

# Cyclic Oxygenates: A New Class of Second-Generation Biofuels for Diesel Engines?<sup>†</sup>

Michael Boot,<sup>\*,‡</sup> Peter Frijters,<sup>‡</sup> Carlo Luijten,<sup>‡</sup> Bart Somers,<sup>‡</sup> Rik Baert,<sup>‡,§</sup>  
Arjan Donkerbroek,<sup>||</sup> Robert J. H. Klein-Douwel,<sup>||</sup> and Nico Dam<sup>||</sup>

*Department of Mechanical Engineering, Eindhoven University of Technology, Post Office Box 513, 5600 MB Eindhoven, The Netherlands, TNO Automotive, Delft, The Netherlands, and Applied Molecular Physics, Institute for Molecules and Materials, Radboud University Nijmegen, Nijmegen, The Netherlands*

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Combustion behavior of various oxygenated fuels has been studied in a DAF heavy-duty (HD) direct-injection (DI) diesel engine. From these fuels, it is well-known that they lead to lower particle (PM) emissions; however, 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 (smoke number) of three oxygenates [viz., 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 an important 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 C<sub>6</sub> oxygenates (e.g., guaiacol, cyclohexanone, phenol, etc.), which can be derived from lignin, is the subject of current investigation. Fuels produced from such biomass (e.g., plant waste or the nonedible part of plants) are referred to as second-generation biofuels and are expected to play a pivotal role in the near future.

## Introduction

For the heavy-duty (HD) diesel industry, it is very difficult to keep up fuel economy while still complying with legislated soot (PM) and nitric oxide (NO<sub>x</sub>) targets. Measures needed to meet future (EPA 10 or EURO 6) emission legislation call for combined measures, such as after treatment (particle filters, deNO<sub>x</sub> catalysts, etc.) and/or exhaust gas recirculation (EGR). Both measures, however, increase pumping losses and therefore lead to lower engine efficiency.

Also, a non-optimal (e.g., retarded) combustion phasing will most likely be needed, which, although favorable to reduce engine-out NO<sub>x</sub> emissions, lowers the thermodynamic efficiency of the engine even further. On the long term (beyond 2015), this methodology will be unfavorable because the industry will face stringent CO<sub>2</sub> legislation as well.

Alternative pathways are still using conventional CI engines but using an oxygenated fuel or even choosing more revolutionary approaches, such as premixed charge compression ignition (PCCI), at modest engine loads. This study will focus on oxygenated fuels used in a conventional HD diesel engine, more specifically, on the impact of oxygenate cetane number (CN) (i.e., reactivity) on the PM performance.

It is the aim of the authors to provide the reader with an overview of the literature that deals with the impact of (oxygenated) fuel reactivity (CN) on the soot formation process. In addition, the authors will present their own work dedicated specifically to this topic.

The dependency of soot formation on CN is important because legislators worldwide are pressing for a minimum CN (i.e., ~50) for biofuels. Although first-generation biofuels (vegetable oils or their esterified counterparts) are generally in compliance with such legislation, second-generation biofuels, produced from lignocellulosic feedstock will most likely fall short of the minimum CN.

The reason why this will be the case becomes clear when one considers the molecular structure of the feedstock. First-generation biofeedstock typically comprises monomers of long-chained molecules, which intrinsically have relatively high CN (i.e., >50). Conversely, molecules that constitute the second-generation biofeedstock are inherently polymers of a cyclic nature.

As will be demonstrated later in the paper, these polymers are built up exclusively from C<sub>4–6</sub> cyclic oxygenates, which are linked together via C–O–C bonds. When the polymer is broken up and treated catalytically, cyclic C<sub>4–6</sub> oxygenates can be produced, which typically have a very low reactivity (CN ~ 5–20). In this study, one such oxygenate, cyclohexanone (X1; CN ~ 10–15), will be compared to conventional (i.e., noncyclic, fossil-based oxygenates) in a 9.2 L DAF HD DI diesel engine

<sup>†</sup> From the Conference on Fuels and Combustion in Engines.

<sup>\*</sup> To whom correspondence should be addressed: Section Combustion Technology, Department of Mechanical Engineering, Eindhoven University of Technology, Post Office Box 513, 5600 MB Eindhoven, The Netherlands. Telephone: +31-40-2475689. E-mail: m.d.boot@tue.nl.

<sup>‡</sup> Eindhoven University of Technology.

<sup>§</sup> TNO Automotive.

<sup>||</sup> Radboud Universiteit Nijmegen.

under various operation conditions. Particularly, the effect of a low CN on smoke opacity and NO<sub>x</sub> emissions is of interest.

### Literature Review: Impact of Cetane Number on Sooting Tendency

There is no consensus in the reviewed literature surrounding the influence of fuel CN on soot emissions. Two trends can be distinguished in the literature: (1) a higher CN leads to less soot,<sup>1–4</sup> and (2) a higher CN leads to more soot.<sup>5–12</sup> To comprehend why two distinct trends are measured, one must discern how the variation in CN was achieved in the experiments. Three main approaches have been identified: (1) variation of aromatic content,<sup>1–5</sup> (2) use of CN boosters,<sup>6–9</sup> and (3) comparison of fuels with equal aromaticity but with a different CN.<sup>10–12</sup>

**Aromatics.** Karonis et al.<sup>1</sup> measured the emitted PM mass from 68 diesel fuels in a single-cylinder diesel engine. The CN range in question was 42–58. The CN correlated well with the aromatic content, with the CN rising as the total aromatic fraction of the fuel decreased. A near linear decrease of PM mass with increasing CN (i.e., decreasing aromatic content) was reported.

Zannis and Hountalas<sup>2</sup> used a single-cylinder Lister LV1 experimental DI diesel engine to compare the smoke opacity of three diesel fuels with a spread in CN from 60 to 64. The variation in CN was attributed to the difference in aromatic content. Smoke opacity was seen to decrease with increasing CN.

Wu et al.<sup>3</sup> added synthetic diesel fuel to commercial diesel fuel at fractions ranging from 0 to 100 vol %. As more purely paraffinic, high CN synthetic fuel was introduced, the aromatic content of the blend decreased, resulting in the gradual rising of the CN from 52 to 75. Smoke opacity, measured from a HD turbocharged DI diesel engine, decreased with increasing CN (i.e., increasing fraction of synthetic fuel).

Bielaczyc et al.<sup>4</sup> tested four specially prepared diesel fuels with varying CN (range of 45–63) in a 2.0 L DI turbocharged common rail diesel engine. The variation in CN is ascribed to the aromatic content. A general trend observed was that the emitted particle mass decreased with increasing CN.

Most authors recognize the conflicting effects that aromatics have on the soot formation process. On the one hand, aromatics are known soot precursors. Moreover, because the formation of the first aromatic ring is generally considered to be the rate-determining step in the formation process, aromatics already present in the fuel have a significant impact on the sooting tendency.

On the other hand, because aromatics are intrinsically relatively inert, the CN of a fuel will decrease with increasing aromatic content. Consequently, longer ignition delays can be expected, and the nonsooting premixed burning period becomes more dominant. Ultimately, however, the former mechanism outweighs the latter, and higher soot emissions are generally observed as the degree of aromaticity is increased.

A notable exception to the trend discussed above can be expected when a high aromaticity coincides with a very low CN. Kalghatgi et al.<sup>5</sup> demonstrated that a DI diesel engine fueled with gasoline (CN ~ 10) can run virtually soot-free in a wide range of operating conditions. The low soot emissions were ascribed to a nearly fully premixed combustion, which was the result of the long incurred ignition delays. It should be noted that low soot was achieved only when the incurred ignition delay was sufficiently long to completely separate the injection and heat-release event. Accordingly, a form of fuel-induced PCCI is realized.

