Detailed Morphological Investigation of Diesel Nano-Particles for Their Efficient Control

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Abstract

In an effort of reducing diesel particulate matter (PM) emissions and consequently protecting environment, PM control technologies, including diesel particulate filter (DPF) systems, have been developed as a practical means of meeting the reinforced PM emissions standards. However, profound understanding of detailed properties of diesel particulates, such as morphology and nano-structures, is still required for developing advanced PM emissions control systems. Therefore, researchers at Argonne National Laboratory developed a unique thermophoretic soot sampling system that can provide diesel PM samples for observation of soot morphology with a transmission electron microscope (TEM). The experimental results showed the different degrees of graphitization of diesel particulates as a function of engine operating conditions, in addition to differences in size and fractal geometry. Differences in soot morphology were observed along the exhaust pipe, where oxidation catalysts were installed. The effects of the aftertreatment system and engine components were examined in detail and quantitatively analyzed in this experimental work. Also, the morphology and nano-structures of diesel particulates were characterized with a variation of chemical properties in diesel fuels, such as sulfur, paraffins, naphthane, and aromatics. One outstandingly interesting observation among many others is a difference in the number of nuclei that consist of core parts of individual primary soot particles, which implies the different number of active sites for soot oxidation. The analyses of dark fringes on the high-resolution soot images, in terms of curvature and interspacing distance, proved that the degree of oxidation is dependent upon the chemical properties of diesel fuel. In the recent experimental work, it was found that a gasoline direct injection (GDI) engine produced soot particles much smaller than those from the conventional diesel combustion. The current experimental work revealed many unknowns of engine combustion-derived nano-particles and suggested potential strategies that could be used to design advanced diesel PM control systems and also useful for regulating future PM emissions standards.

Experimental Descriptions

Particulate samples were collected from a 1.7-liter light-duty diesel engine, where emissions were bypassed to a thermophoretic soot sampling system. The engine was equipped with a common-rail direct fuel injection system, a turbocharged/inter-cooled air intake system, an exhaust gas recirculation (EGR) system, and oxidation catalysts. Argonne researchers first developed the thermophoretic soot sampling system for engine application, which consists of a flow-through sampling chamber, an actuator, solenoid valves, and an electronic remote controller. In principle, particles are collected on the carbon substrate of a copper grid by temperature gradient between particles and the grid. Once soot particles are sampled, the sample grid is directly inserted into a high-resolution TEM for the detailed analysis of soot morphology. The residence time of sampling probe sustaining in exhaust streams was set at the order of tens of milliseconds. The short sampling duration offers such major benefits as no dilution of exhaust stream, non-subjective sampling, and minimal influence to soot properties. Finally, the TEM micrographs were analyzed by a custom data acquisition system to measure particle sizes and fractal geometry [1-2].

Results

This paper summarizes the experimental results obtained for past several years at Argonne under four major subjects: effects of engine operating conditions, effects of engine exhaust components, effects of fuel properties, and characterization of gasoline engine particulates.

Fig. 1(a) - (b) show morphologies representing the diesel particulates sampled at 780 rpm/0% load (idling) and 2500 rpm/70% load. At idling, particles appeared to be nebulous, where individual primary spherules looked fused together. It is speculated that these amorphous soot particles should contain a significant amount of soluble organic compounds (SOCs). Our recent work showed that diesel PM emissions overall contain about 20% SOCs in terms of weight [3]. On the other hand, the particulates sampled at the high engine load appeared to be more distinct. This trend is quite common in conventional diesel combustion. Fig. 1(c) shows the size [primary particle diameter (d_p) and radius of gyration (R_g)] distributions of particulates collected from a heavy-duty and a light-duty diesel engine as a function of exhaust gas temperature (proportional to engine load).

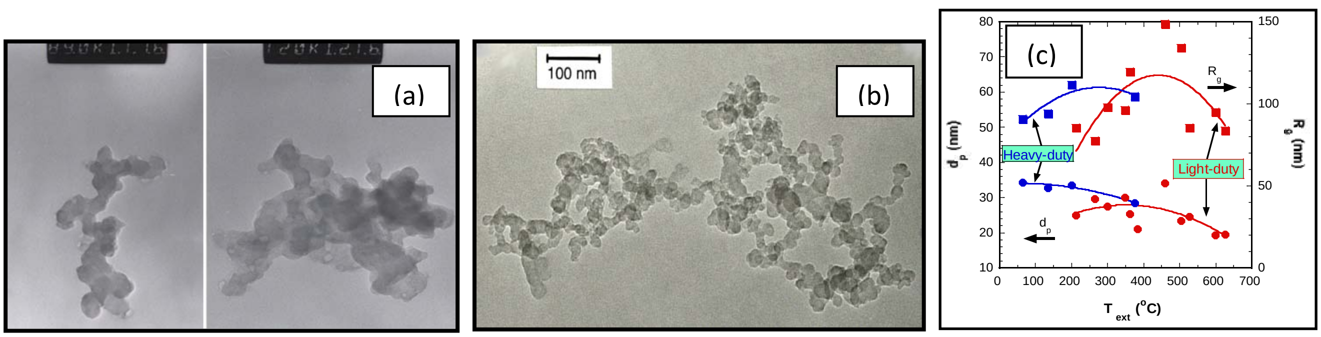

Figure 1. TEM micrographs of diesel particulates collected at idling (a) and 2500 rpm/70% load (b), and particle size distributions as a function of engine operating conditions (c).

Fig. 2 shows the morphology of diesel particles collected after a diesel oxidation catalyst (DOC) in the exhaust system. Overall, the particle shape looks spherical and the particle size is smaller than that of typical engine-out particles. Many particles looked fused together, where bounds between primary particles were unclear. The evolution of particle in size and shape has been examined along the exhaust pipe [4].

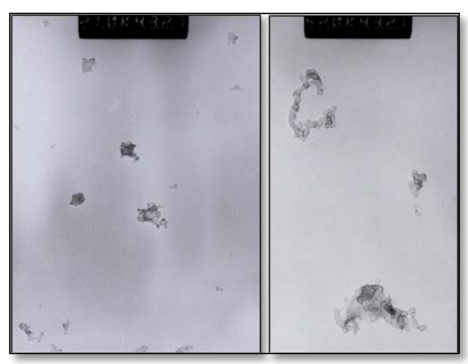

Figure 2. TEM micrograph of diesel particles collected after a DOC.

Diesel fuels were formulated with different concentrations of chemical properties, such as sulfur, n-/iso-paraffin, naphthene, and aromatics. Fig. 3 shows HRTEM images taken at a magnification of 250,000X for particulates collected from the combustion of (a) aromatic-enriched and (b) iso-paraffin-enriched fuels, respectively. These engine-out particles were collected at 2500 rpm/50% load. Significant differences in nanostructures between the two samples were observed: the aromatic fuel-derived particles [Fig. 3(a)] appeared to be larger in diameter (about 30 nm) than iso-paraffin fuel-derived particles (about 15 nm) represented in Fig. 3(b). Each primary particle in Fig. 3(a) has only one nucleus near the center, while the one in Fig. 3(b) has multiple nuclei. Furthermore, the dark fringes of aromatic fuel-derived particles were arranged in a more orderly way, while those of iso-paraffin fuel-derived particles appeared to be wiggly (higher degree of curvature). Differences in the nano-structures will significantly affect the degree of particle oxidation [5].

