NANOPARTICLES CHARACTERISATION AT THE SPARK IGNITION ENGINE EXHAUST

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Abstract

The particles at the exhaust of two Port Fuel Injection Spark Ignition (PFI-SI) engines were characterised in terms of number size distribution and chemical properties. Optical techniques based on the Laser Induced Incandescence (LII) and on the Broadband Ultraviolet - Visible Extinction and Scattering Spectroscopy (BUVESS) were applied. The optical results were compared with those obtained by Electrical Low Pressure Impactor (ELPI). The aim of the work was the characterisation of the nanoparticles emitted by Port Fuel Injection Spark Ignition (PFI - SI) engines in terms of number size distribution and chemical-physical properties. Two PFI - SI engines were used for the experiments: a four-cylinder engine and a research optically accessible single cylinder engine. The experiments were performed at the exhaust of a multi-cylinder SI engine equipped with a three way catalyst (TWC) and in the combustion chamber and at the exhaust of a single-cylinder optical engine. High number concentrations of nanoparticles (D < 50 nm) were detected. The presence of carbonaceous particles at the exhausts was due to the ignition of the fuel film deposits on the intake valves and on the cylinder walls. This was demonstrated by the optical measurements performed in the combustion chamber of the research engine. Different engine operating conditions were considered.

Keywords: *Nanoparticles; Laser Induced Incandescence; Broadband Ultraviolet - Visible Extinction and Scattering Spectroscopy; Electrical Low Pressure Impactor; Spark-Ignition Engine.*

1. Introduction

It is well known that the particles emission from spark ignition (SI) engines is negligible if compared to Diesel one in terms of mass concentration. Conversely, under high load in rich mixture conditions, including cold starts and acceleration, SI engines emit high number of nanoparticles comparable to those from Diesel engines [1, 2]. Thus, Euro 5/6 regulations will introduce PM mass emission standards, numerically equal to those for Diesels, for gasoline cars equipped with direct injection engines [3].

The objective of this work is to detect and characterise the particles emitted by Port Fuel Injection Spark Ignition (PFI SI) engines.

For the experiments, two PFI SI engines were used. The former was a four-cylinder real engine equipped with a three-way catalyst (TWC). It was representative of the highest number of gasoline vehicles present on the Italian roads until the last year [4]. The latter was an optically accessible single cylinder engine [5].

Several complementing technologies were applied at the undiluted exhaust in order to measure particles in a wide range of size, from nanometres until microns.

Two different optical techniques were used: Laser Induced Incandescence (LII) and Broadband Ultraviolet - Visible Extinction and Scattering Spectroscopy (BUVESS), moreover an Electrical Low Pressure Impactor (ELPI) was employed.

The LII is a laser-based technique able to measure the mass and mean diameter of carbonaceous primary particles with a large measurement range, not limited by aggregate size and by complex retrieving procedures [6]. BUVESS is based on the ultraviolet - visible multiwavelength extinction and scattering spectroscopy. The analysis of the BUVESS data gives information about the particles chemical nature and their physical structure. The optical results were compared with those obtained by ELPI.

2. Experimental apparatus

For the experiments two PFI Spark Ignition engines were used, a real engine and a research engine. The real engine was a four-stroke 16 v - 1242 cm^3 engine, with four in-line cylinders, a compression ratio of 10.6:1 and a multipoint electronic injection system. It was equipped with a TWC. More details about the engine are reported in ref. [5].

The research engine was an optically accessible single cylinder engine. It had a displacement of 399 cm^3 and it was equipped with the cylinder head of a new generation of SI engine [7]. More details about the engine are reported in ref. [8]. All the measurements were carried out using EURO 4 commercial gasoline fuel (Octane Number = 95) containing less than 50 ppm of Sulphur.

2.1. Optical setup for optical measurements in the single cylinder engine

The research engine had a flat piston transparent through a quartz window. During the combustion process, the light passed through a quartz window located in the piston and it was reflected toward the optical detection assembly by a 45°inclined UV-visible mirror located in bottom of the engine.

