Accurate Evaluation of Particulate Mass Based on Morphological Analysis

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Objective

The objective of this work is to develop a calibration methodology that can accurately evaluate the mass of particulate emissions corresponding to particle number measurements and propose a gold standard that can directly be applied to future PM emission regulations.

Background and Motivation

As emissions standards have been reinforced, engine manufacturers have dramatically improved the emissions performance of modern transportation diesel engines by using various combustion and emissions control technologies. The use of advanced after-treatment systems, such as the diesel particulate filter (DPF), has substantially reduced tail-pipe particulate matter (PM) emissions to a significantly lower level, one that meets upcoming emissions standards. To comply with more stringent future emissions standards, diesel manufactures will strive to develop even more advanced emission control technologies, and concurrently emissions regulatory agencies will need to provide a proactive agenda, including emissions evaluation protocol and methodology. Because diesel PM mass emissions typically contain detrimental chemicals — such as organics or polycyclic aromatic hydrocarbons (PAHs) — they have a major impact on health, and consequently diesel PM emissions need to continue to be regulated in terms of mass. However, regulating PM emissions from future advanced diesel engines in “mass” is quite a challenge, because they, in successful application of advanced DPF systems, emit PM mass emissions near the barely measurable limit of high-fidelity instruments (an order of a few mg per kWh). Therefore, a new methodology that can accurately evaluate PM mass emissions needs to be developed.

Meanwhile, upcoming Euro-VI PM emissions regulations include standards for particulate number (PN) emissions, which are known to be 6×10^{11} particles per kWh for heavy-duty diesel vehicles. This PN standard is associated only with solid carbon particles larger than or equal to 23 nanometers. A noticeable result from recent PN measurements is that the number of particles from diesel tailpipes varies in a quite broad range as a function of engine operating conditions, which implies that the PN evaluation methodology is capable of resolving particulate emission levels to those of existing and future diesel vehicles. Therefore, converting the PN measurement to corresponding PM mass is proposed to be an effective methodology for the PM mass evaluation of such low-emission diesel vehicles.

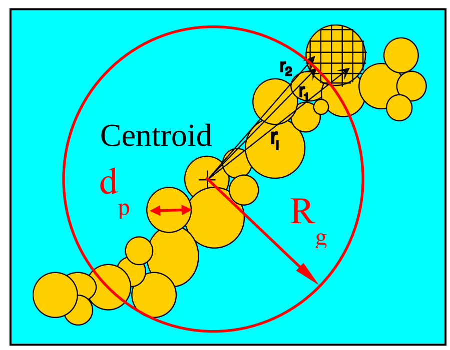
Some manufacturers have developed instruments for measuring PM mass, such as an aerosol particle mass analyzer or a centrifugal particle mass analyzer. However, none of these instruments can accurately resolve effects from the complex fractal geometry of diesel particulates, such as different levels of aerodynamic friction or electric charges. Excess air dilution is another problematic parameter that alters particle mass and geometry. The aerodynamic motion of particles in a long sampling line with excess dilution air creates artificial agglomerations or segregations, which eventually alter the mass measurement. Accuracy in measuring electric charges is also another problem in evaluating the mass of such small nanoparticles in these instruments.

In this proposal, the PI proposes a new approach to evaluate the mass of diesel particulates, essentially based on morphological analysis, which has been investigated first at Argonne National Laboratory for an extended period. Key analyses include size measurement, fractal analysis, and theoretical calculation for the high-magnification TEM images of actual diesel particulates. Results will be evaluated on the basis of statistical analysis and used to evaluate the volume of individual aggregate particles. The mass of an individual particle can be calculated by multiplying the volume and the soot density (the soot density will be evaluated by the research team in CARB). For the evaluation of total mass, the number of particles will be measured by using scanning mobility particle sizer (SMPS). In this project, the PI will first validate the proposed calibration methodology that can evaluate total PM mass based on PN measurements. Then, the methodology will further be validated for a few different engine models as well as various engine operating conditions. Ultimately, the PI intends to provide a gold standard that can replace the current methodology of PM mass measurements for diesel vehicles.

Technical Approach and Milestones

As described above, the total mass of PM emissions can be calculated by multiplying the total volume and density. The evaluation of volume of individual particle relies on measurement of particle size. Although the particle size, such as mobility diameter or aerodynamic diameter, can be measured by commercial instruments, it is not a physical dimension accounting for actual particle geometry. Consequently, the particle volume based on the diameters from commercial instruments will differ from the actual particle volume. In this proposal, therefore, the working team will statistically evaluate the volume of individual aggregate particle by morphological analysis, which will use microscopic images taken by a high-resolution TEM. The total volume of particulate emissions will then be evaluated by the product of the individual particle volume and the total number of particles. The total number of particles will be measured by SMPS, as described below.