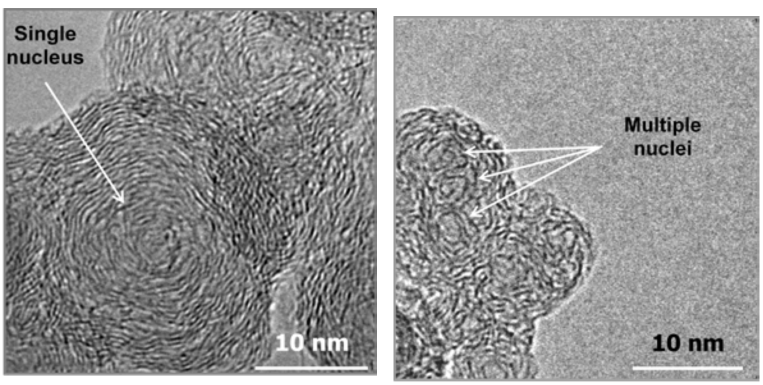

Figure 3. Nanostructures of particles collected from combustion of aromatic-enriched fuel (a) and iso-paraffin-enriched fuel (b), respectively.

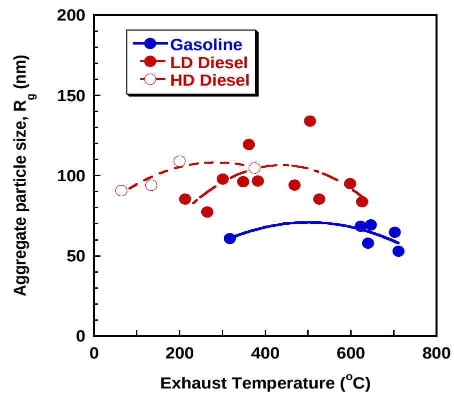

Figure 4. Size distributions of GDI engine particles in comparison with diesel particles

Fig. 4 displays data for the radius of gyration of particles collected from a gasoline direct injection (GDI) engine in comparison with those from diesel engines. The size distributions show apparent dependence on engine operating conditions. The GDI engine particles appeared to be significantly smaller in size than diesel particles (approximately a factor of 0.5).

Acknowledgement

This work has been supported by the Combustion and Emissions Program at the Office of Vehicle Technologies of US Department of Energy.

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August 2, 2010

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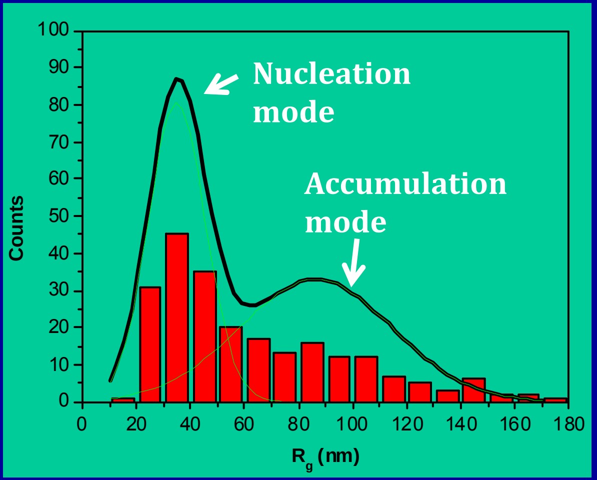
14th ETH-Conference on Combustion Generated Nanoparticles

Outline

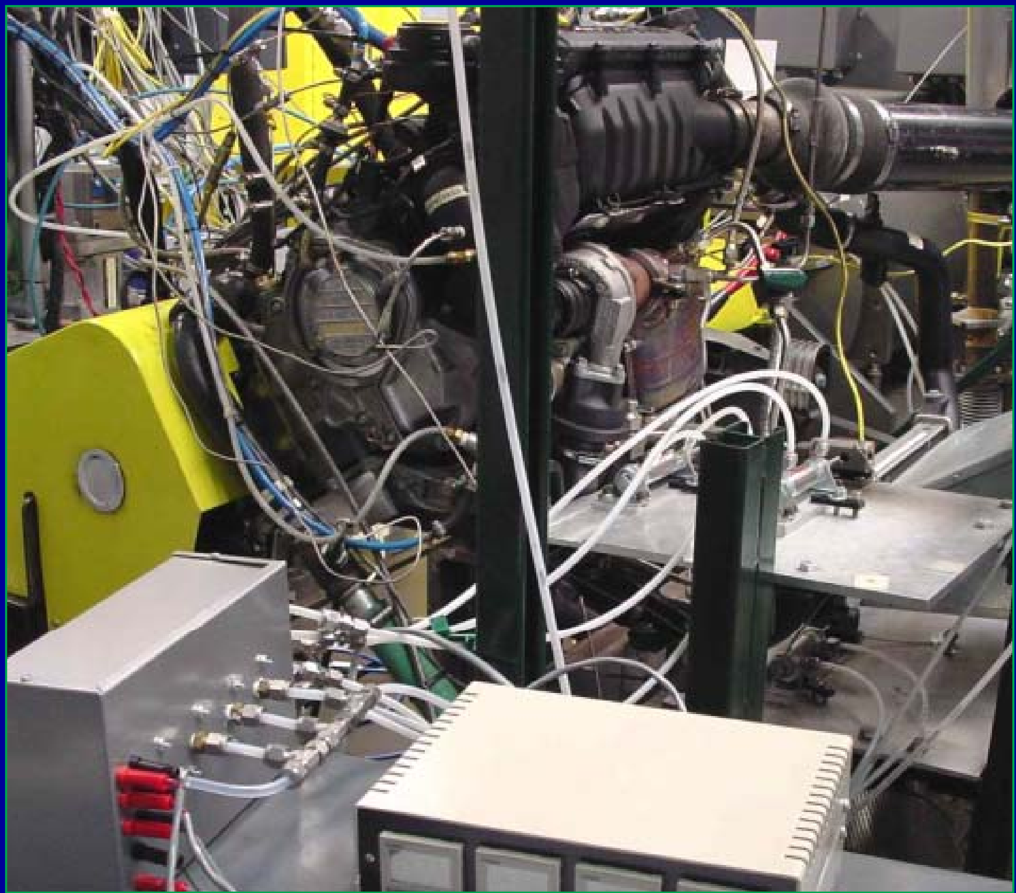
- Motivation
- Argonne's Solution for PM emission characterization
  - Thermophoretic soot sampling and TEM techniques
- Results
  - Effects of engine operating conditions
  - Effects of exhaust components
  - Effects of fuel properties
  - Nano-particles from GDI engine

Motivation

- The mass-based PM emission measurements cannot illustrate details about engine particulates.
- Current $PM_{1.0,\ 2.5,\ 10}$ standards are not enough to regulate nano-particles from internal combustion engines.
  - Most number of diesel particulates fall in $PM_{0.1}$.
- Regulations for the number of PM emissions will be effective soon.
- Current particle measurement instruments cannot define human health impacts.
  - Volume-based non-physical equivalent diameter.
  - Both physical size and chemistry of particulates are key parameters.
- Soot formation mechanisms are still unclear for different combustion types and alternative fuel combustion.
  - HCCI, LTC, GDI, bio-fuel combustion.



