

The Effect of the Position of Oxygen Group to the Aromatic Ring to Emission Performance in a Heavy-Duty Diesel Engine

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ABSTRACT

In this paper, the soot-NO_x trade-off and fuel efficiency of various aromatic oxygenates is investigated in a modern DAF heavy-duty diesel engine. All oxygenates were blended to diesel fuel such that the blend oxygen concentration was 2.59 wt.-%. The oxygenates in question, anisole, benzyl alcohol and 2-phenyl ethanol, have similar heating values and cetane numbers, but differ in the position of the functional oxygen group relative to the aromatic ring. The motivation for this study is that in lignin, a widely available and low-cost biomass feedstock, similar aromatic structures are found with varying position of the oxygen group to the aromatic ring. From the results it becomes clear that both the soot-NO_x trade-off and the volumetric fuel economy (i.e. ml/kWh) is improved for all oxygenates in all investigated work points. In general, the improvement in the soot-NO_x trade-off correlated with the position of the functional oxygen group to the ring, with better overall emission behavior observed as the oxygen group was further from the ring. No distinct trend was observed with respect to fuel economy.

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INTRODUCTION

This study builds on earlier work on cyclic oxygenates. In [1], the authors compare the soot-NO_x trade-off for various classes of oxygenates and conclude that, given a fixed fuel oxygen content, cyclic oxygenates consistently outperform their linear and branched counterparts. In this work, a correlation is presented which shows better emission behavior for lower blend cetane numbers (CN), thereby offering a possible explanation for the above par performance of the inherently low reactive cyclic compounds.

Later, in [2], the authors compare aromatic vs. saturated cyclic oxygenates and report comparable emission behavior between the two. From a production point of view, starting from lignin - itself a polymer of aromatic oxygenates - it would be far more economical to focus on aromatic end-products. Saturated compounds, conversely, would require large amounts of expensive hydrogen to produce. Accordingly, this line of research will focus primarily on aromatic oxygenates.

It is known from literature that there exists a strong connection between fuel molecular structure and the soot formation mechanism. [3,4,5]. In general, compared with saturated hydrocarbons, soot production of fuels with unsaturated (e.g. double, triple or aromatic carbon-carbon bonds) are relatively high.

Some studies [6, 7] have also shown the positive influence of oxygen content in the fuel on the emission behavior. Soot formation can be reduced more or less linearly with increasing oxygen content. Since the carbon atoms are partly bounded to the oxygen atoms already in the fuel, the formation of mono-aromatics, notable soot precursors, can be suppressed.

Though aromatics and oxygenates in general have been extensively researched, it is difficult to find studies that focus on aromatic oxygenates. Admittedly, intentionally adding aromatic compounds to diesel fuel with the purpose of lowering soot emissions is counterintuitive. Nonetheless, positive results in earlier work and the widely available and generally overlooked (i.e. for transport fuel applications) lignin feedstock warrant further investigation into the use of aromatic oxygenates in diesel engines.

Given the heterogeneous nature of lignin, it is important to investigate various types of aromatic oxygenates in order to learn which compounds should be targeted in a future lignin refinery. This study will investigate how the position of the functional oxygen group to the aromatic ring impacts overall engine behavior in a modern DAF heavy-duty diesel engine.

Table 1. Physical properties and heating value for the neat compounds

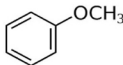
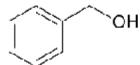
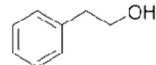
Name of Fuel	Diesel (EN590) [9]	Anisole	Benzyl alcohol	2-Phenyl ethanol
				
CAS no.	-	100-66-3	100-51-6	60-12-8
Scent/odor	-	Anise	Jasmine	Rose
Molecular formula	-	C ₇ H ₈ O	C ₇ H ₈ O	C ₈ H ₁₀ O
Density (at 300K) [kg/L]	0.830	0.995	1.044	1.017
Initial / final boiling point [K]	443 / 634	427	478	493
Molar Mass [kg/mol]	0.233 [9]	0.108	0.108	0.122
HHV [MJ/kg]	44.50	34.97 (according to [10])	34.56 (according to [10])	35.90 (according to [10])
LHV [MJ/kg]	41.50	33.46 (calculated from HHV)	33.05 (calculated from HHV)	34.24 (calculated from HHV)

