Morphology and Microstructures of Diesel Particulates

Kyeong Lee

Transportation Technology R&D Center
Argonne National Laboratory

May 17, 2005

This project has been supported by **Dr. Sidney Diamond** at the DOE Office of FreedomCAR and Vehicle Technologies

2005 CLEERS Conference

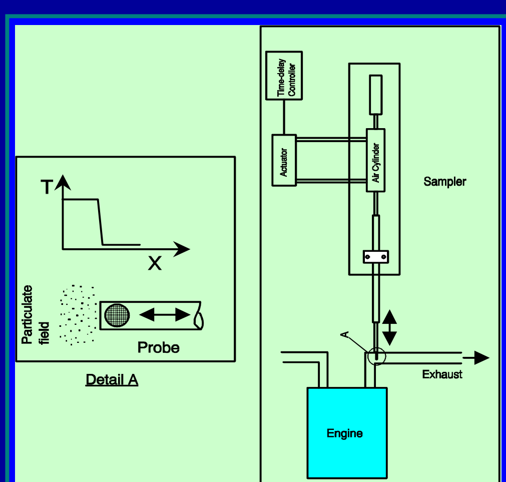
Overview

- Motivation
- Experimental Setup & Techniques
- Results
  - Effects of Engine Operating Conditions
  - Effects of Exhaust System Components
- Other data available in publication

Motivation of Morphological Investigation

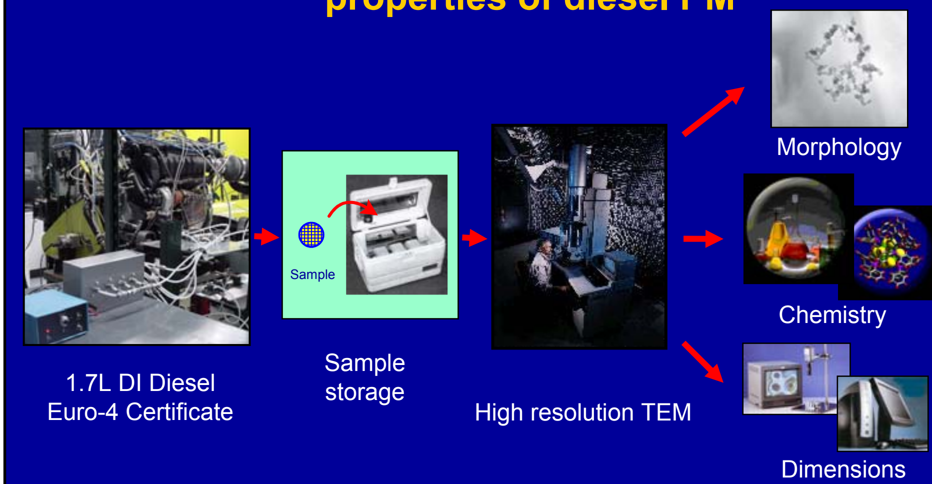
- Development of advanced aftertreatment systems is known to be a promising PM control technology.
- Detailed characterization of diesel PM properties is necessary.
- Conventional techniques of PM analysis do not tell the whole story.
  - Excess amount of diluting air
  - Equivalent diameters (Non-physical dimensions)
  - Incapable of analyzing detailed morphology and structures

Unique thermophoretic sampling system offers many advantages for engine research



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

Thermophoretic sampling and TEM analysis enable us to investigate important properties of diesel PM



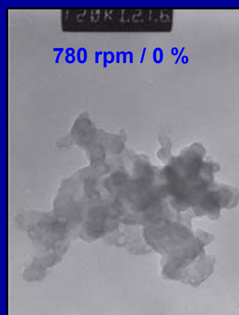
ARGONNE NATIONAL LABORATORY TRANSPORTATION TECHNOLOGY R&D CENTER

Effects of Engine Operating Conditions

ARGONNE NATIONAL LABORATORY TRANSPORTATION TECHNOLOGY R&D CENTER

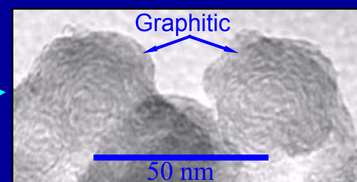
Particulate morphology is strongly affected by engine operating conditions

