Detailed Examination of Physicochemical Properties of Diesel Nanoparticles Undiscovered in the European PMP Protocol

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Objectives

The objectives of this work focus on characterizing the chemistry of diesel particulates, unrevealed properties of diesel nanoparticles, and the effects of Particulate Measurement Programme (PMP) operating parameters on particle chemistry and morphology, and finally providing database that CARB can use as the basis for regulating future PM emissions standards with confidence.

Background and Motivation

Upcoming Euro-VI emissions regulations have reinforced standards for particulate number (PN) emissions as well as mass emissions from diesel vehicles. To evaluate these particulate emissions under a consistent test condition, the European Union has developed the PMP, which requires the use of specific measurement processes and several pieces of key equipment. For instance, parameters to be set include specific temperature of dilution air and sample emissions, and key systems include those for multiple-stage dilution, emissions heating, and removal of organic compounds. Such a complex test protocol is based primarily on requirement that volatile organic fractions (VOFs) be removed, because otherwise they make the PN measurements highly uncertain. VOFs are often detected not only in engine-out emissions, but also during sampling processes. In principle, volatile organics are very unstable in phase, and so that they can readily be condensed to form independent aerosols or absorbed in the particulate matter (PM). These unstable behaviors indeed increase measurement uncertainty for both PN and PM mass. While the PMP protocol quite focuses on PN measurement, many important properties of diesel particulates cannot be analyzed or are overlooked due to the nature of the PMP protocol.

First, one of the most important components of diesel particulates to be monitored is the chemicals in PM. Diesel PM is known to be toxic, often referred to as carcinogenic, but only when it contains organics —particularly acids and polycyclic aromatic hydrocarbons (PAHs) [International Programme on Chemical Safety–EHC171, World Health Organization, Geneva, 1996]. However, the PMP method does not enable a suitable way to measure volatile organics from engine exhaust emissions, as described above. Because an ultimate objective of regulating vehicle emissions is to protect the environment and human life, the chemicals of PM emissions from transportation systems need to be closely monitored, regardless of the measurement methodology.

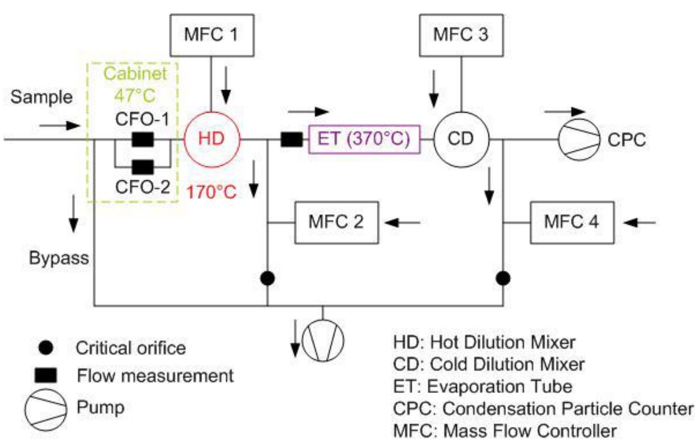
Second, PN standards, based on the PMP protocol, set a limit of 6×10^{11} particles per kWh for heavy-duty diesel vehicles, but only for the solid carbon particles that are equal to or larger than 23 nanometers. Therefore, the importance of nanoparticles smaller than 23 nanometers is overlooked. Indeed, smaller particles increase surface area, which gives harmful chemicals a better chance to be adsorbed onto particle surfaces. In addition, medical scientists have asserted that these small nanoparticles have strong potential to readily pass through the human bronchial system, penetrate pulmonary arteries or veins, and eventually reach the brain. In recent studies, we discovered that modern engines tend to apparently produce higher numbers of such small nanoparticles. Therefore, the pathway and mechanisms of formation and destruction of these nanoparticles must be investigated with accurate analysis of detailed properties.

Third, the PMP method requires that specific parameters for PM sampling be controlled accurately, such as the temperatures of diluting air and air-emissions mixtures, the dilution ratio, the flow rate, and the sample residence time. However, the effects of these parameters on PM measurements (both mass and number) have not been examined comprehensively. In addition, the setting values of these parameters in the PMP protocol — some of which depend on engine size and engine operating mode — have not explicitly been illustrated. Indeed, particle size, morphology, and chemistry can change, depending on dilution ratio and residence time.

In this proposed project, the working team will in detail examine the physicochemical properties of diesel particulates that are usually neglected in PM evaluation by using the PMP method. The team will also identify the effects of operating parameters of PMP components on the properties of particle samples.

Technical Approach and Milestone

The PMP system consists of a series of devices, such as a primary hot-diluter (HD), an evaporation tube (ET), a secondary cold-diluter (CD), and a condensation particle counter (CPC) (see the schematic). The PMP system is designed to enable commercial instruments to count the number of solid particles emitted from engines, by removing most volatile particles present in the exhaust emissions. The effects of operating conditions of these PMP components have not been evaluated comprehensively. In this proposed project, therefore, the working team will discover the effects of PMP key components on particle morphology and chemistry. In addition, the physicochemical properties of organic compounds and small nanoparticles will accurately be examined in use of the analytical methodologies described below. TEM will be a major instrument to be used for analysis of morphology and nanostructures.



