Chemical/physical features of particles emitted from an automotive modern dual-fuel methane-diesel engine.

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Abstract

The even more stringent worldwide emission legislation, the instability of the fuel price and the not very clear limit of fossil fuel reserves, push researcher to develop high efficiency and low emission technologies in the field of internal combustion engines (ICE). The use of alternative fuels together with the adoption of alternative combustion concepts are possible routes to reach these objectives. Fuel decarbonisation and gaseous fuels are two key points for emission lowering including the CO_2. On this way, the dual-fuel (DF) engines for automotive application based on the use of natural gas (NG) and diesel have received increased attention in recent years [1-4]. In DF CI engines, the gaseous fuel is premixed with air in the intake manifold and subsequently compressed as in a conventional diesel engine. A certain amount of high-cetane liquid fuel (conventionally diesel fuel), usually called pilot, is then injected at the end of the compression stroke providing the energy to ignite the mixture and initiate the combustion. The high octane number of NG makes the fuel suitable for CI engines which usually operate with relatively high compression ratio (CR). Furthermore, NG is mainly constituted by methane (CH_4) and has a favorable H/C ratio in terms of CO_2 reduction compared to conventional fuels. From the point of view of NOx and particulate matter (PM) emissions, it was assessed that the DF combustion concept has the benefits to reduce NOx, and generally PM. From previous experiences it was evidenced that in the case of automotive DF engine operating with diesel energy substitution rate (ESR) ≥50%, exhaust PM suppression at engine out is in the order of 60÷80% [5,6]. Therefore, also with high EGR, the DF engine could not match the current Euro 6 PM emission target of 5 mg/km, as clearly reported in [6]. So, the use of a diesel particulate filter (DPF) is required, even if the relevant soot load reduction related to the DF operation mode could increase the interval time between two consecutive regenerations. With this premise, it appears extremely important the evaluation of the chemical, physical and morphological characteristics of the emitted PM, as well as the engine out particles in terms of particle size distribution function (PSDF) and total number. Such information are of high importance for the design of tailored DPF for DF engines and their management during regeneration. They are usually available for conventional diesel engine, but literature concerning properties of the impact of DF operating mode on emitted particles is still not fully exhaustive. Moreover, literature data should be representative of the dynamic operating mode typical of the automotive engines.

On this aim, a research activity was carried out on a modern multi-cylinder automotive engine installed on a test bench and operated in DF mode in dynamic test conditions [7]. The engine was properly calibrated to work in DF mode with a ESR of 50% in almost whole operating area, except at idle. In this preliminary assessment pure methane was employed as gaseous fuel in order to avoid possible effects on PM features from other components of the NG (e.g. CO, H_2, ethane *etc.*), whose can vary in mole fraction depending on the different NG sources. Several devices were employed in order to collect gaseous emissions and PSDF

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during the whole test cycle, and particulate matter samples for chemico-physical analysis. The engine specifications are reported in the following:

Engine type	In-line 4 cylinders, 2 liter of displacement, Turbo VGT
Diesel/gas injection system	CRBosch/Multipoint LANDI Renzo
After-treatment system	Diesel Oxy Catalyst (DOC) plus Close-coupled Catalyzed Diesel Particulate Filter (CC-CDPF)
Maximum Power	113 kW @ 4000 rpm

The counting and sizing of particles were performed by means of a differential mobility spectrometer (Cambustion DMS 500). The exhaust gas for pollutant and particle analysis was sampled at engine outlet downstream of the turbine and 0.5 m downstream the CDPF in order to fully characterize particle numbers and sizes through the whole exhaust system.
The DMS classifies the total PN in nucleation (particles with diameter from about 5 nm to 50 nm) and accumulation (particles with diameter from about 50 nm to 1000 nm) modes.

