Fuel Impacts on Soot Nanostructure and Reactivity

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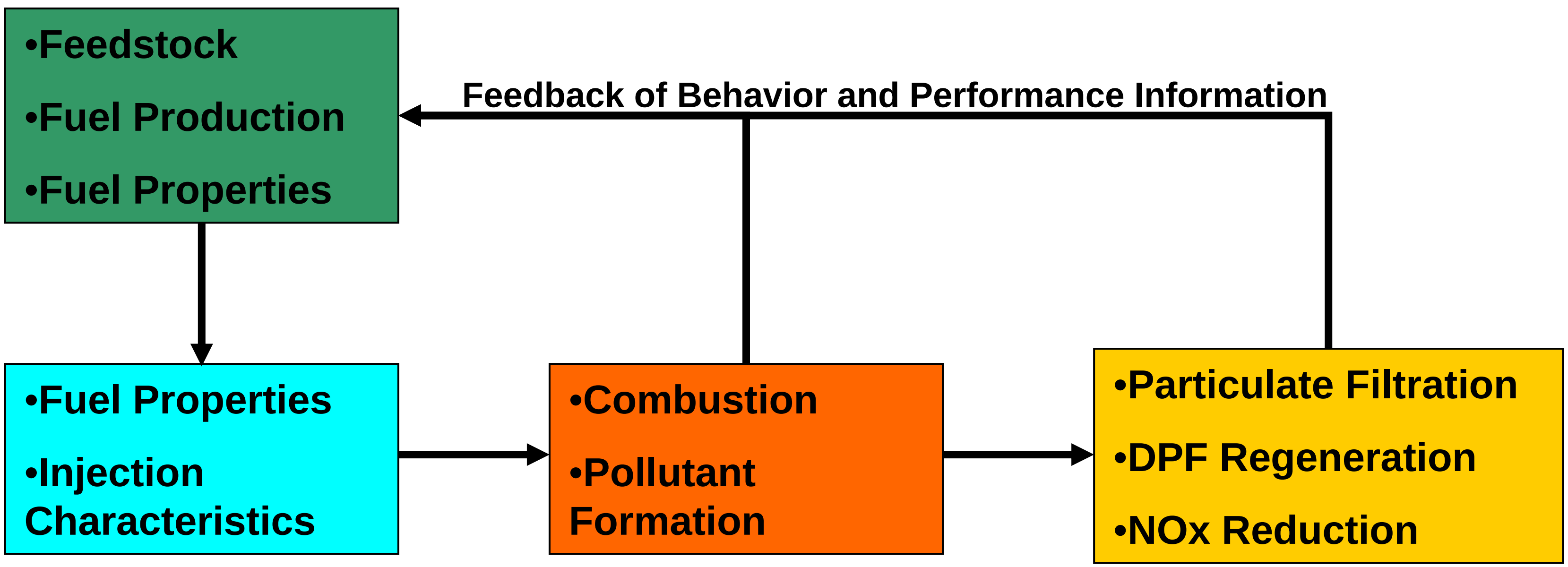
Background

- Observation, reported at DEER 2003, of reduced Break Even Temperature during catalyzed DPF operation with biodiesel blended with a low sulfur (325 ppm) diesel, lower than with ultra low sulfur diesel fuel – what is the source of this difference in PM regeneration process ?
- 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

Objectives:
Ultra Clean Fuels Project

- Determine the interaction between formulation of conventional, renewable, and synthetic diesel fuels and their injection characteristics
- Measure physical properties of fuels that can provide support for understanding injection, combustion, and emissions performance of diesel fuels
- Use injection studies, physical properties, emissions measurements, and in-cylinder visualization to determine optimal fuel formulations
- Link feedstock and fuel production process to physical properties and, thereby, injection, combustion, and emissions performance - characteristics of soot from different fuels