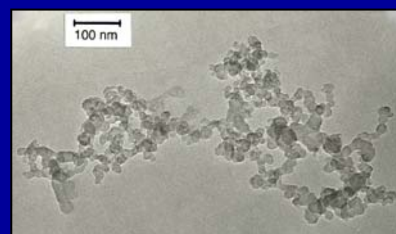
SAE 2003-01-3169



Nebulous
Amorphous

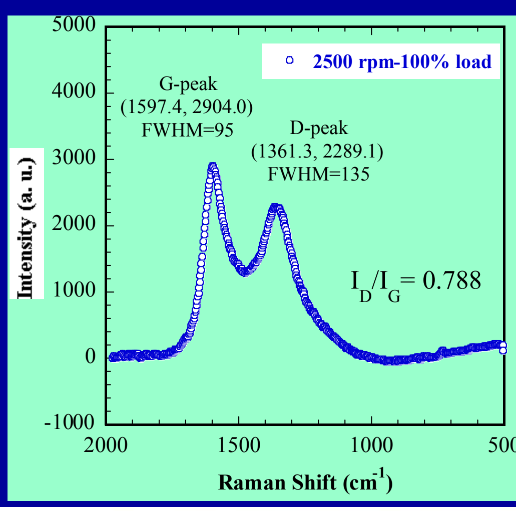
Distinct
Graphitic





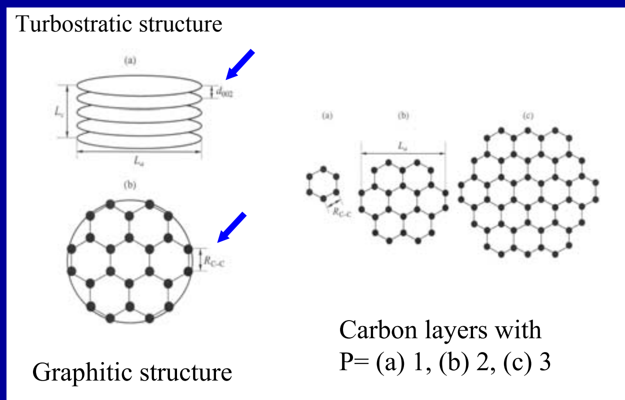
Oxidized Soot

Raman spectra reveal a degree of graphitic structure of diesel particulates



- $I_D / I_G = C \cdot 1 / L_a$ (C = 4.4 nm)
- Average crystal size (L_a): approximately 5.6 nm
- Disorder of crystal structure is proportional to $FWHM_D$.

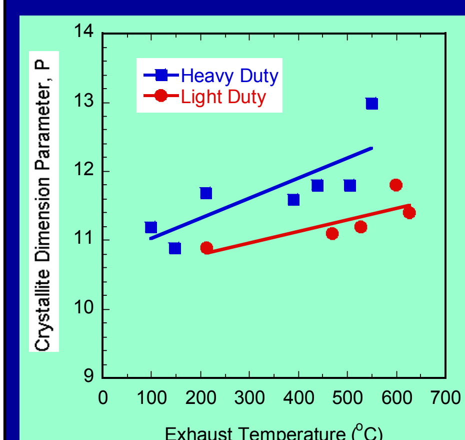
Further analysis with Raman data reveals atomic structures of diesel particulates