Schematic of the PMP system

<u>Suggested operating conditions</u>

- Cabinet temperature: 47°C
- Primary HD temperature: 170°C
- Evaporation tube (ET) temperature: 350°C
- Primary dilution ratio at HD: 10
- Primary dilution air flowrate (MFC1): 11.5 lpm
- Secondary dilution ratio at CD: 15
- Secondary dilution air flowrate(MFC3): 10.5 lpm
- Bypass flowrate: 2 lpm
- CPC with 50% detection efficiency to particles ≥23 nm

1. Chemical analysis of diesel particulates

The working team will find out various organic compounds, such as hydrocarbons including oxygen functional groups, and analyze the amount of each organic compound at several different engine operating conditions. The bulk samples of engine-out diesel PM will be collected on Teflon filters by a gravimetric sampling method before the PMP system. Three different analytical techniques will be used: temperature programmed desorption-mass spectroscopy (TPD-MS), x-ray photoelectron spectroscopy (XPS), and gas chromatography-mass spectroscopy (GC-MS). The TPD-MS and XPS will directly use the bulk samples for analyses, while the GC-MS will need to employ the Soxhlet extraction technique to provide condensed organic samples. We will also measure those organic species at various isothermal temperature conditions to find the temperature dependence. For the measurements, the particulate samples will be thermally treated in the temperature range comparable to the temperature condition of ET by means of the TPD setup or thermogravimetric analyzer (TGA).

2. Characterization of physicochemical properties of sub-23nm nanoparticles

For the analysis, engine-out emissions will be sampled through a differential mobility analyzer (DMA), which classifies different sizes of diesel particulates, without using the PMP setup. Then, the particles or aerosols will be collected on a Teflon filter and processed in the Soxhlet extraction for ultimate analysis of chemistry by GC-MS. Because those nanoparticles may be solid soot, we will also sample them on a TEM grid to analyze their morphology. The TEM samples will be provided from different DMA channels, which enable us to analyze the morphology of different sizes of particles. The degree of crystalline structures and fractal geometry will be determined from high magnification TEM images. These analyses will also be performed for those samples collected on TEM grids in the PMP process, in order to identify the presence of organic aerosols or sub-23nm soot particles.

3. Effects of operating parameters of PMP components on particle morphology and chemistry

In the PMP system, the dilution ratios in HD and CD and the temperature in ET are important parameters affecting the particle number, size, morphology, and the content of organic compounds. Therefore, the working team will analyze those physical parameters from the samples collected on TEM grids in variation of dilution ratio, ET temperature, and sampling position (at the outlets of HD, ET, and CD). The detailed parameters to be evaluated will be the primary particle size (d_p), aggregate particle size (R_g), and fractal dimension (D_f). Argonne has developed a unique digital image processing/data acquisition system with algorithms. The influence of those PMP operating parameters on particle chemistry will also be evaluated by measuring the amount of each organic compound, using TPD-MS, XPS and GC-MS. For this chemistry analysis, bulk PM samples will be collected at the outlets of HD, ET and CD with variation of ET temperature.

Recently, other types of volatile particle remover than ET, such as thermodenuder and catalytic stripper, have been introduced in the research community. It has been informed that those new instruments can improve reliability in removing volatile organics and so enable consistent data acquisition in size. However, it is anticipated that the materials consisting those instruments, such as activated carbon or catalyst, could alter morphology and chemistry of particulates. We will analyze the morphology and chemistry of particulates in replacement of ET with thermodenuder and catalytic stripper, and finally compare the data with those obtained with ET.

Milestone

1st year
- Purchase a Soxhlet extraction system and set up the instruments, inclusive of existing DMA, PMP-type dilution system, TPD-MS, SMPS, TEM sampling system, with a selected heavy-duty diesel engine.
- Perform the chemical analysis of bulk PM samples collected at different engine conditions, using TPD-MS, XPS and GC-MS (to find the oxygen functional groups and organic compounds).
- Analyze the particle size, morphology, and chemistry across each PMP component under typical PMP operating conditions (to evaluate the effects of each component itself as a base reference).

2nd year
- Analyze the morphology and chemistry of sub-23 nm nano-particles.
- Analyze the morphology and chemistry across each PMP component in variation of dilution ratio for different types of diluter (perforated tube or ejector pump).

3rd year
- Evaluate the effects of temperature and residence time of the evaporation tube on PM morphology and chemistry.
- Evaluate the performance of different types of volatile particle removers (evaporation tube, thermodenuder, and catalytic striper) in terms of morphology and chemistry.
- Propose the operating conditions of PMP components that optimize the PMP system operation.