For the spectroscopic investigations, the combustion light emission was focused by a 78 mm focal length, f/3.8 UV Nikon objective onto the micrometer entrance slit of a spectrometer with 150 mm focal length, f/3.8 aperture, 300 groove/mm grating. In order to investigate the natural emissions from the UV to the visible, the central wavelength of the spectrometer was fixed at 350 nm and 500 nm. The output of the spectrometer (254 nm spectral range) was coupled to an intensified cooled CCD (ICCD) camera with an array size of 512 x 512 pixels and 16-bit dynamic range digitization at 100 kHz.

2D flame visualization was obtained by digital CCD color camera system and a 50 mm focal length, f/3.8 lens. The optical assessment allowed a spatial resolution around 0.1 mm/pixel. Spatial distribution of soot temperature and concentration was obtained by the two color method. The soot-emission wavelengths were selected by edge filters. More details about this methodology are reported in [9].

The synchronization between the cameras and the engine was made by the Crank Angle Encoder signal through a unit delay. The exposure time of the cameras was fixed at 41.6 μs that corresponds to 0.5°crank angle (CA) at engine speed of 2000 rpm. The cameras were not cycle resolved detectors and each image was detected at a fixed crank angle of different engine cycles. The dwell time between two consecutive images was set at 41.6 μs.

2.2. Exhaust measurements

At the engine exhaust, the particulate mass concentration was evaluated by an opacimeter. Its probe was placed along the optical measurements pipe. From empirical relations it is possible to convert the opacity percentage in particulate mass concentration [10].

An ELPI system was employed to determine the particles number concentration in the range 7 nm-10 μm through electrical detection of inertially classified charged aerosol particles [11 - 13].

The experimental setup for the optical measurements at the exhaust was placed at 150 cm downstream of the exhaust valves. This distance resulted as the best compromise to reduce the speed of the exhaust flow and to avoid coagulation effects caused by the increase in the residence time in the test section. An optical path length of 150 cm was chosen. The integration of the optical measurements over this path was sufficient to have a good signal to noise ratio.

BUVESS measurements were carried out using a broadband pulsed light source, generated by the emission of a laser induced optical breakdown [14]. The signals were collected and focused on the entrance slit of the spectrometer coupled with the ICCD camera previously described. In order to reduce the statistical uncertainty, the scattering and the extinction measurements were carried out over 100 engine cycles, using laser shots at a frequency repetition of 16.6 Hz. The synchronization between the engine, the ICCD and the light source was controlled by the unit delay with the signal coming from the angle shaft encoder.

A numerical procedure developed in LabView™ environment was used to retrieve the multiwavelength extinction and scattering data. It was based on the minimization of the difference between the experimental and the theoretical spectra and it allowed the evaluation of the number distribution of the particles and to characterize their chemical nature [15]. In order to build up the scattering and extinction theoretical spectra, the refractive index was a necessary input for the procedure. An external database of optical properties accessible by the program was made up using literature data [16 - 21].

LII measurements were carried out exciting by the first harmonic of Q-switched Nd:YAG laser and detecting at 430 nm by band-pass filter. The LII signal was acquired at 90°angle to the direction of the incident beam using the ICCD. In this experiment, the ICCD received an external timing signal from the Nd:YAG pump laser and it detected the LII signal just 10 ns after the laser pulse. The ensemble decay curve was obtained by moving the gate via software.

The binning of pixels on the x and y location was used to improve ICCD sensitivity. In this process, a number of pixels corresponding to the optical access were read out as a single pixel, this increased the number of photons collected per binned pixel. Full Binning allowed using the ICCD chip as a linear image sensor. More details about the optical techniques applied at the engines exhausts are reported in ref [5, 6].

3. Results and discussion

3.1.3.1. Four-cylinder engine

Tab. 1. Four cylinder engine - operating conditions

Speed	Load	SOI	DOI
[rpm]	[%]	CAD ATDC	[ms]
1500	50	202	10.3
2000	50	140	11.0
3000	50	46	10.0
4000	50	-90	11.3
1500	100	208	11.3
2000	100	136	11.2
3000	100	28	10.7
4000	100	-112	12.4

Tab. 1. reports the operating conditions of the four cylinder PFI SI engine. The fuel injection occurred at closed-valve condition and stoichiometric equivalent ratio for all the cases. For each test point, the three-way catalyst (TWC) temperature was higher than the activation one. All the ELPI distributions measured without the TWC showed high nanoparticles number concentrations with a maximum in the range 7-28 nm as reported in Fig. 1. The TWC determined an overall reduction in number concentration with the strongest decrease for particles smaller than 30 nm. Since the diffusive particle loss within the catalyst was low for particles larger than 10 nm, the primary mechanism for the „removal" of these particles was probably the catalytic stripping of the volatile hydrocarbon particle precursors [22].