**CN Boosters.** Lü et al.<sup>6</sup> studied the effect of a CN booster on the sooting tendency (i.e., smoke opacity) of fuels tested in a high-speed DI diesel engine. In all cases, an increased CN booster concentration led to an increase in smoke opacity.

Ladommatos et al.<sup>7</sup> investigated the effect of fuel CN improver on diesel pollutant emissions on a single-cylinder ASTM co-operative research engine with IDI. The CN booster was added in various concentrations to a base fuel, resulting in a CN spread from 40 to 62. Increased smoke opacity was observed as more CN booster was added.

In another study by Lü et al.,<sup>8</sup> the effect of the CN improver on the heat-release rate and emissions was investigated on a high-speed DI diesel engine. The CN booster was added to an ethanol–diesel blend at various concentrations. Measured smoke opacity increased as more CN booster was added to the oxygenated blend.

Schultz et al.<sup>9</sup> studied the influence of the CN booster concentration (iso-propylnitrate) on a one-cylinder engine dedicated for CN testing. CN in this study ranged from 50 to 64, and the measured particle mass increased as more CN improver was added.

In all reviewed literature, the use of a CN booster had a negative impact on soot emission, regardless of the engine type, operating conditions, or base fuel specifications. Most authors attribute this result to a reduction in nonsooting premixed burn duration as a result of shorter ignition delays.

**Equal Aromaticity but Different CN.** Apart from varying the aromatic fraction or introducing a CN booster, one can compare the soot performance of fuels with equal aromatic content but with a different CN. For a given class of saturated hydrocarbons (e.g., *n*-, iso-, and cycloparaffins), CN mainly depends upon the carbon number or molecular weight, with heavier molecules having consistently higher CN.

When saturated classes at a given carbon number are compared, the fuel that is the most “compact” will generally have the lowest CN. Accordingly, the CN will decrease in the order *n*- → iso- → cycloparaffin. For example, the CN of a given straight hydrocarbon (*n*-hexane) can be reduced from 42–45 to 23–34 by introducing branching (3-methylpentane) and further down to 13–18 by cyclization (cyclohexane).

Alternatively, one can increase the CN of hexane to 52–56 or 64–65 by elongating the chain with one (*n*-heptane) or two (*n*-octane) carbon atoms, respectively. In all cases, the molecules are not considered soot precursors, but the variation in CN will have a significant effect on the yielded soot emissions.

(1) Karonis, D.; Lois, E.; Stournas, S.; Zannikos, F. *Energy Fuels* **1998**, *12*, 230–238.

(2) Zannis, T.; Hountalas, D. *Energy Fuels* **2004**, *18*, 659–666.

(3) Wu, T.; Huang, Z.; Zhang, W.; Fang, J.; Yin, Q. *Energy Fuels* **2007**, *21*, 1908–1914.

(4) Bielaczyc, P.; Kozak, M.; Merkisz, J. *SAE Tech. Pap. Ser.* **2003**, 2003-01-1882.

(5) Kalghatgi, G.; Risberg, P.; Ångström, H. *SAE Tech. Pap. Ser.* **2006**, 2006-01-3385.

(6) Lü, X.; Yang, J.; Zhang, W.; Zhen, H. *Energy Fuels* **2005**, *19*, 1879–1888.

(7) Ladommatos, N.; Parsi, M.; Knowles, A. *Fuel* **1996**, *75*, 8–14.

(8) Lü, X.; Yang, J.; Zhang, W.; Huang, Z. *Fuel* **2004**, *83*, 2013–2020.

(9) Schulz, H.; Bandeira De Melo, G.; Ousmanov, F. *Combust. Flame* **1999**, *118*, 179–190.

(10) Svensson, K.; Richards, M.; Mackrory, A.; Tree, D. *SAE Tech. Pap. Ser.* **2005**, 2005-01-0381.

(11) Boot, M. D.; Frijters, P. J. M.; Klein-Douwel, R. J. H.; Baert, R. S. G. *SAE Tech. Pap. Ser.* **2007**, (<http://www.sae.org/technical/papers/2007-01-2018>).

(12) Klein-Douwel, R. J. H.; Donkerbroek, A. J.; van Vliet, A. P.; Boot, M. D.; Somers, L. M. T.; Baert, R. S. G.; Dam, N. J.; ter Meulen, J. J. *Proc. Combust. Inst.* **2009**, *32*, 2817–2825.

Svensson et al.<sup>10</sup> investigated the impact of hydrocarbon molecular structure on soot production (via line-of-sight extinction) of a reacting fuel spray in a constant volume combustion vessel. A comparison between *n*-heptane and *n*-undecane was made, with the former and latter species having a CN of 53–56 and 79–83, respectively. A higher soot concentration was observed for *n*-undecane, which was credited to a shorter ignition delay and less dominant nonsooting premixed burn period.

*n*-Heptane was subsequently compared to toluene, an aromatic molecule with a significantly lower CN of approximately 5–10. Toluene yielded a significantly higher soot concentration, which was attributed to the fact that toluene, being an aromatic, can be considered a soot precursor. The authors conclude with the remark that, depending upon how a change in CN is realized, it can have either a positive or negative impact on soot concentration.

In a study performed by Boot et al.,<sup>11</sup> the low CN hydrocarbon cyclohexane (CN ~ 10) was blended to commercial diesel fuel (CN ~ 55) and subjected to a series of engine experiments in a DAF HD DI diesel engine. The authors reported a significant reduction in smoke opacity compared to the neat base fuel. In related work by Klein-Douwel et al.,<sup>12</sup> cyclohexane was blended to a high CN (~75) synthetic diesel fuel. The soot luminosity resulting from combustion of the blend (CN ~ 45) in a DAF HD DI diesel engine was compared to that of neat synthetic fuel. A clear decrease in soot luminosity was observed as a result of cyclohexane addition.

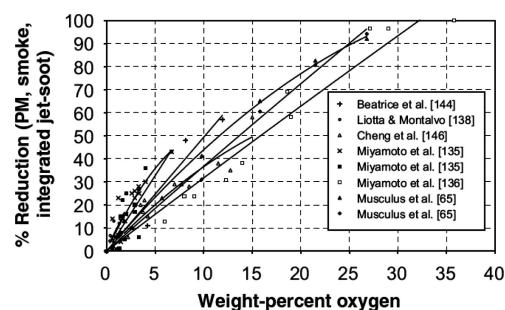
Further insight into the influence of fuel CN on soot formation is provided by Pickett et al.<sup>13</sup> In their experiments, the soot formation process was observed in an optically accessible constant volume combustion chamber via laser extinction and planar laser-induced incandescence. By studying a quasi-steady fuel jet, the aforementioned beneficial impact of a long ignition delay is no longer of significance. Nevertheless, a correlation between the fuel CN and sooting tendency was still found. In general, lower CN fuels produced less soot. The authors attributed this trend to the apparent relation between fuel reactivity (i.e., 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 manifested in less soot being produced.

**Overview.** Aromatics generally lead to a lower CN and increased soot emissions. In other words, when the CN of fuel is increased by removing soot precursors, this will have a beneficial impact on soot. Nevertheless, it should be noted that, when a high aromaticity coincides with a very low CN, the resulting prolonged ignition delays are likely to lead to low soot emissions. This appears only to be the case when the fuel injection process and heat-release event are completely separated, effectively creating a form of PCCI combustion.<sup>5</sup>

In the reviewed literature, CN boosters lead to a higher CN and increased soot emissions. Most authors attribute this trend to a smaller fraction of fuel that is consumed in the nonsooting premixed burn period.