Table 2. CN derivation for the cyclic oxygenates

Name of Fuel/Blend	Diesel	Gasoline	90% Gasoline 10% Anisole	90% gasoline 10% Benzyl alcohol	90% Gasoline 10% 2-Phenyl ethanol	Anisole	Benzyl alcohol	2-Phenyl ethanol
Molecular formula		-	-	-	-	C ₇ H ₈ O	C ₇ H ₈ O	C ₈ H ₁₀ O
Measured MON [11]		86	87	87	86	-	-	-
Measured RON [12]		95	97	97	97	-	-	-
Calculated MON [13]		-	-	-	-	94	93	90
Calculated RON [13]		-	-	-	-	112	108	110
Evaluated CN	56	-	-	-	-	8	9	9

MATERIAL AND METHODS

Chemical and Physical Properties of the Molecules

The three aromatic oxygenates in question are anisole, benzyl alcohol and 2-phenyl ethanol. All of which are considered to be of a low toxicity, given that the U.S. Food and Drug Administration (FDA Part 172, Subpart F) [8] has approved their use as food additives for direct addition to food for human consumption. Relevant physical properties and heating values are presented in Table 1.

From Table 1 can be inferred that the boiling points of the neat oxygenates are on the low side of the diesel boiling

range and that their gravimetric heating values are considerably lower than is the case for diesel.

As shown in Table 2, the CN of the cyclic oxygenates has been derived from the measured MON (ASTM D2700 [11]) and RON (ASTM2699 [12]) values of blends with gasoline.

$$CN = 54.6 - 0.42 \text{ RON}$$

(1)

First, the MON and RON values of the neat oxygenates are calculated according to Kay's mixing rule [13]. Next, the CN follows from equation (1) proposed by Kalghatgi [14]. The three oxygenates are subsequently blended to commercial diesel (EN590) to an equal fuel oxygen content of 2.59 wt.-% (Table 3). Fortunately, albeit coincidental, there is a nice match for the CN as well.

Table 3. Blend properties of test fuels

Name of Blend	Diesel (EN590)	Anisole-15%	Benzyl alcohol-14.4%	2-Phenyl ethanol-16.7%
Base Fuel	Diesel	Diesel	Diesel	Diesel
Base Fuel [vol.-%]	100	85	85.6	83.3
Oxygenate	-	Anisole	Benzyl alcohol	2-phenyl ethanol
Concentration [vol.-%]	-	15	14.4	16.7
Oxygen [wt.-%]	-	2.59	2.59	2.59
Density [kg/l]	0.830	0.855	0.862	0.861
Calculated LHV [MJ/kg]	41.5	39.0	38.8	39.2
LHV [MJ/kg] vs. diesel [%]	-	-6.0	-6.5	-5.5
Calculated LHV [MJ/l]	34.4	33.3	33.4	33.8
LHV [MJ/l] vs. diesel [%]	-	-3.2	-2.9	-1.7
Calculated CN [-]	56	41	41	41
CN vs. diesel [-]	-	-15	-15	-15

Measurement Setup

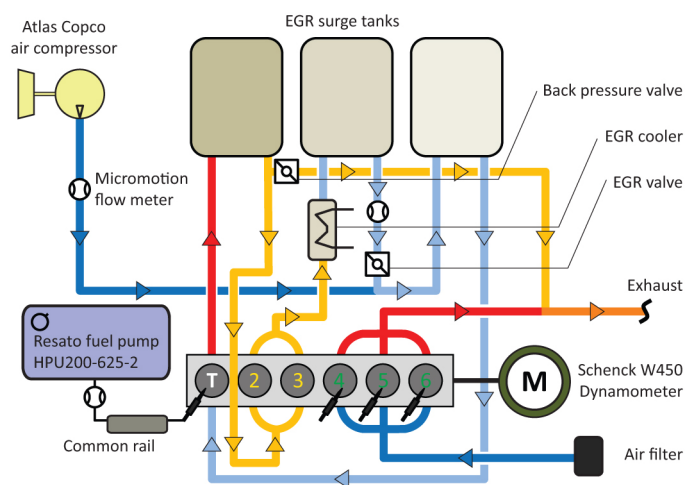
The test engine, CYCLOPS [15], is a dedicated test rig, designed and built at the Eindhoven University of Technology. It is based on a DAF XE 355 C engine. Specifications of this engine are presented in Table 4. Cylinders 4 thru 6 operate under the stock engine control unit, and together with a water-cooled, eddy-current Schenck W450 dynamometer, they are only used to start the engine and control the rotational speed of the test cylinder, i.e. cylinder 1.

