Chemical/physical features of particulate emitted from a Heavy-Duty SI LPG engine

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Abstract

Road traffic emissions are one of the main sources of environmental pollutants affecting urban inhabitants. Investigation focused to develop systems and processes for the reduction of air pollutants is strongly addressed to achieve near zero emissions goal. In the field of internal combustion engines (ICE), the use of alternative fuels together with the adoption of innovative combustion concepts are possible routes to develop high efficient and low emission technologies. Fuel decarbonization and the utilization of gaseous fuels are two top-notch approaches for emission lowering (including CO_2) and for suitable standard regulations settlement.

The major pollutants emitted in engine exhaust gases are particulate matter (PM), CO_2, nitrogen oxides (NO_x), and, to a lower extent, unburned hydrocarbons. PM formation is usually linked to (even local) fuel-rich conditions establishing in some phases during the combustion process (i.e. high engine load conditions).

In this study the performances of a heavy-duty SI gas engine fueled with LPG (propane > 98%) were investigated by sampling and evaluating the chemical, physical and morphological characteristics of the emitted PM (off-line), as well as the engine-out particle size distribution function (PSDF) and total number (PN) (on-line).

The engine specifications are reported in the following:

Engine type	6 cylinder in-line
Displacement	5883 cm^3
Bore x Stroke	102mm x 120mm
Rated torque	630 Nm @ 1500 rpm
Rated power	113 kW @ 1800 rpm
Compression ratio	10.3 : 1

The exhaust gases for pollutants and particle matter analysis were sampled downstream of the engine after the treatment device (three-way catalyst) in order to fully characterize particle numbers and sizes through the whole exhaust system.

Gas exhausts were emitted accordingly to the WHTC homologation procedures (World Harmonized Transient Cycle) combining cold and hot start tests. Gas exhausts from separate cold start and hot start driving cycles (hereinafter WHTC-cold and WHTC-hot, respectively) were also investigated.

The PM was sampled from the exhaust pipeline by isokinetic sampling, collecting the gaseous stream from 14-17 tests repetitions on the same filter, for a sampling time of 30 min each test. The solid particulate, collected on a Teflon filter (Millipore, pore diameter of 0.45 μm) kept at 100 °C was then analyzed as it is. Three kinds of solid particulate samples were collected (replicated trice) to evaluate differences between the PM emitted in WHTC (as representative of the overall engine particle emissions), WHTC-cold and WHTC-hot tests.

The chemical, physical and morphological features of the PM have been off-line analyzed by transmission electron microscopy (bright field TEM imaging, FEI Tecnai G12 Spirit-Twin

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using LaB6 as source at 120 kV), thermogravimetry (thermogravimetric analysis (TGA) performed on a Perkin–Elmer Pyris 1 Thermogravimetric Analyzer under oxidative environment (air) at 30 mL min^{-1} from 50 °C up to 800 °C at a rate of 10 °C min^{-1}) and infrared spectroscopy (FTIR spectra were acquired on PM/KBr pellets (1-2 wt.%) by a Nicolet 5700 spectrometer operating in transmittance mode in the 650−4000 cm^{-1} range). The soot mass emission, the counting and sizing of particles were on-line performed by means of a transient high-sensitive soot photoacoustic sensor (AVL Micro Soot Sensor) and a differential mobility spectrometer (Cambustion DMS500), respectively.

On-line emissions analysis indicates that the PM emissions are inside the homologation limits: about 6 mg/kWh versus 10 mg/kWh. PN_23 (actual standard) e PN_10 (possible future standard) are very close, the particles in the range 10 nm to 23 nm represents less than 20% of the all particles measured. The most part of the particulate emissions (PM e PN) appears to be emitted just after the idle phase when the engine speed and torque increase rapidly; the results are repeatable also considering the two versions of WHTC (WHTC-hot and WHTC-cold). The most part of the particles emitted has a diameter in the range 80 -120 nm (accumulation mode). The ultrafine particles (sub-23 nm) represent less than 20% of all particles emitted. Little differences between WHTC-hot and WHTC-cold tests are found: in WHTC-cold a higher amount of sub-23 nm particles were detected.

The micro and nano-texture of the samples were investigated by TEM (Figure 1).