A comparison of fuels with an equal aromaticity but with a different CN will typically show a trend wherein the higher CN fuels lead to higher soot emissions. It is believed that this trend can be credited to a smaller fraction of fuel, which is consumed in the nonsooting premixed burn period.

A correlation appears to exist between fuel reactivity (i.e., CN) and FLOL. In general, the lower the CN, the longer the



**Figure 1.** Soot reduction versus fuel oxygen: a literature review.<sup>14</sup> NB references in the legend correspond to those used in the original publication.

FLOL, the more favorable the equivalence ratio in the particle synthesis zone, and ultimately, the lower the soot production. Although this relation seems intuitively correct, it should be noted that more research in this particular area is still needed to further substantiate the aforementioned correlation.

### Literature Review: Impact of Fuel Oxygen on Sooting Tendency

Over the past 15 years, a large number of studies have demonstrated that blending oxygenated hydrocarbons with diesel can be a very effective route for PM reduction. A wide variety of such oxygenates have been tested, and the results have been described in a large number of publications. Only a few of them will be referred to here.

**Fuel Oxygen Concentration.** In the majority of these, a strong relation was found between fuel oxygen content and the amount of PM produced.<sup>11,12,14–26</sup>

Tree and Svensson<sup>14</sup> for example collected data on this dependency for 21 oxygenates from a large number of independent studies (Figure 1). Soot-free combustion is typically observed, regardless of oxygenate structure, when the fuel oxygen concentration is between 30 and 40 wt %. From this data, it can be concluded however that, a general trend notwithstanding, fuel oxygen content alone cannot account for the observed reduction in PM.

It is clear from this figure that, for a given fuel oxygen mass fraction, there are indeed significant differences in PM reduction. Although this can be traced back to the specific molecular structure of the oxygenates in question, no consensus can be

(14) Tree, D.; Svensson, K. *Prog. Energy Combust. Sci.* **2007**, *33*, 272–309.

(15) Song, J.; Zello, V.; Boehman, A.; Waller, F. *Energy Fuels* **2004**, *18*, 1282–1290.

(16) Liotta, F.; Montalvo, D. *SAE Tech. Pap. Ser.* **1993**, 932734.

(17) Beatrice, C.; Bertoli, C.; Del Giacomo, N. *Combust. Sci. Technol.* **1998**, *137*, 31–50.

(18) Miyamoto, N.; Ogawa, H.; Nurun, N. M.; Obata, K.; Arima, T. *SAE Tech. Pap. Ser.* **1998**, 980506.

(19) Mueller, C.; Martin, G. *SAE Tech. Pap. Ser.* **2002**, 2002-01-1631.

(20) Gonzalez, M.; Piel, W.; Asmus, T.; Clark, W.; Garbak, J.; Liney, E.; Natarajan, M.; Naegeli, D.; Yost, D.; Frame, E.; Wallace, J. *SAE Tech. Pap. Ser.* **2001**, 2001-01-3632.

(21) Stoner, M.; Litzinger, T. *SAE Tech. Pap. Ser.* **1999**, 1999-01-1475.

(22) Ren, Y.; Huang, Z.; Miao, H.; Di, Y.; Jiang, D.; Zeng, K.; Liu, B.; Wang, X. *Fuel* **2008**, *87*, 2691–2697.

(23) Murayama, T.; Zheng, M.; Cikahisa, T. *SAE Tech. Pap. Ser.* **1995**, 952518.

(24) Song, J.; Cheenakorn, K.; Wang, J.; Perez, J.; Boehman, A.; Young, P.; Waller, F. *Energy Fuels* **2002**, *16*, 294–301.

(25) Bertoli, C.; Beatrice, C.; Migliaccio, M.; Del Giacomo, N. *SAE Tech. Pap. Ser.* **1998**, 982492.

(26) Frijters, P.; Baert, R. *Int. J. Vehicle Des.* **2006**, *41*, 242–255.

(27) Musculus, M.; Dec, J.; Tree, D. *SAE Tech. Pap. Ser.* **2002**, 2002-01-0889.

(13) Pickett, L.; Siebers, D. *SAE Tech. Pap. Ser.* **2003**, 2003-01-3080.



found in the literature as to the explanation hereof. There is some indication, however, that oxygenate effectiveness is linked to the distribution of oxygen atoms in the oxygenated molecules.

**Oxygenate Effectiveness.** The beneficial impact of fuel oxygen on particulate emissions is often credited to enhanced “trapping” or sequestering of fuel carbon into nonsooting species (e.g., partially oxidized  $C_1$ – $C_2$  hydrocarbons). In other words, by means of already chemically bonding oxygen to carbon in the fuel, fewer carbon atoms are available to mature into (potential) soot precursors (e.g., ethylene, acetylene). At a fixed fuel-oxygen level, however, carbon sequestration was often found to depend heavily upon the type of functional oxygen group(s) (e.g., alcohols, ethers, and esters) involved.

In many studies, oxygenates in which each oxygen atom is connected to two carbon atoms tend to yield the lowest soot emissions.<sup>15–20</sup> One can imagine that, in alternative distributions, an oxygen atom may trap only one ( $C=O$ ) or one-half ( $O-C-O$ ) of a carbon atom instead of up to two ( $C-O-C$ ) carbon atoms in the preferred embodiment.

Oxygenate classes that are in accordance with the optimal sequestering configuration are ethers. Many authors who investigated the impact of oxygenate molecular structure on sooting tendency report that ethers are the most effective. Herein, tripropylene glycol methyl ether (TP) and glycol ethers (also known as glymes) are named as being particularly effective at reducing soot emissions.<sup>15–20</sup>

Conversely, there are studies that show classes other than (glycol) ethers (i.e., classes with lower expected sequestering efficiencies) to be the most effective.<sup>11,12,21,22</sup>

Stoner and Litzinger<sup>21</sup> for example reported that, in an optically accessible DI diesel engine, in-cylinder soot concentrations (measured via laser light extinction) were lower for maleates (i.e., esters;  $O-C=O$ ) than was the case for glycol ethers.

Boot et al.<sup>11</sup> conclude that, in a DAF HD DI diesel engine, regardless of engine operating conditions, a cyclic ketone (cyclohexanone;  $C=O$ ) leads to lower smoke opacities than both glymes and ethers even though the fuel oxygen concentration was kept constant.

In a related study by Klein-Douwel et al.,<sup>12</sup> cyclohexanone was blended to a synthetic diesel fuel. The soot luminosity resulting from combustion of the blend in a DAF HD DI diesel engine was compared to that of an ether (TP) blend with the same synthetic fuel. The authors report significantly lower soot luminosity for the cyclohexanone blend, a constant fuel oxygen content notwithstanding.

Ren et al.<sup>22</sup> studied the combustion and emissions of a DI diesel engine fueled with various diesel–oxygenate blends. Low CN oxygenates (for example, ethanol) performed better with respect to smoke opacity than high CN fuels (for example, diglyme).

**Combination of Fuel Oxygen and EGR.** Although soot emissions attenuate strongly with the introduction of fuel oxygen,  $NO_x$  emissions are typically left little affected by the use of oxygenates. An exception to this observation can be found when the range of CN of investigated oxygenated blends is relatively large.<sup>11,12</sup> It has been proposed by many authors<sup>11,18,23–25</sup> to combine the use of oxygenates with EGR. Accordingly, soot and  $NO_x$  can be addressed simultaneously. The negative effect of lower flame temperature (via EGR) on soot oxidation is (partially) countered by the enhanced suppression of particle formation (via fuel oxygen).