Research Strategy

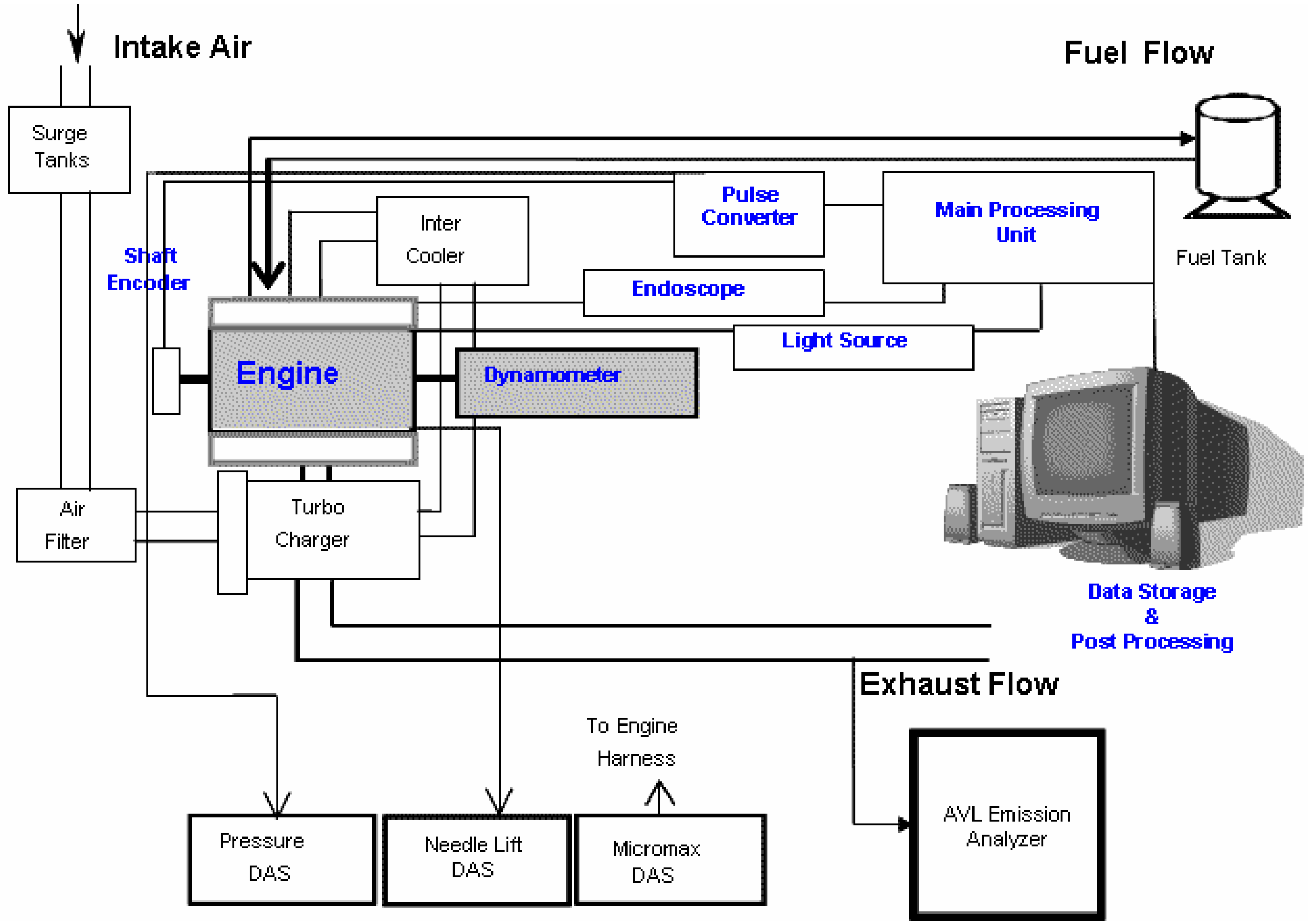


- **Spray Visualization Chamber**
- **Bulk Modulus of Compressibility**

- **AVL 513D Engine Videoscope**
- **Particulate and Gaseous Emissions**

- **Various Aftertreatment Strategies**

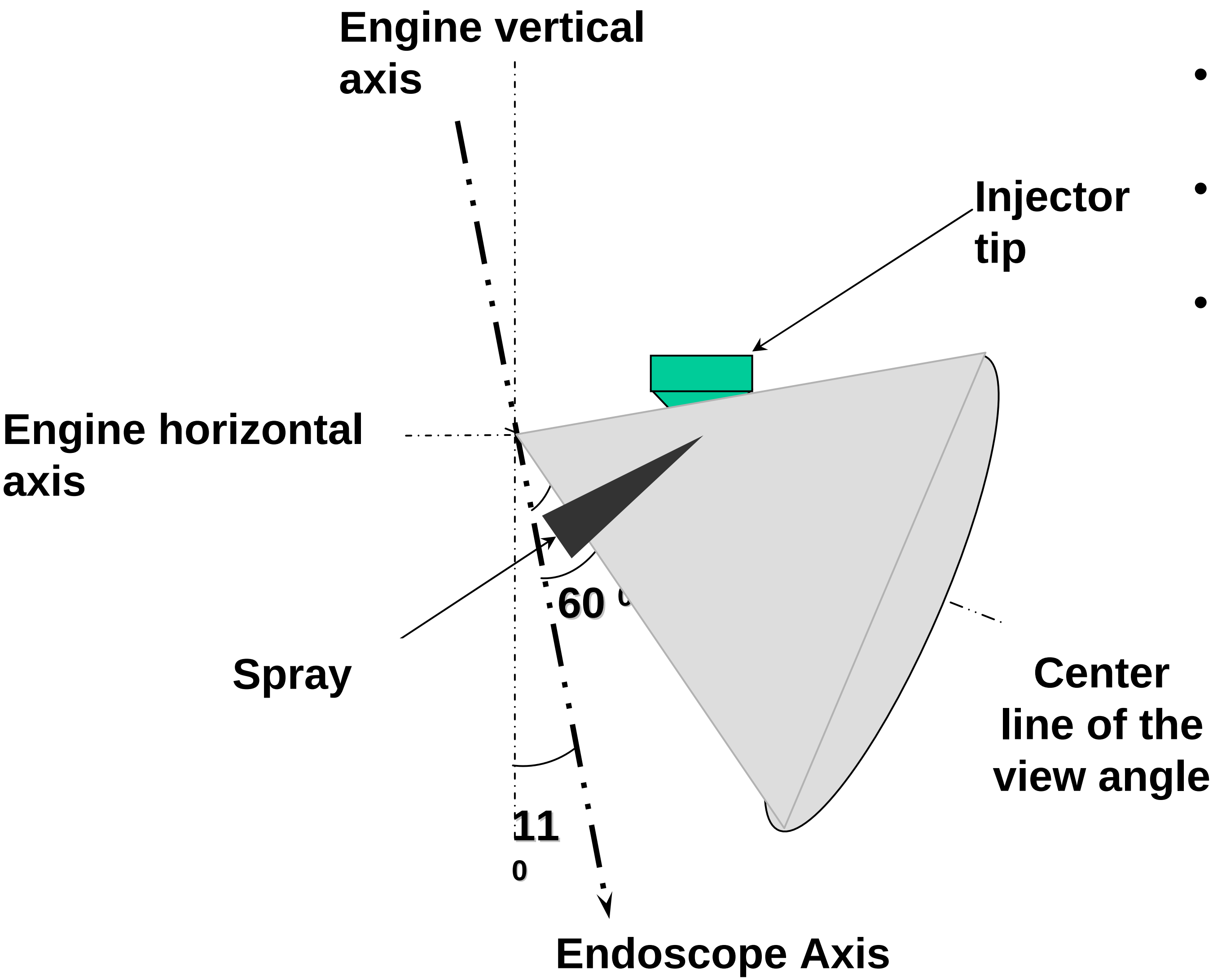
Schematic Diagram of the Cummins ISB Test Stand



Outline: Ultra Clean Transportation Fuels from Natural Gas

- In-cylinder visualization of various diesel fuels in the cummins ISB 5.9L engine
- Influence of fuels, injection timing, combustion, and emissions on the performance of aftertreatment devices → characteristics of soot from different fuels

Viewing Window of Endoscope

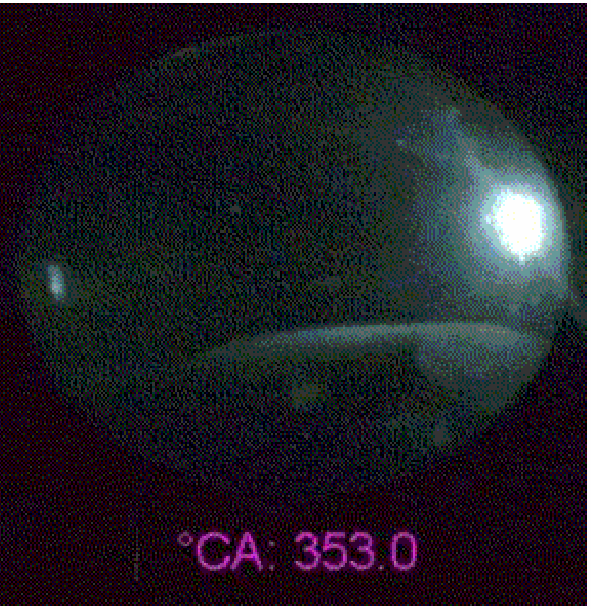


- Endoscopes 0, 30 and 60 deg
- Strobe lights 0, 30 and 70 deg
- Viewing window of endoscope is 80 deg