Thermophoretic PM sampling system was first developed for engine application at Argonne

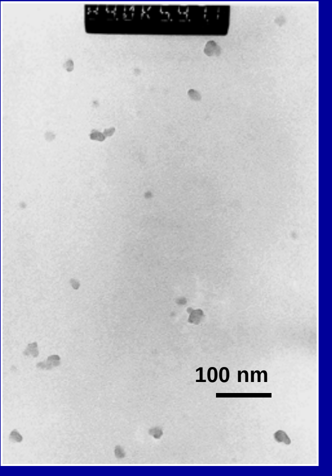


Thermophoretic sampling system installed on a diesel engine

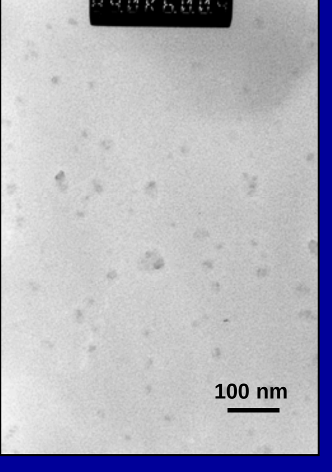
Advantages

- No air dilution
- Non-subjective sampling
- Minimal influence to PM properties (20 ms sampling time)
- No extra treatment
- Detailed analysis of morphology, microstructures, physical dimensions

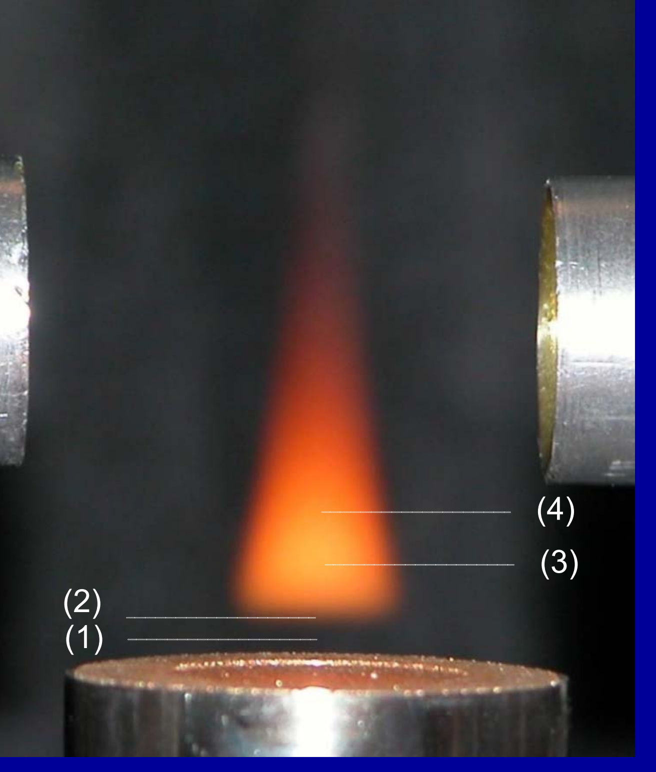
Thermophoretic sampling system and TEM enable us to reveal fundamentals in soot growth