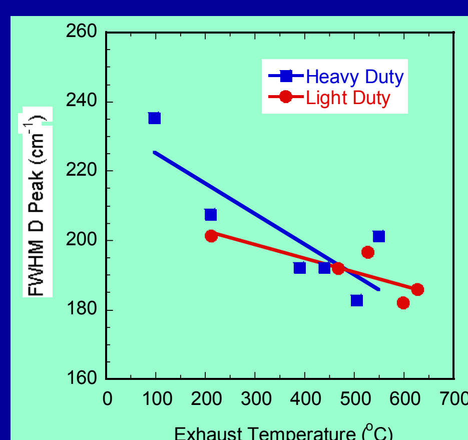


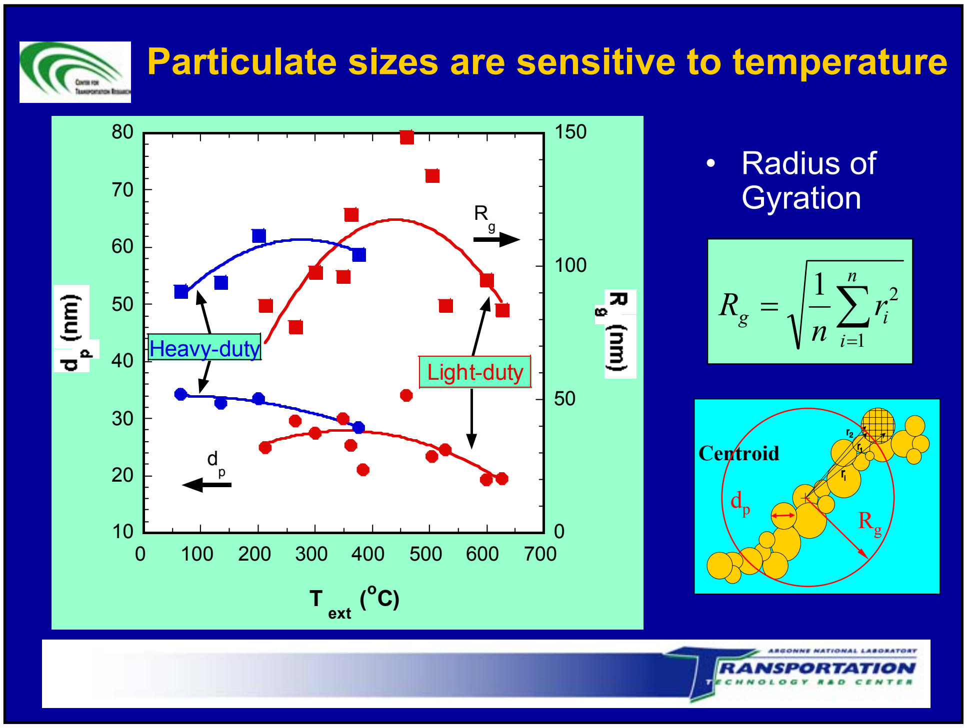
- L_a = 5.6 nm
- P = 12
- 864 carbon atoms per layer
- Interlayer distance:
  - $d_{002} \approx 0.34$ nm
  - $R_{c\text{-}c}$ = 0.141 nm

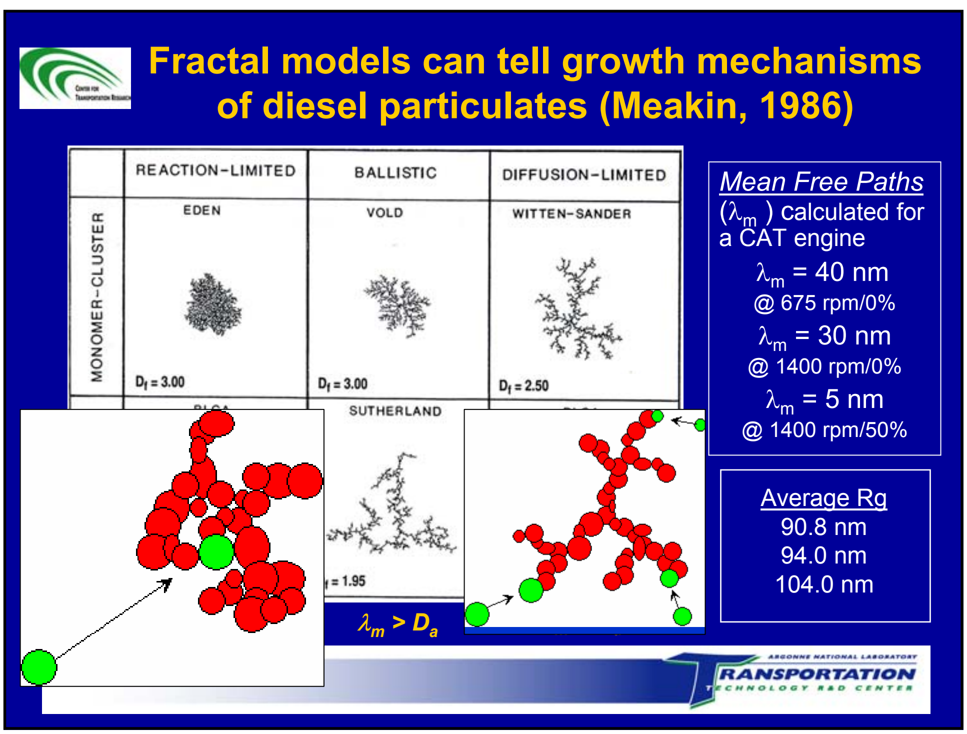
- Typical graphite
  - d_{002} = 0.3354
  - $R_{c\text{-}c}$ = 0.1422

