ARGONNE NATIONAL LABORATORY

TRANSPORTATION TECHNOLOGY R&D CENTER

Characterization of Particulate Sizes, Microstructures and Fractal Geometry of a Light Duty Diesel Engine via Thermophoretic Sampling

Kyoeng Lee, Jinyu Zhu and Raj Sekar

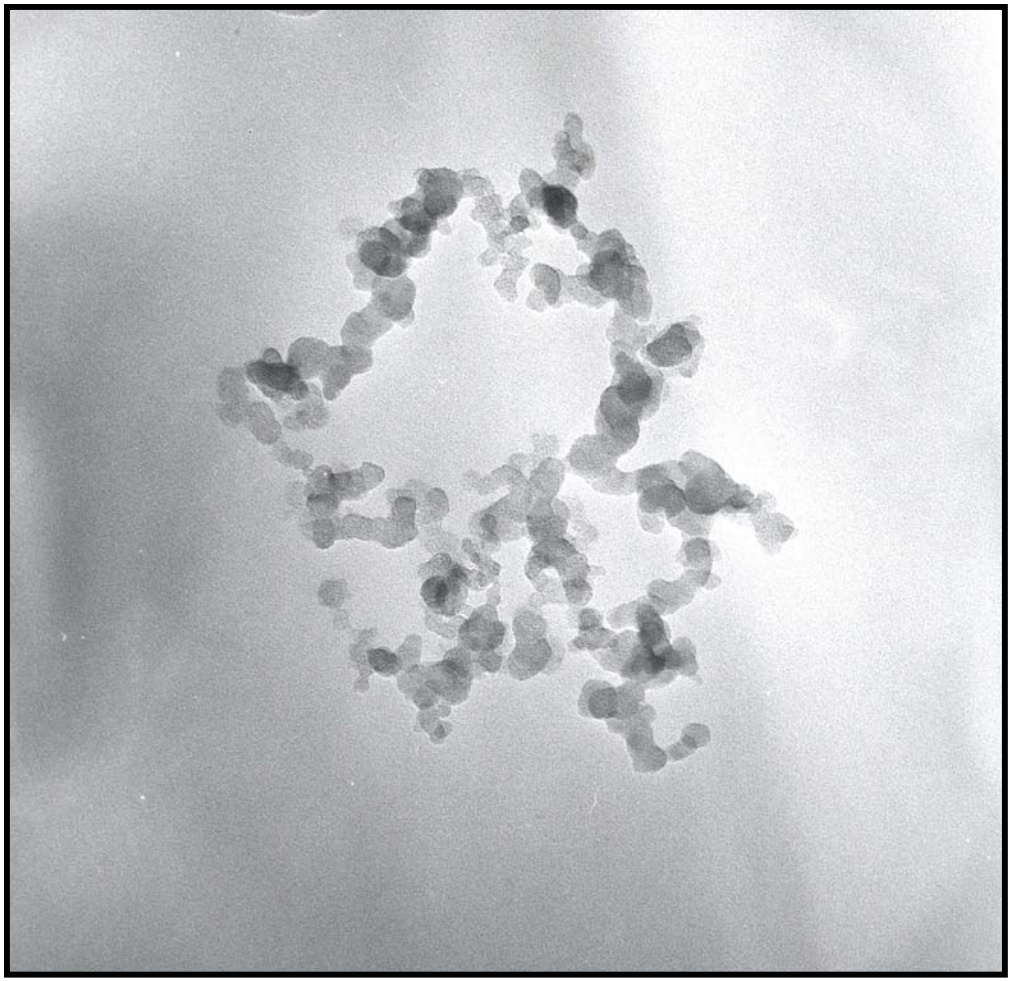
Center for Transportation Research

Argonne National Laboratory

April 7, 2003

Presented at 13th CRC On-Road Vehicle Emissions Workshop

Diesel Particulates



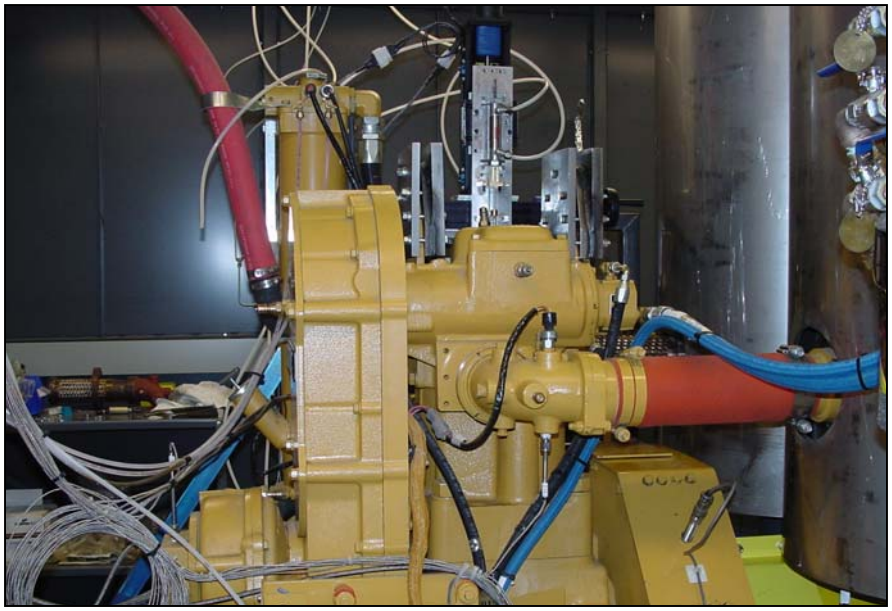
Human health and environment impacts of PM call for detailed investigations

- 2007 PM standards for heavy-duty diesel vehicles
  - 0.01 g/bhp-hr (90 % reduction) / Low sulfur content fuel
  - Aftertreatment systems required
- Future regulations for PM sizes
- Major research targets
  - Formation/destruction mechanisms of PM
  - Accurate sampling techniques
  - Particle sizes, structures and chemistry
- Morphological investigation reveals details of diesel particulates, which has not been available.