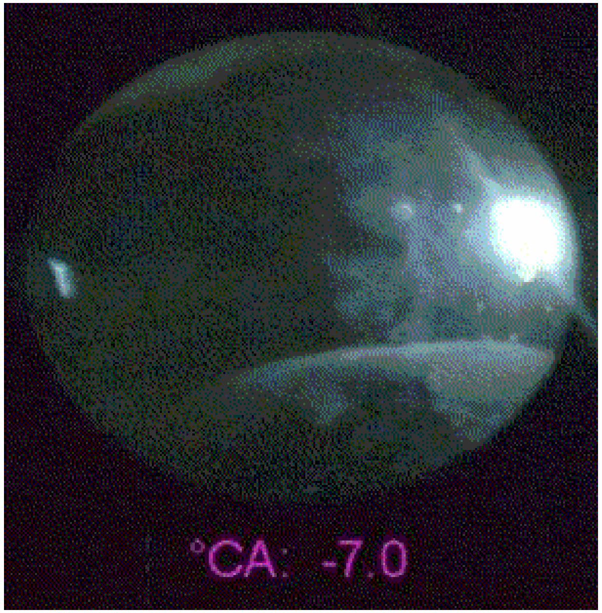
Spray and Combustion

10% Load and 1800 RPM in Cummins 5.9L ISB

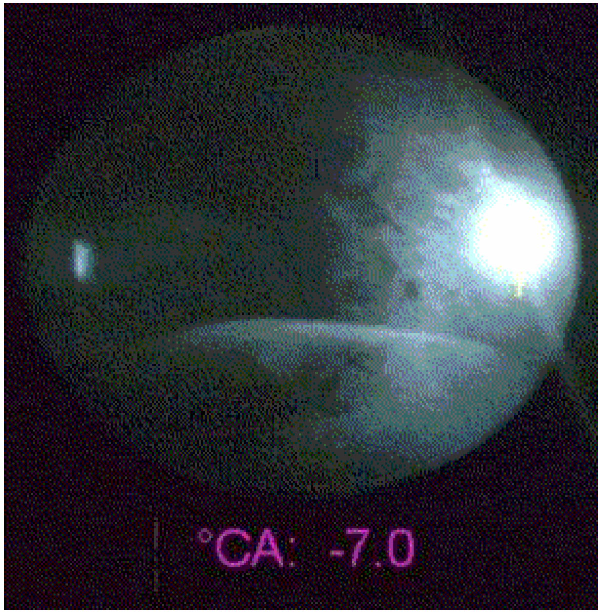
BP 15



BP 15 + 40 % Biodiesel



B100



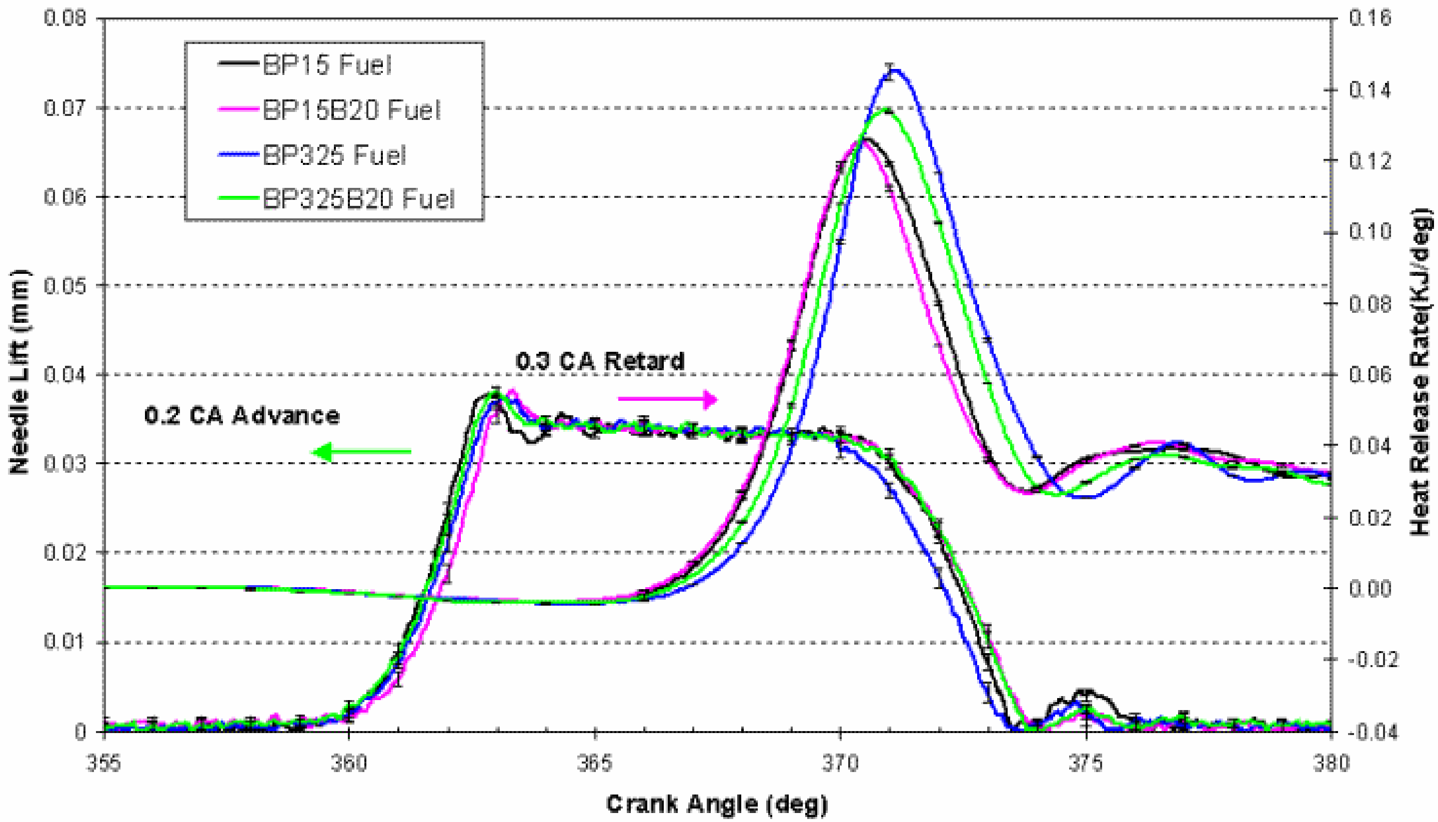
Comparison of Start of Combustion

BP15

FT 100

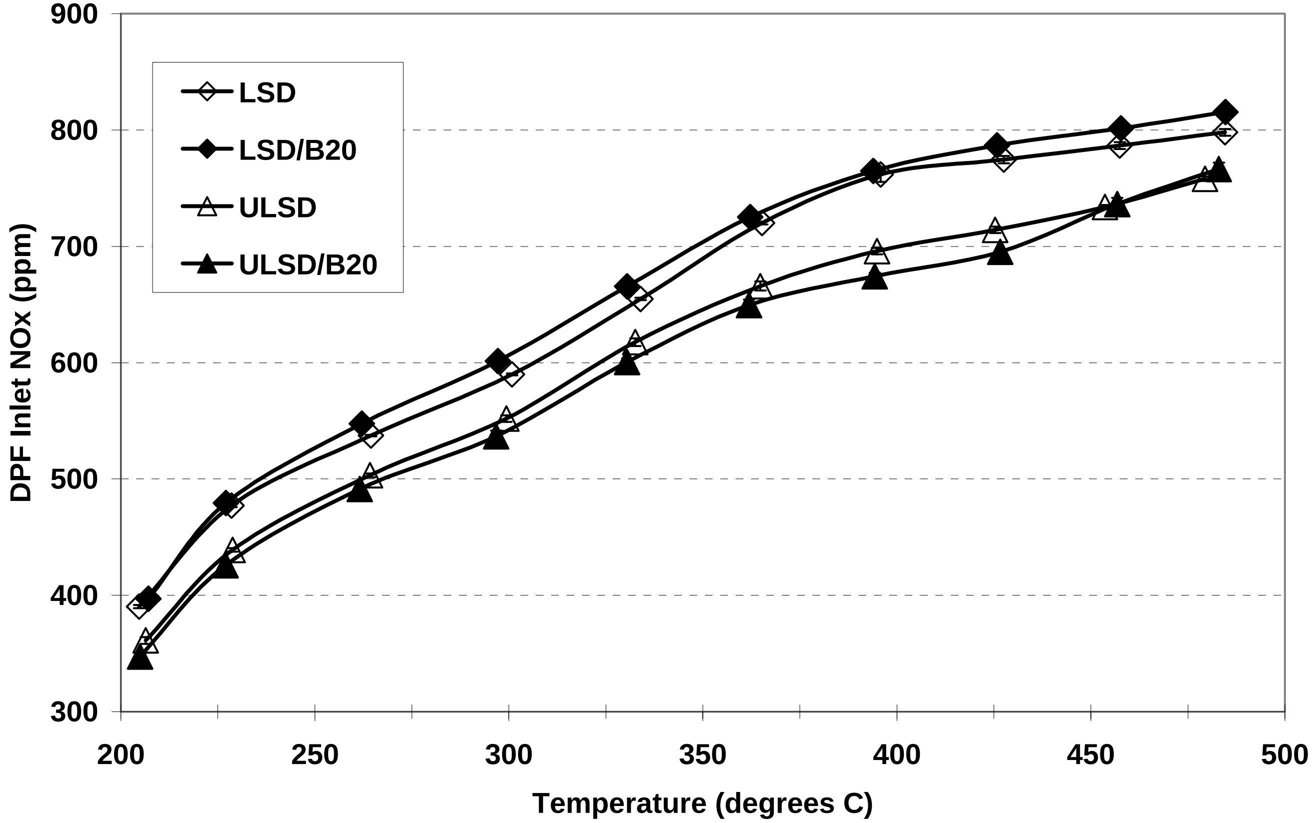
Injection and Rate of Heat Release Analyses

