E}\right) - \ln[p(y)] = \ln(A) - \left(\frac{1}{n}\right) \ln[-\ln(1 - X)]$$

Estimation of soot reaction order, n , for (a) MCE0 soot and (b) MCE20 soot



$$\underbrace{\ln\left(\frac{\beta R}{E}\right) - \ln[p(y)]}_{\text{y-axis}} = \ln(A) - \underbrace{\left(\frac{1}{n}\right) \ln[-\ln(1-X)]}_{\text{x-axis}}$$

Slope of each line yields a value for (n) at a given β



Soot Oxidation Kinetics Summary

	F0	F15	SCE0	SCE8	MCE0	MCE20
E_a (kJ/mol)	165	165	152	153	165	165
A (1/s)	7.3E8	1.3E9	1.86E8	2.7E8	2.8E8	4.3E8
n	0.79	0.79	0.90	1.0	0.97	0.77

E_a is not affected by soot properties



RDS is the same & soot follows the same oxidation mechanism irrespective of its formation condition

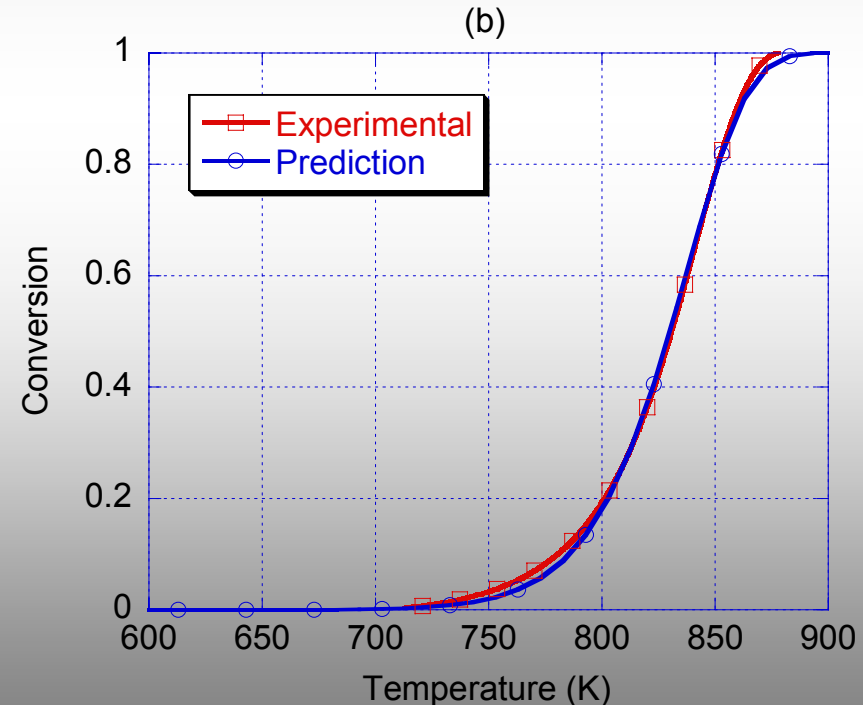
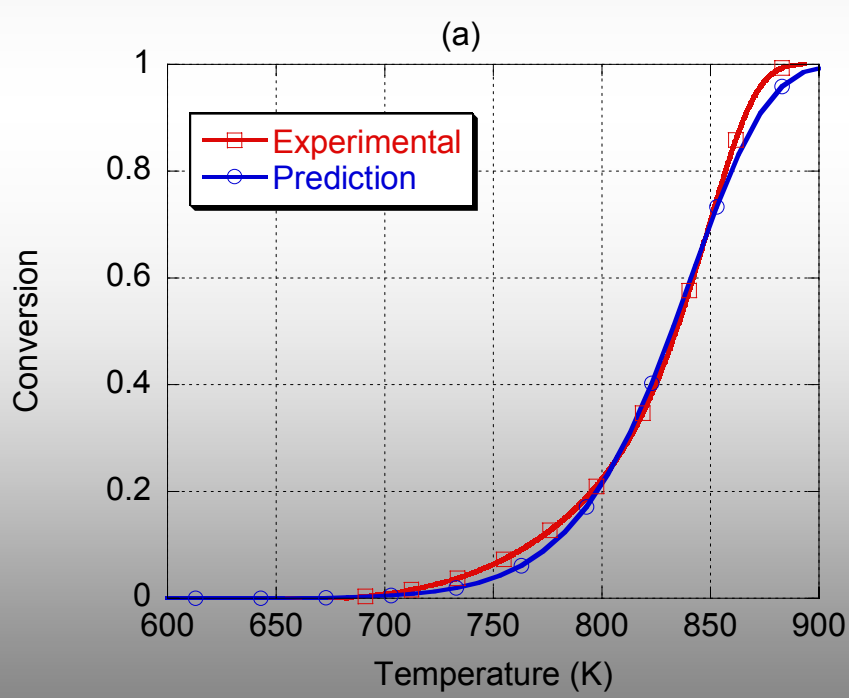
Formation of oxygen complex
 $2C_s + O_2 \rightarrow 2C_s(O)$