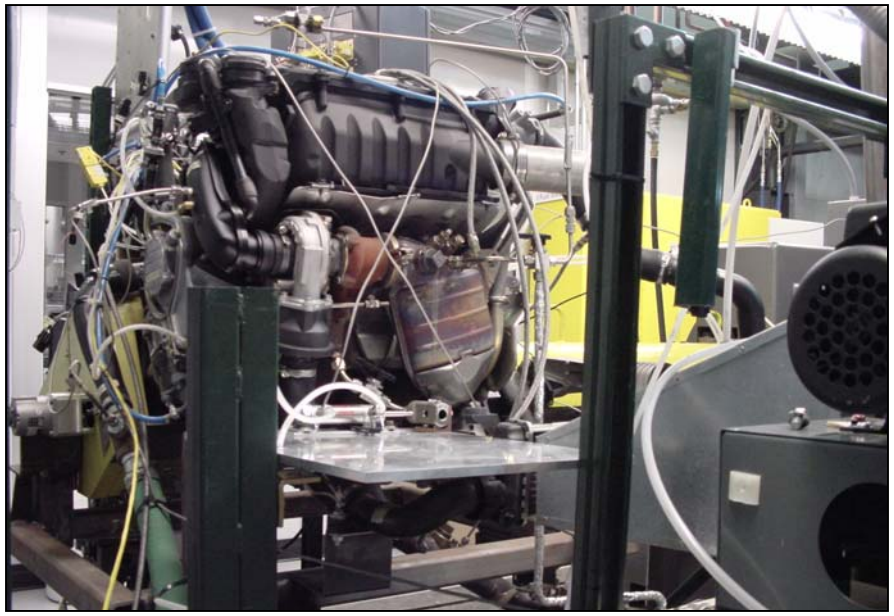
Thermophoretic sampling and TEM enable us to measure actual physical dimensions and microstructures of PM

- Commercially available apparatus
  - Electrical aerosol analyzer (EAA)
  - Scanning mobility particle sizer (SMPS)
  - Impactor
- Thermophoretic sampling/TEM
  - Short residence time
  - No air dilution
  - No extra treatments for analysis of morphology and chemistry
  - Measurement of actual physical dimensions
    - Primary & aggregate particles

Thermophoretic sampling is a necessary component for detailed investigations of PM



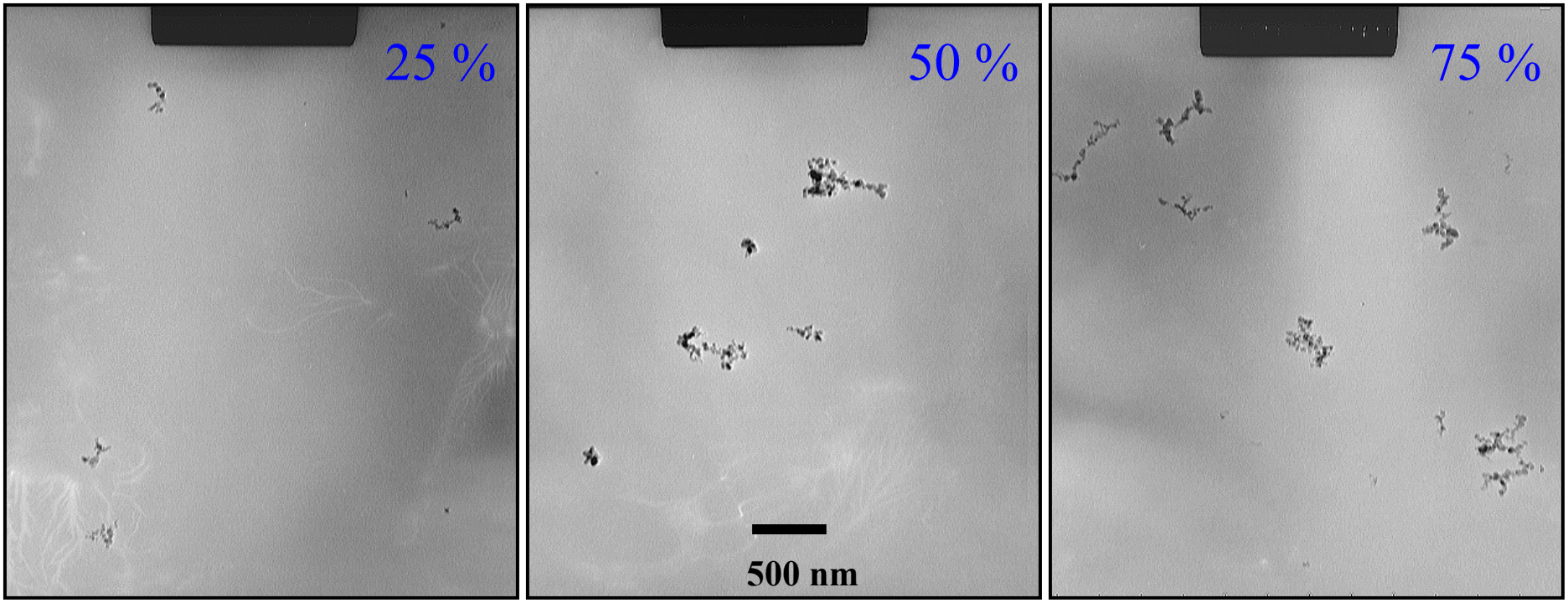
2.4 L Single-Cylinder DI Diesel Engine (Supercharged, Unit Injection)