Size and disorder of crystal structures are sensitive to temperature

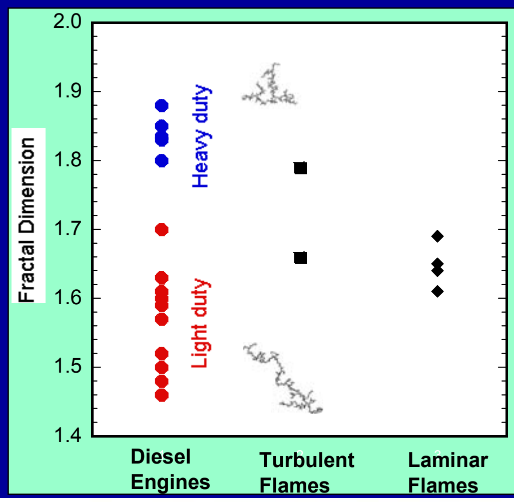





Particulate sizes are sensitive to temperature
80
70
60
50
40
30
20
10
d_p (nm)
150
100
50
0
R_g (nm)
0 100 200 300 400 500 600 700
T_ext (°C)
R_g
d_p
Heavy-duty
Light-duty
• Radius of Gyration
$R_g = \sqrt{\frac{1}{n}\sum_{i=1}^{n} r_i^2}$
Centroid
d_p
R_g
RANSPORTATION
TECHNOLOGY R&D CENTER
ARGONNE NATIONAL LABORATORY


Fractal models can tell growth mechanisms of diesel particulates (Meakin, 1986)
REACTION-LIMITED
BALLISTIC
DIFFUSION-LIMITED
MONOMER-CLUSTER
EDEN
VOLD
WITTEN-SANDER
D_f = 3.00
D_f = 3.00
D_f = 2.50
SUTHERLAND
= 1.95
λ_m > D_a
Mean Free Paths (λ_m) calculated for a CAT engine
λ_m = 40 nm
@ 675 rpm/0%
λ_m = 30 nm
@ 1400 rpm/0%
λ_m = 5 nm
@ 1400 rpm/50%
Average Rg
90.8 nm
94.0 nm
104.0 nm
RANSPORTATION
TECHNOLOGY R&D CENTER
ARGONNE NATIONAL LABORATORY

Light duty diesel engine produced more chain-like shape particulates

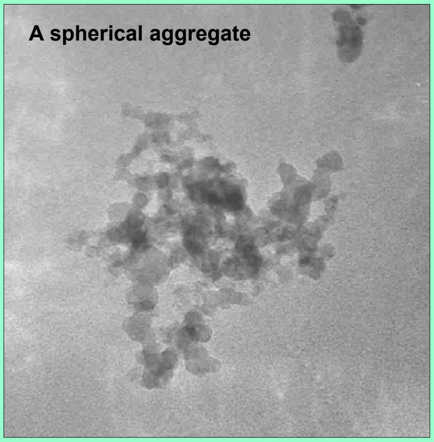


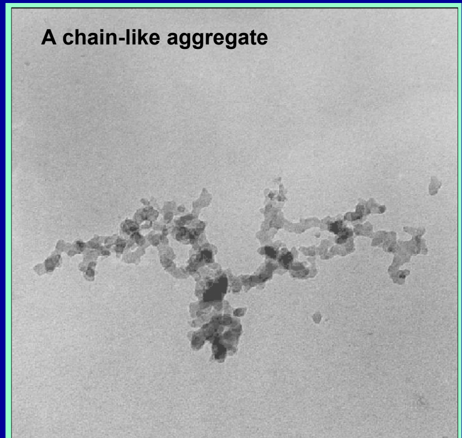
- Morphology of diesel particulates was standardized.
- Heavy-duty diesel PM → more compact
- Light-duty diesel PM → more chain-like shaped

Effects of engine speed was relatively less important for particle growth

- Engine speed-dependent experiment
  - Caterpillar 3401 HDD model – single-cylinder engine
    - Max. power of 75 HP @ 1800 rpm
    - Max. torque of 396 Nm @1400rpm
  - 900, 1400 and 1800 rpm
  - Constant exhaust temperature
  - Constant air-fuel ratio of ~65
- Results
  - d_p = 32.5 nm (σ =1.0 nm)
  - R_g = 109.1 nm (σ = 3.5 nm)
- Characteristic time available for particle agglomeration was relatively less important for particle growth. Combustion temperature was a more important parameter.