Diesel and B20 Test Fuels in the Cummins 5.9L ISB



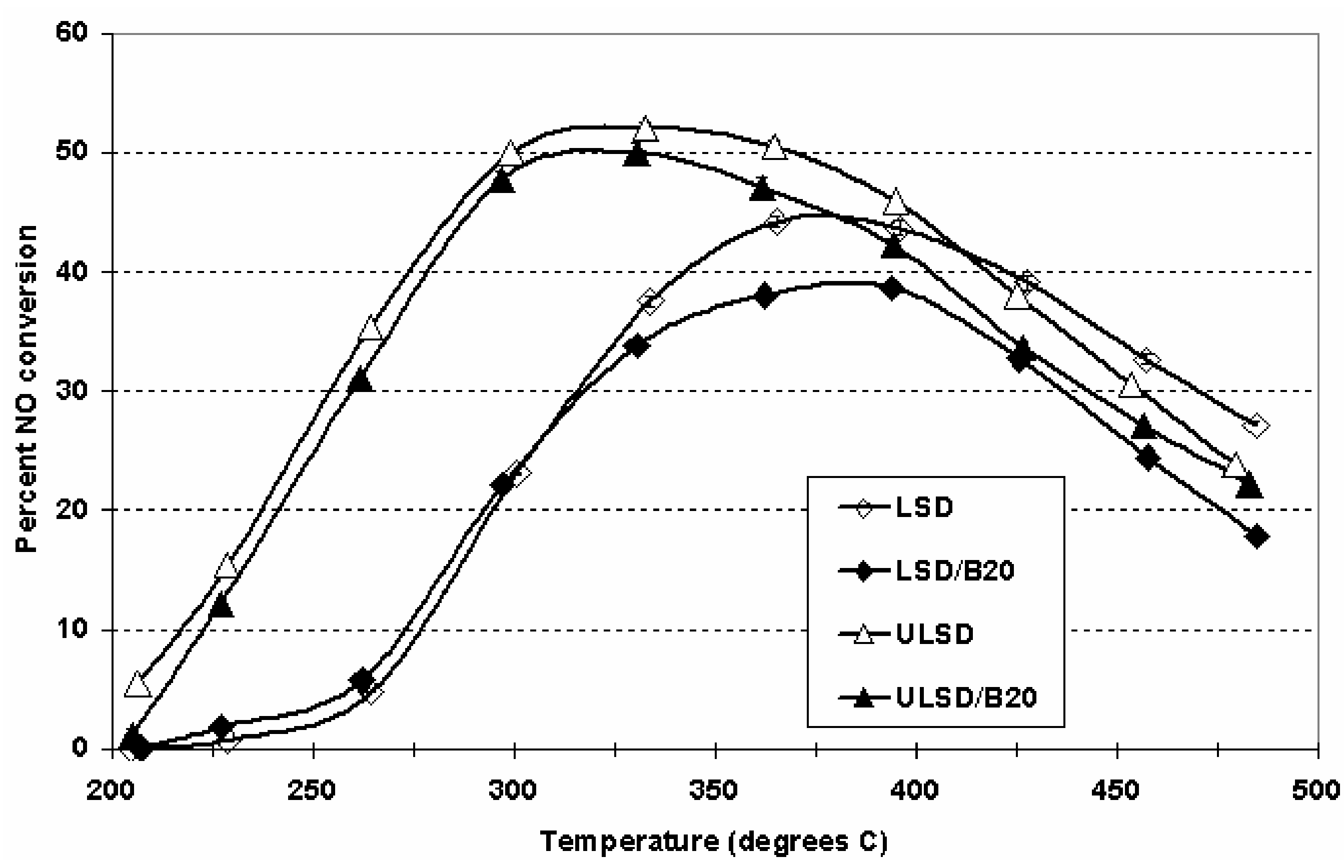
Fuel Composition Effects on Emissions

BP-325 and BP-15 Test Fuels in the Cummins 5.9L ISB

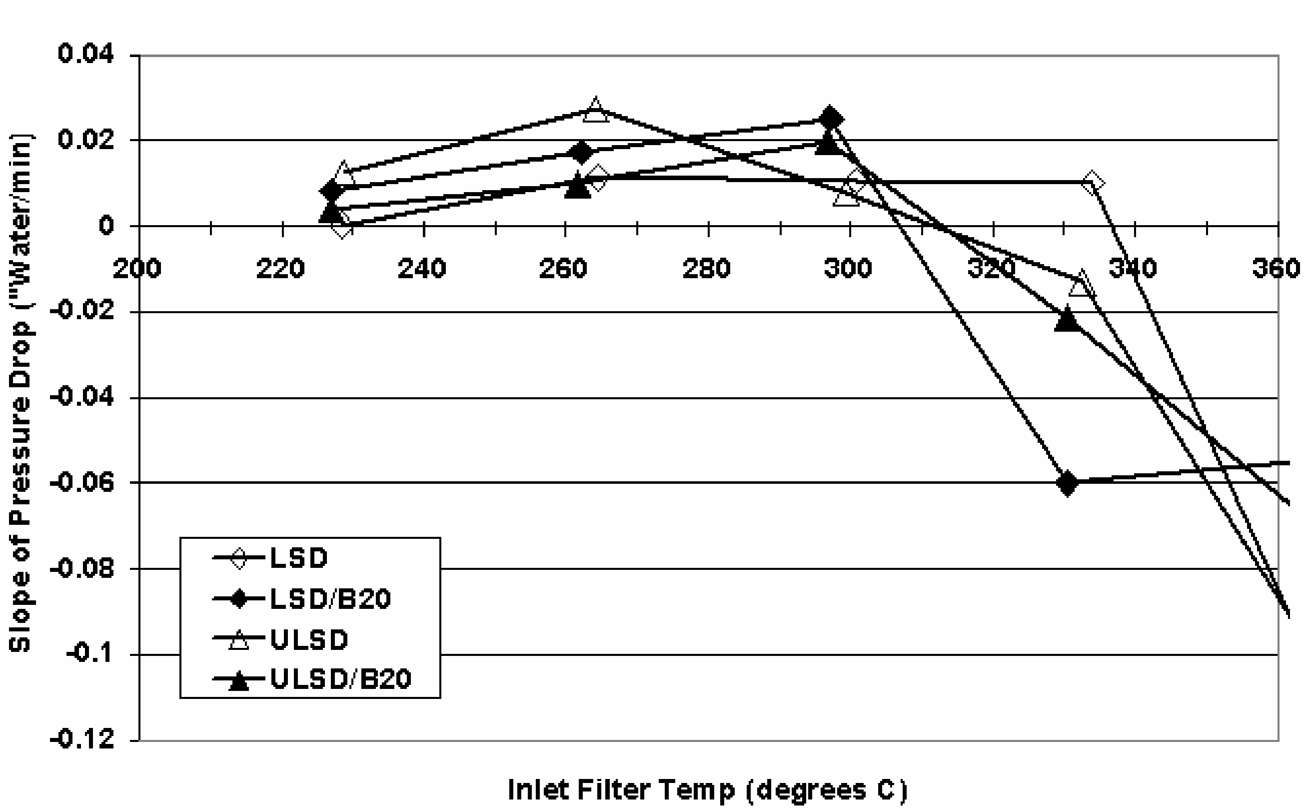


Fuel Composition Effects on Emissions

BP-325 and BP-15 Test Fuels in the Cummins 5.9L ISB

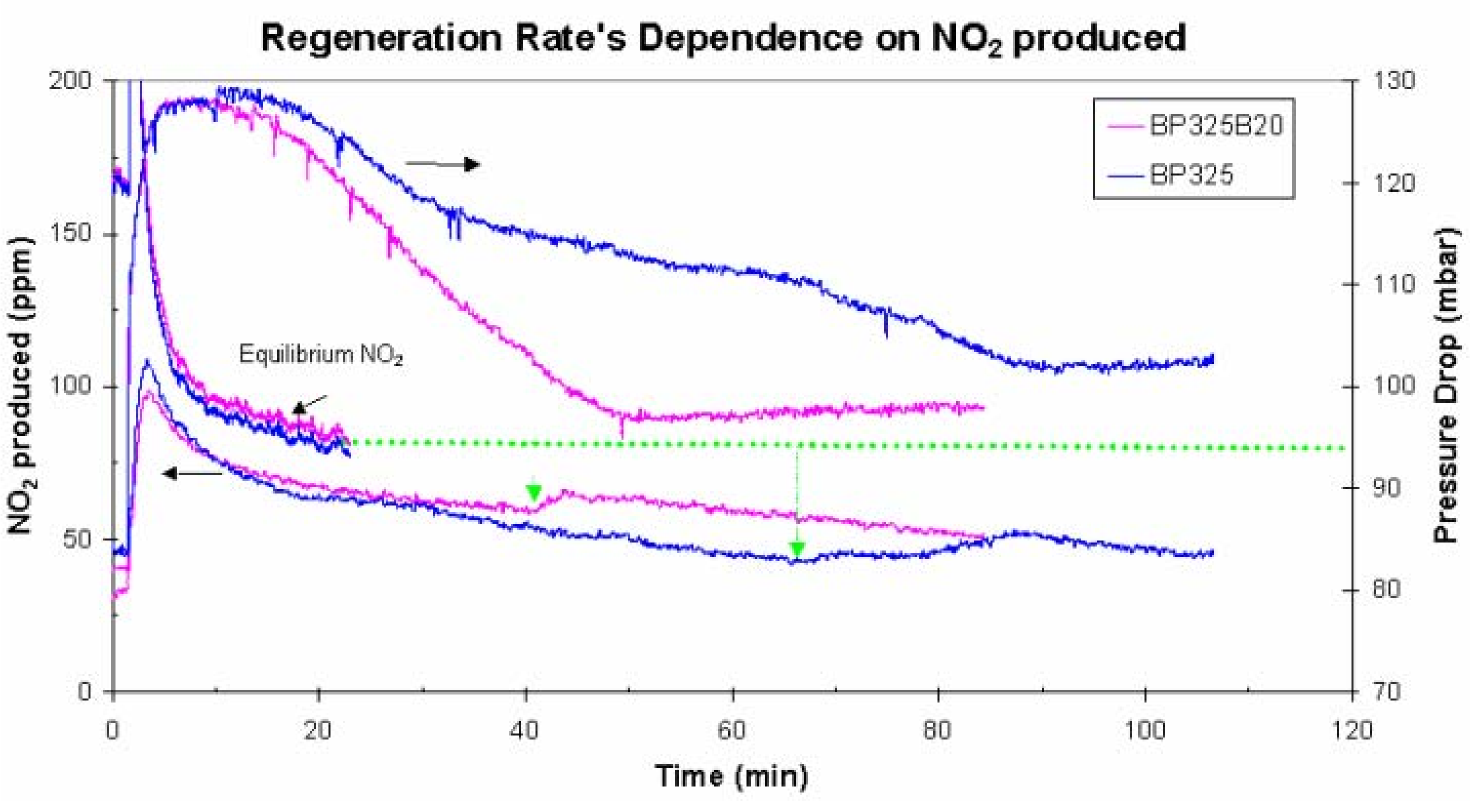


Fuel Composition Effects on Emissions
BP-325 and BP-15 Test Fuels in the Cummins 5.9L ISB

