MODELING OF DIESEL PARTICULATE SIZE DISTRIBUTIONS WITH OXIDATIVE FRAGMENTATION AND COAGULATION

Margaritis Kostoglou and Athanasios G. Konstandopoulos

Aerosol & Particle Technology Laboratory

CERTH/CPERI, P.O. Box 361, Thermi Thessaloniki 57 001, Greece

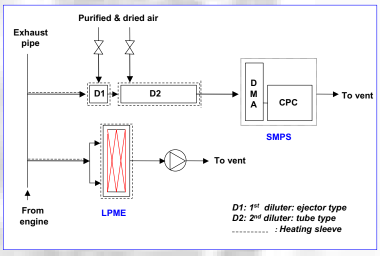
Phone: +30 2310 498192 Fax: +30 2310 498190 E-mail: agk@cperi.certh.gr http://apt.cperi.certh.gr

MOTIVATION

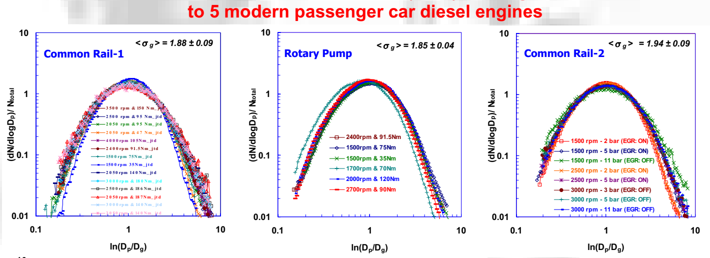
Recently, it has been shown (Harris and Maricq, 2002) that soot particle size distributions from various types of diesel engines, running on different fuels under a wide range of operating conditions, can be approximated by a "signature distribution" when the number-based particle size distribution (PSD) is normalized with respect to the total particle number concentration and the particle size is scaled with respect to the mean particle size. Harris and Maricq (2002) have also shown that the shape of the measured "signature" PSD is close to that predicted by the steady-state solution of the aggregation-fragmentation equation with Brownian coagulation in the continuum regime. The fractal dimension of soot aggregates was assumed to be D_f = 2 and a binary fragmentation of the soot aggregates into equal-sized fragments was assumed with a rate proportional to the size of the aggregate raised to the exponent $1/D_f$. To reach this conclusion 15000 size classes were employed to solve the population balance equation. The purpose of the present work is to study the problem incorporating a more-physically motivated fragmentation mechanism and accounting for the relative magnitude between aggregation and fragmentation (or equivalently for the extent of coagulation as given by the measured number of primary particles in the aggregates). In addition, a theoretical analysis in the large aggregate (continuum) limit is performed that obtains analytically the shape of the steady-state distribution.

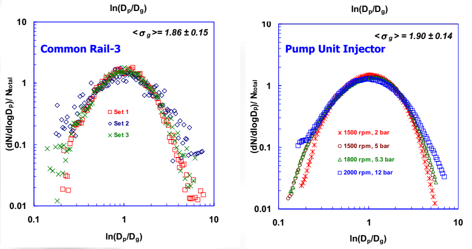
EXPERIMENTAL

Soot aggregate size distributions have been measured in the exhaust of modern turbo-charged direct injection diesel engines, employing a Scanning Mobility Particle Sizer (SMPS) and a Long Path Multiwavelength Extinction (LPME) analyser as described in Nikitidis et al. (2001). The experimental set-up is shown below. The resulting size distributions have been plotted in the coordinates suggested by Harris and Maricq (2002).



Application of Harris and Maricq (2002) plotting method to 5 modern passenger car diesel engines

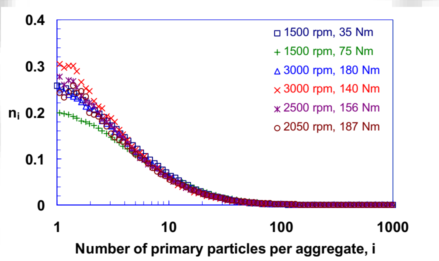




Fuel Injection System	s_g	STD
Common Rail-1	1.88	± 0.09
Common Rail-2	1.94	± 0.09
Common Rail-3	1.86	± 0.15
Pump Unit Injector	1.90	± 0.14
Rotary Pump	1.85	± 0.04
Average	**1.89**	**± 0.08**