Decomposition of oxygen complex
 $C_s(O) \rightarrow CO + C_s$
 $2C_s(O) \rightarrow CO_2 + C_s$

Pre-exponential factor (A) correlates with the observed decrease of (L_a) → increased (ASA)
 Effects of active sites are incorporated implicitly in (A)

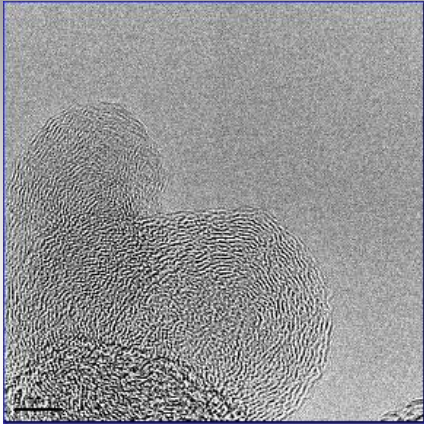
Soot Oxidation Simplified Model

Soot oxidation is described By:
$$X = 1 - \exp \left[- \left[\frac{AE_a}{\beta R} \frac{\exp\left(\frac{-E_a}{RT}\right)}{\left(\frac{E_a}{RT}\right)^2} \right]^{\frac{1}{n}} \right]$$

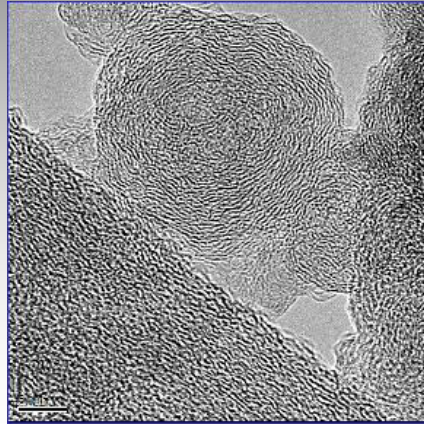


Comparison between experimental and predicted curves at constant heating rate of 1.5°C/min for
(a) MCE0 soot, and (b) MCE20 soot.

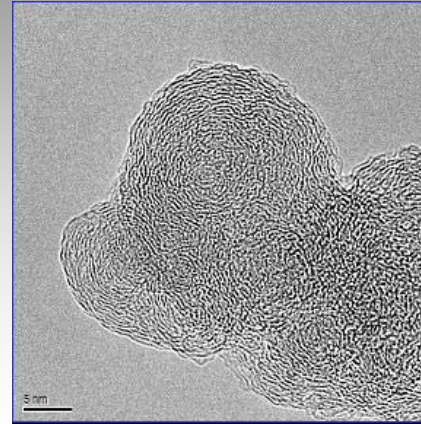
Oxidation consequence of soot generated under 0% EGR