1.7 L Turbocharged 4-cylinder DI Diesel Engine (EGR, Common-Rail)

TEM reveals details of diesel particulate morphology and structures

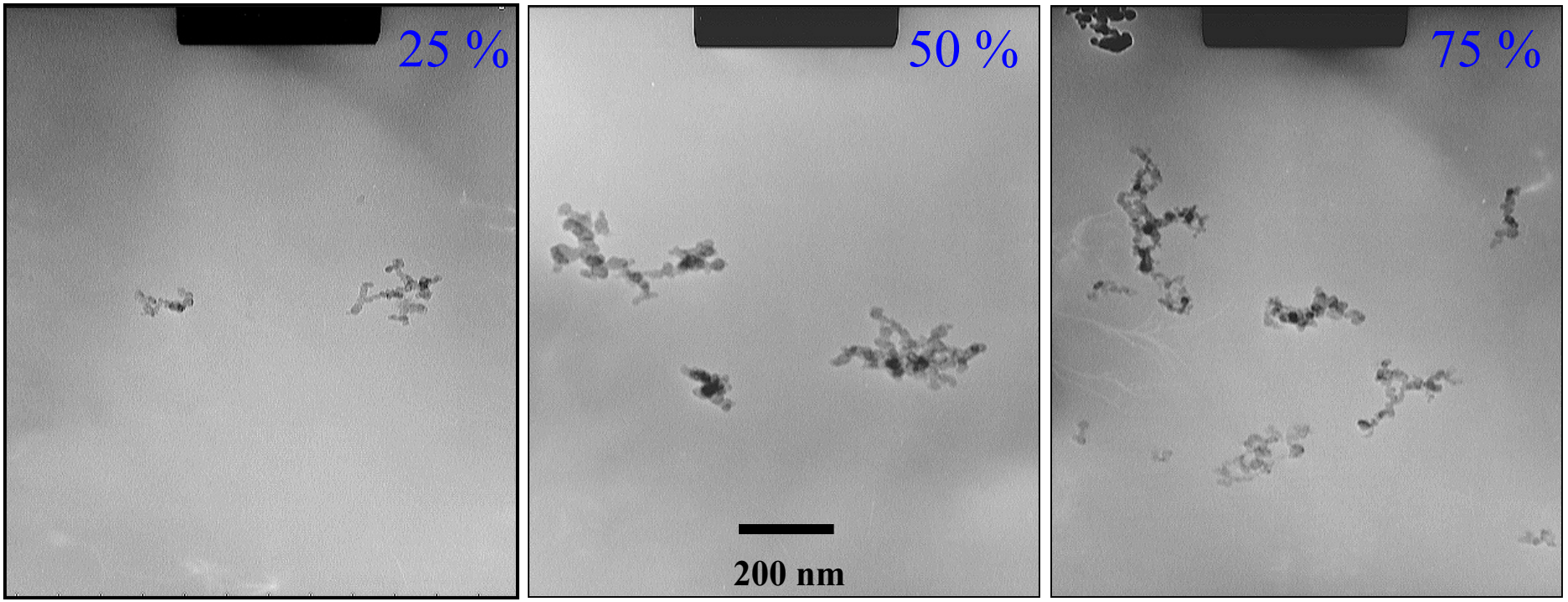
1000 rpm (17KX)



- Particle morphology: Near-spherical to chain-like
- Particle size and number density increases with engine load.

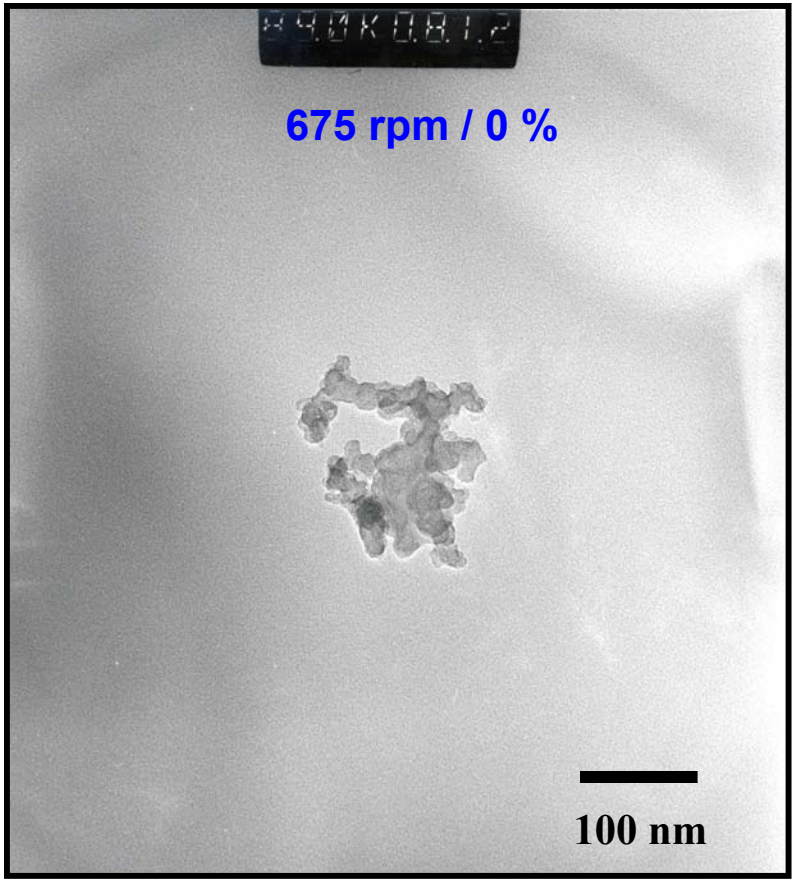
Continued

4000 rpm (52KX)