TRANSFORMATION OF DISTRIBUTIONS

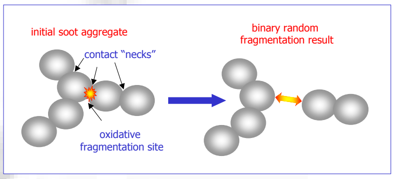
To make a clear connection to the extent of coagulation, the particle size metric employed in the present work is the number of primary particles per aggregate, *i*. This is determined from the aggregate mobility diameter using an average primary particle diameter of 32 nm, as determined from independent soot cake permeability measurements and a soot aggregate fractal dimension of 2.4 (Park et al., 2003). The method has been described in Nikitidis et al (2001). Some of the transformed distributions are shown below. These transformed distributions deviate from a universal shape especially for smaller aggregate sizes in the range below 100 nm (consisting of about 30 primary particles and less). Notably carbonaceous aggregates (predominantly from diesel combustion sources) found in the atmosphere typically contain less than about 250 primary particles (Xiong and Friedlander, 2001).



REFERENCES

- Harris, S. J. & Maricq, M. M. (2002). The Role of Fragmentation in Defining the Signature Size Distribution of Diesel Soot. *J. Aerosol Science*, 33, 935–942.
- Nikitidis, M. S., Konstandopoulos, A. G., Zahoransky, R. A. & Laile, E. (2001). Correlation of Measurements of a New Long Optical Path Length Particle Sensor against Gravimetric and Electrical Mobility based Particle Measurements in Diesel Exhaust, *SAE_NA Tech Paper 2001-01-073*, in 5th *Int. Conf. On Internal Combustion Engines*, Capri (Istituto Motori, Naples).
- Park, K., Cao, F., Kittelson, D. B. & McMurry, P. H. (2003). Relationship Between Particle Mass and Mobility for Diesel Exhaust Particles, *Environmental Science and Technology*, 37, 577-583.
- Xiong, C. & Friedlander, S. K. (2001). Morphological Properties of Atmospheric Aerosol Aggregates, *PNAS*, 98(21), 11851-11856.

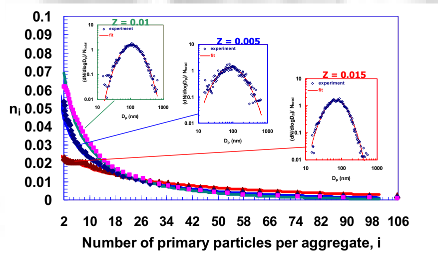
MATHEMATICAL MODEL



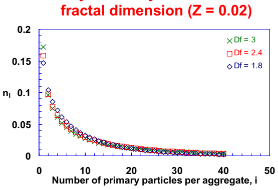
Fragmentation of the soot aggregates is assumed to occur due to the surface oxidation of the small solid contacts responsible for holding the primary particles together in the aggregate. As the contact "necks" are much smaller than the primary particle size, fragmentation can occur before significant reduction of the primary particle size takes place. The neck sizes (i.e. the contact areas) are assumed to follow a uniform size distribution and to be spatially distributed randomly over the aggregate. Consequently the necks are disappearing continuously, potentially creating at each instant two random-sized fragments. In other words the physically based neck oxidation mechanism leads to a continuous, binary random fragmentation process. The number of bonds (necks) in the aggregate increases with the size of the aggregate but as the aggregate becomes more open (i.e. with a smaller fractal dimension) the possibility of oxidation of an interparticle bond to lead into the fragmentation of the aggregate increases. This behaviour can be conveniently represented by a fragmentation rate proportional to the number of primary particles with a fragmentation exponent b = $1/D_f$ as used by Harris and Maricq (2002). The evolution of the concentration of the aggregates undergoing simultaneously aggregation and break-up is given in dimensionless form by (1):

$$\frac{d\overline{n}_i}{d\tau}=\frac{1}{2}\sum_{j=1}^{i-1}[j^{-1/D_f}+(i-j)^{-1/D_f}][j^{1/D_f}+(i-j)^{1/D_f}]\overline{n}_j\overline{n}_{i-j}-\overline{n}_i\sum_{j=1}^{\infty}(j^{-1/D_f}+i^{-1/D_f})(j^{1/D_f}+i^{1/D_f})\overline{n}_j+Z\sum_{j=i+1}^{\infty}\frac{2j^{1/D_f}}{j-1}\overline{n}_j-Zi^{1/D_f}\overline{n}_i(1-\delta_{i,1}) \quad (1)$$