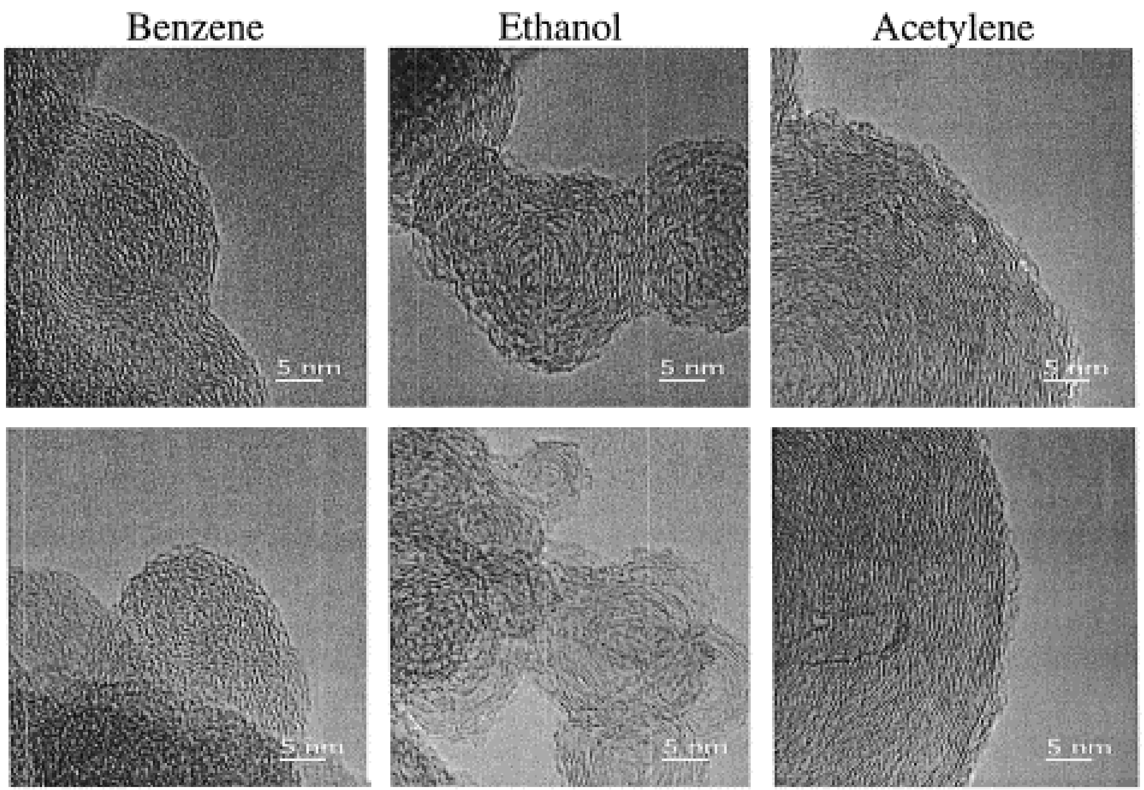


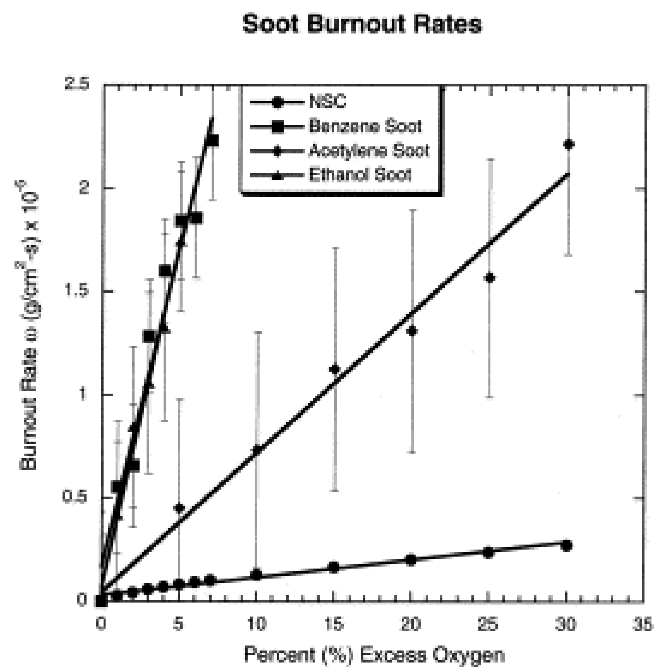
Fuel Composition Effects on Emissions

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



Fuel Effects on Soot Structure and Reactivity

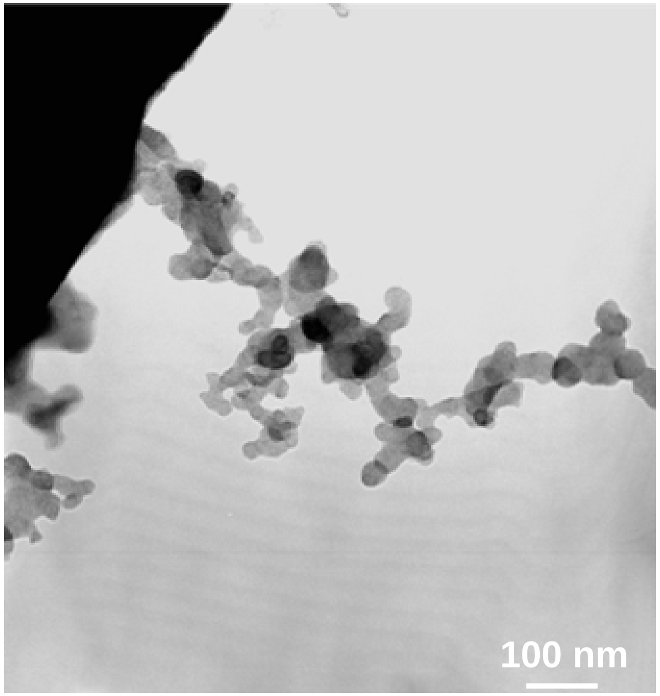




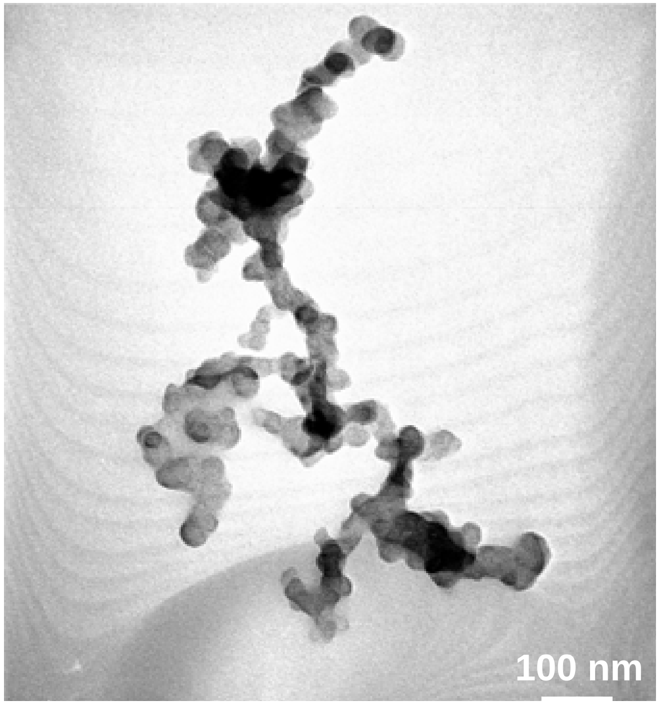
Vander Wal and Tomasek, *Comb & Flame*, Vol. 134, 2003