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


A spherical aggregate

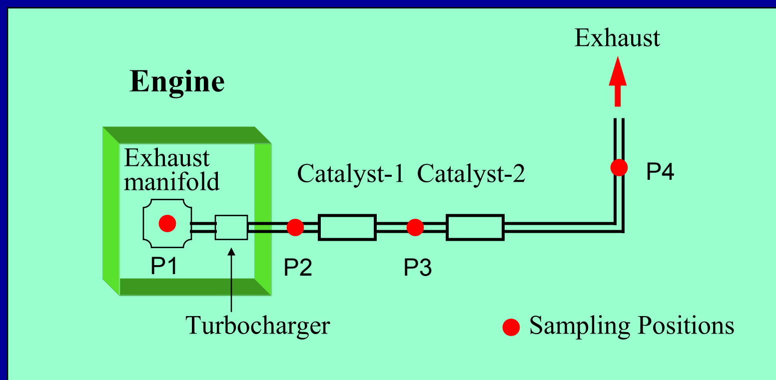

A chain-like aggregate

ARGONNE NATIONAL LABORATORY TRANSPORTATION TECHNOLOGY R&D CENTER

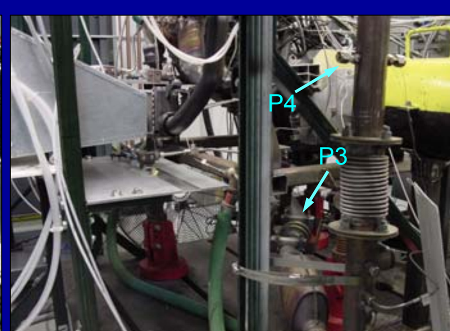
Effects of Exhaust Components

ARGONNE NATIONAL LABORATORY TRANSPORTATION TECHNOLOGY R&D CENTER

Simultaneous PM sampling along the exhaust pipe enables us to characterize the effects of exhaust components on soot properties



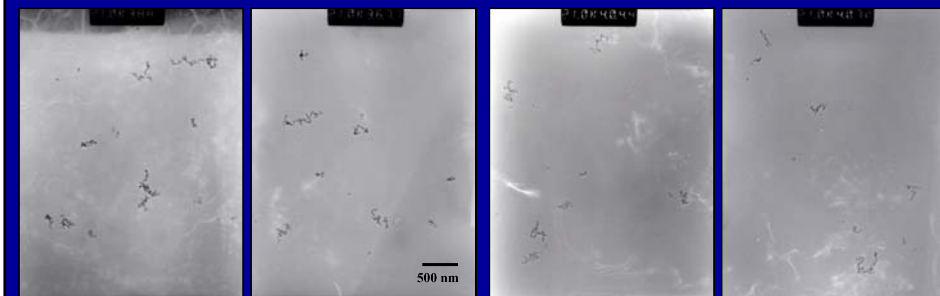
PM sampling system installed along the exhaust pipe



Turbocharged / Intercooled DI Diesel
1.7 L 4-cyl. / 66 kW @4200 rpm
Common-rail Injection / EGR

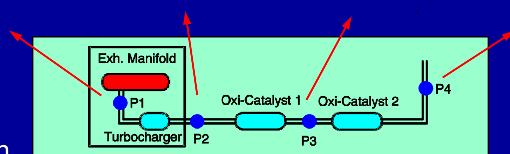
- No air dilution
- Non-subjective sampling
- Minimal influence to PM properties
- No extra treatment

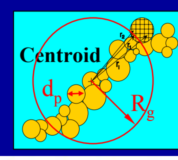
PM morphology changes along the exhaust pipe



