AN OFF-LINE APPROACH FOR THE EVALUATION OF PARTICLE SIZE DISTRIBUTION EMITTED FROM A MODERN DIESEL ENGINE

M. Alfè*, C. Guido, S. Di Iorio**, C. Beatrice**, V. Fraioli**, M. Lazzaro****

alfe@irc.cnr.it

* CNR – IRC, P.le V. Tecchio 80, 80125 Napoli, Italy

** CNR – IM, via G. Marconi 8, 80125 Napoli, Italy

Introduction

The automotive diesel engine has reached in the last years a high improvement in terms of performance and emissions [1]. The real issue for modern diesel engines still lies in the compliance with future pollutant emissions regulation, in particular, with the increasingly stringent reduction on particulate matter emissions levels, not only in terms of mass, but also on the number of emitted particles. In particular, an increase of the number of particles smaller than 100nm (ultrafine particles) was observed in the new generation engines [2]. Taking into account that ultrafine particles have low impact on the total emitted mass, but become predominant in a concentration number analysis [3] this issue led to the formulation of standards regulations including limits also on particle number [4]. In this sense, a detailed analysis of the particle distribution at the exhaust of a diesel engine has been carried out, testing the engine in several operative conditions and evaluating the influence of combustion characteristics on particle distribution.

The present paper is dedicated to the study of the soot particle emissions at the exhaust of an automotive diesel engine. An off-line approach was employed and compared with a consolidated on-line method for particulate emissions characterization (Differential Mobility Spectrometer Cambustion DMS 500).

The evolution of the particles molecular weight (MW) distribution was studied off-line as a function of the UV-Visible absorption by means of Size Exclusion Chromatography (SEC) [5, 6]. The SEC methodology was applied for the first time to study the particulate emission of a real engine running at different low/partial load operative points. The adopted engine was a EURO5 diesel engine, running in three low, medium and high speed/load operative points, representative of the New European Driving Cycle (NEDC) procedure. The analysis of particle emission upstream the particulate filter was performed taking into account the presence of the Exhaust Gas Recirculation (EGR).

Experimental devices and test methodology

The measurements were carried out at the exhaust of a EURO5 light duty diesel engine, installed on a dyno test bench. The engine displacement represents the most

popular size of diesel engine for passenger car in the European market. The main characteristics of the engine are listed in Table 1.

Table 1. Main features of the engine.

Engine type	CR MultiJet In-line 4 cylinders 16 valves
Bore [mm] x Stroke [mm] x Compression Ratio	82.0 x 90.0 x 16.5
Injection system	Bosch Common rail
Catalyst system	Closed-couple DOC plus underfloor DPF
Maximum Power	112 kW @ 4200 rpm

The engine is equipped with an open Engine Control Unit (ECU) to control all engine parameters such as the injection strategy, EGR, etc.. [7]. The engine is fully instrumented for indicated signal measurements in each cylinder. At the exhaust, smoke was measured by a high-resolution (0.01 FSN) smoke meter (AVL415S), dry soot was detected by means of the AVL Micro soot sensor (AVL483), while gaseous emissions were measured upstream and downstream the oxidation catalyst by means of an analysis test bench (AVL-CEB-2). A Differential Mobility Spectrometer (Cambustion DMS 500) has been used for on-line counting and sizing of the particles. The measurement principle of DMS500 is based on a deflection of electrically charged particles combined with electrical counting [8]. After the first dilution, the sample was transported to the DMS500 through a heated sampling line. The first and the second dilution ratios set points were 10:1 and 20:1, respectively. The temperature of the heated line was set at 40°C.

Total particulate was collected from the raw exhaust stream in the outlet manifold of the engine by isokinetic sampling. The sampling line comprised a Teflon filter (Whatman, pore diameter 0.45 μm) heated at 100 °C for the collection of solid particulates and in an ice-cooled trap for the collection of condensable compound that went through the filter. The solid particulate collected on the filter was extracted with dichloromethane (DCM) in order to recover the residues of condensable species adsorbed on it. The carbonaceous solid after DCM extraction was named soot. The DCM-extract was added to the condensable species collected in the ice-cooled trap, DCM-extract and soot samples were dried and weighted.