Table 4. Specifications of Cyclops Engine

Base engine	6 cylinder HDDI diesel
Test Cylinder	1 isolated for combustion studies
Bore [mm]	130
Stroke [mm]	158
Compression ratio [-]	15
Bowl diameter [mm]	100

When data acquisition is idle, for instance during engine warm-up or in between measurements, only the three propelling cylinders are fired. Once warmed up and operating at the desired engine speed, combustion phenomena and emission formation can be studied in the test cylinder. Apart for the shared cam- and crankshaft and the lubrication and coolant circuits, the test cylinder operates autonomously from the propelling cylinders. Fed by an Atlas Copco air compressor, the intake air pressure of the test cylinder can be boosted up to 5 bar. The fresh air mass flow is measured with a Micro Motion Coriolis mass flow meter. Non-firing

cylinders 2 and 3 function as exhaust gas recirculation (EGR) pumps (see Figure 1, the schematic layout of the setup). Their purpose is to generate adequate EGR flow, even at elevated charge pressures.

**Figure 1. Cyclops engine test rig**

Fueling of cylinder 1 is provided by a double-acting air-driven Resato HPU200-625-2 pump, which can deliver a fuel pressure up to 4200 bar. An accumulator is placed near (~ 0.2 m) the fuel injector to mimic the volume of a typical common rail and dampen pressure fluctuations originating from the pump. The fuel mass flow is measured with a Micro Motion mass flow meter.

For measuring gaseous exhaust emissions, a Horiba Mexa 7100 DEGR emission measurement system is used. Exhaust smoke level (in Filter Smoke Number or FSN units) is measured using an AVL 415 smoke meter three times per

Table 5. Operating points

Intake pressure [bar]	1		1.5	
Aim load (IMEP) [bar]	7.5		12	
EGR [wt%]	0	30	0	30
Aim λ [-]	1.45	1.00	1.60	1.15
SOI [deg CA aTDC]	-5	-5	-5	-5
	-10	-10	-10	-10
	-15	-15	-15	-15

Table 6. Calculated stoichiometric ratio of the blends

Blend	Diesel (EN590)	Anisole-15%	Benzyl alcohol-14.4%	2-Phenyl ethanol-16.7%
Base Fuel	Diesel	Diesel	Diesel	Diesel
Additive	Diesel	Anisole	Benzyl alcohol	2-Phenyl ethanol
Stoichiometric ratio of additive	14.3	10.8	10.8	11.3
Stoichiometric ratio of blend	14.3	13.8	13.8	13.8

operating point, of which the average value is logged. The engine is equipped with all common engine sensors, such as intake and exhaust pressures and temperatures, and oil and water temperature. This quasi steady-state engine data, together with air, fuel and EGR flows, as well as the regulated gaseous emissions, are recorded at 20 Hz for a period of 40 seconds by means of an in-house data acquisition system (TUEACS) [15]. The average of these measurements is taken as the value for the operating point under investigation.

Finally, a SMETEC Combi crank angle resolved data acquisition system [16] is used to record and process in-cylinder pressure (measured with an AVL GU12C uncooled pressure transducer), intake pressure, fuel pressure and temperature and injector current. All of these channels are logged with a resolution of 0.1 °CA for 50 consecutive cycles. From this data, the average and standard deviation of important combustion parameters, such as CA10, CA50 and IMEP, can be calculated with the associated SMETEC software.