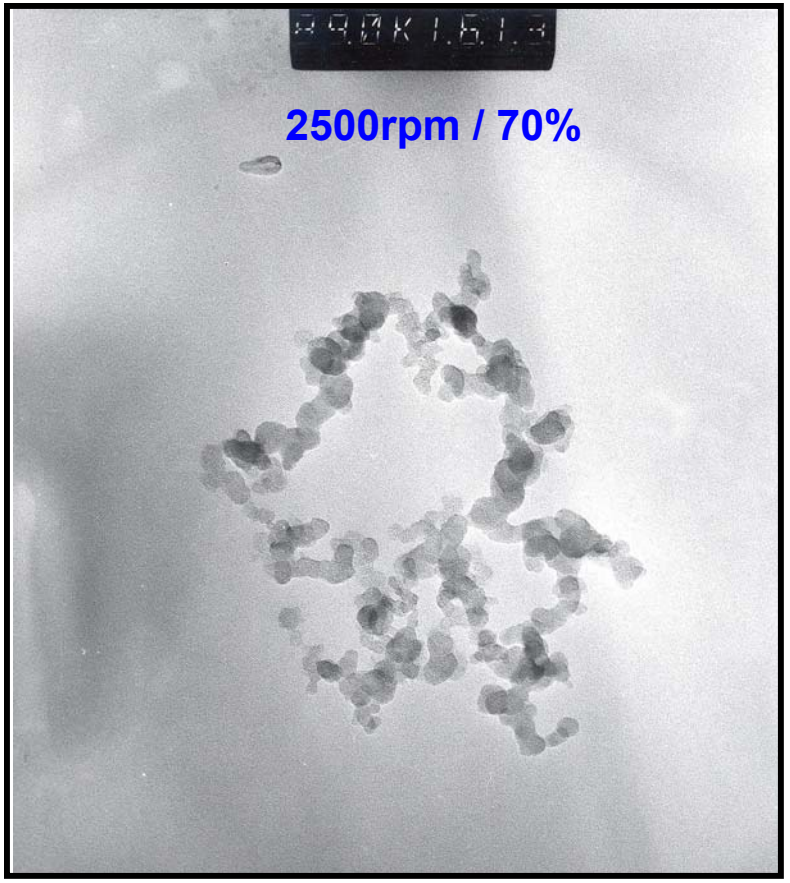


- Particle size initially increases with load and decreases.
- Number density keeps increasing with load.
- EGR was off in operation.