Soot and DCM-extract were suspended in N-methyl pyrrolidone (NMP) using an ultrasonic bath and analyzed by SEC to get information on the particle size distribution. SEC analysis was carried out on two different SEC columns able to furnish a reliable MW distribution in a wide range of MW (100-1E10u). PL-gel styrenedivinylbenzene individual pore column (low-MW SEC column, linear range from 100 to 1E5 u, corresponding to 0.6 ÷ 5 nm diameters, injection volume 250 μl, flow rate 0.5 mL/min, 60°C) was used to investigate the MW region (10-1E4u) [5] and a Jordi Gel divinylbenzene (DVB) Solid Bead non-porous column (high-MW SEC column, linear range from 1E5 and 1E10 u, corresponding to 5 ÷ 100 nm particle diameters, injection volume 10 μl, flow rate 1 mL/min, room temperature) was used in the particle-size region (1E5-1E10u) [6]. The on-line detection of the

species eluted from the SEC column was carried out using a UV–visible Diode Array detector measuring the absorbance signal at λ = 350 nm. The solvent used as eluent was NMP.

The measurements were carried out in three steady-state test points reasonably representative of the low, medium and high engine speed/load conditions in the NEDC. The analysis of particle emission upstream the particulate filter was performed varying the EGR levels, from zero to the EURO5 level. The operating conditions are reported in the Table 2.

Table 2. Engine operating conditions.

	Engine speed [rpm]	BMEP [bar]	SOIPilot [cad BTDC]	SOImain [cad BTDC]	Prail [bar]	EGR [%]
L1	1500	2	16	0.5	350	0
L2	1500	2	17	1.5	350	38
M1	2000	5	25	2	766	0
M2	2000	5	26	3.3	766	26
H1	2500	8	30	3.5	1124	0
H2	2500	8	33	6	1124	20

Results

The DMS particles distribution are reported plotting PSDF versus particle equivalent diameter, while the SEC chromatograms, usually reported as a function of the elution time, are plotted as a function of the MW by transforming the elution time into MW on the basis of the SEC calibration curves [5, 6]. The estimation of the diameter was obtained by assuming spherical shape and a density of 1.8 g/cm^3. Figure 1 reports a typical MW distribution of total particulate.

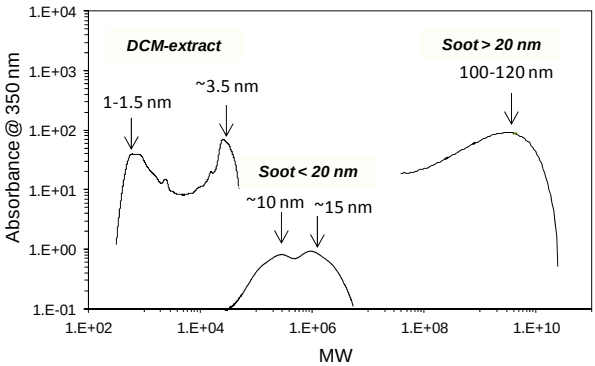

Figure 1. Typical MW distribution profile of total particulate in the 100-1E10u range obtained by SEC.

The species contained in the DCM-extract are characterized by a bimodal MW distribution in the 100-300 u and in the 1E4-3E4 u range (3-4 nm). The lower MW distribution has been further analyzed by gas chromatography/mass spectrometry (not shown) and interpreted as mostly composed by linear paraffin in the range C13-C24 (indicator of unburnt fuel) and oxygenated aromatic compounds

(indicator of partially burnt fuel). Soot MW distribution consists of a predominant peak in the particle-size region at ~1E10u (soot chain-like aggregates, 100-160 nm in diameter as confirmed by Dynamic Light Scattering measurements). Two additional lower MW distribution peaked at 1E5u (~ 10 nm) and at 1E6u (~15 nm) are detected.

The particle size distribution functions (PSDF) detected by DMS500 in all the mentioned engine operating conditions (Table 2) are compared with the MW distribution obtained by SEC approach and reported in Figure 2. The data are grouped displaying, for each figure, on the left hand side, PSDF by DMS and on the right SEC plots. The particle distribution inferred by SEC for each engine load condition is multiplied by the concentration of DCM-extract and soot.