Variation in Heavy Hydrocarbon Fraction

Soot Morphology



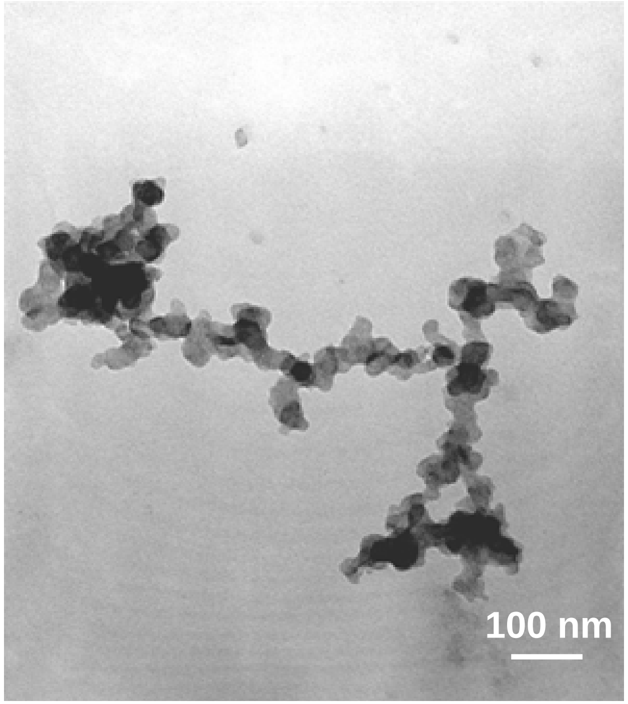
(a) BP325 Derived PM



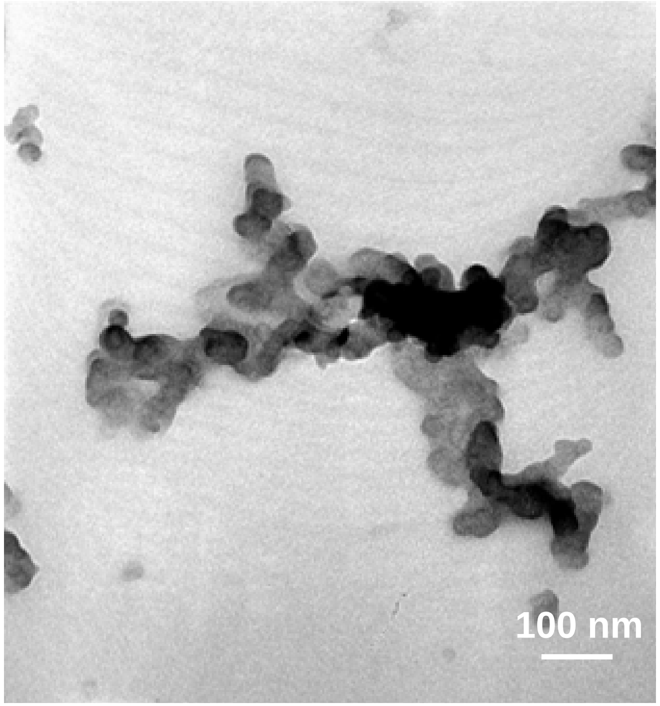
(b) BP325B20 Derived PM

Variation in Heavy Hydrocarbon Fraction

Soot Morphology



(c) BP15 Derived PM



(d) BP15B20 Derived PM

Compositional Analysis

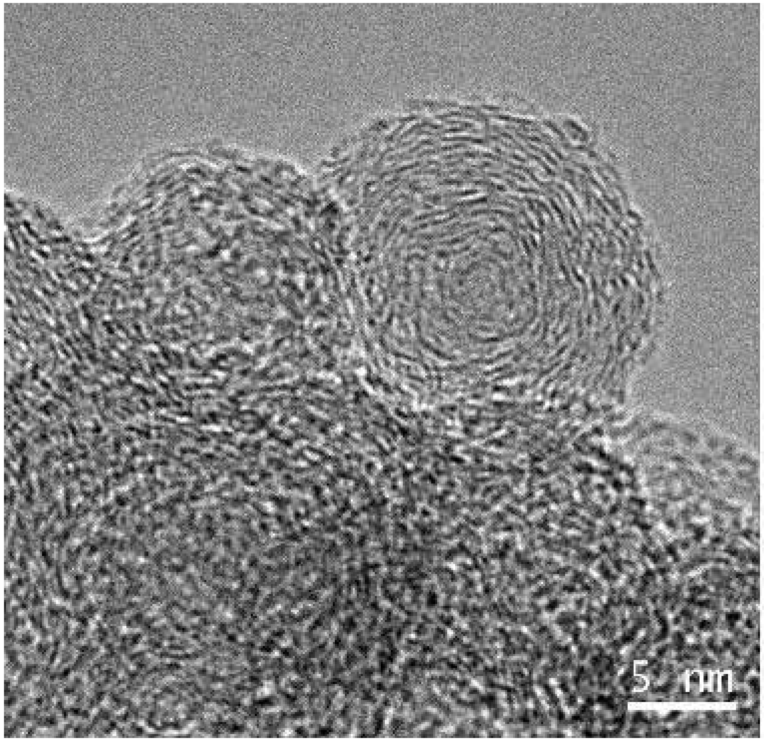
Fuels	PM emission (g/h)	SOF content (%)	Dry soot Reduction (%) relative to BP325
BP325	29.4	52.4	
BP325-B20	25.1	57.6	24
BP15	26.6	57.8	20
BP15-B20	27.8	61.1	23

Soxhlet Extraction and Gravimetric Analysis

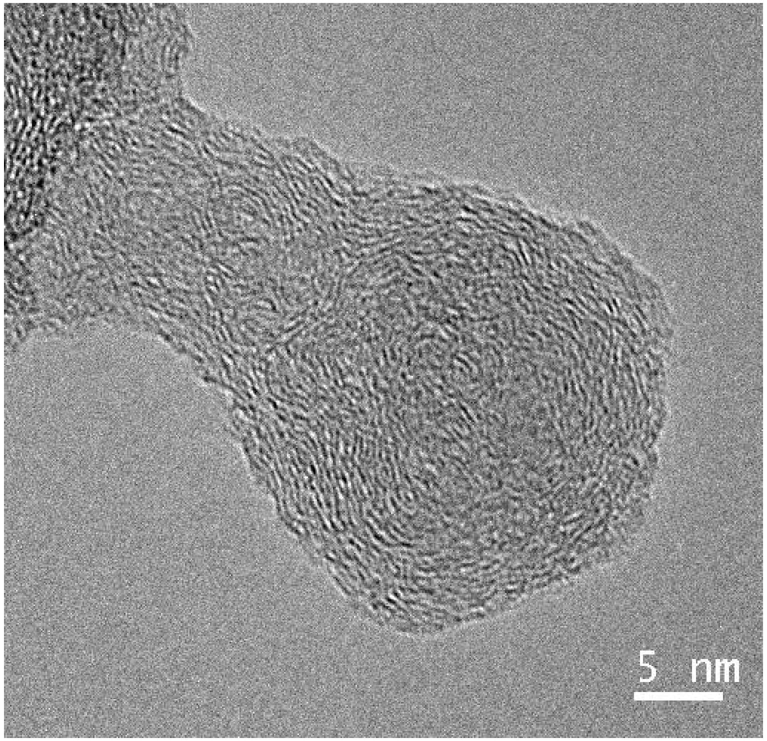
Fuels	Organic Carbon (150~300ºC)	Organic Carbon (300~450 ºC)	Element Carbon (450~750 ºC)
BP325	23	42	35
BP325-B20	32	48	20
BP15	32	48	20
BP15-B20	27	53	20

Thermal Carbon Analyzer

Soot Nanostructure – Less Ordered Nanostructure Corresponds to Enhanced Reactivity



(a) BP15 Derived PM

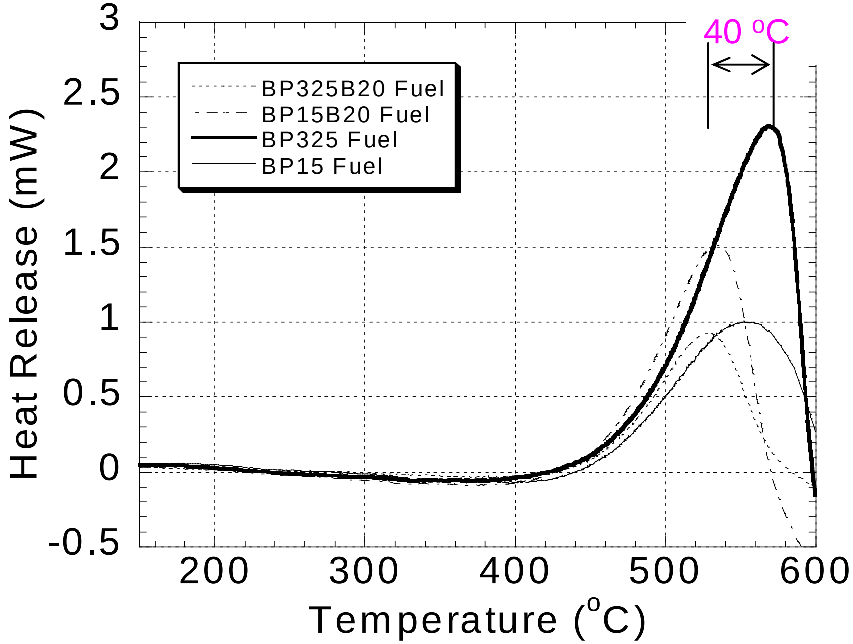


(b) BP15B20 Derived PM

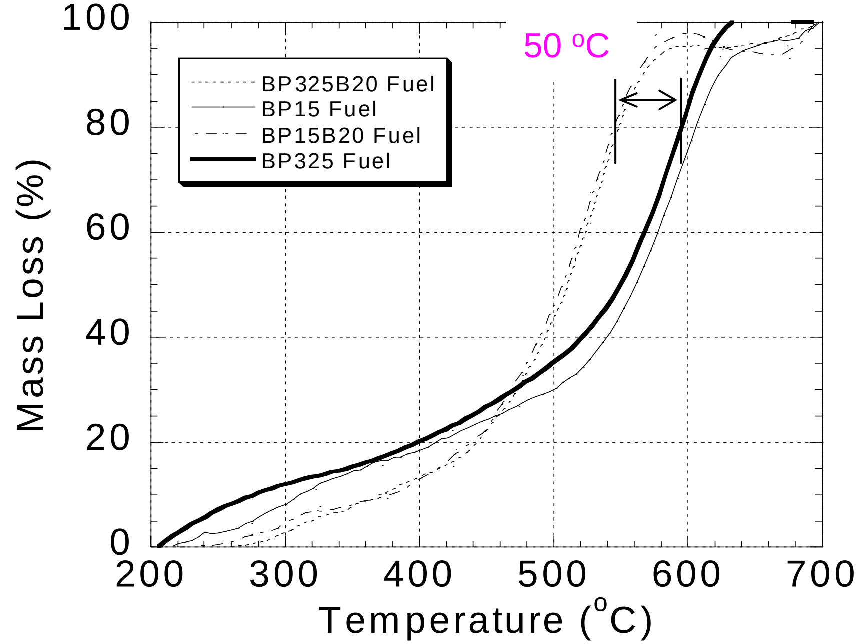
Soot Nanostructure and Its Effect on Reactivity