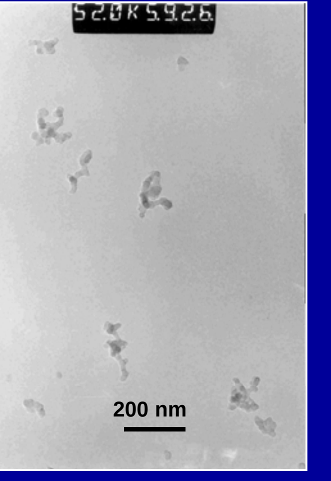
(2) 6 mm



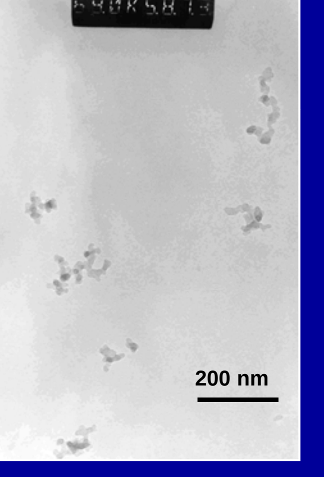
(1) H=4 mm



Ethylene
Laminar Pre-mixed Flame

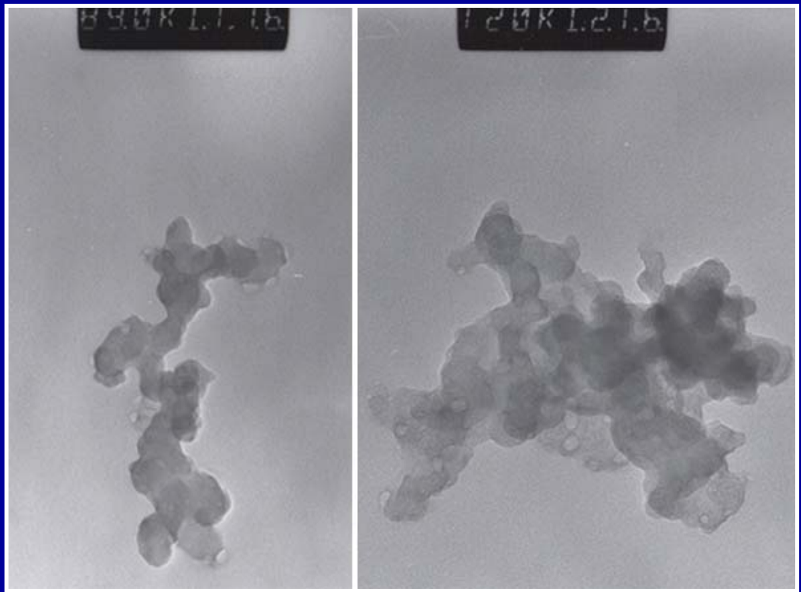


(4) 14 mm



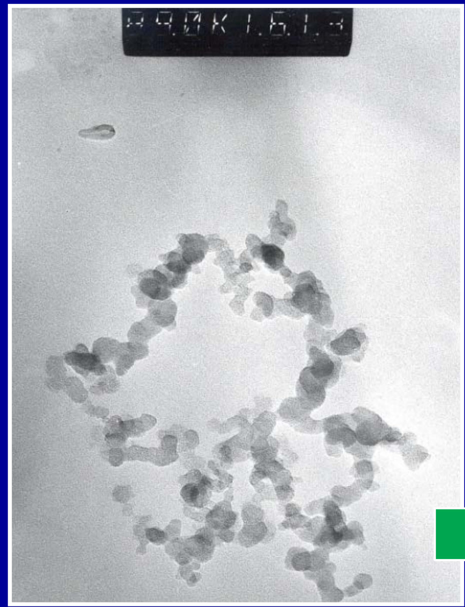
(3) 10 mm

Particulate morphology strongly depends on engine operating conditions



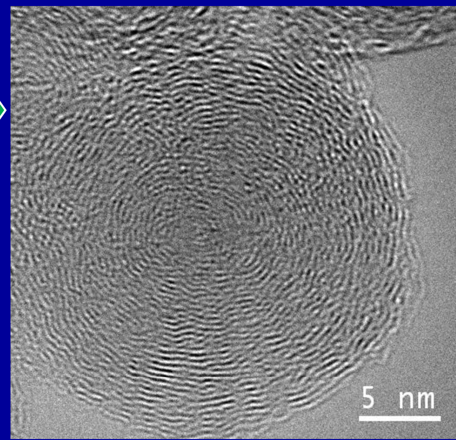
780 rpm / 0 %

Nebulous & Amorphous

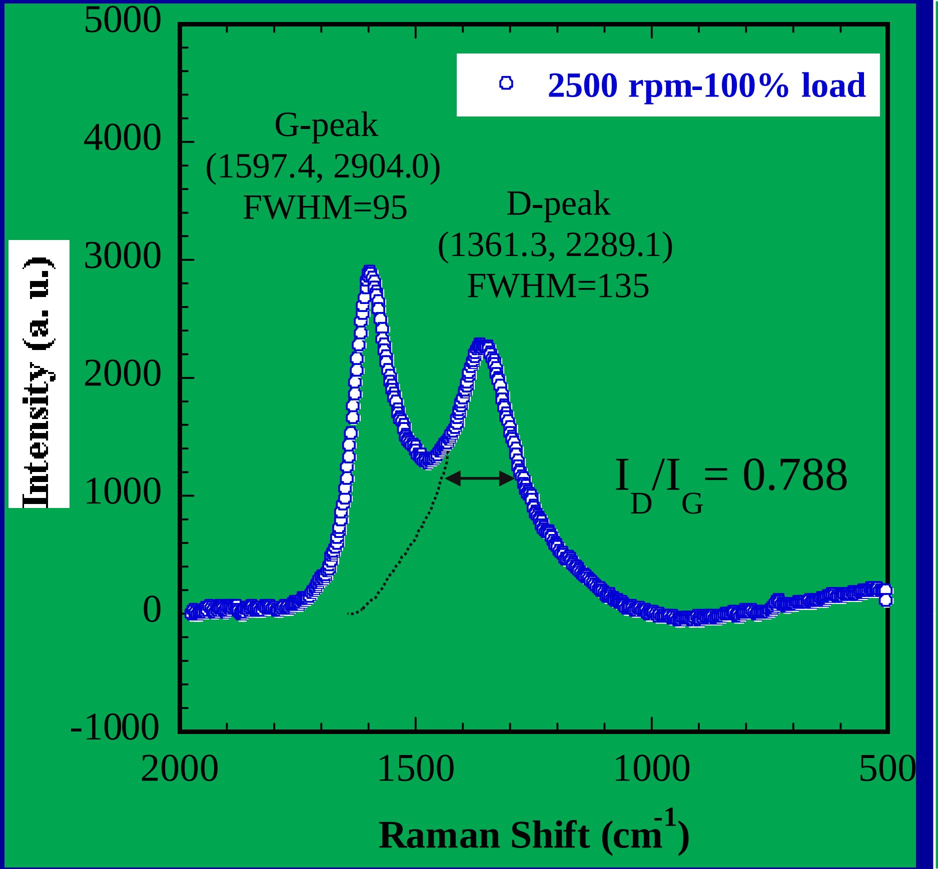


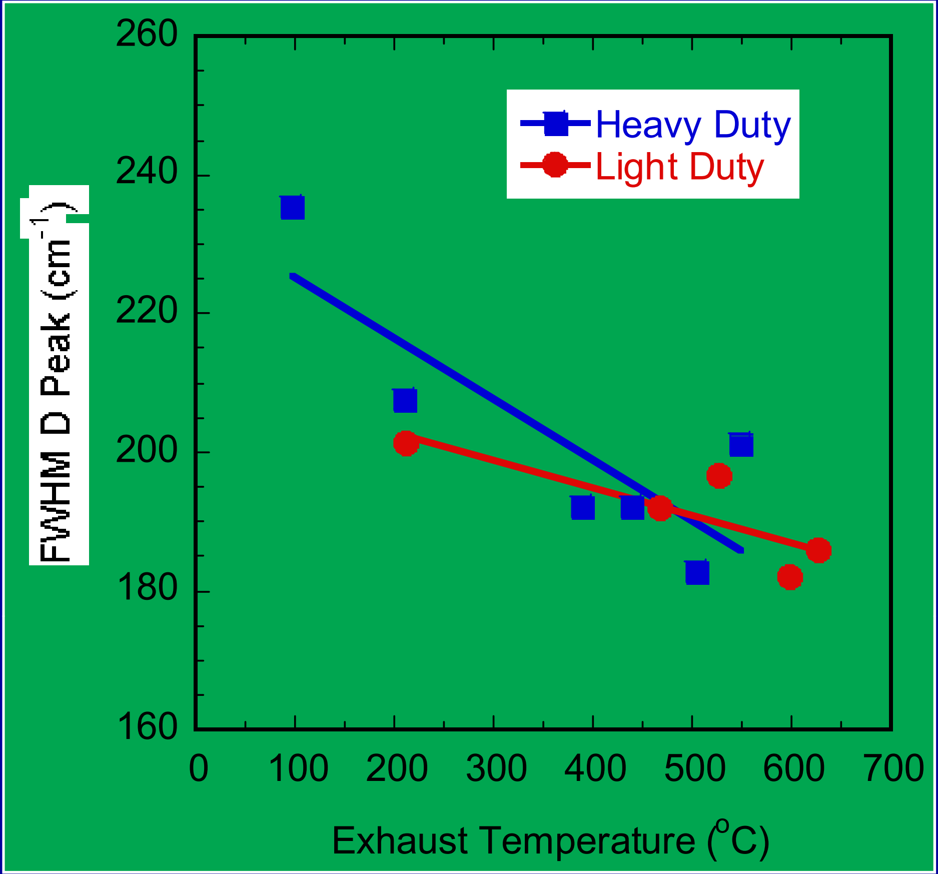
2500rpm / 70%

Distinct & Graphitic



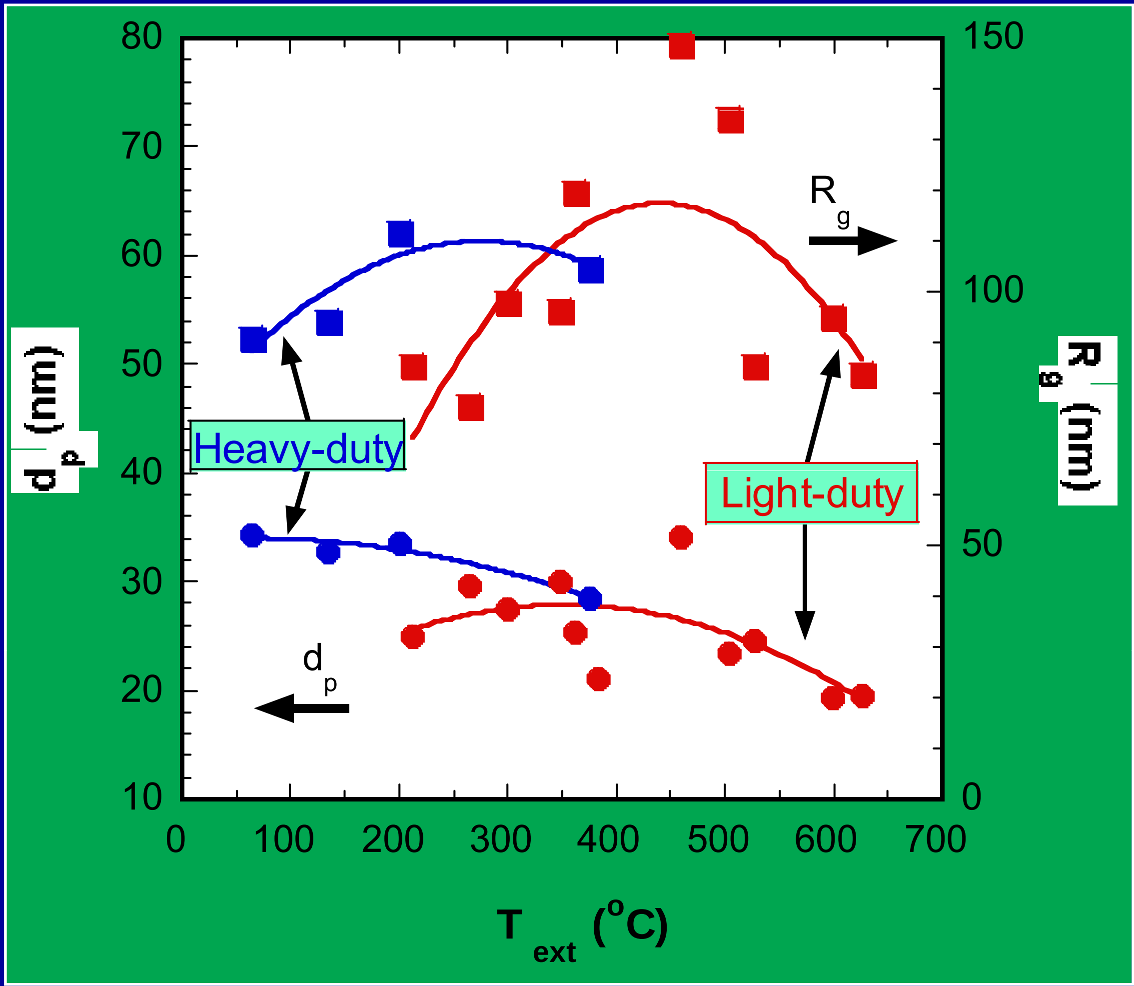
Disorder of crystal structures decreases with engine operating conditions