Murayama et al.<sup>23</sup> studied the combined use of EGR and oxygenated fuel (dimethyl carbonate) on smoke opacity in a

low-emission DI diesel engine. The authors conclude that the expected sharp rise of smoke opacity, typically observed when using EGR to reduce  $NO_x$ , can be partially countered by the simultaneous use of fuel oxygen.

Song et al.<sup>24</sup> examined the effect of oxygenated fuel (e.g., glycol ethers) on the combustion and emissions in a light-duty turbocharged DI diesel engine. At low load, the combination of high levels of EGR and fuel oxygen leads to a concurrent decline in both particle mass and nitric oxide emissions. The authors attributed these findings to suppression of soot precursors and a reduction of the flame temperature, respectively.

In a similar study performed by Bertoli et al.,<sup>25</sup> the influence of fuel oxygenation and EGR on engine-out emissions was investigated on a single-cylinder DI diesel engine. Pertaining to the combined use of EGR and oxygenation, a simultaneous reduction of particle mass and nitric oxides is reported. In addition, the authors conclude that fuel composition becomes less important at high EGR levels (30 wt %) and is negligible at 45 wt %.

The favorable impact of the combination of EGR and oxygenates on emissions has also been observed by Miyamoto et al.<sup>18</sup> In the used single-cylinder DI diesel engine, the smoke increase because of EGR is significantly suppressed by the presence of fuel oxygen.

Boot et al.<sup>11</sup> examined the influence of oxygenated fuel and the use of EGR on the sooting tendency of the combustion process on a HD DI diesel engine. The authors reported that the adverse smoke– $NO_x$  tradeoff typically observed when implementing an EGR circuit is improved when oxygenates are blended to commercial diesel fuel.

**Overview.** In general, soot emissions tend to drop more or less linearly with the amount of oxygen present in the fuel. Near zero-soot operation is found in several studies when the fuel oxygen is in excess of 30–40 wt %.

In all reviewed literature, differences in soot performance are observed between various oxygenates with a constant fuel oxygen content.

Many authors<sup>15–20</sup> believe the soot performance of an oxygenate at a given fuel oxygen content is affected by the (qualitatively estimated) carbon sequestering efficiency. In general, oxygenates in which the individual oxygen atoms are connected to two carbon atoms [e.g., (glycol) ethers], the optimal configuration with respect to sequestering potential, tend to yield the lowest soot emissions.

In general, the negative impact of EGR on soot emissions can be at least partially countered by the simultaneous use of oxygenated fuels.

No clear correlation between oxygenate CN and soot emissions could be found in the reviewed literature. A general observation that can be made when studying the seemingly conflicting literature, a few exceptions notwithstanding, is that, when the spread in CN is relatively low, the oxygenate with the better (expected) sequestering efficiency [e.g., (glycol) ethers] will produce the least soot. Alternatively, when the range of investigated CN is wider, soot emissions tend to decrease with a decreasing CN. This positive correlation between low CN and soot is likely linked to a higher premixed burnt fraction and/or a longer FLOL (see the Overview of the previous section).

As discussed earlier, results of Pickett et al.<sup>13</sup> suggest that, for given operating conditions, the FLOL is a function of mainly the CN. Conversely, the oxygen content of the fuel does not appear to be of importance in this respect. For a given FLOL, however, the presence of fuel oxygen will naturally lower the

**Table 1. Test Engine Specifications<sup>11</sup>**

engine	DAF PE235C 4V
bore/stroke	118/140 mm
number of cylinders	6
compression ratio	16
FIE type	pump line nozzle (PLD)
turbocharger	yes, VNT
charge cooling	air-to-water
EGR	yes, with cDPF
maximum power	235 kW at 2100 RPM
maximum torque	1325 Nm at 1500 RPM
oxidation catalyst	yes
emission norm	Euro 3

equivalence ratio in the flame, effectively shifting it into a more favorable region in the well-known temperature ( $T$ )–equivalence ratio ( $\phi$ ) map. Considering the fact that oxygenates, such as glymes, which have a considerably higher CN than diesel fuel, can still lead to significantly lower soot emissions, it is plausible that the presence of fuel oxygen outweighs the negative effect of a lower degree of mixing, because of both the (expected) shorter FLOL and shorter ignition delay. According to this theorem, low CN oxygenates should therefore hold an advantage over their high CN counterparts via enhanced mixing as a result of both the extended ignition delay and longer FLOL. The main objective of this and ongoing work is to test this hypothesis.

### Experimental Setup and Test Procedure

For the engine tests, a modified Euro-3 DAF PE235C HD DI diesel engine was used. Specifications of the engine and a schematic representation of the engine can be found in Table 1 and Figure 2, respectively.

This 9.2 L engine has an electronically controlled unit pump-type fuel injection system, capable of delivering over 1400 bar injection pressure. This engine was redesigned for lower engine-out emissions (Euro-4) on regular diesel fuel. To this end, an external EGR system was implemented (Figure 2). In the EGR circuit, a catalytic diesel particulate filter (cDPF) was mounted.

Downstream, in the exhaust circuit, a diesel oxidation catalyst (DOC) was installed to be able to measure dry PM (i.e., smoke opacity) emissions. To optimize (within limits) the air-to-fuel ratio (AFR) for a given amount of EGR or  $\text{NO}_x$  level, the fixed geometry turbocharger was replaced by a variable nozzle turbine (VNT) turbocharger. Note that standard air-to-air charge air cooling (CAC) has been replaced with air-to-water cooling.

Engine torque and speed were kept constant when switching between fuels, mimicking the driver's desire for constant vehicle

**Table 2. Base Fuel Properties**

base fuel	acronym	CN	aromatics (wt %)
Swedish class 1	SW1	53	5–10
EN590	D	56	20–25
synthetic diesel	S	75	0

performance independent of fuel quality. In addition, the standard fuel injection equipment (FIE) was not modified. Taking into account that the FIE of the test engine was cam-driven and the relatively low heating values and fuel densities of various test blends, this implied longer injection durations for some fuels. This was particularly the case for the low boiling ethanol blends. The formation of vapor bubbles in the FIE lead to elongated injection durations to maintain the desired engine torque/speed.

Moreover, the VNT/EGR-valve position was not altered when switching fuels. Naturally, this will have some effect on the engine gas exchange process (i.e., AFR and EGR) and combustion phasing. This, in turn, will affect the corresponding  $\text{NO}_x$  emissions.<sup>11,26</sup> In this work, however, the authors aim to establish emission trends rather than to compare exact values. The aforementioned effect of gas exchange on  $\text{NO}_x$  is therefore not considered an issue in this study.

A description of the used emission measurement equipment and other relevant data acquisition is provided elsewhere.<sup>11,26</sup>

### Fuel Matrix

A total of 15 blends have been prepared between various base fuels and neat oxygenates, with fuel oxygen levels ranging from 5 to 15 wt %.<sup>11,26</sup> In Table 2 below, the acronyms and CN of the tested base fuels, neat oxygenates, and blends can be found. A blend acronym has the following format: base fuel-oxygenate fuel-fuel oxygen wt % (e.g., D-ET-15).

