Sooting Behavior of Oxygenated Fuels in a Diffusion Burner

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Abstract
Different strategies are being investigated towards reducing engine-out emission levels of soot and NOx of modern Diesel engines. A fuel-based strategy currently under investigation, entails the use of low cetane number (CN; i.e. low reactive) oxygenates. Previous research has shown that low CN oxygenates (e.g. cyclohexanone, X1), compared to their higher CN counterparts, perform exceptionally well with respect to abating soot emissions. An accepted mechanism, which could account for the observed reduction, is associated with the ignition delay (ID). As the ID effect does not apply to burners, experiments with various oxygenated blends over a wide range of CN’s in a yellow (diffusion) flame burner have been conducted to establish whether or not this is the only mechanism responsible for the measured soot reduction. From the experiments can be observed that emitted soot mass is closely correlated to CN in burners as well. Accordingly, the results suggest that another mechanism is, at least partially, responsible for the observed reduction in emitted soot mass.

Introduction
The drive for increasingly lower regulated emissions (CO, UHC, NO\textsubscript{x}, and soot) will result in the implementation of powerful catalytic aftertreatment technology on next generation Diesel engines. At the same time reducing engine-out emission levels is still a major development effort as this will relax the requirements on the aftertreatment system and at the same time could result in a larger overall cost-of-ownership (in particular fuel and eventual additive consumption).

Of the different paths towards reducing engine-out emission levels, fuel-based strategies are among the promising. For more than hundred years, engines have been optimized to cope with the available fossil-based fuels. When looking at fuel-based strategies, the engine is taken as a given, and fuels are designed which have optimal properties for the prevailing combustion process. An important enabler for such tailored fuels in the future will be the development of synthetic fuels (XTL = ‘anything to liquid’). Basically, XTL entails the gasification of an arbitrary, preferably renewable, source of hydrocarbons to a desired liquid fuel via specialized catalytic routes. This opens the possibility to produce a dedicated fuel, tailored specifically for the conventional combustion engines.

In this paper a brief recapitulation of previous work on such a tailored fuel is given. From this summary it will become clear that some questions still remain open. The burner setup which is used to shed some light on these questions will be presented and a discussion on experimental results and final conclusions will follow.

Background
Previous work [1-3,6] by some of the authors has demonstrated that it is possible to achieve near-zero soot and NOx emissions in modern diesel engines with cyclic oxygenated fuels (e.g. cyclohexanone, X1). Several questions, however, have remained unanswered thus far. A brief overview is presented below.

A first study on X1 was published in [1]. This paper reports on the combustion properties of a large number of blends of different types of oxygenates with a low-sulfur EN-590 type diesel fuel, a Swedish Class 1 fuel and a synthetic diesel, respectively. Oxygen mass fraction of the blends varied between 0 and 15 \%. Tests were performed on a modern multi-cylinder heavy-duty DAF engine equipped with cooled exhaust gas recirculation (EGR) for enabling NO\textsubscript{x}-levels between 2.0 and 3.5 g/kWh on EN-590 diesel fuel.

![Figure 1: Percentage of soot reduction versus fuel oxygen wt-%](image-url)

Figure 1: Percentage of soot reduction versus fuel oxygen wt-%, collected from numerous experiments reported in the literature and compared to the results of the present study [1].

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The results (Figure 1) confirmed the importance of oxygen weight fraction in the fuel blend, but at the same time illustrate the effect of chemical structure. At an equal oxygen content, some oxygenates (X1) are twice as effective in reducing soot as other well-known oxygenates (dibutyl maleate (DB) and tripropylene glycol monomethyl ether (TP)).

It became clear that X1 had excellent combustion properties. The mechanism responsible for the observed soot reduction, however, was not yet understood. High-speed imaging, spectroscopy and thermodynamical characterization were therefore applied to an optically accessible, heavy-duty diesel engine in order to compare sooting and chemiluminescence behavior of various oxygenated fuels [2].