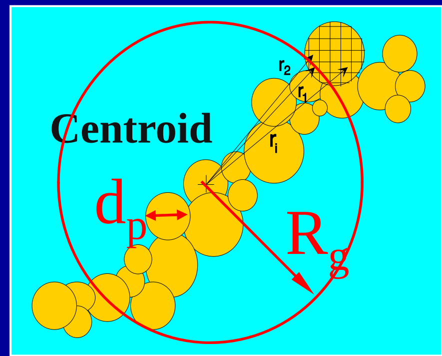




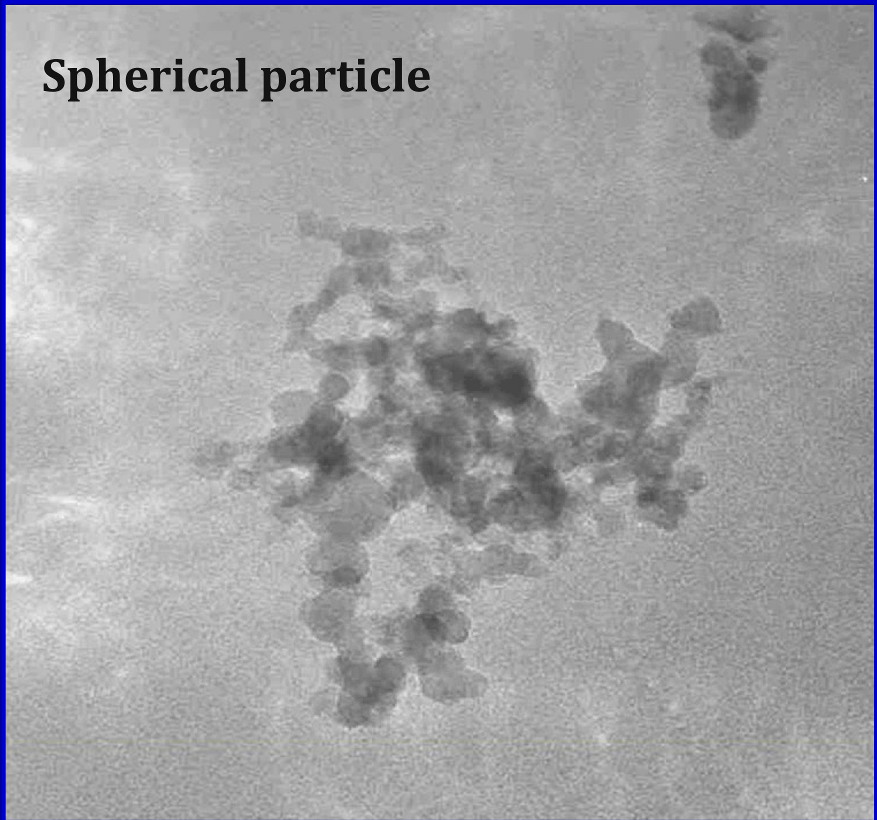
Degree of disorder is proportional to FWHM of D peak, and therefore …

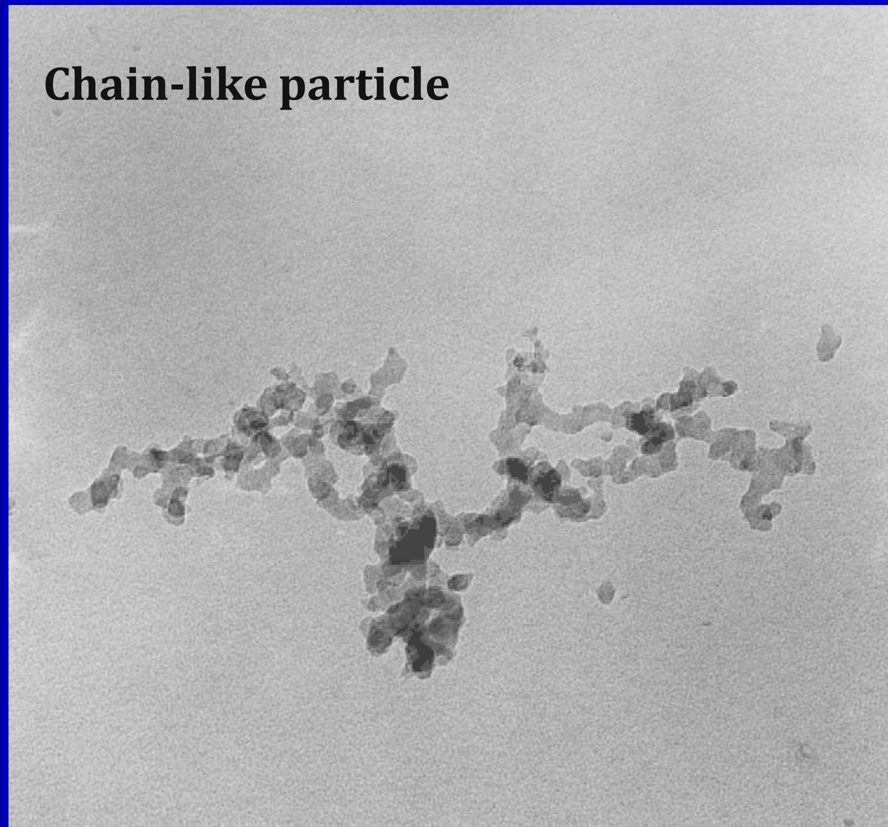
Particle sizes are strongly affected by engine operating conditions