Significant differences in morphology were observed depending on engine load

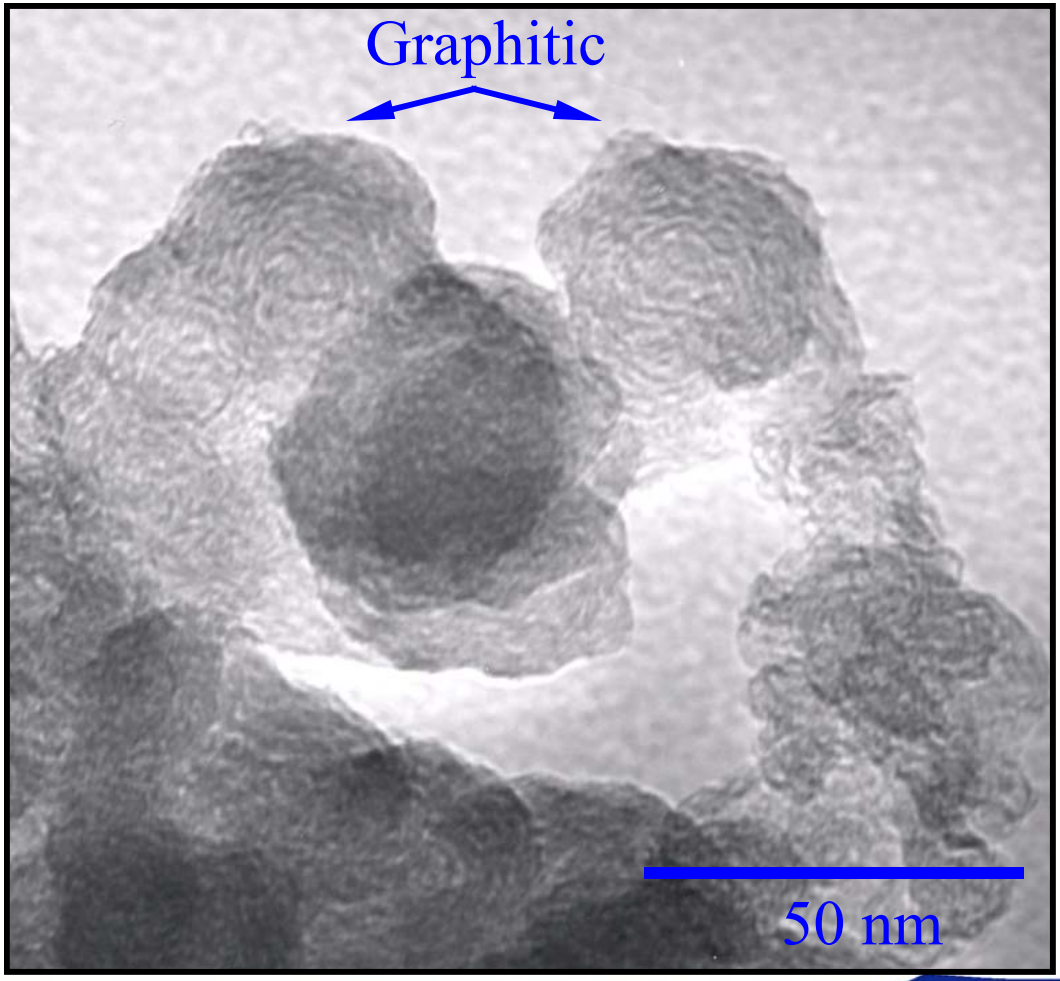


Nebulous

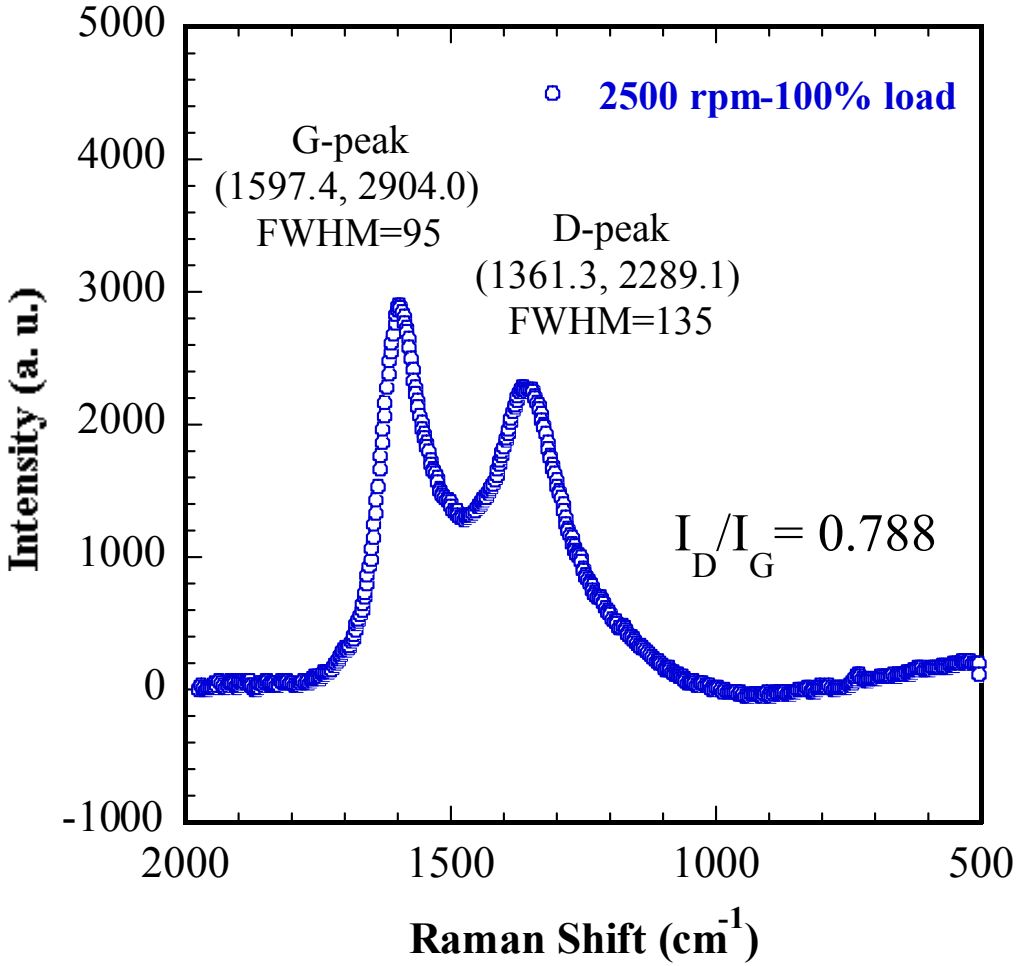


Distinct

High-resolution TEM reveals microstructure of primary particles



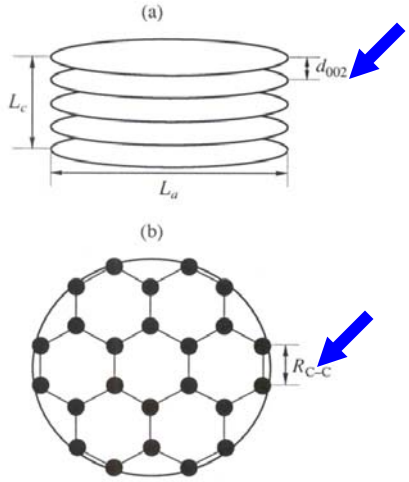
Raman spectra reveal a degree of graphitic structure of diesel particulates



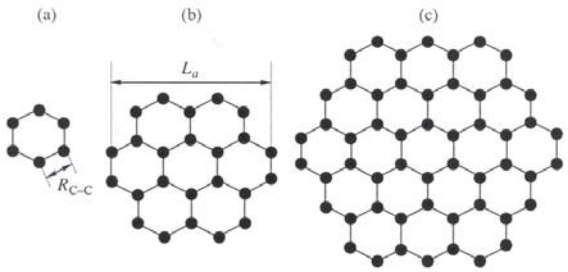
- $I_D / I_G = C \bullet 1 / L_a$
  (C = 4.4 nm)
- Average crystal size (L_a): approximately 5.6 nm
- Disorder of crystal structure decreases with increasing loads