Low temperature Reactivity from DSC/TGA test

- under 21% oxygen gas with treated samples



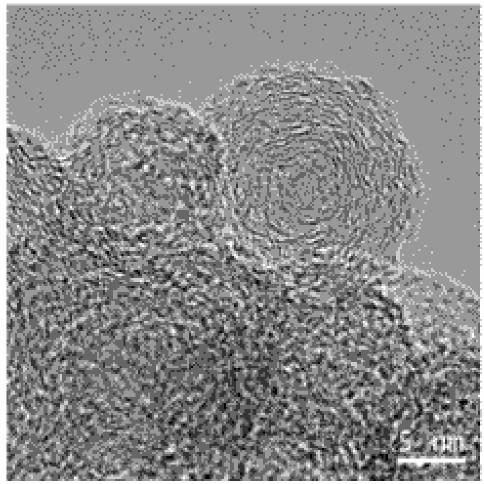
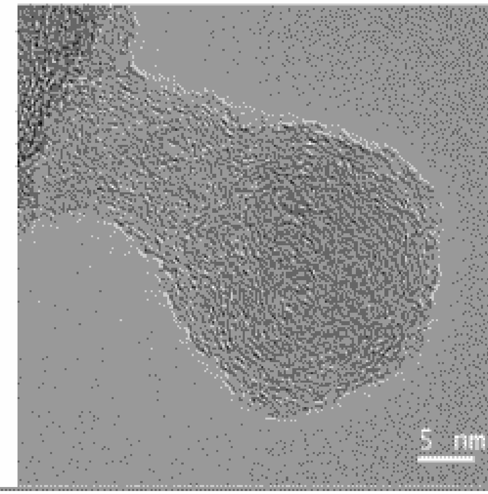
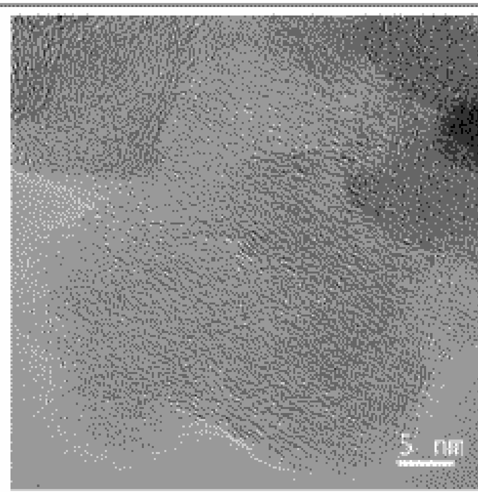
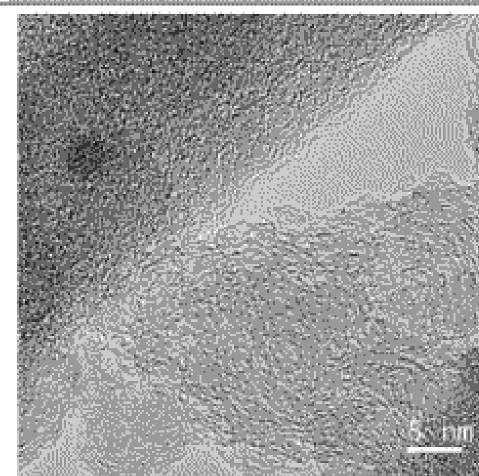
(a) Burning rate DSC curve



(b) Mass reduction TGA curve

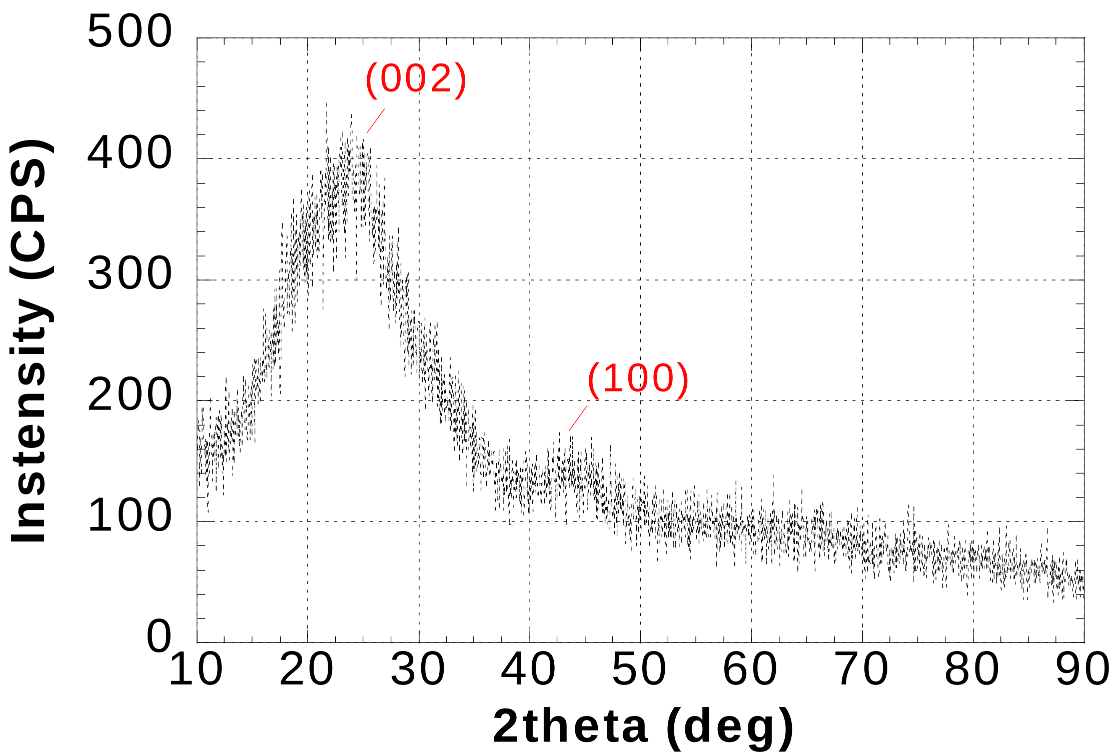
Soot Nanostructure –

Less Ordered Nanostructure Corresponds to Enhanced Reactivity

Time	BP15 soot	B20 soot
No burn-off		
After 30 mins @ 500 °C		

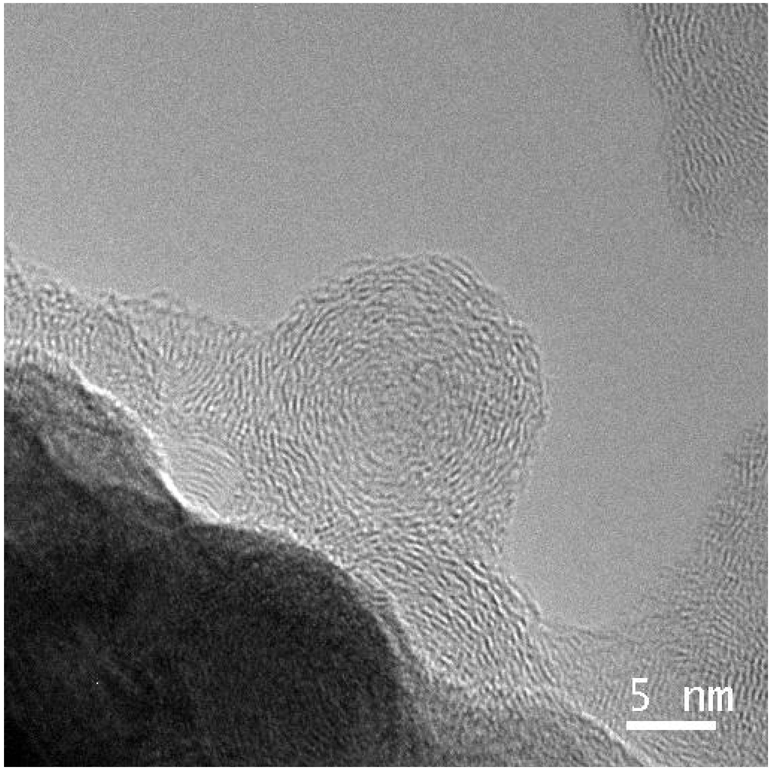
Soot Nanostructure

XRD Analysis of BP-15 Soot Shows a More Ordered Nanostructure

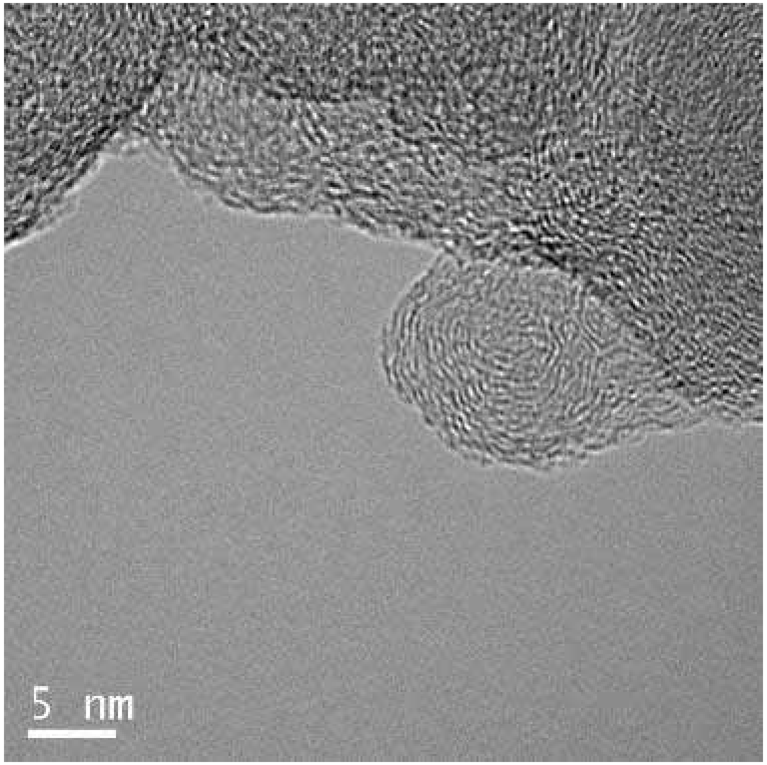


Soot Nanostructure

Do Neat Alternative Diesel Fuels Yield Less Ordered Nanostructure ?