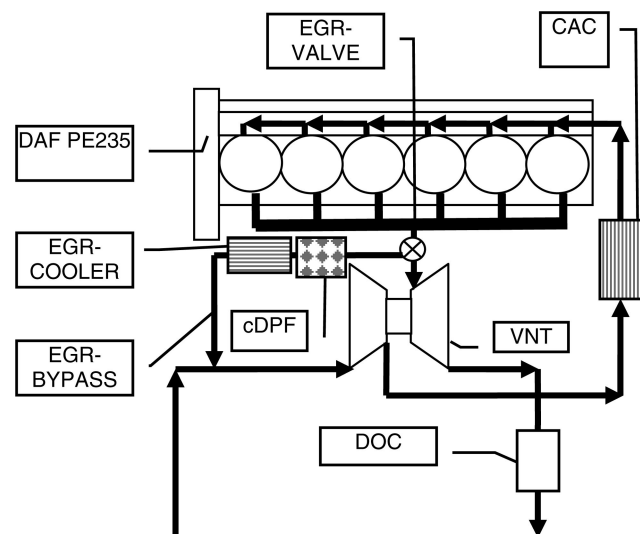
From earlier experimental results,<sup>11,26</sup> it has been concluded that tripropylene glycol methyl ether (TP) and dibutyl maleate (DB) were among the best performing oxygenates. These oxygenates, blended with SW1 to a fuel oxygen content of 9 wt %, have been compared to a third oxygenate, cyclohexanone (X1). X1 is a member of a hitherto scarcely discussed class, viz., cyclic oxygenates. These results have been discussed earlier as well.<sup>11</sup>

X1 has been blended with D, which has a CN and density comparable to those of SW1. CN for all blends other than the X1 blends has been determined by Shell Global Solutions. The CN for the X1 blend has been determined by applying Kay's mixing rule (i.e., a linear dependence on mole fractions).

Contrary to TP and DB, X1 is a cyclic rather than branched (TP) or linear (DB) molecule. It is well-known that such a cyclic character results in a relatively poor reactivity (low CN), as can be seen in Table 3. It is believed that, by investigating so wide a range in CN, more insight can be obtained with respect to the effect of fuel reactivity on the smoke opacity performance of oxygenated fuels.

### Experimental Results

Experimental results discussed in this study have been measured in the so-called ROSI<sup>26</sup> work point (i.e., 1650 rpm at 463 N m). For this particular engine, this is a representative engine operating point for typical use during highway cruising. For all experiments, the start of injector actuation (SOA) has been fixed at  $-13$  degrees crank angle ( $^\circ\text{CA}$ ) after top-dead-center (aTDC). The default EGR level was set at 15 wt %. Unless mentioned otherwise, the data presented in this section was measured in the ROSI work point at the aforementioned EGR and SOA settings.



**Figure 2.** Test engine lay-out and details of the EGR system and aftertreatment.<sup>11</sup>

Table 3. Neat Oxygenate Properties

oxygenate	acronym	CN	density (kg/m <sup>3</sup> )	T <sub>boil</sub> (K)	oxygen (wt %)	LHV (MJ/kg)
ethanol	ET	8	0.82	351	38.8	27.7
cyclohexanone	X1	10	0.95	428	16.3	33.6
dibutyl maleate	DB	28	0.99	554	26	28.23
ethanol with CN booster	ET+	55	0.82	351	34.8	27.7
tripropylene glycol methyl ether	TP	65	0.96	515	31	32.5
triglyme	TG	120	0.99	489	26	26.2

**Impact of Fuel CN on Ignition Delay.** As discussed earlier, fuel reactivity will have an impact on the premixed burn period. In Figure 3, the measured ignition delays (via heat-release analysis) are plotted against their respective CN for all fuels listed in Table 4 in the ROSI work point. The ignition delay is defined as the difference in crank angles or time between the points of 50% injector needle lift (opening) and start of heat release (computed from the measured in-cylinder pressure) at a threshold of 30 J/°CA.

It can be seen that a clear correlation exists between ignition delay and CN regardless of fuel oxygen content and/or base fuel characteristics. Ignition delays become rapidly shorter as the CN of fuel in question rises. Accordingly, fuels with a low and high CN will lead to a large and small nonsooting premixed burn fraction, respectively.

**Impact of Aromatic Content and CN Boosters on NO<sub>x</sub>/Smoke Tradeoff.** As discussed in the literature review, a boost in CN can have either a positive or negative impact on particle emissions (e.g., smoke opacity) depending upon how it is realized. Plotted in Figure 4 below are the smoke and NO<sub>x</sub> emissions for the three base fuels produced in the ROSI work point. It can be seen that a reduction in the aromatic content of the base fuel from 20–25 wt % (D) to 5–10 wt % (SW1) and finally to 0 (S) has a positive impact on smoke opacity. In this case, the reduction in smoke opacity coincides with an increase in CN.

An additional decrease in smoke can be achieved by blending an oxygenate (e.g., ET) to SW1. Conversely, when a CN improver is added to the oxygenated blend, the smoke opacity

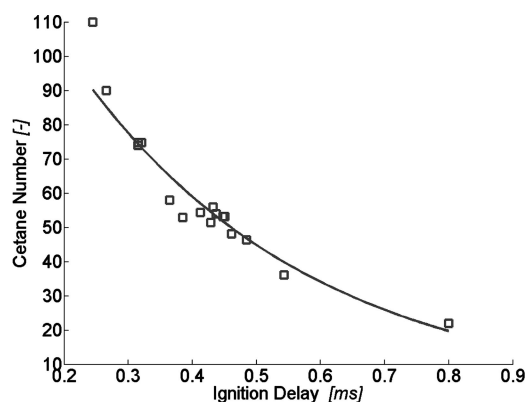


Figure 3. CN versus ignition delay for a wide range of oxygenates blended to various fuel oxygen contents (e.g., 5–15 wt %) with various base fuels.

Table 4. Oxygenated Blend Properties

blend	CN	blend	CN
SW1-ET+-6	51	SW1-ET-9	36
SW1-DB-6	48	S-TG-9	90
SW1-TP-6	53	S-TP-9	75
S-ET+-6	58	D-X1-9	22
D-X1-5	33	S-TG-15	110
SW1-ET+-9	53	S-TP-15	74
SW1-TP-9	54	SW1-TP-15	54
SW1-DB-9	46		

appears to be negatively affected. Both trends are in accordance with the reviewed literature discussed earlier.

**Impact of Fuel Oxygen on NO<sub>x</sub>/Smoke Tradeoff.** In comparison to the base fuel, the NO<sub>x</sub>/smoke opacity tradeoff improved significantly when increasing the fuel oxygen content. In Figure 5, this is best observed when considering a constant (e.g., ~3 g kW<sup>-1</sup> h<sup>-1</sup>) NO<sub>x</sub> value. The significant reduction of smoke opacity with increasing fuel oxygen content is in line with the reviewed literature discussed earlier.

**Impact of Blend CN on NO<sub>x</sub>/Smoke Tradeoff.** To isolate the effect of CN on smoke and NO<sub>x</sub>, only oxygenated blends containing 9 wt % fuel oxygen were considered in the following analysis.

In Figure 6 and 7, it can be seen that, for a given base fuel, there is some indication that smoke opacity and NO<sub>x</sub> emissions tend to increase and decrease, respectively, with increasing CN. This appears to be the case for the X1, DB, TP, and triglyme (TG) blends. Such trends can be expected when considering the impact of CN on the ignition delay or premixed burn fraction discussed earlier.

Exceptions to the trend were the ethanol blends. During engine testing, some vapor bubble formation in the FIE was observed when running on the ethanol (ET) blends. As a result, the injection duration was typically somewhat longer, retarding the combustion process and ultimately leading to lower than

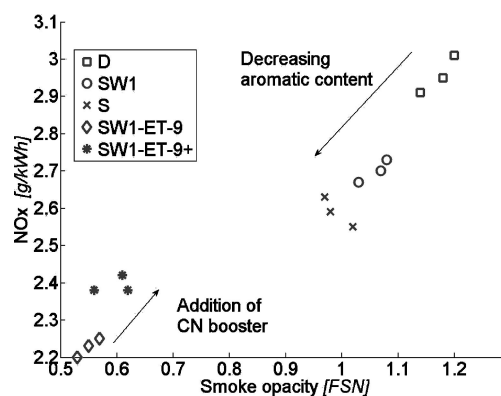


Figure 4. NO<sub>x</sub> versus smoke opacity for the three base fuels and the 9 wt % O ethanol blend (with and without a CN improver).