Conversely, the TWC had effects on the number decrease of larger particles (D > 50 nm) as well. Due to their size and probable composition, they were likely to be in a solid particulate phase in the exhaust. Thus, the most likely mechanism for the removal was the inertial impaction at the catalyst channel faces. Downstream of the TWC, at 1500 and 2000 rpm, the highest particles number concentration was measured by ELPI below 28 nm size range. At 3000 and 4000 rpm the size distributions were characterised by a maximum around 60 nm. This size distribution was closed to the typical size distribution of carbonaceous particles detected by ELPI at the exhaust of Common Rail Diesel engines as reported in [6]. For all the engine conditions, a little fraction of particles larger than 300 nm was detected. They can be produced by lube oil blow-by [23].

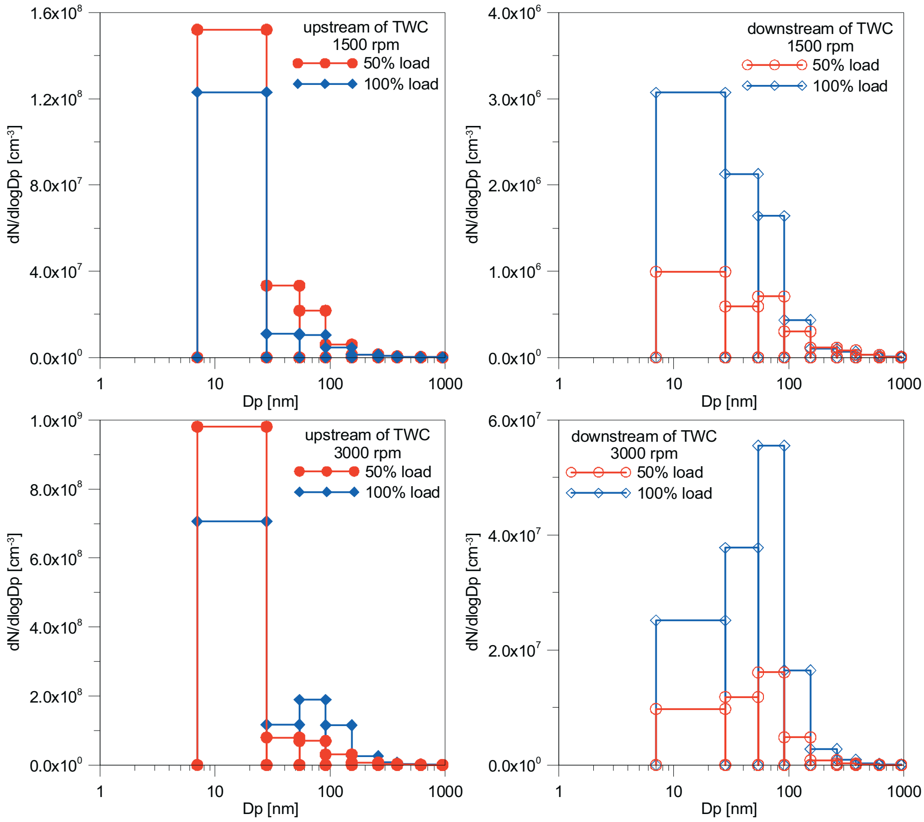

Fig. 1. Particles number concentrations measured by ELPI upstream and downstream of the TWC