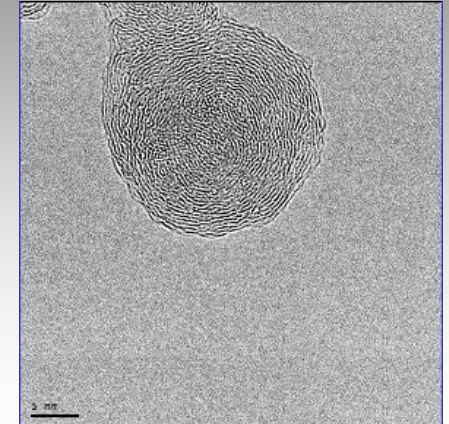
unreacted



25% oxidized

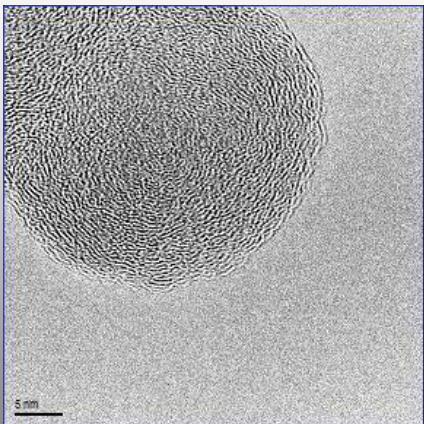


50% oxidized

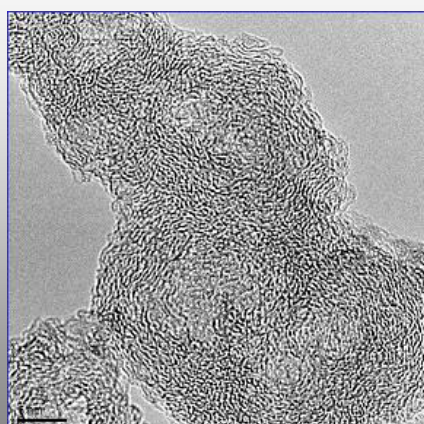


75% oxidized

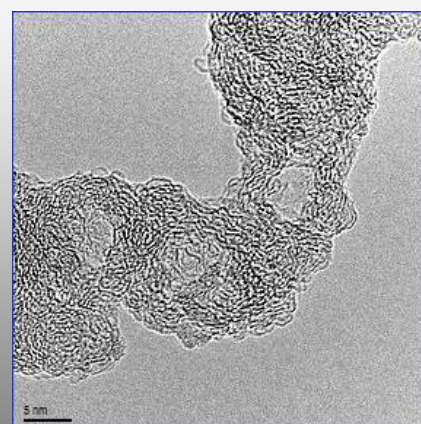
Oxidation consequence of soot generated under 20% EGR



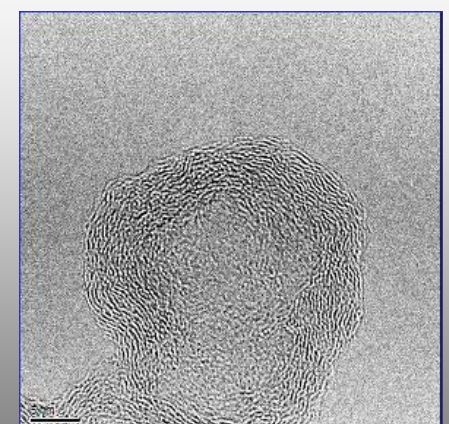
unreacted



25% oxidized



50% oxidized



75% oxidized

CONCLUSIONS

CONCLUSIONS:

- ❖ **The addition of EGR**
 - **enhances the oxidative reactivity of the soot**
 - **has no effect on the activation energy of soot oxidation, the observed increased in reactivity is attributed solely to the increase of active sites which are incorporated implicitly in the pre-exponential factor**
 - **facilitates oxygen dissociation on soot surfaces**
 - **does not affect the rate-limiting step of the oxidation reaction**

ACKNOWLEDGMENTS

- ❖ **Linda Blevins (former project manager) and Phil Westmoreland (current project manager) of National Science Foundation (Grant# CTS-0553339)**
- ❖ **US DOE-National Energy Technology Laboratory**
- ❖ **This presentation was prepared with partial support from the U.S. Department of Energy under Contract No. DE-FC26-03NT41828. The Government reserves for itself and others acting on its behalf a royalty-free, nonexclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit, and perform this copyrighted paper.**
- ❖ **Ryan Harrier and Keith Cavallini of CAV Engineering**
- ❖ **Barry Dobar and Diana Dupuie of VM Motori NA**
- ❖ **Yu Zhang, Vince Zello, Dr. Joe Kulik (Materials Research Institute) and Prof. John Badding (Dept. of Chemistry) of Penn State University**



Thank you for your attention!