In the field of second generation biofuels, ethanol is receiving a growing attention as a valid alternative to conventional fuels in internal combustion engines thanks to its storage facility, availability and handling. The most common use of ethanol is for gasoline engine applications, but the interest in burning ethanol in diesel engine is increasing [1]. Several methods and systems have been examined in order to evaluate the applicability of ethanol in compression ignition engines, including dual fuel (DF) injection. In DF configuration, the port fuel injection (fumigation) of ethanol is coupled with the direct injection of the conventional diesel fuel [2]. Besides the well-known effects of DF ethanol-diesel system on regulated engine raw pollutant emissions (HCs, CO, NO\textsubscript{x} and PM), ethanol fumigation is very effective also in the reduction of the number of the emitted particles. This study address the impact of the dual-fuel ethanol-diesel combustion system on size, number, nanostructure, reactivity and chemical features of the emitted carbonaceous particles [3]. These aspects are relevant on the design and management of the engine-DPF system of a potential DF ethanol-diesel engine.

**Experimental section**

*Testing methodology*. The tests were conducted on a single cylinder research engine provided with a modern architecture and properly modified in a DF configuration [2,3]. The selected test points, critical in terms of soot emissions, were representative of the medium speed (2000 rpm) and medium/high load (7-12 bar IMEP) operating conditions and are significant in the typical operation area of the automotive diesel engines performing the New European Driving Cycle (NEDC). The selected test points were performed using engine calibration parameters (injection, boost, swirl, etc.) and exhaust recirculation gases (EGR) values derived from the real Euro 5 compliant four-cylinder engine of equal unit displacement. Table 1 reports the operating conditions applied.
Table 1. Test points.

<table>
<thead>
<tr>
<th>Test points</th>
<th>RPM</th>
<th>IMEP</th>
<th>BMEP</th>
<th>Rail pressure</th>
<th>EGR</th>
<th>EtOH mass</th>
<th>Equiv. ratio</th>
<th>Total fuel mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000x5</td>
<td>2000</td>
<td>2000</td>
<td>7</td>
<td>5</td>
<td>28</td>
<td>0-17-30</td>
<td>0.69 -0.67-0.66</td>
<td>1.13-1.20-1.28</td>
</tr>
<tr>
<td>2000x10</td>
<td>2000</td>
<td>12</td>
<td>10</td>
<td>1230</td>
<td>18.5</td>
<td>0-20-34</td>
<td>0.73-0.71-0.69</td>
<td>1.85-1.96-2.07</td>
</tr>
</tbody>
</table>

Soot sampling and pre-treatment. Total particulate was collected from the exhaust pipe by isokinetic sampling for 30–60 min on a Teflon filter (pore diameter 0.45 μm) heated at 100 °C. The solid particulate collected on the filter was washed with dichloromethane (DCM) to remove condensable species and fuel residuals (soluble organic fraction, SOF). The carbonaceous solid after DCM extraction (soot) was dried, weighted and characterized. Soot spectral features were evaluated in N-methyl pyrrolidinone (NMP) suspensions.

Results and discussion

Combustion analysis. Figure 1 shows the effect on pressure and rate of the apparent heat release (RoHR) evolutions when different ethanol percentages are used for both the engine operating points.

In both cases, independently of the fuel quantity injected with the pilot injection [2], the start of the pilot combustion shows a delay when employing ethanol. This is explainable by the lower in-cylinder charge reactivity [2,3]. It is well assessed that the main factors that affect the charge reactivity (longer ignition delay) are: i) the lower compression temperature due to the cooling effect of the ethanol vaporization in the intake runner; ii) the dilution effect of premixed ethanol that reduce the oxygen concentration in the diesel pilot ignition zone [1,4,5]. As a consequence, at 2000x5, moving to the DF mode, the longer ignition delay shifts the main combustion phase to more premixed conditions. At 2000x10, part of premixed ethanol burns after the diesel pilot combustion as clearly shown by the increase of the RoHR traces during the dwell time (Fig. 1). This produces an
increment of the bulk temperature in the combustion chamber which consequently reduces the ignition delay of the main injected fuel. 

In Table 2 the specific emissions in both operating conditions are reported.

**Table 2.** Specific emission and global efficiencies at 2000 rpm and 5, 10 bar of BMEP for three different ethanol percentages.

<table>
<thead>
<tr>
<th>EtOH mass [%]</th>
<th>CO [g/kWh]</th>
<th>HC [g/kWh]</th>
<th>NOx [g/kWh]</th>
<th>PM [g/kWh]</th>
<th>Fuel efficiency [%]</th>
<th>SOF [%]</th>
<th>Soot [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000x5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2.1</td>
<td>0.3</td>
<td>0.72</td>
<td>0.15</td>
<td>42.2</td>
<td>18.8</td>
<td>81.2</td>
</tr>
<tr>
<td>17</td>
<td>4.4</td>
<td>2.0</td>
<td>0.77</td>
<td>0.10</td>
<td>41.6</td>
<td>29.1</td>
<td>70.9</td>
</tr>
<tr>
<td>30</td>
<td>6.4</td>
<td>3.4</td>
<td>0.60</td>
<td>0.07</td>
<td>41.5</td>
<td>34.6</td>
<td>65.4</td>
</tr>
<tr>
<td>2000x10</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.8</td>
<td>0.3</td>
<td>1.5</td>
<td>0.08</td>
<td>43.4</td>
<td>20.0</td>
<td>80.0</td>
</tr>
<tr>
<td>20</td>
<td>4.4</td>
<td>1.0</td>
<td>1.9</td>
<td>0.04</td>
<td>44.3</td>
<td>13.2</td>
<td>86.8</td>
</tr>
<tr>
<td>34</td>
<td>7.8</td>
<td>1.5</td>
<td>1.8</td>
<td>0.02</td>
<td>44.4</td>
<td>16.5</td>
<td>83.5</td>
</tr>
</tbody>
</table>

