Cyclic Oxygenates: A New Class of Clean Second Generation Biofuels?

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ABSTRACT: Combustion behaviour of various oxygenated fuels has been studied in a DAF heavy-duty diesel engine. From oxygenates is well known that fuel-bonded oxygen leads to lower particle (PM) emissions. It is evident that, for a given fuel oxygen mass fraction, there are significant differences in PM reduction. Although this can be traced back to the specific molecular structure of the oxygenate in question, no consensus can be found in the literature as to the explanation hereof. In this study, the sooting tendency (e.g. smoke number) of three oxygenates (e.g. tripropylene glycol methyl ether (TP), dibutyl maleate (DB) and cyclohexanone (X1)) was compared to that of commercial diesel fuel (EN590, D).

The results suggest that the Cetane Number (CN) (i.e. fuel reactivity) may play a role. 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 respectively. Cyclic oxygenates are abundant in nature. Cellulose, the most common organic compound on earth, is the best-known example. Although it is not trivial, liquid cyclic oxygenates can be made from lignocellulosic biomass. Particularly the production of X1 from the phenol-like lignin molecules is subject of current investigation. Fuels produced from such biomass (e.g. plant waste or non-edible part of plants) are referred to as second generation biofuels.

**Background**

Problem Statement

Soot emissions decrease with fuel oxygen %

Performance is influenced by oxygenate structure

**Research Goal**

Investigate how oxygenate molecular structure impacts soot emissions

What structure is (most) beneficial for oxygenate soot performance?

Why is this the case?

**Approach**

Phase 1: Investigate the soot performance of 11 conventional (e.g. non-cyclic) oxygenates in a heavy-duty diesel engine

Phase 2: Compare soot performance of best performing non-cyclic oxygenates to that of a cyclic oxygenate

Phase 3: Perform a second series of measurements in an optically accessible test engine (not discussed here)

Phase 4: Investigate viable pathways to produce cyclic oxygenates

**Experimental Setup**

engine specifications

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bore/Stroke (mm)</td>
<td>119/140</td>
</tr>
<tr>
<td>No. of cylinders</td>
<td>6</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>15:1 (nom.)</td>
</tr>
<tr>
<td>PIS type</td>
<td>PDI-Fortune Line nozzle</td>
</tr>
<tr>
<td>Turbomachinery</td>
<td>Fixed geometry</td>
</tr>
<tr>
<td>Charge cooling</td>
<td>air-to-air</td>
</tr>
<tr>
<td>Max. power</td>
<td>276 kW at 2,150 rpm</td>
</tr>
<tr>
<td>Max. torque</td>
<td>1,289 Nm at 1,800 rpm</td>
</tr>
</tbody>
</table>

**Fuel Matrix**

Phase 2: selected oxygenates

<table>
<thead>
<tr>
<th>Oxygenate</th>
<th>Chemical Structure</th>
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</thead>
<tbody>
<tr>
<td>Tripropylene glycol monomethyl ether (TP)</td>
<td></td>
</tr>
<tr>
<td>Dibutyl maleate (DB)</td>
<td></td>
</tr>
<tr>
<td>Cyclohexanone (X1)</td>
<td></td>
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</tbody>
</table>

All oxygenates were blended with commercially available diesel fuel (e.g. Swedish Class 1 (SW1) or EN590 (D)). Blend oxygen content was always 9 wt-%: SW1-TP-9 (CN = 54) SW1-DB-9 (CN = 46) D-X1-9 (CN = 33)

**Results**

NOx/soot-trend vs. EGR level and oxygenate type

Workpoint 1650 rpm @ 463 Nm Start of injection 13 CAs/TDC

**Discussion**

Influence of EGR-level and blend CN

**Discussion**

Comparison to literature data

**Potential 2nd Gen. Biofeedstock**

for cyclic oxygenates

**Conclusions**

Differentiation in oxygenate performance increases significantly as more EGR is applied

At high EGR levels, soot emissions are seen to drop more or less linearly with decreasing CN

An explanation for the improved soot performance is that longer ignition delays intrinsic to low CN fuels, result in a higher degree of premixing of fuel and air and consequently in lower soot emissions

One low CN (cyclic) oxygenate (X1) performed exceptionally well X1 can be produced from second generation biomass