Influence of Sampling Method and Ageing of Fractal Aggregates on their Morphological Parameters

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Context and aim of the study

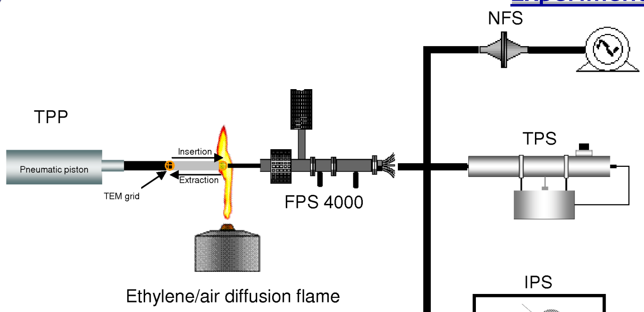
- Soot particles of hydrocarbons or organic matter are of strong interest in the fields of environmental science, fire science, air filtration and combustion science.

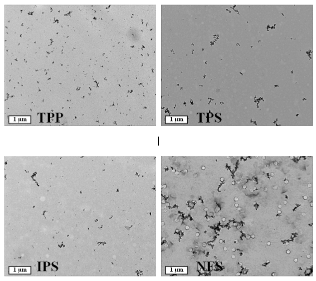
- The morphological analysis of such aggregates is generally based on Transmission Electron Microscopy (TEM) but few works deal with the influence of sampling and storage protocols on soot morphology prior to the TEM observation.

-The aim of this work was to compare the fractal characteristics D_f and k_f, the primary particle and gyration diameters D_{pp} and D_g and the overlap coefficient C_{ov} of carbon nanoparticles aggregates sampled by means of four commonly used techniques.

- The influence of the storage conditions on the soot morphology has been also investigated for more than 350 days.

Experimental facility and conditions





TEM micrographs of soot particles sampled using the different devices

- Diffusion flame of ethylene/air

- Thermophoretic Piston Probe (TPP) inserting TEM grids (Formvar/Carbon on 300 mesh Copper grids Agar Scientific S162) in flame.

- 3 others sampling devices implemented at the outlet of a dilution device (FPS4000):

  - Deposition by filtration on nuclepore membrane (0.2 µm) followed by a specific after-treatment (NFS).

  - Deposition on TEM grids using a Thermophoretic Particle Sampler (TPS).

  - Deposition by inserting TEM grids perpendicular to the aerosol flow (IPS).

- Storage away from light in a low humidity/nitrogen filled cell and in ambient air.

- Morphological analysis at different storage duration with a JEOL 100CXII 100 kV and according to Köylü et al. (1995) and Brasil et al. (1999):

  * Primary particle D_{pp}, gyration D_g diameters and number of monomers N_{pp}:

$$R_{g2D} = \sqrt{\frac{1}{Nb_{pixel}} \sum (x - x_B)^2 + (y - y_B)^2} \qquad N_{pp} = k_a \cdot \left(\frac{S_{ag}}{S_{pp}}\right)^{\alpha}$$

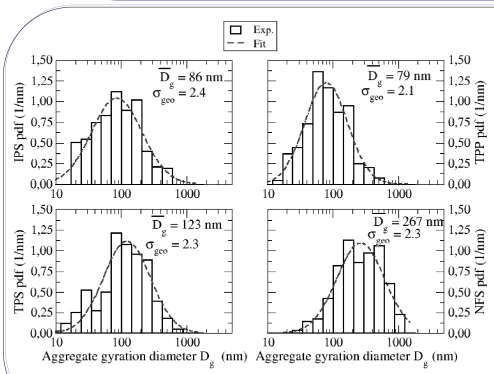
  * Fractal dimension D_f and fractal prefactor k_f:

$$N_{pp} = k_f \cdot \left(\frac{D_g}{D_{pp}}\right)^{D_f}$$

  * Overlapping coefficient C_{ov}:

$$C_{ov,P} = \frac{\overline{D_{pp} - d_{ij}}}{D_{pp}} \qquad C_{ov} = \varsigma_1 . \overline{C_{ov,P}} - \varsigma_2$$

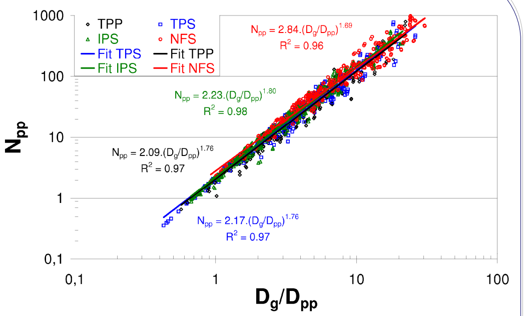
Influence of sampling method



Probability density functions in terms of gyration diameter

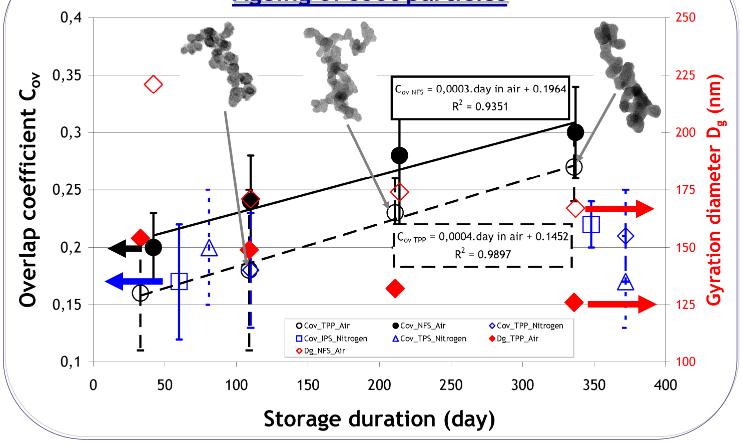
Morphological parameters as a function of sampling methods

Sampling method	$\overline{D_{pp}}$ (nm)	C_{ov}	D_f	k_f	D_g (nm, σ_g)
TPP	24.4 (5.2)	0.18 (0.05)	1.76	2.09	79 (2.1)
TPS	26.9 (5.9)	0.20 (0.04)	1.76	2.17	123 (2.3)
IPS	26.8 (5.8)	0.17 (0.05)	1.80	2.23	86 (2.4)
NFS	37.1 (6.6)	0.23 (0.03)	1.69	2.84	267 (2.3)



Fractal relationships obtained for the different sampling methods

Ageing of soot particles



Conclusions

- Good agreement on D_{pp}, D_f and k_f between TPP, TPS, IPS and literature values.

- Significant discrepancy for D_g between TPP, TPS, IPS and NFS.

- After-treatment induced for NFS sampling overestimates D_{pp}, D_g and C_{ov}.

- Ageing of soot particles in ambient conditions occurs and significantly modified the morphology of soot particles:

  * C_{ov} and D_g respectively increases and decreases with storage duration.

  * While k_f and D_{pp} slightly evolve, D_f seems to be independent of the storage conditions.

- Storage of samples in a low humidity and nitrogen filled chamber significantly mitigated the ageing of soot particles.

- Further investigations will be carried out to describe the soot microstructure and chemical composition evolutions during the ambient ageing of soot.

Reference:

Brasil A.M., Farias T. L., and Carvalho M.G. (1999). A recipe for image characterization of fractal-like aggregates. *Journal of Aerosol Science*. 30: 1379-1389.

Köylü Ü.Ö., Faeth G.M., Farias T.L. and Carvalho M.G. (1995). Fractal and projected structure properties of soot aggregates. *Combustion and Flame*. 100: 621-633.

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