For morphological analysis, particles will be collected on a TEM grid from the emissions stream of each channel of a differential mobility analyzer (DMA), which is associated with a low pressure impactor (LPI). DMA is a commercial instrument that classifies particles in specific size ranges at each channel, which enables us to measure the total number of particles at each channel, using a condensation particle counter (CPC). The particle sampling will take place at the exit of each channel. Then, the particle images taken by a TEM will be analyzed to evaluate the primary particle size (d_p), aggregate particle size (R_g), and number of primary particles per aggregate (n), using a digital image processing/data acquisition system developed at Argonne. The definitions of these parameters are as follows.



Schematic of an aggregate particle

The near-spherical primary particle diameter, d_p, will directly be measured from the TEM image. The radius of gyration of each aggregate, which takes into account the shape factor of aggregate, is defined as

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

where r_i is the distance from the centroid of an aggregate to the center of an individual primary particle, and n is the number of primary particles consisting of the aggregate particle. R_g is calculated from the pixel information of digitalized binary images by the image processing software.

The number of primary particles per aggregate (n_{2D}) is determined on the two-dimensional plane of TEM image by the equation:

$$n_{2D} = \left(\frac{A_a}{A_p}\right)^{1.09} \qquad (2)$$

where A_a and A_p are the projected areas of aggregate and primary particle, respectively, which will be measured from the TEM images by the software. A correlation between the n_{2D} and DMA-measured particle sizes will be found. This correlation will be found for different engine operating conditions to obtain an engine operating conditions-independent value. Using the d_p and n_{2D}, the volume of aggregate particles sampled at a specified DMA channel, which lie in a specific size range, can be calculated.

$$V_i = n_{2D,i} \cdot \frac{\pi}{6} d_p^3 \quad (3)$$

The volumes of aggregate particles at other DMA channels will be evaluated in the same manner.

To evaluate the total volume of aggregate particles collected in a specific sampling time, we need to evaluate the total number of particles by finding a correlation between the DMA data, which inform the number of particle from each sampling channel (N_i) in association of SMPS, and the morphological data ($n_{2D,i}$ *or* V_i). Once the correlation is found, the total volume of particles can be calculated for a specific sampling time:

$$V_{total,2D} = \sum_{i=1}^{n} V_i \cdot N_i \quad (4)$$

Since the primary particle number density (n_{2D}) is obtained by the two-dimensional fractal theory, it needs to be corrected to three-dimensional, which now enables us to evaluate the number of primaries per aggregate in a three-dimensional space:

$$n_{3D} = k_a \cdot n_{2D} \quad (5)$$

where k_a is a correction factor experimentally determined in a range of 1.0 to 1.81. This correction factor can be evaluated in comparison of the particle mass calculated by the 2-D fractal theory and the actual mass measured by a gravimetric soot sampling technique. Finally, the total volume of particulates can be calculated with the 3-D correction as,

$$V_{total} = k_a \cdot V_{total,2D} \quad (6)$$

In the meantime, typical commercial instruments provide size information in terms of particle electric charge- or volume-equivalent diameters, which will apparently differ from the actual physical size. As an additional effort, therefore, it is valuable to find correlations between the mobility diameters measured by SMPS and the physical diameters (radii of gyration) measured by the image processing with TEM images.

$$R_g = k_s \cdot d_M \quad (7)$$

where d_M is a mobility diameter measured by SMPS at a DMA channel and k_s is a correlation factor.

Milestones

1st year:

- Purchase and set up instruments, such as DMA, dilution system, SMPS, TEM sampling system, with a selected heavy-duty diesel engine (single-cylinder version of CAT 3406).
- Evaluate d_p, R_g, n from TEM samples and perform SMPS measurements at different DMA channels in the entire mobility diameter range of CPC (10 – 1000 nm).
- Evaluate the total particle volume to predict particle mass at a specific engine condition.
- Find the 3-D correlation factor, k_a, and the correction factor (k_s) from the correlation between SMPS data and morphology data.
- Find PM mass corresponding to each PN measurement at a specific engine condition.

2nd year:

- Repeat the analyses done for the first year at different engine operating conditions to validate the engine operating conditions-independent correlation between n_{2D} and particle size.
- Evaluate the factors, k_a and k_s, for different engine operating conditions to obtain engine condition-independent values.
- Find PM mass corresponding to each PN measurement at various engine conditions.

- Validate the mass evaluation for the PN data obtained at transient vehicle operation cycles (set a gold standard calibration).

3rd year:
- Repeat the same analyses as above with a different diesel engine model (6-cylinder stock diesel engine) to validate the data.
- Validate the mass evaluation for the PN data obtained at transient vehicle operation cycles.