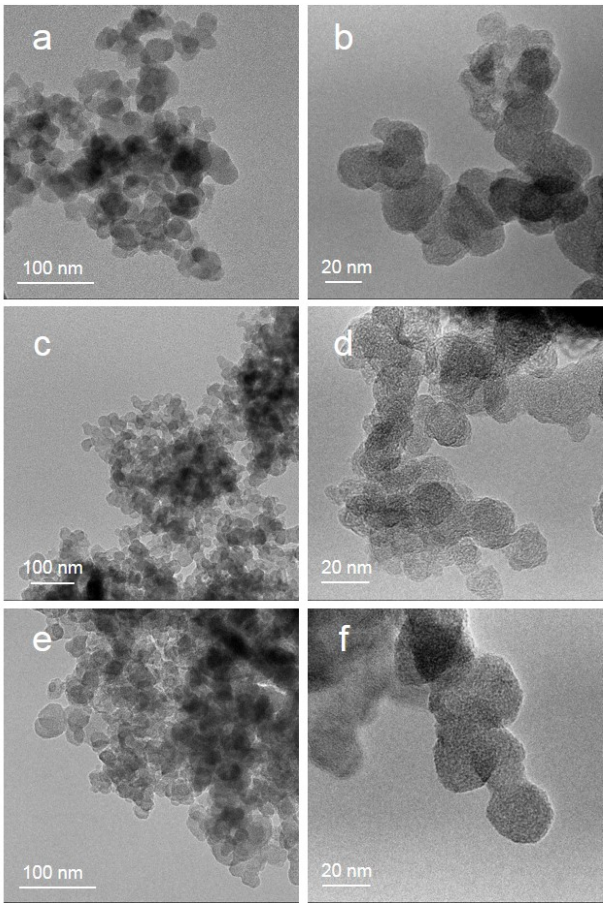

Figure 1. TEM images ad different magnification (a, b) WHTC-cold; (c, d) WHTC-hot; (e, f) WHTC.

Overall the shape of the aggregates and the structure of the particles resemble those of particulate matter produced by high temperatures combustion process (internal combustion engines or flames) [1-3]. The PM appears composed by carbonaceous grape-like structures

with a negligible presence of metals impurity (engine wear, oil residuals), as checked by energy dispersive X-ray (EDX) analysis. In all the soot aggregates the primary particles are clearly discernible and their diameter appears quite widely distributed (average diameter 5-25 nm). The irregular soot edges suggest the presence of sp^3 carbon and possible oxygen presence in the carbonaceous network.

No variation in the distribution of primary particles dimension is clearly discernible in the soot sampled along the three WHTC tests, indicating that different engine starting conditions (cold and hot) negligible affect the formation of the nuclei cores in the early stage of the soot formation. This is even truer looking the interior structure of soot, that appears (at least at this magnification degree) quite unaffected.

The thermal behavior of the samples was investigated under oxidative conditions by thermogravimetric analysis (Figure 2). Looking at the TGA profiles, in all the cases the particulate matter is completely burnt in the temperatures range between 500 and 650 °C leaving a negligible ashes amount.

