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Filtration and coagulation efficiency of sub-10 nm combustion-generated particles

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ABSTRACT

Particle size distributions are measured at the exhaust of a passenger-car diesel engine burning a Sulphur-free diesel oil. Different operating conditions of loads and engine speed, representative of low-loads are analyzed.

Particles with sizes ranging from few nanometers up 1 μm are generated during diesel combustion. Operating conditions strongly affect the size distribution of the particles but overall they maintain a bimodality with a first mode, identified as nucleation mode, in the form of sub-10 nm particles, and a second mode in the form of soot particles and agglomerates. The lower is the engine load, the lower the emission of mass concentration of particulate matter but the higher the emission of particle numbers. Measurements performed in not-firing conditions confirmed that particles are generated during combustion more than by lube oil or mechanical friction.

Filter efficiency with regard to the different particle sizes is evaluated by measuring particle size distributions before and after a diesel particulate filter. Results show that sub-10 nm particles are not sufficiently removed by the filter. Filter capture is almost complete for particles with sizes greater than 10 nm but the collection efficiency decreases to values of the order of 40–50% for sub-10 nm particles. This is of concern particularly when using fuels or operating conditions that produce a huge number of sub-10 nm particles not removed by the filter and hence emitted from the engine. The objective of the study is not to measure the filtration efficiency of a specific after-treatment system but to give a general warning on the capability of current particulate filters in removing sub-10 nm particles.

1. Introduction

Particulate matter emitted from combustion systems is a complex mixture of volatile and non-volatile species. In the ultrafine range, combustion generated particles are found in a bimodal size distribution with a nucleation mode, particles with sizes below 10 nm, and an accumulation mode, larger sizes soot particles [1–3]. Combustion researchers have developed in the years a combination of advanced technologies and new fuel formulations to reduce particulate emission. These improvements turned into an increased combustion efficiency and in a significant reduction of the mass of the emitted particles. However, the number concentration of the particles, recently regulated by European legislation, still remains high and it is of concern for a safe use of combustion devices. The total number of particles emitted can be mainly if not entirely attributed to nucleation particles that are negligible in terms of mass [4].

The nature of the nucleation particles is still under debate [5,6]. Nucleation mode particles emitted from combustion devices, particularly internal combustion engines, are often considered to be mostly "liquid" nanoparticles consisting of water and semivolatile organic and sulfur compounds. They are believed to form during dilution of the exhaust gases [7,8] mainly due to condensation process. Consequently, their presence in the exhaust pipelines and their emission in the atmosphere seems to be sensitive to dilution conditions, temperature and humidity of the dilution air [9]. These particles are often considered as an artifact of the measurement systems rather than a concern for the emission control.

Some recent works performed at the exhaust of engines and vehicles reported the presence of "solid core" particles in the nucleation mode that do not evaporate at high dilution or in a heated tube thermal denuder [10–12]. These exhausted "solid core" nucleation mode particles are formed at flame temperatures in the combustion chamber, have sizes of the order of 2–5 nm and are made by amorphous carbon [13]. They are consistent with those measured in laboratory flames which are considered soot precursor nuclei and for which a large literature exists [13–17]. Hence, the emission in the atmosphere of nanoparticles

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belonging to the nucleation mode is directly connected to the combustion process rather than to the presence of impurity such as sulfur or metal compounds or artifacts due to dilution conditions, temperature and humidity of the air.

The sub-10 nm particles may become centrally important to air quality. In fact, sub-10 nm particles have up to orders of magnitude higher surface area to mass ratios compared to particles and aggregates of tens and hundreds of nanometers [18–22]. This surface area can be covered with adsorbed volatile and semi-volatile organic species. It is important to note that particle surface area is in general thought to scale best with the surface reactivity, bioactivity and toxicity of poorly soluble particles [20]. Also, the organic content is often an additional major driver of the pulmonary inflammatory response. Thus, the health effect of sub-10 nm particles might go beyond what may be expected from their very low mass concentrations. Overall, the reduction of particulate mass emission rate not automatically lead to a reduction in toxic effects and a substantial improve in air quality as the emission of huge amounts of nanoparticles with insignificant mass as well as reactive gases may increase the biological, cytotoxic and inflammatory potential of these aerosols.

Exhaust after-treatment systems are currently unable to efficiently remove nanoparticles and gases from combustion exhausts [23–27]. According to the gas-kinetic theory, particles are believed to be collected by Brownian deposition with an increasing efficiency as particle size decreases. However, at nanometric sizes, it has been found that the filter efficiency significantly decreased rather than continuing to increase, as a net result of particle bounce. In fact, when thermal impact velocity of a particle exceeds the critical sticking velocity, the particle bounces-off filter surfaces instead of being captured. This process has been invoked also to explain the very low coagulation efficiency, at high and intermediate temperatures, of sub-10 nm particles generated from flames and engines [28,29]. Therefore, it is important to investigate nanoparticle filtration at temperature such as that encountered at the exhaust of combustion processes.