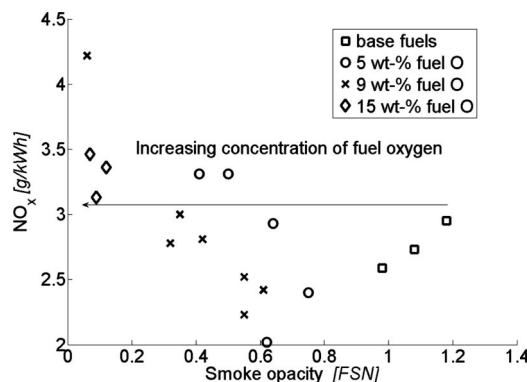


Figure 5. NO<sub>x</sub> versus smoke opacity for all oxygenated blends (at various fuel O wt %) and base fuels.

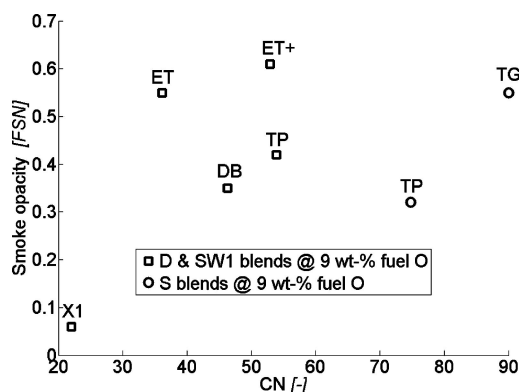


Figure 6. Smoke opacity versus CN for all 9 wt % fuel oxygen blends.

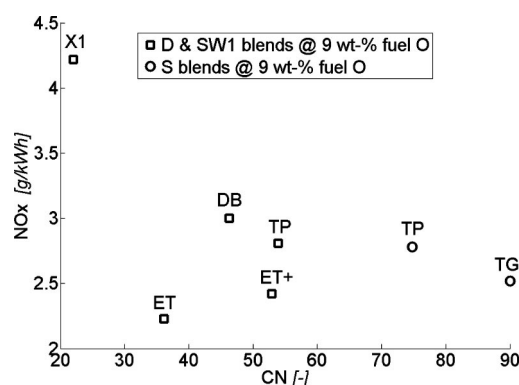


Figure 7.  $\text{NO}_x$  versus CN for all 9 wt % fuel oxygen blends.

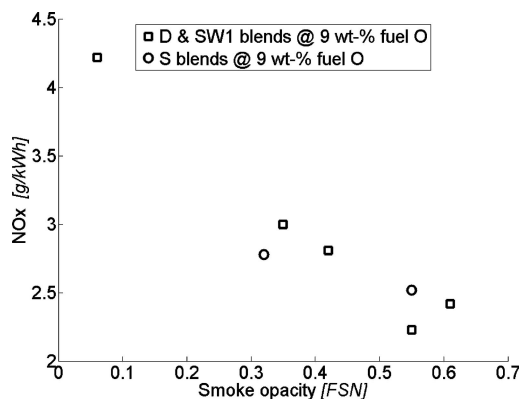


Figure 8.  $\text{NO}_x$  versus smoke for all 9 wt % fuel oxygen oxygenated blends.

expected  $\text{NO}_x$  (Figure 7) and higher than expected smoke opacity (Figure 6).

A more distinct trend is obtained, however, when plotting the  $\text{NO}_x$  emissions against the smoke opacity (Figure 8). Here, a clear tradeoff can be observed regardless of the base fuel used and blend CN. The lowest smoke values are obtained for the fuels that yield the highest  $\text{NO}_x$  emissions in accordance with the well-known diesel dilemma.

**Influence of EGR on  $\text{NO}_x$ /Smoke Tradeoff.** As can be observed from Figure 9, at a given fuel oxygen level, low smoke opacity can be obtained at the expense of  $\text{NO}_x$  emissions. To mitigate the adverse effect on  $\text{NO}_x$ , the EGR level was increased in steps of 2.5 wt % from 15 to 22.5 wt %. In this section, only the best performing oxygenated blends, with respect to smoke opacity, are considered. It should be noted that, even with the higher EGR ratios, the engine-out unburnt hydrocarbon and carbon monoxide emissions were within euro IV/V limits.<sup>11</sup>

As could be expected, a significant reduction in  $\text{NO}_x$  can be

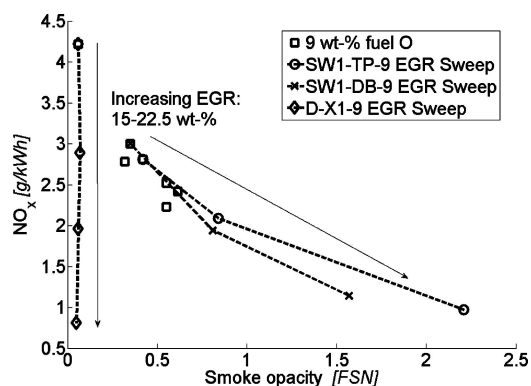


Figure 9.  $\text{NO}_x$  versus smoke opacity at various levels of EGR.

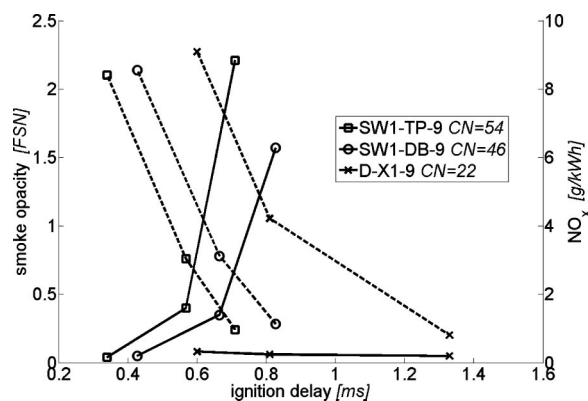


Figure 10. Smoke opacity (solid line) and  $\text{NO}_x$  (dashed line) versus increasing ignition delay (e.g., because of EGR).

realized by boosting the EGR fraction. Unfortunately, for the TP and DB blends, this coincides with the typical sharp rise in smoke opacity. Conversely, the X1 blend appears to be left largely unaffected by the otherwise adverse effect of EGR on smoke.

In Figure 10, smoke opacity and  $\text{NO}_x$  emissions are plotted against increasing ignition delay (e.g., because of EGR). From left to right, the three data points per fuel correspond to the respective emission values at 0, 15, and 25 wt % EGR. From this figure, it becomes clear that, while all blends display a similar reaction to EGR with respect to  $\text{NO}_x$ , the negative impact of EGR on smoke seen for TP and DB is not observed for the X1 blend.

When switching between fuels, the injection duration was varied such that engine torque and speed were maintained at the ROSI work point. From the reference EGR level of 15 wt %, the EGR level was gradually increased up to approximately 25 wt %. For all fuels considered, the impact of increased EGR is clear, i.e., higher fuel consumption and lower thermal efficiency (Figure 11). This effect is well-known and is generally attributed to the associated retarded combustion phasing and increased pumping losses.

As could be expected, the presence of 9 wt % fuel oxygen negatively impacts fuel consumption (i.e., approximately by 10%). All three oxygenates show comparable behavior here. When expressed in energy consumption, however, all fuels including the non-oxygenated base fuel yield similar results (Figure 11). In fact, the distinctions are too small, considering the uncertainty of the LHV in particular, to draw any further conclusions. It is evident from these results that the breaking of the  $\text{NO}_x$ –PM curve does not come at the expense of thermal efficiency (when compared to the base fuel).