Engine Operating Points

All tests are performed at 1200 r/min, with a fuel injection pressure and temperature set to 1500 bar and 30 °C, respectively. As shown in Table 5, because of peak cylinder pressure limitations, the operating points are based on two intake pressure points with two mixture strengths. Finally, injection timings (SOI), separated by 5 °CA intervals, are chosen.

Stoichiometric Ratio Calibration

Because the C-H-O ratios differ widely amongst the test fuels, the stoichiometric ratio of each blend should be evaluated for accurate lambda calculation. The stoichiometric

ratio of EN590 diesel is roughly 14.3. The air composition is supposed to contain 20.95% O₂ and 78.09% N₂, so that [N₂]/[O₂] = 3.773 when other trace gases are neglected. If the hydrocarbon is described as C_cH_hO_o, the combustion reaction equation in case of complete combustion can be written as:

$$C_c H_h O_o + (c + h/4 - o/2)(O_2 + 3.773 N_2) = c \cdot CO_2 + h/2 \cdot H_2O + 3.773(c + h/4 - o/2) N_2 \quad (2)$$

The stoichiometric ratio can then be written as:

$$(34.41 \cdot (4c + h - 2o)) / (12c + h + 16o) \quad (3)$$

Furthermore, constants *c*, *h* and *o* of each blend can be calculated according to the volume fraction of the compositions, resulting in the stoichiometric ratios listed in Table 6. Note that the values for the three mixtures are almost identical.

RESULT AND DISCUSSION

Soot-NO Trade-Off

As shown in Figures 2, 3, 4, 5, the soot emissions of the three oxygenates blends, for a given fuel injection timing, are consistently lower than is the case for diesel. NO_x, conversely, is generally slightly higher for a given timing. Lower soot at the expense of NO_x is expected behavior for lower CN fuels, given a more pronounced premixed combustion phase incurred by the inherently longer ignition delay. Although all fuels show comparable soot-NO_x trends on a qualitatively level, the curves for the oxygenates are considerably more favorable in absolute terms.

Generally, in the operation points without EGR, an increase in the distance between oxygen and the ring, will

lead to lower soot with often only a marginal sacrifice of NO_x. Moreover, it should be noticed that the oxygen atom is in different functional groups (ether and alcohols) in these oxygenates, this difference may also contribute to the lower soot seen for anisole (ether), which will be discussed further in a later paper. In the operation points with EGR, this order of soot reduction still holds, but now appears to come at a far clearer expense of NO_x. From earlier work on oxygenates [1, 2] it is known that fuel identity is more apparent at the lower combustion temperatures that result from EGR.

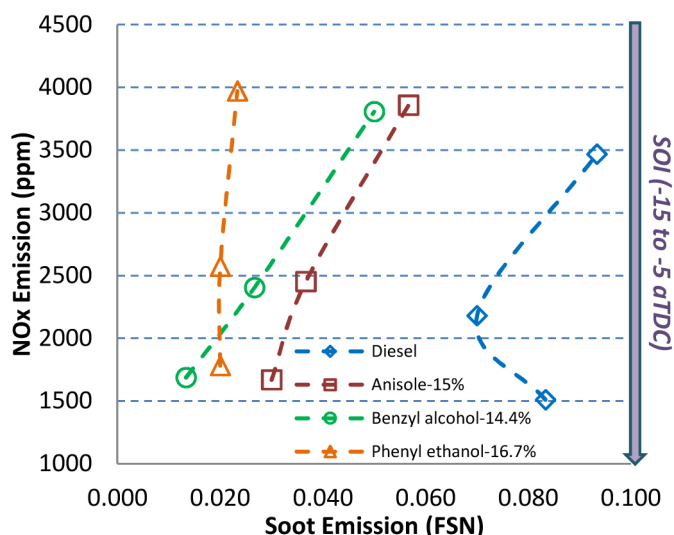


Figure.2. NO_x vs. soot emission at 7.5 bar gross IMEP, no EGR, and $\lambda=1.45$, for diesel (blue diamonds), Anisole-15% (red squares), Benzyl alcohol-14.4% (green circles) and 2-Phenyl ethanol 16.7% (orange triangles)