(a) FT100 Derived PM



(b) B100 Derived PM

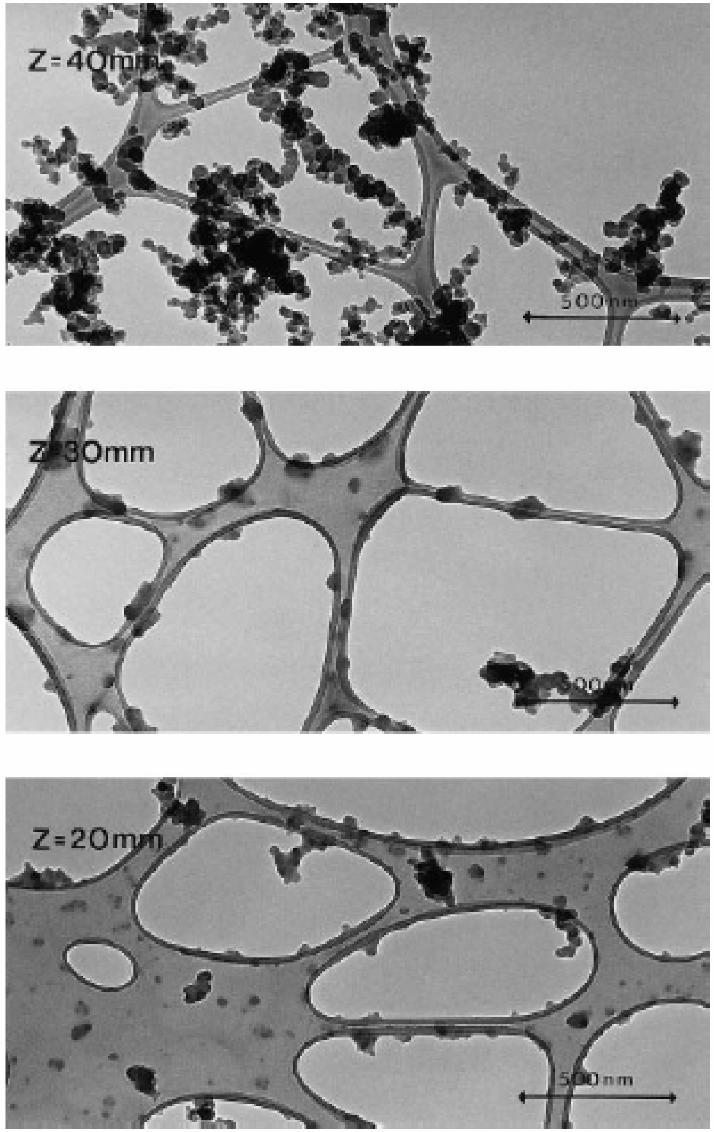


Fig. 1. Micrographs of particulate material captured on lacy carbon grids sampled from the centerline of the ethene diffusion flame. The transition from precursor particles to soot aggregates occurs between $Z = 30$ and 40 mm.

Palmer, H. B., and Cullis, C. F., in Chemistry and Physics of Carbon, Vol. 1, (P. L. Walker, Jr. and P. A. Thrower, Eds.) Marcel Dekker, 1965, pp. 265–325.

“...properties of carbons formed in flames are remarkably little affected by the type of flame, the nature of the fuel being burnt and the other conditions under which they are produced. Any complete theory of carbon formation must of course be able to account for this striking experimental finding.”

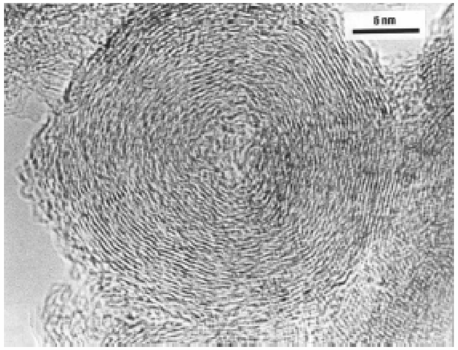


FIG. 1. Example of the well-known shell/core nanostructure of many primary soot particles. HRTEM fringe image of ethylene soot courtesy of Lenore Rainey at MIT and Professor Adel Sarofim at the University of Utah.

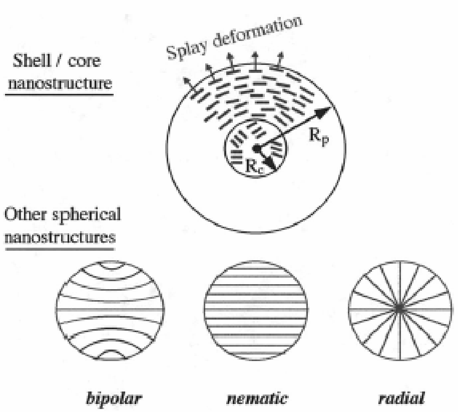


FIG. 2. Possible nanostructures in spherical carbon bodies shown as two-dimensional cross-sections, including bipolar [8,13], radial, and nematic [14]. Each of these carbon nanostructures has an analogue among low molecular weight, rod-like liquid crystalline systems confined to spherical geometries [15].

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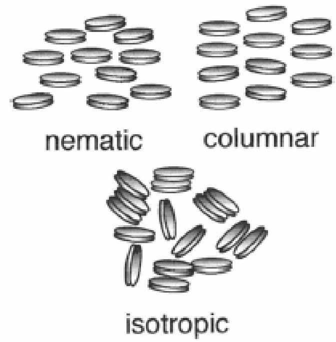


FIG. 3. Simple discotic phases. The nematic and columnar phases are liquid crystalline phases containing orientational order but incomplete long-range positional order. The nematic is the simplest liquid crystalline phase, possessing no modes of long-range positional order.

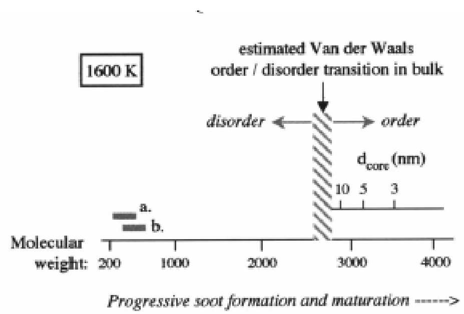
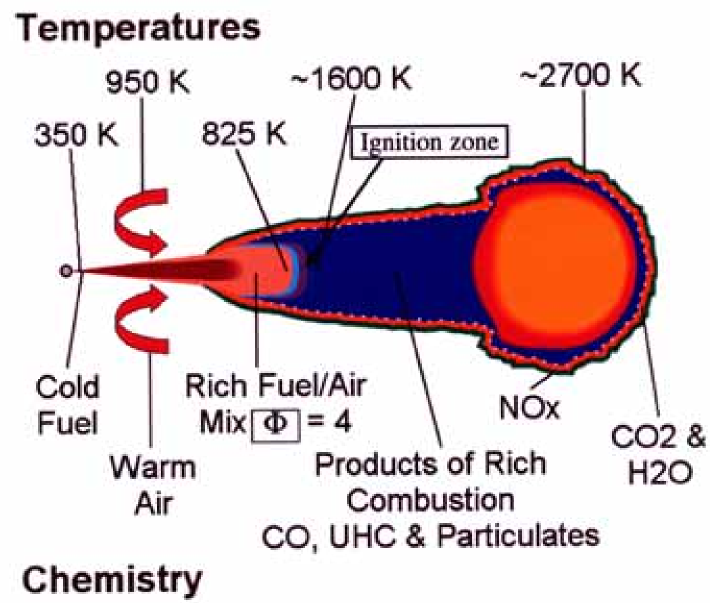


FIG. 9. Example one-dimensional phase diagram relevant to soot formation processes. Equilibrium relations are given as a function of molecular weight at an example local flame temperature of 1600 K. The vertical line gives an estimate of the threshold molecular weight for the disorder → order transition in the bulk (unstrained) condensed phase based on extrapolation of a relation for pitch transitions [17] to higher temperatures and higher molecular weights. The plot also shows the isotropic core diameter as a function of molecular weight in the region above the transition point, where increasing molecular weight allows an increasing degree of strain to be accommodated in the ordered phase. Bars a and b show example molecular weights of early flame condensation products as determined by laser microprobe mass spectrometry [27].



C. K. Westbrook

Conclusions

- Biodiesel Fuels
  - Soot nanostructure for B20 fuel blends is less ordered and contributes to more reactive PM
  - Preliminary results show B100 does not yield the same shift to a less order soot nanostructure as B20 does
- Fischer-Tropsch Fuels
  - The structure and luminosity of the diesel spray flame with FT diesel is not significantly different from that with ultra low sulfur diesel
  - Soot nanostructure for FT100 is not different than for conventional diesel fuel
- Aggregate Effects on Emissions Control
  - Higher engine-out NOx and higher PM-SOF can enhance DPF regeneration and lower the Break Even Temperature (BET)
  - NOx/PM ratio and PM composition/reactivity are key issues in DPF regeneration

Future Work

- Ultra Clean Fuels Program
  - Examine COP Fischer-Tropsch Diesel Products Neat and in Blends, Including Blended with Biodiesel, in the Cummins ISB 5.9L Turbodiesel Engine
  - Includes Property Evaluation (✓), Combustion & Emissions Tests, Exhaust Aftertreatment and In-Cylinder Visualization (✓)
  - Examine Optimization of Engine Control Parameters to Maximize the Benefits from the Unique Properties of the COP F-T Diesel
- Other Related Work
  - Characterize the Impact of Engine Operating Conditions (EGR, Inj. Timing, Charge Composition) on Soot Nanostructure and Link to the Surface Chemistry of Soot

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