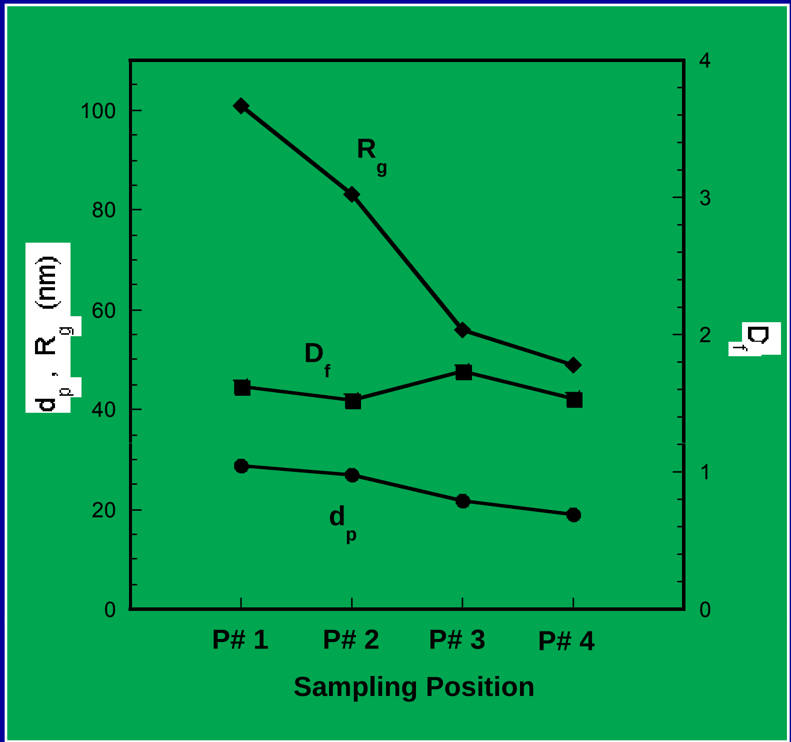


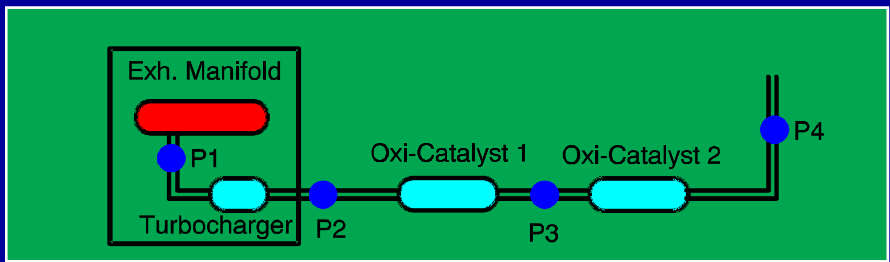
First observation of 3-D PM structures reveals details of complex diesel particulates





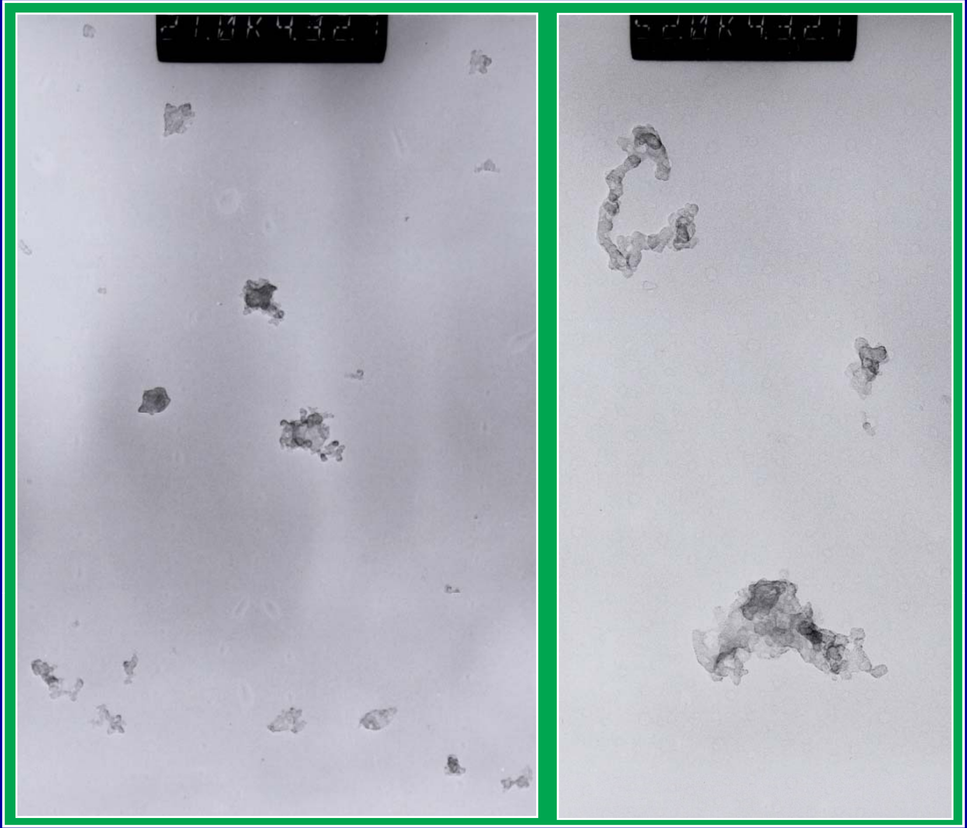
Particle sizes and shape change along the exhaust pipe





- PM size reduction:
  - $d_p \rightarrow 33\ \%$
  - $R_g \rightarrow 50\ \%$
- Particles became more spherical after passing the catalyst.
- Catalytic oxidation and aerodynamic interaction are dominant factors for the size reduction.