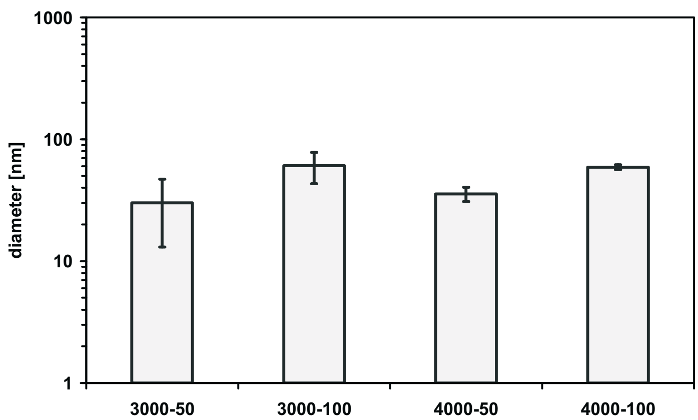

Fig. 2. Average diameters of carbonaceous particles obtained by LII downstream of the TWC

ELPI does not provide information about the particles chemical nature. In order to obtain a more complete particles characterisation, LII and BUVESS were applied at the engine exhaust downstream of the TWC. The carbonaceous particles were detected by LII measurements at high speeds and they showed average diameters in the range 30-60 nm as reported in Fig. 2.

LII is sensitive only to carbonaceous primary particles; thus, in order to evaluate the chemical-physical nature of particles for all the engine operating conditions, BUVESS measurements were performed (Fig. 3). At high speeds, two modes were evaluated: the first one was composed by soot particles with 30 nm mean diameter [18]. The second mode was characterised by carbonaceous organic particles with mean diameter below 15 nm [21]. Recent experiments detected organic nanoparticles smaller than 10 nm in flames and at the exhaust of few passenger cars[21, 24, 25]. With respect to the vehicles, they outlined that these nanoparticles were formed in the combustion chamber; some of them could survive to oxidation in the combustion chamber and in the TWC and then they could be emitted at the exhaust. On the other hand, other research results [23] suggested that these particles could be volatile ones resulting from the nucleation of gas phase hydrocarbons during the dilution process.

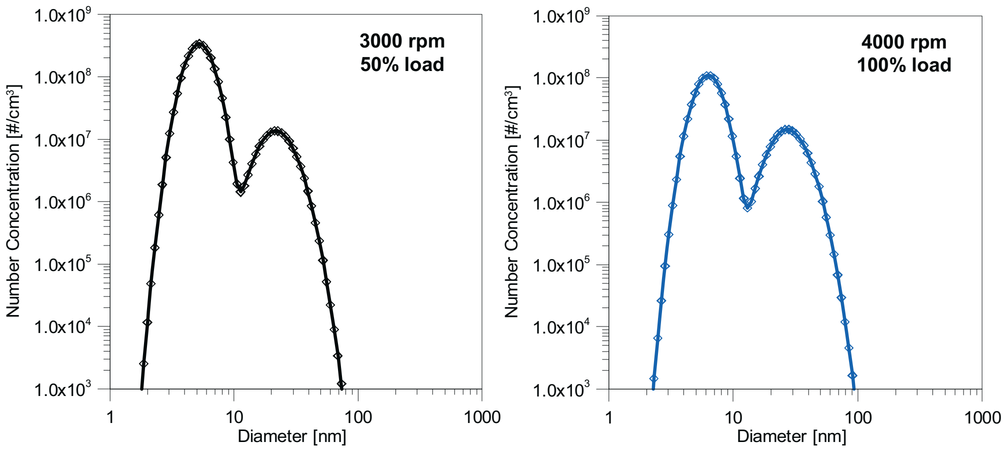

Fig. 3. Particles size distributions obtained by BUVESS downstream of the TWC

3.2 Research mono-cylinder engine

Several previous experiments demonstrated, in agreement with the literature, that in the port fuel injection spark-ignited engines thin films of liquid fuel formed on the valves surface and on the cylinder walls [26 - 31]. Once formed, the fuel films develop dynamically under the influence of gas flow and valve movement, creating locally rich-zones. Due to the interaction of these zones with the propagating spark-ignited flame, diffusion-controlled flames are induced.

In order to understand if there was a link between this phenomenon and the nanoparticles detected at the exhaust of the PFI SI engines, optical investigations were performed in the cylinder of the research engine [8]. Operating conditions comparable with the four-cylinder PFI SI engine ones were considered.