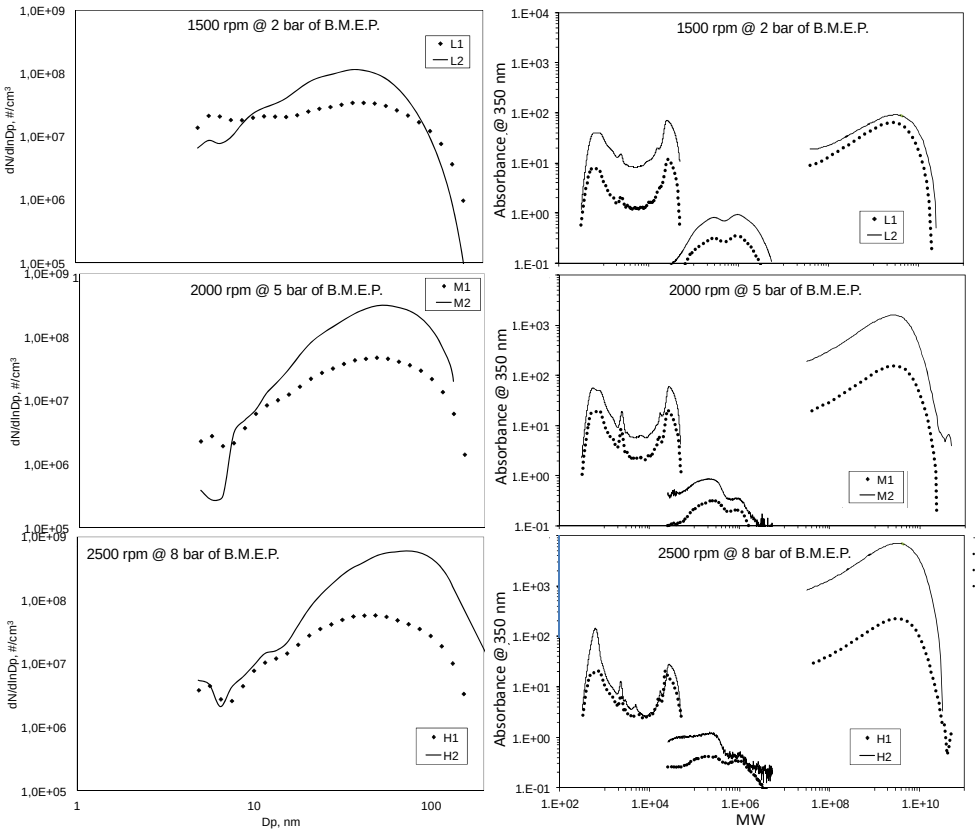

Figure 2. PSDF measured by DMS (on the left) and SEC profiles as a function of the sample absorbance (λ = 350 nm) (on the right) in all test conditions.

For each engine load condition, the same effect of EGR presence on the all measured profiles is obtained: the detected quantities of the high MW distribution generally get higher values. This scenario is coherent with the well known increment of soot production when EGR is adopted. It is noteworthy that the SEC

approach is capable of properly follow the engine behavior, confirming the trends detected by DMS. Comparing the three rows of Figure 2 as regards the particles larger than 20 nm, both the techniques display an increased distance between the profiles relative to cases w/o EGR and those for cases with EGR. A similar behavior is observed by increasing engine speed and load, thus confirming the reliability of this methodology.
Examining the particles smaller than 20nm, both the techniques exhibit similar trend, varying the operative conditions. The profiles relative to the DCM soluble fraction, display an opposite trend with respect to the larger particles. In fact, as long as the speed/load are increased, the difference between the low MW molecules/particles emission in the cases 1 and 2 gets lower.
The above described trends are consistent with the results given by MicroSoot sensor and HC Multi-FID analyzer, reported in Figure 3. More in detail, the trend of HC emissions is coherent with the lowest MW trend (attributed to linear paraffin in the range C13-C24 and oxygenated aromatic compounds) and an increase in the emitted soot mass concentration is obtained adding EGR and increasing the engine speed/load, in agreement with the results of Figure 2.

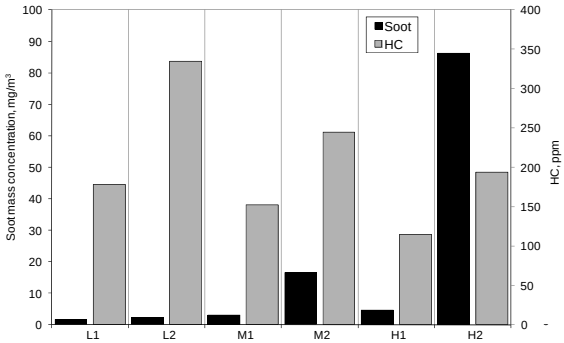

Figure 3. Engine out soot mass concentration and HC emissions in all test conditions.

Conclusions

The present work illustrates some results of an experimental investigation devoted to the application of different techniques for the analysis of soot particles emitted by an automotive diesel engine. In particular the focus is the reliability of the SEC approach, currently devoted to the study of the evolution of particle size distribution during the processes of soot formation in laminar flames, to an exhaust gas emitted by a diesel engine of current technology. SEC approach offers the possibility to enrich the pool of information by exploring intervals of molecular weights not easily detectable with on-line conventional techniques. Future developments can foresee the application of the SEC approach to engine operating conditions of specific interest (like PCCI, LTC mode) and/or employing alternative fuels.

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