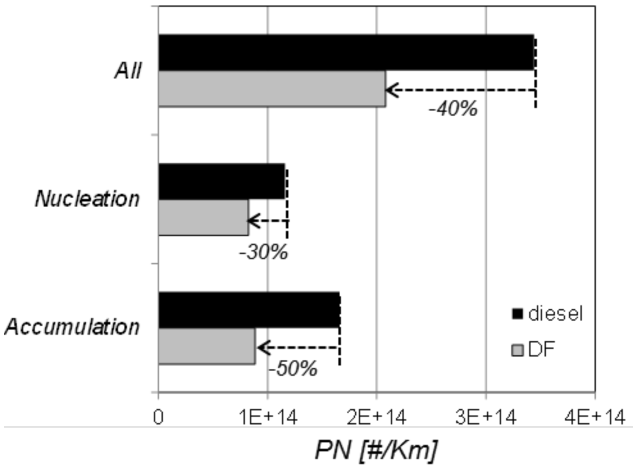

Figure 1. Total, Nucleation and Accumulation Particle Number during the whole test cycle *, for Diesel and Dual Fuel combustion modes.*

A remarkable reduction of total engine out PN emission was accounted moving from D to DF mode (Figure 1). The main reduction regarded the accumulation mode particles, but a significant reduction is evident also in terms of smaller particles (nucleation mode). This is a very interesting aspect of DF application, not only in terms of reduced workload for the DPF system but also taking into account the growing concern on nanoparticles emissions from internal combustion engines in the urban area, both from an environmental and health points of view. Downstream the CDPF, the PN measures were always at the limit of threshold detection of the measurement chain, so any significant comparison was possible between the two combustion configurations.
Total particulate was collected at the engine tailpipe by isokinetic sampling (30–60 min, depending on the fuels and engine operating conditions). The solid particulate, collected on a Teflon filter keep heated at 100 °C, was extracted with dichloromethane (DCM) in order to remove condensable species and fuel residuals. The carbonaceous solid after DCM extraction (soot) was dried and characterized by different analytical techniques.

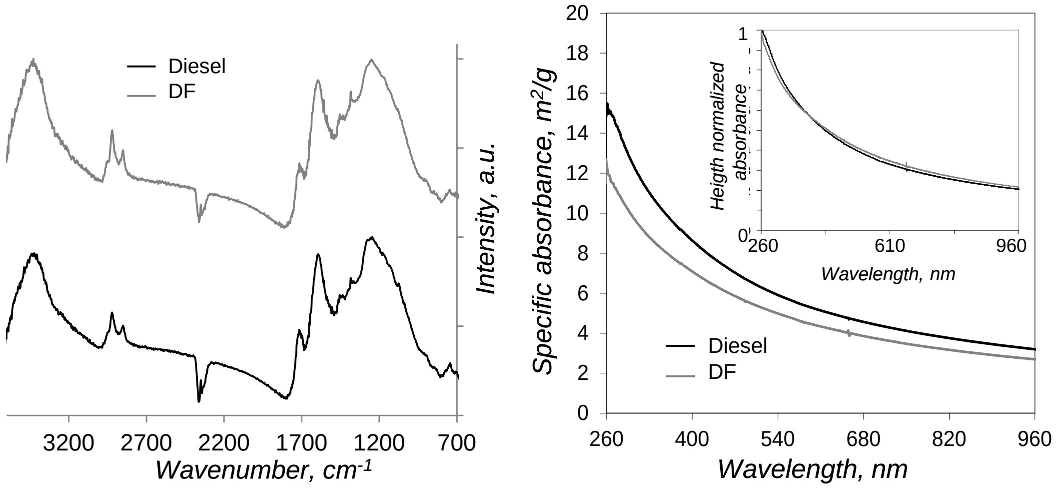

Fig. 2. Left panel: FTIR spectra of diesel soot and dual-fuel NG-diesel soot; right panel: UV-Vis spectra of diesel soot and dual-fuel NG-diesel soot.