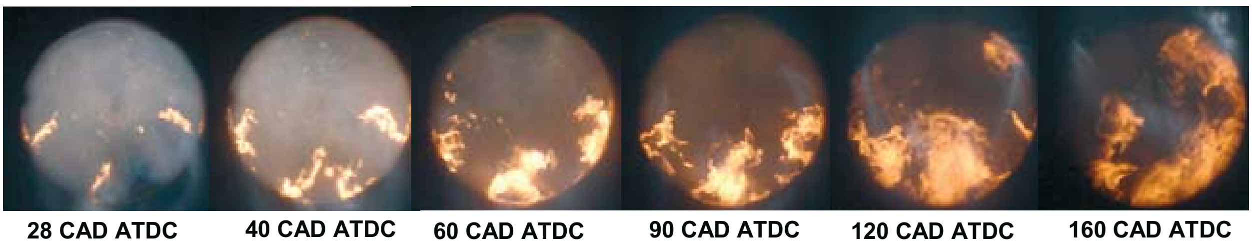

Fig. 4. Flame visible emission detected in the optical engine

Fig. 4. reports the flame emissions detected at medium speed and load, closed valve injection and stoichiometric air-fuel ratio in the combustion chamber of the optical engine. Around 28 CAD ATDC the flame front interaction with the fuel deposits on the intake valves induced the ignition of strongly intense diffusion-controlled flames. They persisted in the late combustion phase until the opening of the exhaust valves that started at 155 CAD ATDC.

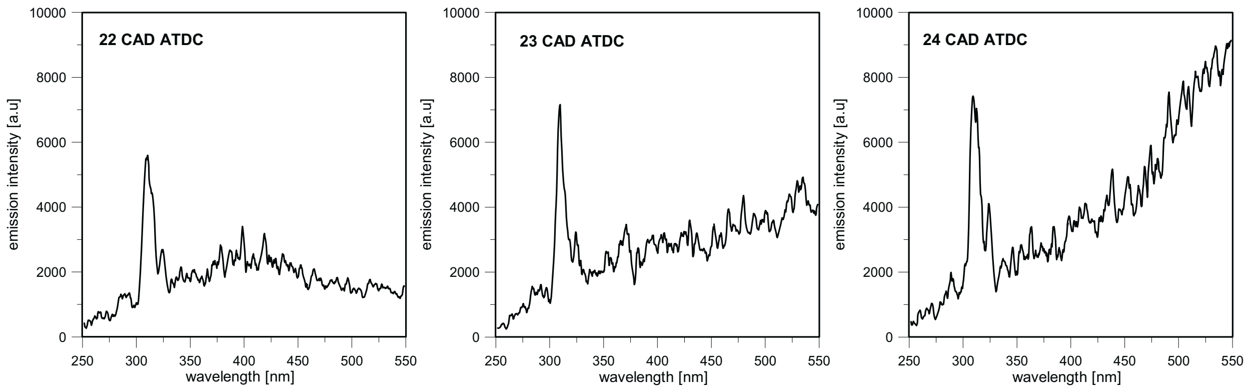

Fig. 5. Natural emission spectra detected in the region near the intake valves in the optical engine

Spectroscopic investigations allowed to have information about the chemical compounds that were involved in the inception and evolution of these flames. Fig. 5 shows the natural emission spectra detected in the region between the intake valves. The OH radical's band at 309 nm is well resolved in all the spectra [32]. OH is widely present in the chamber during all the combustion process; it is marker of high temperature combustion and chemical reactions. At 22 CAD after the start of spark (ASOS), CO-O emission could be observed as a broadband around 400 nm [32]. In less than 1 CAD, around 23 CAD ASOS, a spectral signal that increased with the wavelength above 400 nm was detected. This could indicate the formation of carbonaceous structures that represented soot precursors because, successively, the spectrum evolved showing the blackbody-like emission typical of the soot particles [33].

In order to evaluate the effect of the diffusion-controlled flames in terms of soot time and spatial evolution, two-colour pyrometry was applied and the results were reported in Fig. 6. It can be noted that at the opening of the exhaust valves high soot concentration was detectable. This effect was due to an uncompleted oxidation caused by the too low temperatures in the combustion chamber.