It may be concluded that, as expected, the application of EGR has a positive and negative effect on the  $\text{NO}_x$  and smoke opacity,



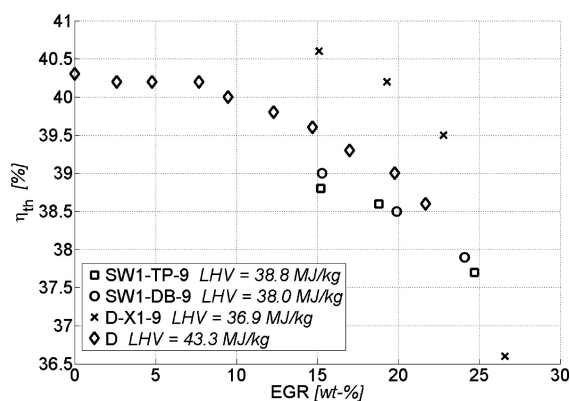


Figure 11. Thermal efficiency versus EGR.

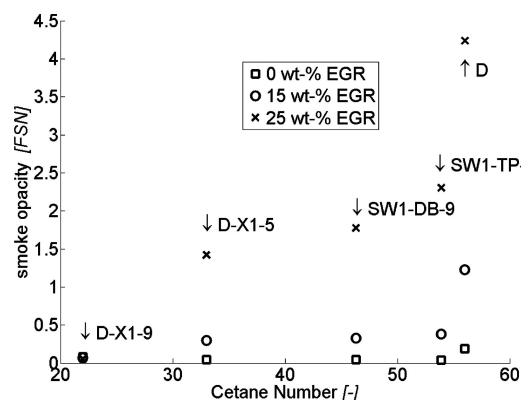


Figure 12. Smoke opacity versus CN plotted for various 9 wt % fuel oxygen blends at three different EGR levels.

respectively. This effect is exacerbated by the fact that the AFR drops as more EGR is fed into the cylinders. The presence of fuel oxygen appears to improve this tradeoff irrespective of the oxygenate concentration or molecular structure. Considerable differences, however, are observed between the various oxygenates, with X1 performing considerably better than TP and DB. These distinctions appear to be masked at low EGR/high  $\text{NO}_x$  values and are amplified at high EGR/low  $\text{NO}_x$  levels (Figure 10). These conclusions have been drawn earlier by Boot et al.<sup>11</sup> and will be readdressed in the Discussion below. It should be noted that an opposite trend was reported by Bertoli et al.,<sup>25</sup> who concluded that fuel composition becomes less important with respect to soot at high EGR levels (30 wt %) and is negligible at 45 wt %.

## Discussion

**Effect of CN Number.** As stated earlier, the main research goal of this study was to investigate the impact of fuel reactivity, expressed here as the CN on smoke opacity. In this Discussion, smoke opacity will be taken as an indication of emitted PM mass.

From Figure 12, it may be deduced that fuel identity is essentially masked at low EGR levels. In this case,  $\text{NO}_x$  emissions are relatively high (Figure 10) and most PM formed is likely to be readily oxidized in the diffusion flame and postflame gases. Conversely, at high EGR,  $\text{NO}_x$  emissions are low, suggesting low flame temperatures and poorer PM oxidation. Here, more influence of the PM formation tendency of the fuel can be expected. This expectation is supported by the data in Figure 12, where it can be seen that smoke opacity becomes increasingly sensitive to fuel identity as more EGR is applied.

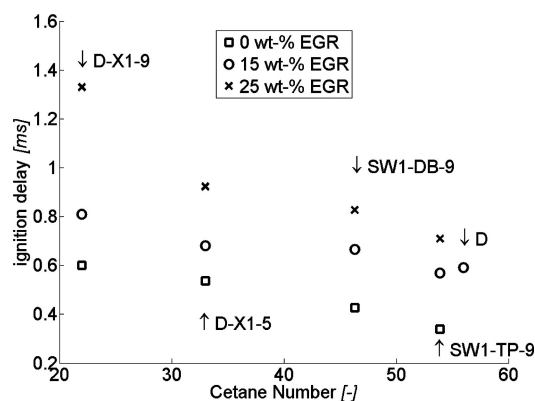


Figure 13. Ignition delay versus CN plotted for various 9 wt % fuel oxygen blends at three different EGR levels.

Table 5. Injection and Ignition Events

blend	SOD ( $^{\circ}\text{CA}$ aTDC)	EOD ( $^{\circ}\text{CA}$ aTDC)	SOC ( $^{\circ}\text{CA}$ aTDC)
D	-3.6	8.8	0.7
D-X1-9	-3.3	9.7	5.2
SW1-DB-9	-2.9	10.5	1.9
SW1-TP-9	-2.9	10.4	1.4

When investigating the difference in PM performance, one observes that PM emissions correlate quite well with the CN of the fuels. Indeed, PM emissions, at a given EGR level, are seen to decrease in the order SW1-TP-9, SW1-DB-9, and D-X1-9, the CN of which being 54, 46, and 22 respectively. It is striking that the difference in PM performance between the various oxygenates (e.g., at 25 wt % EGR) is nearly 2 orders of magnitude (Figure 12). To emphasize this distinction, the data for X1 at a lower fuel oxygen wt % (e.g., 5) is plotted in Figure 12 as well. It can be observed that, the greater than 40% difference in fuel oxygen wt % notwithstanding, the DB-9 and X1-5 blends share a similar PM performance. These results suggest that not only fuel oxygen content but also oxygenate reactivity or CN play a significant role in the PM lifecycle, especially at high EGR levels. For the oxygenated blends at 25 wt % EGR, smoke opacity increases more or less proportionately with the CN. A possible explanation for this strong dependency upon CN will be discussed below.

A consequence of using EGR and/or lower CN fuel is that the resulting ignition delay (i.e., time between the start of injection and start of combustion) becomes more extended (Figure 13).

As a rule, longer ignition delays translate into more premixing of fuel and air prior to auto-ignition. It is generally accepted that most fuel that is injected prior to auto-ignition (i.e., during the ignition delay) will not participate in the PM formation process. By studying Figures 12 and 13 together, it can be concluded that longer ignition delays indeed coincide with lower smoke opacity. When EGR is applied, with respect to PM emissions, the positive effect of more premixing is generally offset by the negative effect of lower flame temperatures. Accordingly, as can be seen in Figure 12, an increase in EGR results in a sharp increase in smoke opacity.

It should be noted that, the longer ignition delays notwithstanding, there still exists considerable overlap between the fuel injection and combustion event. The data in Table 5 show that the start of combustion (SOC) occurs (e.g., for 15 wt % EGR) well before the end of fuel delivery (EOD). From Figure 10, it can be concluded that at this EGR level the breaking of the  $\text{NO}_x$ /PM tradeoff is already well-established for the X1 blend. Conversely, for premixed combustion concepts, such as homogeneous charge compression ignition (HCCI), Nissan's modu-



lated kinetics (MK), and Volkswagen's combined combustion system (CCS), the aforementioned events are as a rule separated.

NB while the start of injector actuation (SOA) has been fixed at  $-13$  crank angle degrees ( $^{\circ}\text{CA}$ ) after top-dead-center (aTDC) for all experiments, the actual start of delivery (SOD) is nearly  $10^{\circ}$  later because of delaying effects in the pump-line-nozzle (PLD) fuel injection system.