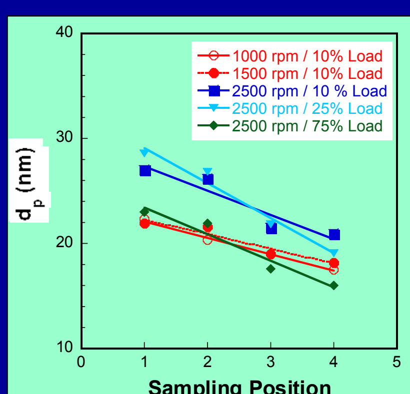
2500 rpm
25% load

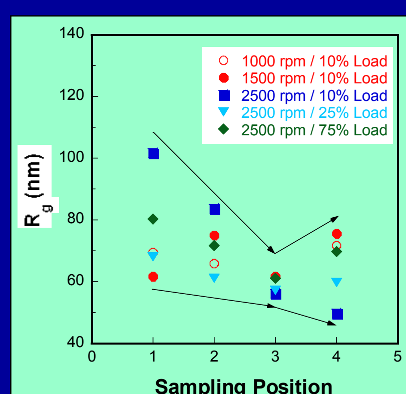
Particle size
& concentration





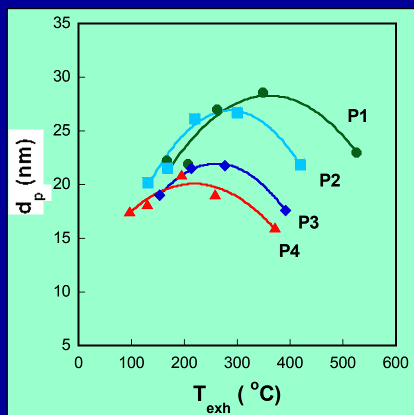
Sizes of both primary and aggregate particles significantly change along the exhaust pipe

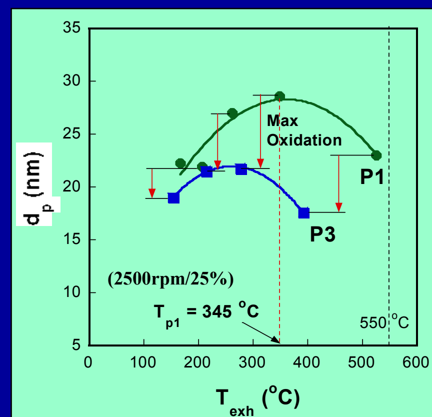




- d_p linearly decrease along the exhaust pipe.
- R_g were affected most significantly by the catalyst and tail pipe.

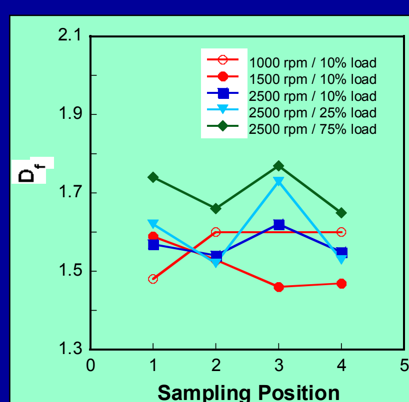
Maximum oxidation of primary particles occurred at a lower temperature than typically believed





ARGONNE NATIONAL LABORATORY TRANSPORTATION TECHNOLOGY R&D CENTER

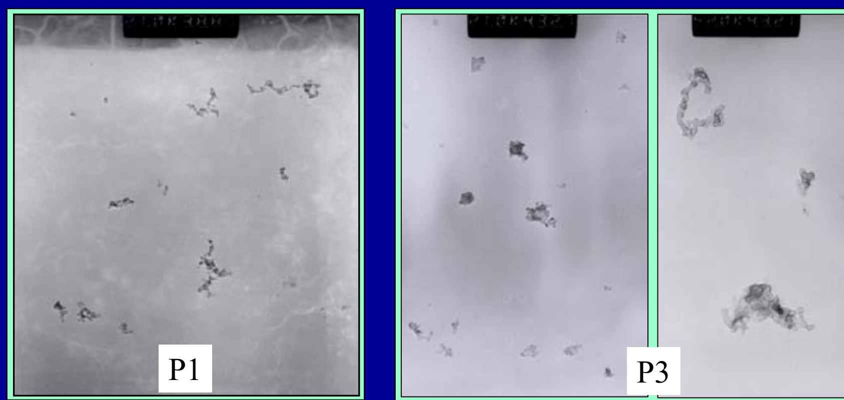
Particle geometry was also affected most by the oxidation catalyst



- Particles become more spherical after the 1st catalytic (P3), and then tend to be more stretched at the tail pipe that should be caused by aerodynamic interaction.

ARGONNE NATIONAL LABORATORY TRANSPORTATION TECHNOLOGY R&D CENTER

Morphological observation verified the significant change of fractal geometry



- Spherical shape of particles at P3 verified the increase of D_f.

Other data available since 2000

- Effects of EGR [SAE 2005-01-0195]
- Morphology and Geometry of Soot Particles generated from CAT's Diesel Simulating Combustor [SAE 2004-01-3044]
- Morphology and Microstructures of Diesel Particulates [29th and 30th (Int'l) Combustion Symposiums, 2002 & 2004]
- Morphology of Gasoline Engine Particulates [Unpublished yet]

ARGONNE NATIONAL LABORATORY
TRANSPORTATION
TECHNOLOGY R&D CENTER