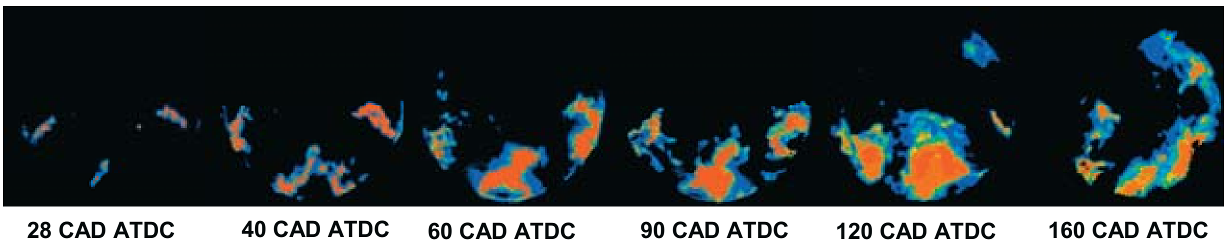

Fig. 6. Soot distributions measured by two-colour pyrometry in the optical engine

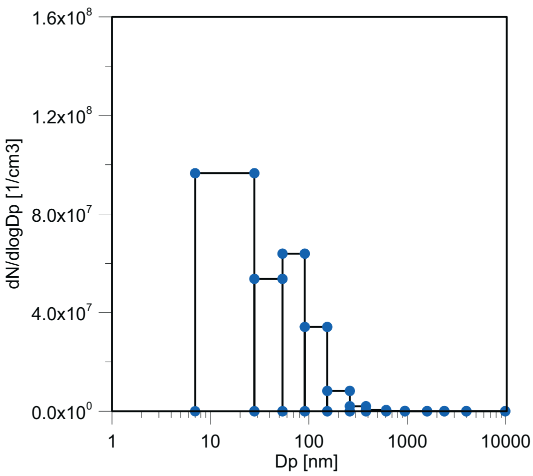

Fig. 7. Particles number concentration measured by ELPI at the optical engine exhaust

To correlate the particulate formation in the combustion chamber with the particle size distributions at the exhaust, ELPI measurements were performed during the in-cylinder optical measurements. The result is reported in Fig. 7. As just observed for the multi-cylinder engine, the highest number of particles was measured on the ELPI first stage (7-28 nm). A second mode of particles with a mean diameter around 60 nm was detected. It could be due to the soot particles produced by the diffusion-controlled flames in the combustion chamber.

It should be noted that the investigated optical engine lacks of aftertreatment device. On the other hand, since the nanoparticles cannot be removed by three way catalysts, it seems to be necessary to optimise the engine operating conditions taking into account the lowest emissions of nanoparticles.

5. Conclusions

The aim of the work was the characterisation of the nanoparticles emitted by Port Fuel Injection Spark Ignition (PFI - SI) engines in terms of number size distribution and chemical-physical properties. Two PFI - SI engines were used for the experiments: a four-cylinder engine and a research optically accessible single cylinder engine.

Two optical techniques based on Laser Induced Incandescence (LII), Broadband Ultraviolet - Visible Extinction and Scattering Spectroscopy (BUVESS) were used at the exhaust of the real engine. The optical results were compared with the Electrical Low Pressure Impactor (ELPI) size distributions.

High number concentrations of nanoparticles (D < 50 nm) were measured for all the engine operating conditions. In particular BUVESS detected two modes size distributions. The first mode was composed by soot particles with 30 nm mean diameter; the second one was constituted by carbonaceous organic particles with mean diameter below 15 nm. These results were in very good agreement with the ELPI ones.

In order to understand the origin of the nanoparticles emitted by the multi-cylinder engine, several investigations were performed in the research engine both in the cylinder and at the exhaust. The natural emission spectroscopy and visible flame imaging coupled with two-colour pyrometry demonstrated that the main sources of carbonaceous particles were the diffusion controlled flames. These were due to the burning of the fuel films formed on the valves surface and on the cylinder walls. The particulate formed in the combustion chamber was correlated with the particle size distributions at the exhaust by ELPI measurements. These showed high number concentrations of particles smaller than 30 nm and around 60 nm. This result agrees with the multi-cylinder one.

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