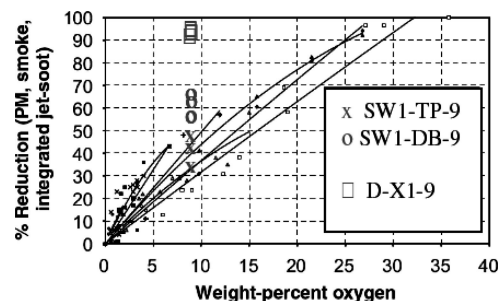
Alternatively, as discussed earlier, there is some indication in the literature that lower CN fuels lead to longer flame-lift-off-lengths. Longer FLOLs in turn allow for more air to be entrained into the fuel jet prior to combustion. Accordingly, a more favorable (i.e., lower) equivalence ratio can be expected in the particle synthesis zone downstream of the FLOL,<sup>13</sup> ultimately creating a less conducive environment for soot production.

To put these results in a broader perspective, relevant data from Figure 10 has been superimposed (Figure 14) onto the literature overview presented in Figure 1. An explanation for the omission of cyclic oxygenates and low CN oxygenates in general from fuel matrices in other studies may lie in the dogma that a high CN is beneficial for PM emissions. Although true for conventional fossil fuels, where increased CN is achieved by virtue of the removal of notorious soot precursors [i.e., (poly) aromatics], the presented data clearly suggests otherwise for oxygenated fuels. Moreover, such a pronounced influence of CN as presented in Figures 12 and 13 is visible only for high EGR/low  $\text{NO}_x$  levels.

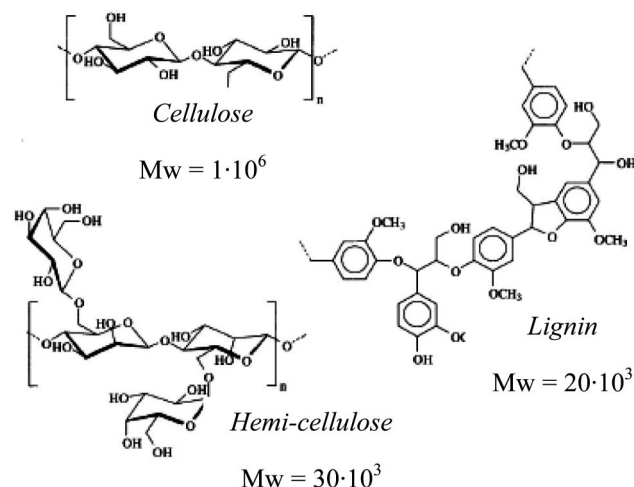
In light of the good results obtained with the X1 blend, the use of cyclic oxygenates in combustion processes has been secured by the Eindhoven University of Technology in three patents. The subject of the current investigation is to develop a commercially viable production route for  $\text{C}_6$  cyclic oxygenates, such as X1, from a biological feedstock. A preliminary study is presented in the following section.

**Production Routes for Cyclic Oxygenates.** Cyclic paraffins are the most abundant (30–60 wt %) chemical compounds in crude oil.<sup>28</sup> Rings with 6 carbon atoms (e.g., cyclohexane) are the most dominant species by far. Partial oxidation of cyclohexane to X1 is quite straightforward, which might explain why cyclohexanone (X1) could be purchased at less than a fourth of the price of TP and DB. What is more, distillates such as diesel, jet fuel, and heating oil, contain at least about 20 vol %, generally from about 20 to about 40 vol %, of six-membered cyclic paraffins. In other words, an economically viable feedstock for X1 is available at any neighborhood gas station. Even on-site and/or on-board refining is within the realm of possibilities.

Even more ambitious is the production of cyclic oxygenates (e.g., X1) from a biological feedstock, more specifically, from lignocellulosic biomass (also known as plant waste/residue). Principal components of such biomass include cellulose (35–50%), hemicellulose (25–30%), and lignin (15–30%),<sup>29</sup> as can be seen in Figure 15, all of which are five- and six-membered cyclic oxygenates. Unfortunately, these compounds are large polymers with molecular weights 2–4 orders of magnitude higher than conventional fuels.<sup>29</sup> The production of liquid cyclic oxygenates from such heavy molecules is not straightforward.



**Figure 14.** Reduction versus fuel oxygen wt %, collected from numerous experiments reported in the literature<sup>14</sup> and compared to the results of the present study.



**Figure 15.** Cyclic oxygenated structures of the various lignocellulosic molecules. Molecular weight (MW) in g/mol.<sup>29</sup>

Meier and Berns<sup>30</sup> discuss the isolation of phenol from the phenol-like lignin molecules and report conversion rates of 12.8%. Jianliang et al.,<sup>31</sup> in turn, studied the conversion of phenol ( $\text{C}_6\text{H}_6\text{O}$ ) to cyclohexanone (X1) and reported conversion rates in excess of 80%.

Hewgill and Legge<sup>32</sup> have isolated the model component for lignin, guaiacol [ $\text{C}_6\text{H}_4(\text{OH})(\text{OCH}_3)$ ], with an efficiency of 88%. Cyclohexanol ( $\text{C}_6\text{H}_{12}\text{O}$ ) can be subsequently produced via direct hydrogenation.

It deserves attention that all species discussed above are  $\text{C}_6$  cyclic oxygenates (like X1) and soluble (to a certain extent) in commercial diesel fuel. The CN of these  $\text{C}_6$  molecules is in the range of 5–20 and is expected to have a similar smoke opacity performance as X1.

The design of a commercially viable production process of these species is a current subject of investigation. In the meantime, the above species will be purchased in neat form and tested in a HD DI diesel engine by some of the authors in the near future.

## Conclusions

When the extraordinary sooting behavior of the cyclic oxygenate cyclohexanone (X1) was first observed, many fuel properties were considered as potentially responsible. Foremost herein were the fuel reactivity, oxygen content, and functional oxygen groups (e.g., so-called carbon sequestering efficiency).

(28) Kvesitadze, G.; Khatisashvili, G.; Sadunishvili, T.; Ramsden, J. *Biochemical Mechanisms of Detoxification in Higher Plants*; Springer: Heidelberg, Germany, 2006; pp 19–48.

(29) Santen, R.; Centi, G. *Catalysis for Renewables*; Wiley-VCH: Weinheim, Germany, 2007; pp 21–29.

(30) Meier, D.; Oasmaa, A.; Peacocke, G. *Biomass Bioenergy* **1994**, *7*, 99–105.

(31) Jianliang, L.; Hui, L.; Hexing, L. *Chin. J. Catal.* **2007**, *28*, 312–316.

(32) Hewgill, F.; Legge, F. *Wood Sci. Technol.* **1976**, *10*, 125–129.

The main objective of this work was to examine earlier data more closely in an attempt to ascertain which of the above parameters is the most important. From the Discussion, it follows that the impact of fuel reactivity (CN) on soot, via its derivatives flame-lift-off-length (FLOL) and ignition delay, appears to outweigh that of carbon sequestering efficiency and, in some cases, even that of the amount of oxygen present in the fuel. The results suggest that the importance of CN grows as higher levels of EGR are applied.

With respect to the breaking of the  $\text{NO}_x/\text{PM}$  curve, the authors have demonstrated that for the D-X1-9 blend this occurs at EGR levels as low as 15 wt %. At such low EGR, there exist still considerable overlap between fuel injection and heat release. For combustion concepts geared toward creating a homogeneous mixture (e.g., HCCI, MK, and CCS), breaking of the  $\text{NO}_x/\text{PM}$  curve has indeed also been observed. Such combustion concepts, however, are characterized by the absence of the aforementioned overlap.

There are process routes known from the literature to produce X1 and similar  $\text{C}_6$  cyclic oxygenates from lignocellulosic material. An investigation of a viable production route is the subject of current investigation. When produced from such feedstock, X1 or similar  $\text{C}_6$  cyclic oxygenates will qualify as second-generation biofuels.

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