Further microscopic analysis reveals atomic structures of diesel particulates

Turbostratic structure



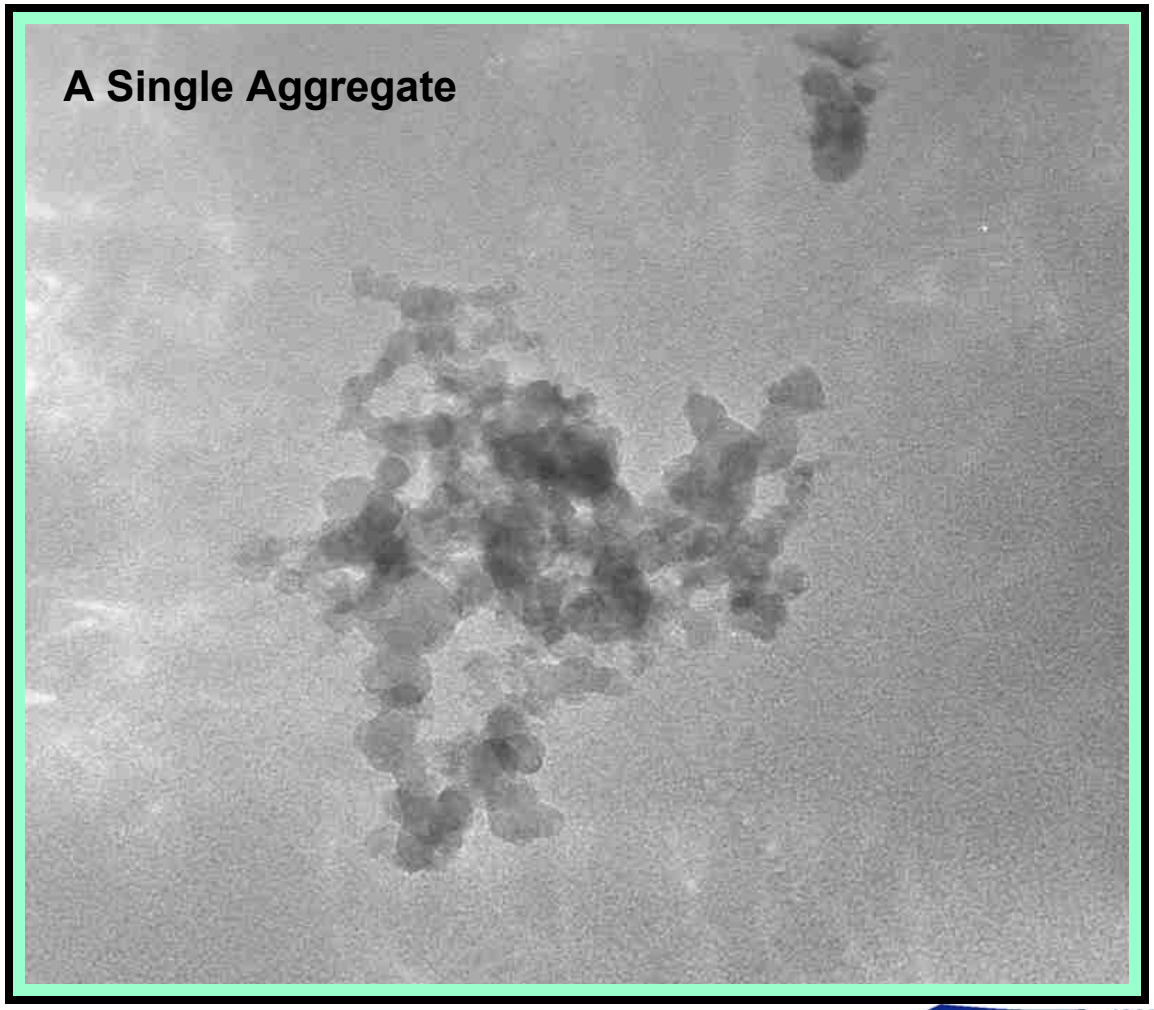
Graphitic structure



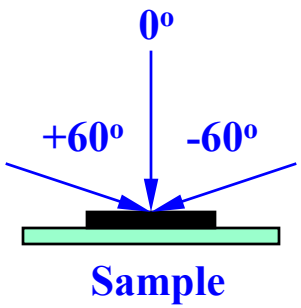
Carbon layers with
P= (a) 1, (b) 2, (c) 3

- L_a = 5.6 nm
- P = 12
- 864 carbon atoms per layer
- Interlayer distance:
  $d_{002} \approx 0.34$ nm
- R_{c-c} = 0.141 nm