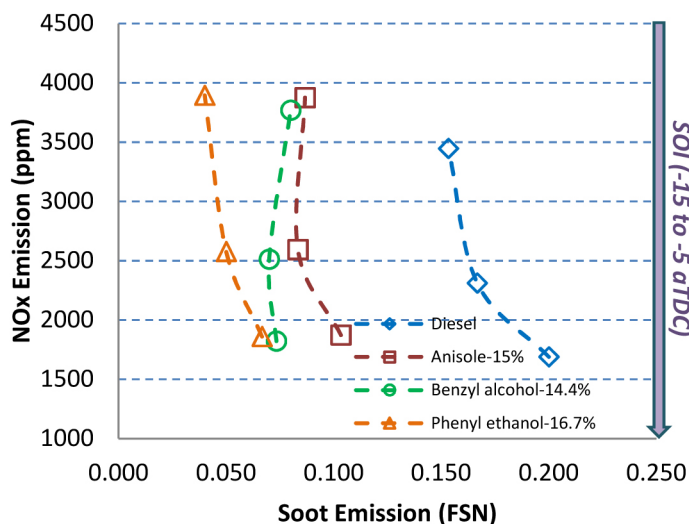


Figure.3. NO_x vs. soot emission at 12 bar gross IMEP, no EGR, and $\lambda=1.60$, for diesel (blue diamonds), Anisole-15% (red squares), Benzyl alcohol-14.4% (green circles) and 2-Phenyl ethanol 16.7% (orange triangles)

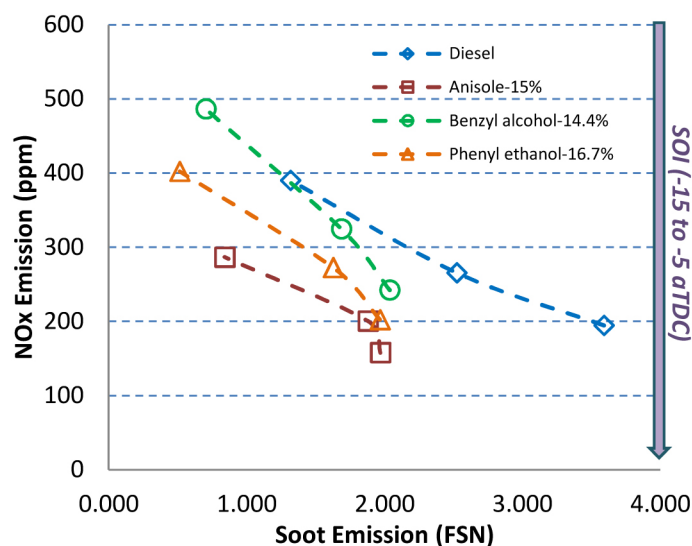


Figure.4. NO_x vs. soot emission at 7.5 bar gross IMEP, 30 wt% EGR, and $\lambda=1.00$, for diesel (blue diamonds), Anisole-15% (red squares), Benzyl alcohol-14.4% (green circles) and 2-Phenyl ethanol 16.7% (orange triangles)