The start of hot combustion was derived from OH* and CH* chemiluminescence, as observed through a spectrograph that was used to separate the molecular signals from thermal soot radiation. Both species occur at about the same time, CH* signal being weaker. Soot incandescence was observed two-dimensionally at 0.3 crank angle resolution (200 images/cycle). Ignition delays, derived from soot incandescence and chemiluminescence, were compared to those determined from heat release. In line with earlier work [1] large differences in sooting behavior were observed between oxygenated fuels at an equal fuel oxygen content [2], see figure 2.

The heat release rate and exhaust NO concentrations were used as indicators of average and peak temperatures, respectively. Both the fuel molecular structure and its oxygen content were reported to be important for soot abatement, a low reactive cyclic structure having the most significant effect.

Another conclusion drawn from the optical experiments was that the cyclic molecule X1 had a considerably longer ignition delay (ID), related to its relatively low cetane number (CN, measure for reactivity) of ~10. It is well known from literature that longer ID’s tend to have a favorable effect on soot emissions. Accordingly, it was decided to re-examine data from [1] to establish whether or not a correlation could be found between the soot emissions and ID.

The results, reported in [3] indicate that the low CN (via ID) may indeed play an important role with respect to soot suppression. More specifically, the low reactive oxygenate X1, with its cyclic carbon chain, was found to perform exceptionally well compared to the more reactive linear and branched oxygenates DB and TP (Figure 3).

Figure 2: Six consecutive (inversed) frames of a high-speed video recording of soot luminosity of TP (left) and X1 (right) blends at 9 wt-% fuel oxygen [2]. The dark areas correspond to clusters of radiating soot.

Figure 3: Smoke opacity (solid lines: FSN, measure for soot) and NOx (dashed lines) versus ID for 9 wt-% fuel oxygen blends of X1, DB and TP at three different EGR levels (i.e. from left to right: 0, 15 and 25 wt-%) [3].

Specific Objectives

To verify whether or not ignition delay is the dominant factor in the above par soot reduction potential of low CN X1 blends, it was decided to perform a series of experiments on stationary burners with various fuels, having a wide range in CN. Contrary to the situation in engines, fuels burnt in stationary burners do not incur an ID. Accordingly, the presence of a correlation between CN and soot would suggest a different, hitherto unknown, mechanism is at work.
Figure 4: Schematic drawing of the test setup.

**Fuel Matrix**

The base fuel (D) used for the blends is a commercially available low sulphur fuel oil with a sulphur content of 9 ppm. This base fuel oil is blended with oxygenates up to an oxygen concentration of 9 wt % in the blend. As oxygenates different types of compounds are used: an alcohol (hexanole (HX)), a cyclic ketone (X1) and an ether (Tri Propylene Glycol Methyl Ether (TP)), see Table 1. As a result a matrix with a range of functional oxygen groups and CN is formed (Table 2).

Table 1: Properties of neat compounds

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>X1</th>
<th>HX</th>
<th>TP</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>0.95</td>
<td>0.81</td>
<td>0.97</td>
<td>0.84</td>
</tr>
<tr>
<td>Molar mass</td>
<td>g/mol</td>
<td>98</td>
<td>102</td>
<td>206</td>
<td>-</td>
</tr>
<tr>
<td>CN</td>
<td></td>
<td>10</td>
<td>23</td>
<td>65</td>
<td>50</td>
</tr>
<tr>
<td>Oxygen wt-%</td>
<td></td>
<td>16</td>
<td>16</td>
<td>31</td>
<td>-</td>
</tr>
<tr>
<td>Functional oxygen group</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Knowing the properties of the pure species, it is assumed that the blend CN (Table 2) can be roughly estimated using the Kay mixing rule [3, 4]:

\[
CN = \sum_{i} x_{i} CN_{i},
\]

wherein \(x_{i}\) and \(CN_{i}\) denote the mole fraction and CN of species \(i\) respectively.

Table 2: Properties of tested blends. Note the fractions refer to the oxygenate content in the blend.