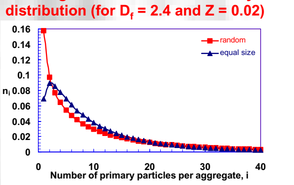
where $d_{i,j}$ is Kronecker's delta, $\overline{n}_i=n_i/N_o$, n_i is the concentration of aggregates consisting of *i* primary particles (i-mers), N_o is the total concentration of primary particles, $\tau=B_oN_ot$, *t* is time, $B_{i,j}=B_o(i^{-1/D_f}+j^{-1/D_f})(i^{1/D_f}+j^{1/D_f})$ is the coagulation rate between the i-mers and j-mers for Brownian coagulation of fractal aggregates in the continuum regime, with $B_o=4k_BT/3\mu$, k_B, T and μ are Boltzmann's constant, the temperature and the gas viscosity respectively. S_i is the fragmentation frequency of an i-mer, $S_i=Ai^b=Ai^{1/D_f}$, $C_{i,j}=2/(j-1)$, the fragmentation kernel for binary random fragmentation and the parameter $Z=A/B_oN_o$. The system of equations (1) is truncated at a large enough value of *i* and is integrated numerically until a steady state is reached which is independent from the initial condition. Obviously, the steady state size distribution is determined by just one parameter (i.e. *Z*). Three size distributions of aggregates in terms of $\overline{n}_i$ based on experimental measurements at three steady state engine operating points: (1500 rpm, 75 Nm), (1500 rpm, 30 Nm), and (2400 rpm, 91 Nm) and the theoretical size distribution for Z=0.0015, 0.005 and 0.01 respectively, are shown below.



Sensitivity of steady-state distribution to fractal dimension (Z = 0.02)



Effect of fragmentation mode on steady-state distribution (for D_f = 2.4 and Z = 0.02)



LARGE AGGREGATE (CONTINUUM) LIMIT

If the steady-state size distribution is such that its characteristic aggregate size is much larger than the primary particle (monomer) size or equivalently it contains a small number of oligomers, a continuous population balance can be applied. This limit corresponds to the numerical solutions with 15000 size classes obtained by Harris and Maricq (2002). It can be shown that invoking a lognormal assumption it is possible to obtain analytically the geometric standard deviation, of the size distribution as:

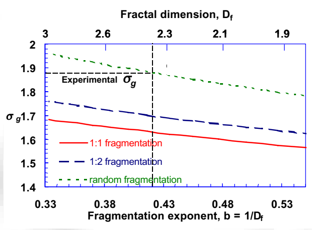
$$2\ln\sigma_g=\frac{1}{1+b}\ln\left(\frac{2(\nu-1)}{1-J_2}\right)$$

where ν is the number of fragments resulting from the fragmentation and J_2 is the second moment of the homogeneous fragmentation kernel. For random binary fragmentation J_2 = 2/3 and ν = 2 leading to the simple result: $\ln\sigma_g=\ln(6)/2(1+b)$. In this limit a number of results is now rigorously proven:

- the non-dependence of the distribution on *Z* supporting the numerical observations of Harris and Maricq (2002).
- the insensitivity of the distribution on the coagulation kernel in the continuum regime.
- the small sensitivity of the distribution on the fragmentation exponent.

The figure on the right shows the dependence of σ_g for different fragmentation modes on the fragmentation exponent *b*.

σ_g dependence in the continuum limit on b



CONCLUSIONS

Employing a physically motivated oxidative fragmentation mechanism and the laws of fractal aggregate coagulation it is possible to parameterise the shape of the size distribution of diesel soot particles in terms of the dimensionless number *Z*, which expresses the relative magnitude of fragmentation and coagulation processes. In the continuous (large aggregate) limit the shape of the size distribution does not depend on *Z* but only on the fragmentation exponent, *b* and it is obtained analytically, substantiating observations based on recent computationally intensive numerical simulations. The analytic results in this limit support the choice of the random binary fragmentation mechanism since it is the only mechanism that gives values consistent with the experimental value of 1.89 and this occurs for a *b* = 0.42 or equivalently D_f = 2.4.