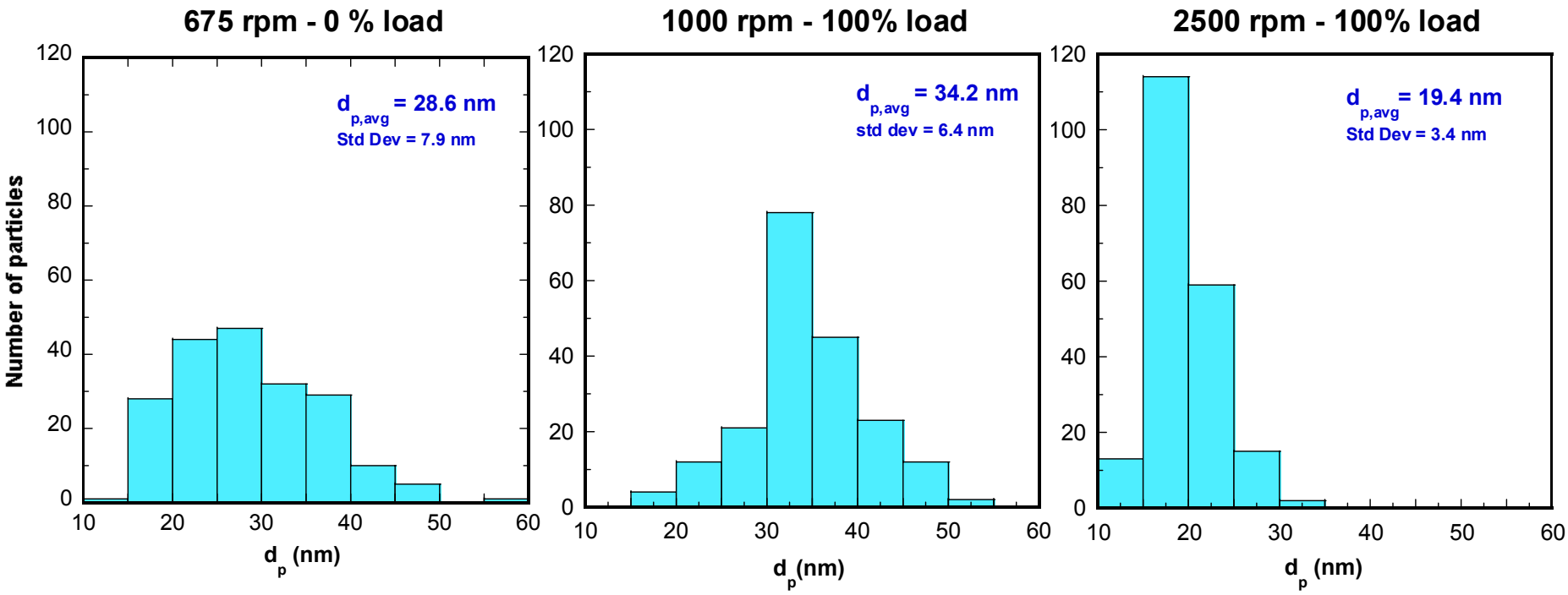
TEM lends us to observe 3-D structures of particulate morphology



Viewing angles

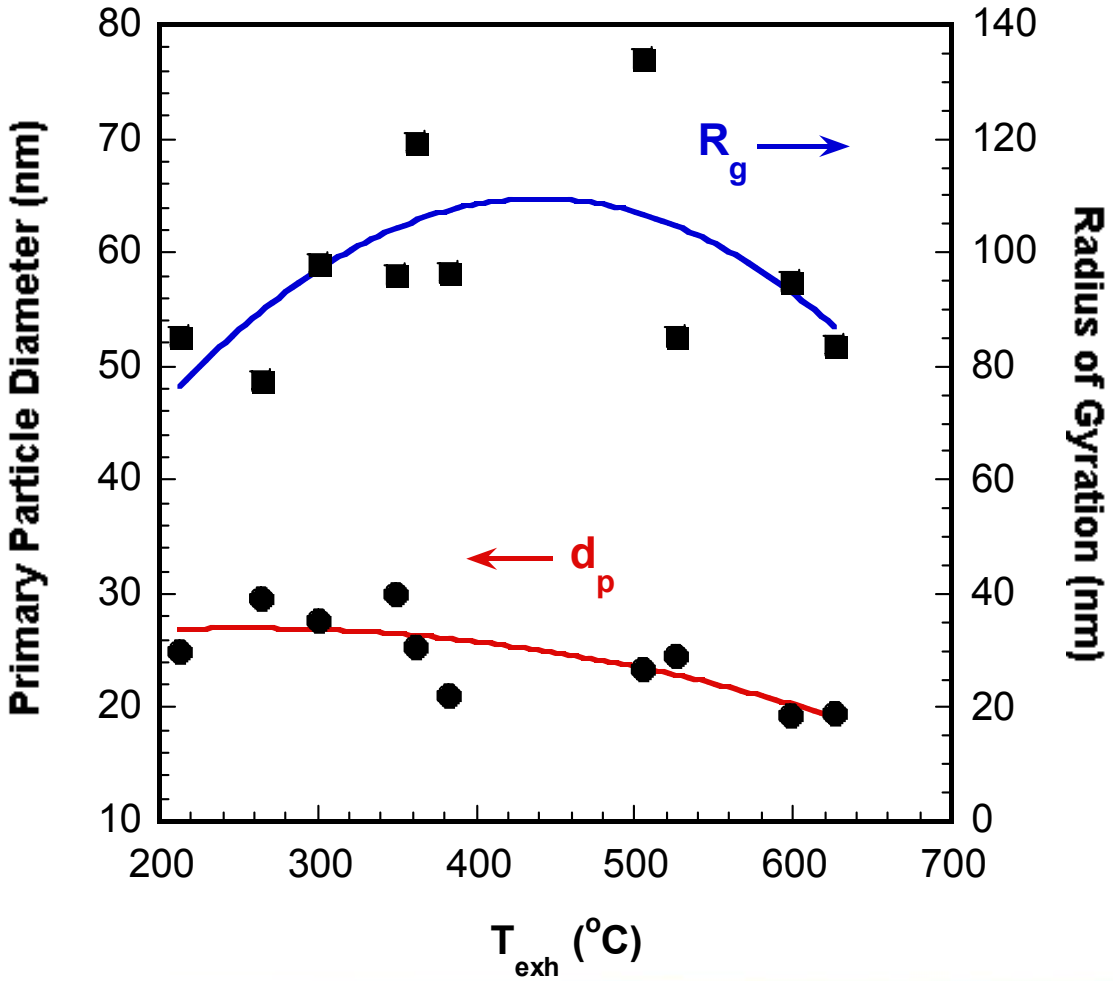


Primary particle sizes are significantly affected by engine operating conditions



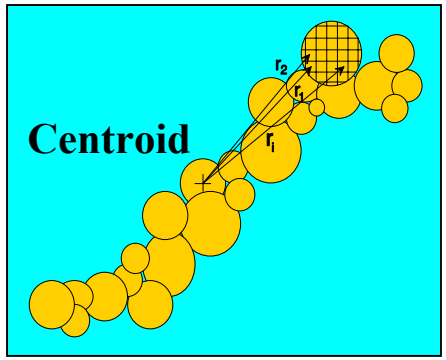
- Idling: Both young and aged soot particles exist.
- High loading: Significant oxidation due to high temperature
- T_{exh} = 140, 460 and 600 ^{o}C, respectively.