<table>
<thead>
<tr>
<th>Blend property</th>
<th>D-X1-9</th>
<th>D-HX-9</th>
<th>D-TP-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. fraction</td>
<td>0.52</td>
<td>0.58</td>
<td>0.24</td>
</tr>
<tr>
<td>Mass fraction</td>
<td>0.55</td>
<td>0.57</td>
<td>0.27</td>
</tr>
<tr>
<td>Molar fraction</td>
<td>0.70</td>
<td>0.71</td>
<td>0.25</td>
</tr>
<tr>
<td>CN</td>
<td>21</td>
<td>31</td>
<td>54</td>
</tr>
</tbody>
</table>

**Experimental Setup**

The combustion of the oxygenated blend fuels is accomplished in a yellow flame burner in stationary mode at its nominal heat input of 18 kW, mounted on a low temperature boiler providing an exhaust gas temperature of 130 °C. In their standard configuration with an equivalence ratio of about \(\phi = 0.83\) the soot number measured in accordance with the German standard DIN 51402, part 1, reaches values between 0 and 1 (on a scale from 0 to 10). In order to see an effect as large as possible comparing the soot
emissions of standard and oxygenated fuels, the equivalence ratio of the burner is adjusted to $\phi = 0.96$, which rises the soot number of the exhaust gas to values between 3 and 4.

Previous to each test run the burner and the boiler are checked for soot deposits and cleaned if necessary. After each test with one of the oxygenated fuels a run with pure fuel oil is done to check and, if necessary, adjust the settings of the yellow flame burner.

The determination of the total suspended particles (TSP) is executed by differential weighing of filter membranes before and after exposure to the soot-loaded exhaust gas, following the European standard EN 13284-1 (April 2002).

The pressure loss due to the filter is compensated by an additional fan placed between the filter and the burner. Due to the compression heat of the fan the intake air is heated up to about 30 °C.

In the chimney there are sensors for pressure and temperature of the exhaust gas as well as a sampling point feeding the gas analysis system. A partial flow of the exhaust gas is extracted iso-kinetically by the probe head and lead through the measurement filter. The filter housing is heated to the temperature of the exhaust gas in order to avoid condensation of vapor components on the filter. The design of the probe head and the filter housing is according to the requirements of the VDI (Verein Deutscher Ingenieure) directive 2066, part 7.

Because the rotary vane pump and the gas meter are not resistant to corrosion due to humidity and aggressive gas components, the exhaust gas is cooled, scrubbed and dried downstream of the filter. The adjustment of the partial gas flow in order to ensure iso-kinetic extraction is done by a choke valve just before the pump. The determination of the exhaust gas flow rate at the probe head is done by calculating the flow rate from the heat input and the equivalence ratio. The fuel-related data necessary for this calculation, such as the specific exhaust gas flow etc., are determined by an elementary analysis of the fuel. For the present setup this method has proven more accurate than direct measurement of the exhaust gas flow rate (due to the high turbulence of the gas flow which complicates measurement using a Prandtl-probe).

Filtration of the particles from the partial gas flow takes place by a Teflon-coated borosilicate fibre membrane with a filtration efficiency of DOP 0.3 µm = 96.4 % according to ASTM D 2986-95A and a temperature resistance up to 315 °C. According to the requirements of EN 13284-1 (April 2002) the filter membranes are dried at a temperature of 180 °C for 1 hour and equilibrated several hours in an exsiccator before the initial weighing. In the time between the initial weighing and the application in the filter housing the membranes are stored in the exsiccator (i.e. dryer).

Directly after removal from their housing, the loaded filters are dried for 1 h at a temperature of 160 °C and subsequently equilibrated inside the exsiccator. Each weighing of the loaded membranes is executed at least twice with an additional drying cycle between the weighings. This procedure is repeated until two subsequent weighings give identical results in order to ensure a complete evaporation of volatile components and a good repeatability of the measurement.

It should be noted that atmospheric conditions are considered here, rather than the typical high pressure environment that prevails in the combustion chamber of an engine. It is assumed, however, that pressure has only a modest effect on the diffusion flame.

### Experimental Results

In Figure 5, the results of the measurements with the oxygenated fuels related to the tests with the pure fuel oil are shown. For comparison of the results the particle mass on the filters is related to the heat input of the fuel and given in mg/MJ. Each of the tests is conducted with a duration of half an hour, the test settings are mentioned in the previous section. In order to get at least a minimum of statistics and estimate the repeatability of the results, each test is carried out between two and five times.