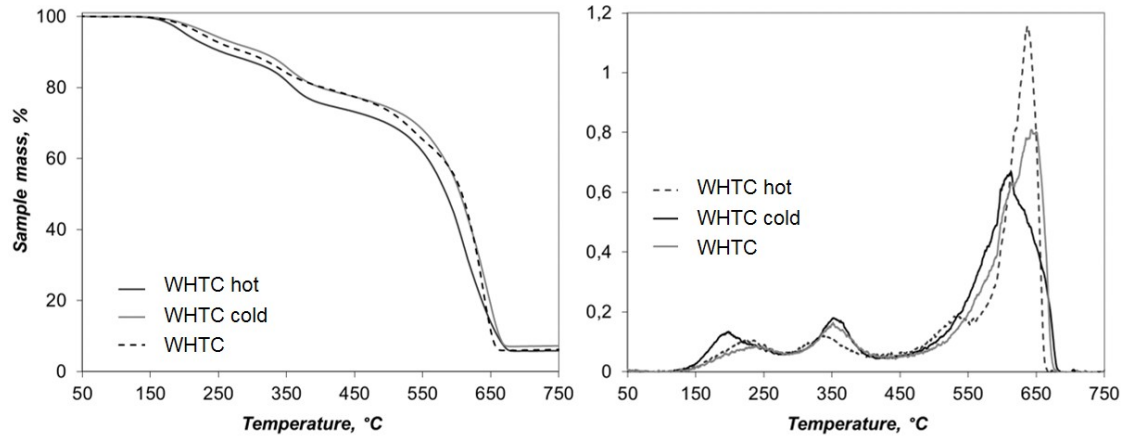

Figure 2. (left) TGA profiles; (right) DTG curves

Three main events characterize the DTG profiles of all the samples: i) a progressive weight decrease up to 10-20% between 150-300 °C ascribable to the devolatilization of the lighter components (oil residuals, polycyclic aromatic hydrocarbons); ii) a progressive weight decrease up to 10-15% between 300-450 °C ascribable to the devolatilization /decomposition of the higher molecular weight components (tar-like species) and iii) a rapid weight decrease up to 60% between 450-680 °C due to the combustion of solid phase (soot particles). Soot oxidation takes place in the temperature range typical of diesel soot oxidation [1, 4] but at a lower temperature with respect to a nanostructured furnace carbon black (690 °C) [5] which exhibits a more graphitized texture.

The surface chemistry of the soot particles was investigated by infrared spectroscopy and the resulting data are reported in Figure 3. The FTIR spectra are baseline corrected, height normalized and shifted for clarity. In accordance with previous findings [1, 4] the shape of the FTIR spectra reflects the complex character of the carbonaceous networks constituting the soot particles [5]. The spectral profiles of the three samples are quite similar. Overall the spectra evidenced a very low presence of aliphatic chains (C-H functional groups, mainly $-CH_2-$) attributable to residuals of unburned or partially burned oil (gathered in the 2850 - 3050 cm^{-1} region), differently to those observed in as-sampled particulate from diesel-fueled engines [6-7]. In the spectral region between 3100 and 3600 cm^{-1} broad signals of exchangeable protons were found (unbounded water residuals) and in the 1800 - 900 cm^{-1} region overlapping signals of stretchings and bendings of many different functional groups (C=O of carbonylic and carboxylic groups, C-OH, C-H, C=C, C-C) are detected. It is worth of note that in the spectrum of the sample belonging to the WHTC tests the highest peak due to the C=O stretching mode is

detected (peaked at 1720 cm^{-1}), suggesting a more oxygenated character. In the region between 900 and 700 cm^{-1} low intense and poor defined bending absorptions of "out of plane" aromatic C-H groups are found [5]. The similarity in the shape and the intensity of the signals among the three spectra suggests that the surface chemistry of the soot particles is not influenced by start versions.

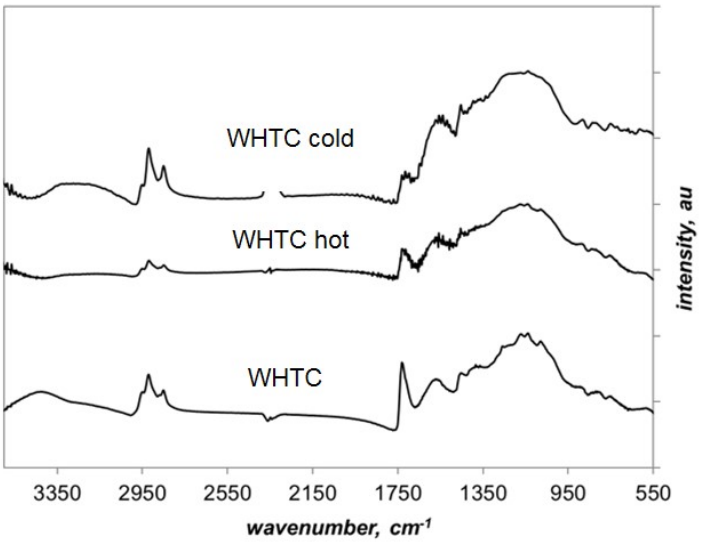

Figure 3. FTIR spectra

Overall, this preliminary survey on soot sampled averaging WHTC tests and discriminating between cold and hot starts on LPG-fueled heavy-duty gas engine indicated that the start version has a limited effect on soot characteristics, both looking at micro-nanotextures and surface chemistry. Moreover, the highlighted similarity with the PM of modern diesel engines envisages a reliable usage of the same after-treatment soot trap systems designed for modern diesel engines.

References

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