The FTIR spectra, acquired in the transmittance mode on solid samples in KBr pellets (Figure 2, left panel) are baseline corrected, height normalized and shifted for clarity. The shape of both FTIR spectra is representative of the presence of complex carbonaceous networks [8]. In both the FTIR spectra the signals were mainly located in four regions: a region between 3100 and 3600 cm^{-1} containing signals of exchangeable protons from alcohol, phenol, carboxylic acid groups and adsorbed water, a region between 2850 and 3050 cm^{-1} containing signals due to the stretchings of aromatic and aliphatic C-H groups, mainly $-CH_2-$, (attributable to residuals of unburned or partially burned fuel), a region between 1800 and 900 cm^{-1} containing overlapped signals of stretching and bending absorptions of many different functional groups (C=O of carbonylic and carboxylic groups, C-OH, C-H, C=C, C-C) and a region between 900 and 700 cm^{-1} containing bending absorptions of "out of plane" aromatic C-H groups [8,9]. No significative differences were observed by comparing the shape and the relative intensities of the signals of both soot samples, indicating that the surface chemistry of the soot particles is not influenced by the dual fuel configuration. This result agrees with previous studies on the effect on soot structure related to ethanol fumigation [10].

Dynamic Light Scattering (DLS) measurements, performed in N-methyl pyrrolidone (NMP) suspension, allowed the estimation of the hydrodynamic diameter of the soot particles. The evaluation of this parameter is of keen interest since the particles dimensions, together with the surface chemistry characteristics, are strictly connected to the penetration degree into the human respiratory apparatus and subsequent channeling by biological fluids after sticking on the respiratory apparatus mucosa. The mean hydrodynamic diameter of soot isolated from engine operated in diesel mode was 121.3 nm while that of soot isolated from engine operated in dual fuel configuration is larger (138.7 nm). This trend on hydrodynamic diameter agreed with previous work on the soot collected from an engine operated in dual fuel configuration with ethanol [10]. The analyzed soots appeared quite monodispersed, being the polydispersity index lower than 0.1.

The UV-Vis spectra of both soot samples in NMP suspension are reported in Figure 2 (right panel). Specific absorbance is expressed on a mass basis (m^2/g). As typical of carbonaceous materials produced in combustion environment [8], a broad shape extending in the visible region ascribable to a large condensation degree of the aromatic moieties was found for both soot samples investigated in this work. The specific absorption (sensitive to the sp^2/sp^3 ratio) of the dual-fuel soot, both in the UV (300 nm) and in the visible (500 nm) regions, is slightly lower compared to diesel soot (Figure 2 right panel). This finding indicates a possible influence of the methane in the soot formation process [11]. It is worth to note that overall both

soot samples exhibited specific absorptions higher than those of carbons with a high graphitization degree and a good level of structuration (furnace carbon blacks, mature soot from benzene laminar flame [8]). Despite the differences between the specific absorptions, the shape of the spectra appears quite similar (height normalized spectra Figure 2, right, inset), thus indicating no detectable variation in the graphitic arrangement of the particles.
Soot reactivity was evaluated by thermogravimetric analysis (TGA) in oxidative environment (air). Soot oxidation took place in the 500-550 °C range for both soot samples and it occurred in a temperature range typical of diesel soot oxidation [10] but at a lower temperature with respect to standard carbon black (690 °C) [8]. A progressive weight decreasing up to 10-20% ascribable to the loss of oxygen functional groups and/or physisorbed molecules strongly adsorbed on soot surface and not completely removed by the DCM extraction was detected before the complete oxidation of the soot. A very low amount of ashes was detected (between 2-4 wt%) for both soot samples and ascribable to engine wear. Overall the TG profiles and the bulk oxidation temperatures are comparable (577 °C for pure diesel soot and 588 °C for methane DF soot) indicating that the DF configuration did not significantly affected the soot combustion behavior.
In conclusion this study outlined a sort of uninfluenced of the CH_4 on the reactivity of collected soot and a relevant impact of CH_4 on PM and PSDF reduction in the test cycle but not on the average size. The results here disclosed appear very interesting in view of the coupling a DF NG–diesel engine with the currently in-use DPF, with the benefits on management and durability of the DPF thanks to a lower regeneration frequency due to the soot emission lower levels expected from the use of the DF engine.

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