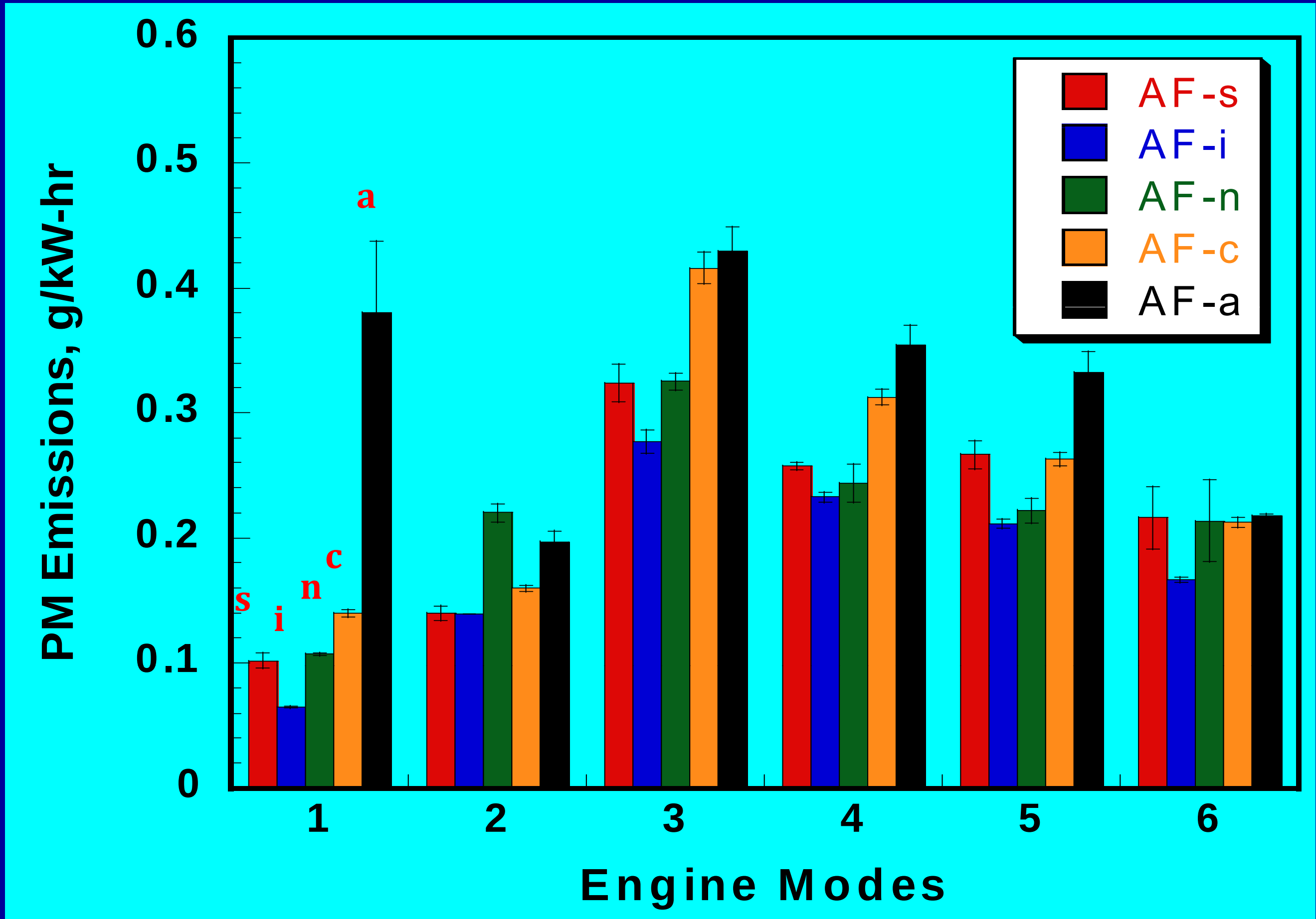
Microscopy revealed the catalytic reaction changed particle morphology as well as sizes



Particles sampled at P# 3

Particles sampled at P# 1

PM emissions are quite dependent on fuel property and engine operating conditions



RPM /Load

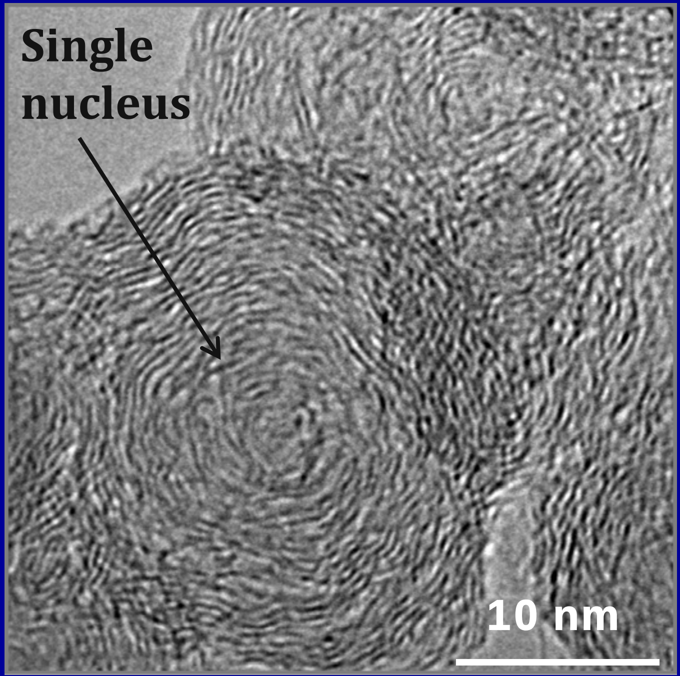
1. 1000 /25%
2. 1000 /50%
3. 1000 /75%
4. 2500 /25%
5. 2500 /50%
6. 2500 /75%

s: high sulfur (500 ppm)
i: low-s high iso-paraffin
n: low-s high n-paraffin
c: high cyclo-paraffin (naphthene)
a: high aromatic

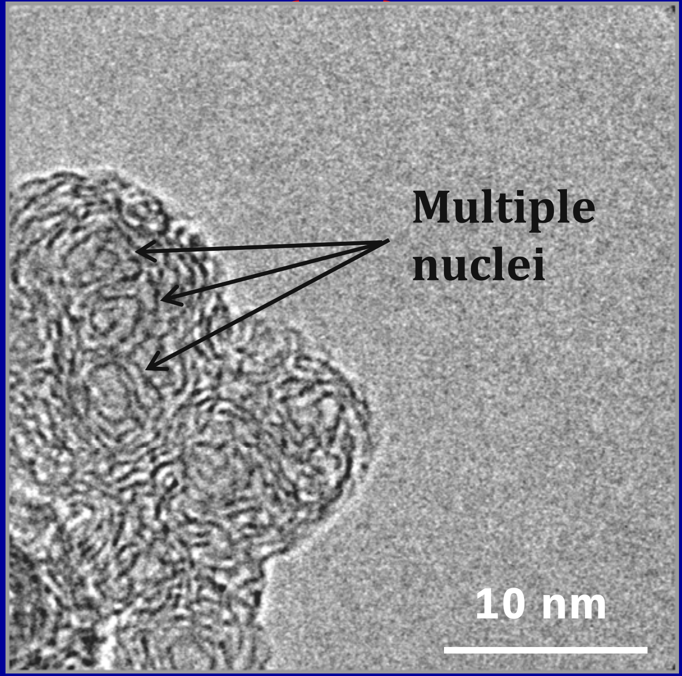
- At constant CN and volatility, both aromatics and naphthene contents increased PM emissions most significantly.

Fuel chemical properties alter particle nanostructures

Aromatic-enriched (AE)