In this study, particle size distributions were measured in the exhaust manifold of a diesel engine run in different operating conditions before and after the particulate filter. From these measurements, a size-dependent collection efficiency of the filter is retrieved and the result is interpreted on the basis of a particle adhesion model. The size-dependent collection efficiency is related to the peculiar coagulation efficiency of particles as evaluated in laboratory premixed flames.

2. Experiments

The investigation was carried out on a Euro-4 1.9-liter passenger car Diesel engine with maximum power of 110 kW for which two load configurations were used. The engine was operated on a dynamometer test bench at three steady-state conditions namely at 3.5 kW and 1500 rpm, 6.5 kW and 1800 rpm and 10.5 kW and 2300 rpm. These operative conditions correspond to 8%, 12% and 15% of the maximum load at the given engine speed and are classified as low engine loads.

Engine was equipped with an electronically controlled common rail injection system and a commercial uncoated Diesel Particulate Filter (DPF). The 1.9-l engine was also equipped with standard Diesel Oxidation Catalyst (DOC) system. The engine was loaded by an electrical dynamometer to measure the torque output. Experiments were performed with Sulfur-free (less than 5 ppm) diesel oils. Before starting the tests, the engines were warmed-up until the coolant water reached 350 K.

Aerosol samples were collected at about 1 m from the engine exhaust valves, before and after the DPF. Measurements were performed by using an Engine Exhaust Particle Sizer 3090 (EEPS) developed by TSI that measures particles down to 6 nm. Particles smaller than 6 nm would be collected with a very low efficiency with the used instruments and their detection would be strongly influenced by diffusion losses in the sampling line and by particle charging efficiency, so that we have neglected their detection in this study.

Before entering the measuring system, the sampled exhaust aerosol was diluted by means of a Dekati Engine Exhaust Diluter (DEED) to avoid particle coagulation in the sampling line. The sample was first diluted with air heated above 420 K, then passed through an evaporation chamber at a temperature above 570 K for removing volatile species. After the thermal conditioning, the sample was further diluted to reduce the particle concentration along with the temperature to a suitable level for the aerosol particle sensors. A dilution ratio of 100 was chosen for which particle size distributions (PSDs) remain unchanged, thus achieving a critical dilution.

The heated sampling line conveyed particles to the EEPS where particles were positively charged to a predictable level using a corona charger. Charged particles were then separated according to their electrical mobility. Finally, an electrometer registered a current which was converted in a PSD using a proper matrix taking into account that the engine exhaust particles, specifically carbonaceous agglomerates, differ from spherical particles because agglomerates uptake more charge than spheres at a given mobility diameter.

3. Results and discussion

Particle size distributions measured at the exhausts of the investigated engine before the DPF at the two extreme power conditions examined are reported in Fig. 1. PSDs in all the examined conditions are clearly bimodal. The relative importance of the two distinct modes depends on the engine operating conditions. In particular, the large formation of soot aggregates with sizes greater than 20 nm (not shown in the figure) is measured at higher load conditions whereas the at the low load condition there is a greater importance of smaller particles. The cumulative PSDs reported in Fig. 2 clearly show the relevance of the smallest particles at lower load.

The peculiar bimodality of the PSDs at the engine exhaust has been already reported in the literature [10,11]. However, nuclei mode is often attributed to the condensation of semivolatile hydrocarbons on metallic nanoparticles deriving from piston friction or to acid-base reactions occurring in the engine exhausts because of the presence of sulfuric or nitric acids (these latter formed by reaction of the Sulfur contained in the fuel or the Nitrogen in the combustion air [11]).

In this experiment, we have used Sulphur free fuels (less than 5 ppm) so that the contribution of Sulphur to particle nucleation can be disregarded. To account for the contribution of unburned fuel and lube oil we have measured Raman spectra of the material collected on Teflon filters at the exhaust of the engine before the DPF both during

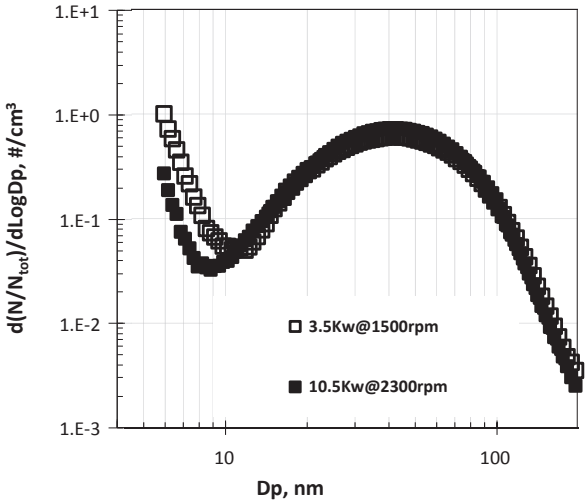

Fig. 1. PSDs measured before the DPF in two operating conditions: 3.5 kW @1500 rpm (□) and 10.5 kW @2300 rpm (■).