The emissions trends versus ethanol substitution rates are in line with previous results on the same engine configuration and with those reported in literature [2,5,6]. HC and CO emissions sharply rise with ethanol addition mainly due to the low fuel oxidation rate in the squish volume of the combustion chamber, while NO\textsubscript{x} emissions are mainly controlled by the EGR. The main NO\textsubscript{x} controller at 2000x5 remains the EGR. At 2000x10 the higher NO\textsubscript{x} value is confirmed since the shift of combustion to more premixed conditions is prevalent on the EGR effect. 

As expected, great advantages on the PM suppression are evidenced in both cases. The PM reduction is strictly related to the reduced quantity of direct injected diesel, which burns in diffusion mode, and to the lower local equivalence ratios (fuel/air) in the combustion chamber [2,3,7]. Particle size distribution function (PSDF) profiles are shown in Fig. 2 in the 10-500 nm range.

**Figure 2.** PSDF profiles in the 10-500 nm range.

In line with PM mass measurements, the PSDF profiles show that, independently of the speed and load, the ethanol addition contributes to the reduction of the number of emitted particles. The lower particulate emissions compared to diesel
mode are due to [4]: i) lower C/H mass ratio of the burning mixture because of the ethanol lower carbon to hydrogen ratio compared to diesel fuel. The lower C/H mass ratio reduces the tendency to form soot precursors under fuel rich combustion conditions; ii) longer ignition delay that involves more diesel fuel burning in the premixed mode; iii) lower diesel fuel combusting in the diffusion mode as part of the fuel is replaced by ethanol.

Soot characterization. Table 2 shows the mass distribution of soluble organic fraction (SOF) and non-volatile fraction (soot) collected on the filter. At the high engine load the SOF keeps quite constant than those at the low engine load. At the low engine load, the percentage of SOF is higher and increases with the increase of injected ethanol. This trend is attributed to the cooling effect of ethanol that lower the combustion pressure and temperature in the combustion chamber, leading to more unburned hydrocarbons [3].

Figure 3 reports TEM images of the soot particles emitted DF mode at high ethanol level. Images of soot emitted in diesel mode are also given for comparison. Soot consists of irregularly shaped compact aggregates with a secondary structure consisting of almost spherical primary particles (15-20 nm). The primary particles dimensions do not vary, even at high ethanol level.

**Figure 3.** TEM images of the soot particles emitted at 2000 rpm and 5 bar (a,c: diesel mode; b,d: DF mode at high ethanol loading) and 10 bar (e,g: diesel mode; f,h: DF mode at high ethanol loading).

TG profiles of soot in an oxidative environment (air) are reported in Fig. 4 (left panel). The TG profiles exhibit a 10-20% weight loss between 150 and 450 °C, ascribable to the loss of oxygen functional groups and/or physisorbed molecules. Soot oxidation takes place in the 500-550 °C range and occurs, in both engine loads, at a lower temperature with respect to standard carbon black (690 °C) and soot formed in flame environment (600-650 °C) [8], clearly indicating a lower thermal stability of the graphitic core. A 9-10 wt. % of ashes for all soot samples
indicates the presence of inorganic impurities that lower the activation energy for soot oxidation. A higher weight loss is observed by increasing the ethanol level and it was attributed to a variation of soot bulk proprieties as a consequence of a slightly increase in the oxygenation degree.

ATR-IR spectra of diesel soot are reported in Fig. 4. The diesel soot spectra at both points exhibit bands due to the vibrations of oxygen functional groups (1650-1750 cm\(^{-1}\), C=O stretching vibrations from carbonyl and carboxylic groups) and graphitic domains (1500-1600 cm\(^{-1}\), skeletal vibration of the \(\text{sp}^2\) moieties). The broad band in the 1300-1100 cm\(^{-1}\) region is ascribable to the overlapping of C-OH and C-O stretching vibrations [9]. Weak and broad signals in the 2950-2850 cm\(^{-1}\) region, attributable to aliphatic groups (mainly methylene) are also detected, probably residuals of unburned or partially burned fuel. Bands of oxygen functional groups (1650-1750 cm\(^{-1}\)) are present even in the case of engine burning pure diesel.

Height normalized UV-Vis spectra of soot [3] indicate the presence of highly conjugated systems as detected for complex carbon-based materials produced in combustion processes [8]. The spectra appear quite similar, again confirming the previous findings. The specific soot absorption (sensitive to the \(\text{sp}^2/\text{sp}^3\) ratio) of diesel soot are comparable, both in the UV (300 nm) and in the visible region (500 nm), to those of carbons with a high graphitization degree and a good level of structuration (furnace carbon blacks, mature soot from benzene laminar flame [8]).
The specific absorption progressively decreases with the ethanol level increase, in both the operating conditions. This indicates a decrease of sp²/sp³ ratio (i.e. a lower graphitization and aromaticity degree) and it is consistent with the decrease of the temperature of soot oxidation.

**Conclusion**
The chemico-physical characterization of soot particles clearly indicates that soot features, including the oxygen incorporation and nanostructure, slightly vary with the increasing amount of injected ethanol, even at high ethanol loading. The results on the soot oxidation stability, confirmed by the soot specific absorption analysis, appear very interesting in view of the coupling a potential DF ethanol-diesel engine with the particulate diesel filter (DPF).

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**References**

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