The tests with D-TP-9 show nearly identical results to D without improvement of particulate matter emissions. The filters are as black as with pure fuel oil. The weighing confirms the optical impression. In contrast to the test with D-TP-9 there is an improvement using D-HX-9. The particle emissions decrease obviously, the filters are coloured dark grey. The mean of the three tests is 0.10 mg/MJ.

In the last test with this blend two problems occurred: the sealing of the filter holder broke and the oil nozzle changed its behaviour. The damages on the oil nozzle could not be identified by inspection using a microscope, but the emissions with pure fuel oil increased severely and the burner could no longer be adjusted to the previous settings. The damaged components were replaced with new ones and the burner settings adjusted to the standard (see previous section).

The best results concerning the particle emissions are achieved with D-X1-9, the value is 0.03 mg/MJ and the filters are light grey. But with this fuel similar problems occurred as with D-HX-9, i.e. the oil nozzle broke and a leakage at the sealing of the oil pump occurred.
Figure 5: Averaged test results with the oxygenated fuels compared to pure fuel oil. Test duration is half an hour, equivalence ratio $\phi = 0.96$. The error bars display the total range of the individual measurements. Featured above each fuel is a photograph of the collected filter sample.

**Discussion**

As stipulated earlier, the specific objective of this work is to verify whether the ID is the dominant factor with respect to the above par soot reduction potential of the low CN X1 blends reported in earlier work [1-3]. According to this theory, oxygenates with a different CN but equal oxygen wt-% should yield similar soot emissions. Soot, after all, is largely a function of the incurred ignition delay, which is not applicable for stationary diffusion burners for long periods (e.g. 30 minutes).

When comparing the various oxygenated fuels it is evident from the results that there are, however, still clear distinctions in soot tendency, the absence of an ID notwithstanding. Moreover, as was the case in the engine experiments, the soot emissions now correlate with blend CN as well (Figure 6). More specifically, the soot emissions are seen to decrease sharply with decreasing CN or fuel reactivity.

Another striking observation is the more or less equal performance of the D-TP-9 blend and the diesel base fuel (D). Although both have a similar CN, one would expect the presence of 9 wt-% fuel oxygen in the former blend would have a positive effect on soot, as is the case in most engine experiments cited in literature (Figure 1). Apparently, at least in a stationary burner, the CN is of more significance with respect to soot than the available fuel oxygen. Bearing in mind the insignificance of the ID effect, the mechanism of the soot reduction observed in Figure 6 is not straightforward.

Some insight into the influence of fuel CN on soot formation in diffusion flames is provided by Pickett and Siebers [5]. In their experiments, the soot formation process was observed in an optically accessible constant volume combustion chamber via laser extinction and planar laser-induced incandescence. By studying a quasi-steady fuel jet, as is the case in the diffusion burner, the beneficial impact of
a long ID is no longer relevant. Nevertheless, a correlation between the fuel CN and sooting tendency was found. In general, in line with the data in Figure 6, lower CN fuels produced less soot. The authors attributed this trend to the apparent relation between fuel reactivity (e.g., CN) and flame-lift-off-length (FLOL). According to the authors, a longer FLOL will yield a more favorable equivalence ratio in the soot synthesis zone, which lies downstream of the FLOL. Lower CN fuels yield longer FLOL, which in turn manifests itself in less soot being produced. An investigation into the relation between CN and FLOL in engines is currently subject of research by some of the authors.

Conclusions
Based on the experimental data the following conclusions are drawn:

• The Cetane Number (CN) of oxygenated blends plays an important role in the emitted soot mass in stationary diffusion burners.
• Given an equal CN, the presence of fuel oxygen does not appear to have the same positive effect on soot as is commonly experienced in engines [1-3].
• A clear correlation between soot and blend CN is observed, regardless of the presence of different functional oxygen groups (e.g. ether, ketone and alcohol).
• There are indications from literature that low CN may have a beneficial impact on soot in diffusion flames, via an elongation of the flame lift-off length (FLOL). Accordingly, more air is entrained upstream of the soot synthesis zone.
• This, together with the observations reported in the present work, would explain the results of engine experiments [1-3] where, for the same ignition delay (ID), low CN oxygenated fuels showed lower soot levels than oxygenates with similar oxygen mass fraction but higher CN.

References