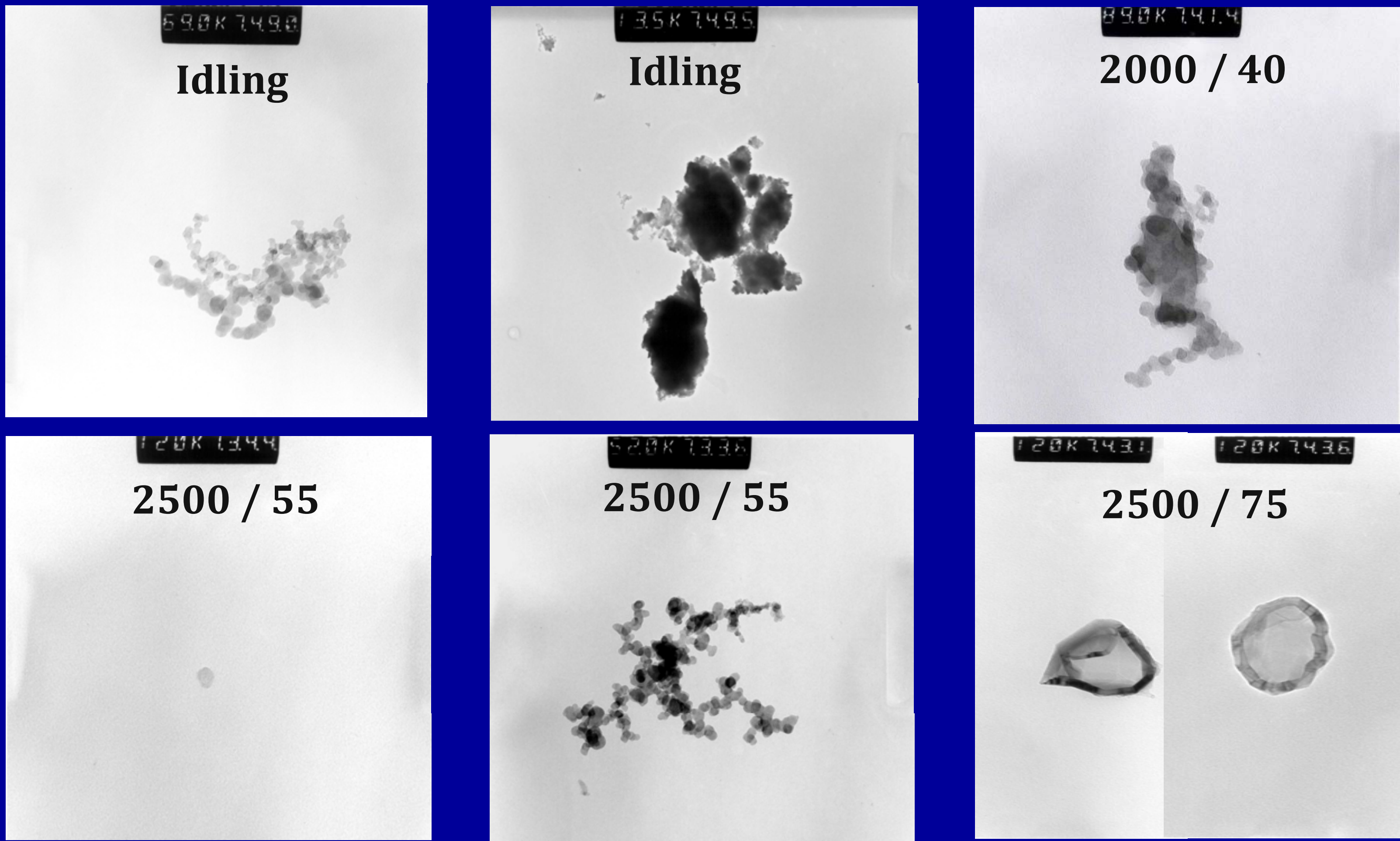
Iso-paraffin-enriched (IPE)



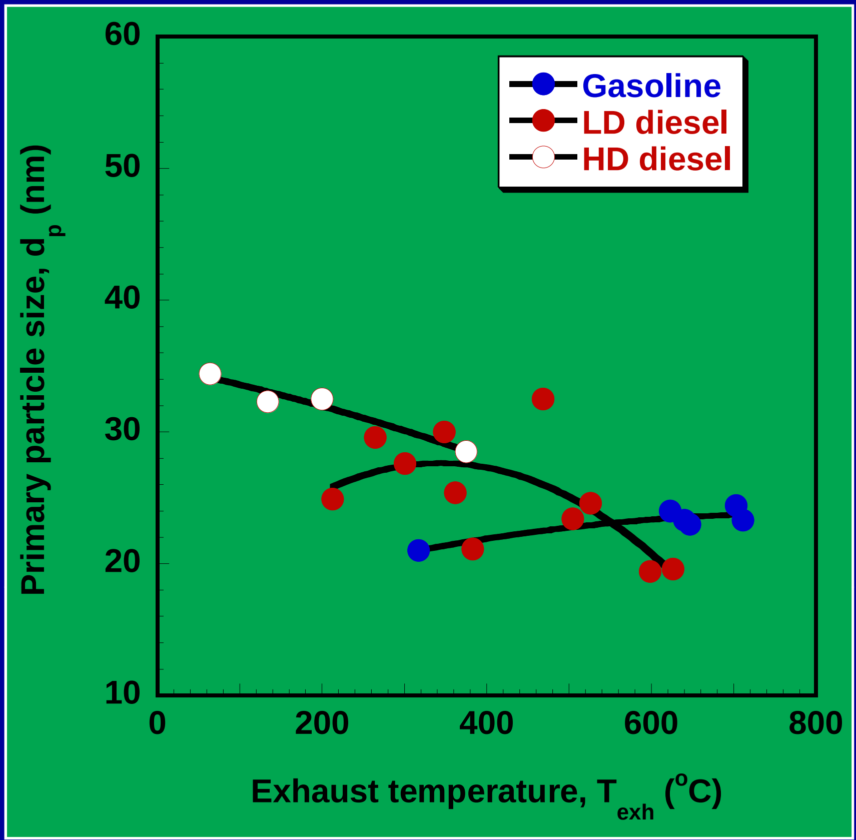
2500 rpm and 50% load

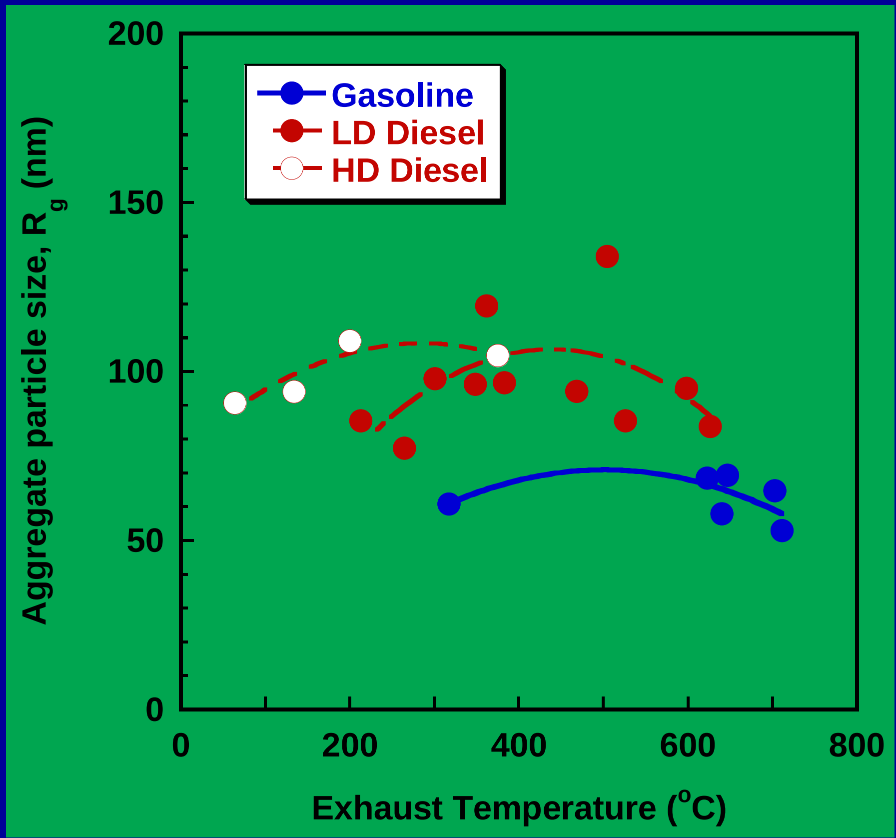
- AE soot indicated highly-ordered graphitic structures.
- IPE soot displayed a wiggly fringe pattern and wider interspacing distances.
  → possibly higher oxidation rate

Particulates from a lean-burn GDI engine showed more complex morphologies



GDI engine particles are much smaller than diesel particles





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