Particulate sizes are sensitive to temperature

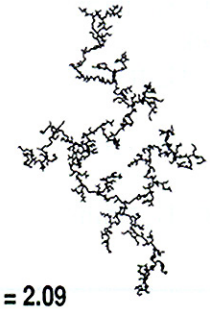
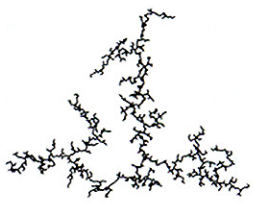
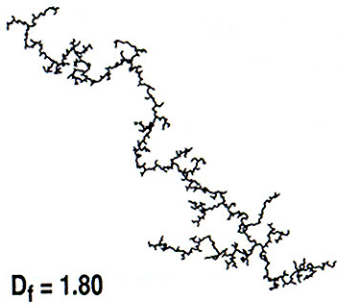


- Radius of Gyration

$$R_g = \sqrt{\frac{1}{n}\sum_{i=1}^{n} r_i^2}$$



Fractal dimension indicates how aggregate particles are formed

	REACTION-LIMITED	BALLISTIC	DIFFUSION-LIMITED
MONOMER-CLUSTER	EDEN  $D_f = 3.00$	VOLD  $D_f = 3.00$	WITTEN-SANDER  $D_f = 2.50$
CLUSTER-CLUSTER	RLCA  $D_f = 2.09$	SUTHERLAND  $D_f = 1.95$	DLCA  $D_f = 1.80$

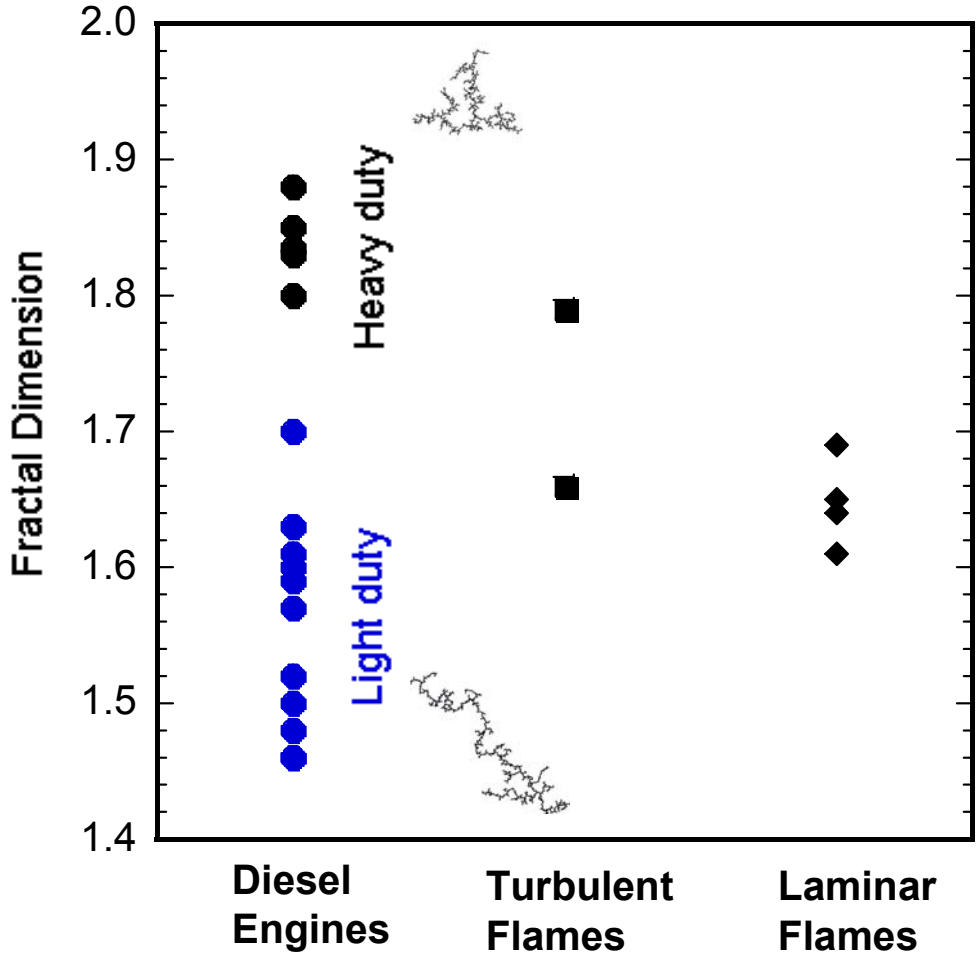
$$n = k_f \left(\frac{R_g}{d_p} \right)^{D_f}$$

n: **Number of primary particles per aggregate**

$$n = \left(\frac{A_a}{A_p} \right)^{\alpha}$$

α =1.09

Morphology of diesel particulates was standardized via fractal analysis



- Heavy-duty diesel PM → more compact
- Light-duty diesel PM → More chain-like shape
- Diffusion-limited particle formation mechanism suggested

Challenging questions remain for future work

- Can we find correlations with the aerodynamic or mobility diameters measured by commercially available apparatus?
- How would aftertreatment systems affect PM sizes and morphology along the exhaust pipe?
- How do different properties in diesel fuel affect particulate morphology?
- How do PM morphology differences affect human health?

Acknowledgement

Dr. Sidney Diamond

This project is supported by the Office of FreedomCar and Vehicle Technologies of the U.S. Department of Energy.