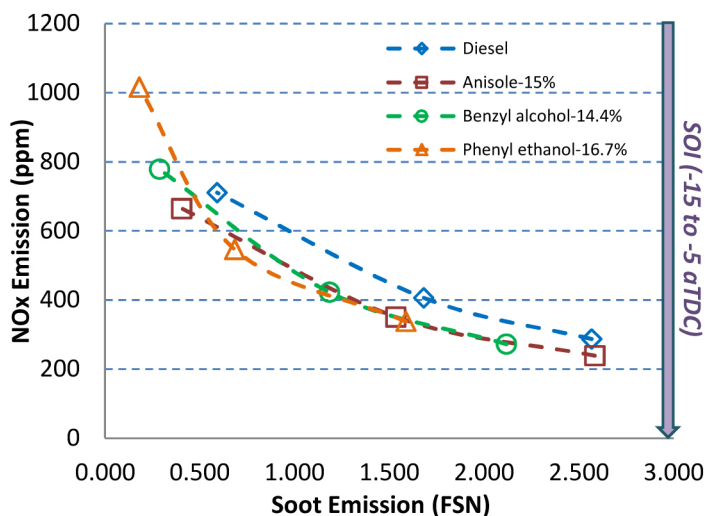


Figure.5. NO_x vs. soot emission at 12 bar gross IMEP, 30 wt% EGR, and $\lambda=1.15$, for diesel (blue diamonds), Anisole-15% (red squares), Benzyl alcohol-14.4% (green circles) and 2-Phenyl ethanol 16.7% (orange triangles)

For reasons of clarity, the normalized soot emissions are presented in Figures 6,7,8,9.

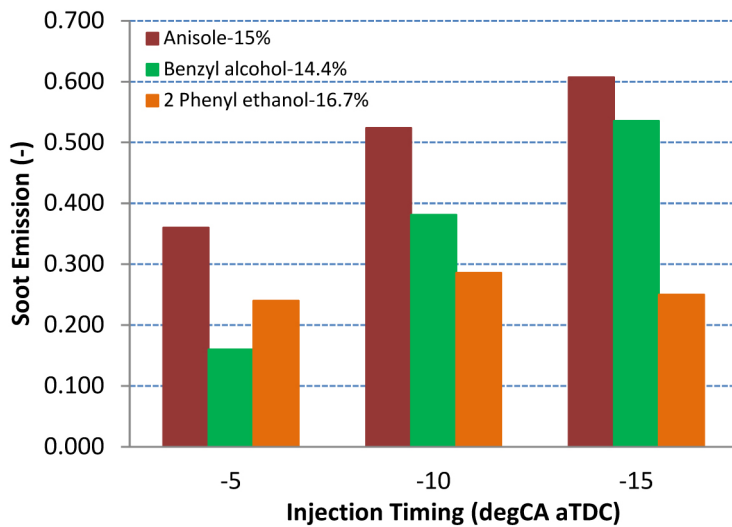


Fig.6. Normalized Soot Emission (Soot emission of pure diesel=1.0) at 7.5 bar gross IMEP, no EGR, and $\lambda=1.45$, for Anisole-15% (red bars), Benzyl alcohol-14.4% (green bars) and 2-Phenyl ethanol 16.7% (orange bars)

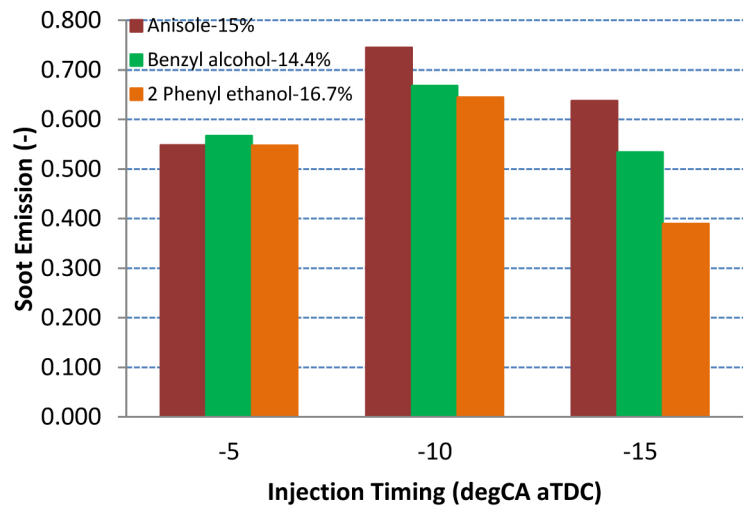


Fig.8. Normalized Soot Emission (Soot emission of pure diesel=1.0) at 7.5 bar gross IMEP, 30 wt% EGR, and $\lambda=1.00$, for Anisole-15% (red bars), Benzyl alcohol-14.4% (green bars) and 2-Phenyl ethanol 16.7% (orange bars)

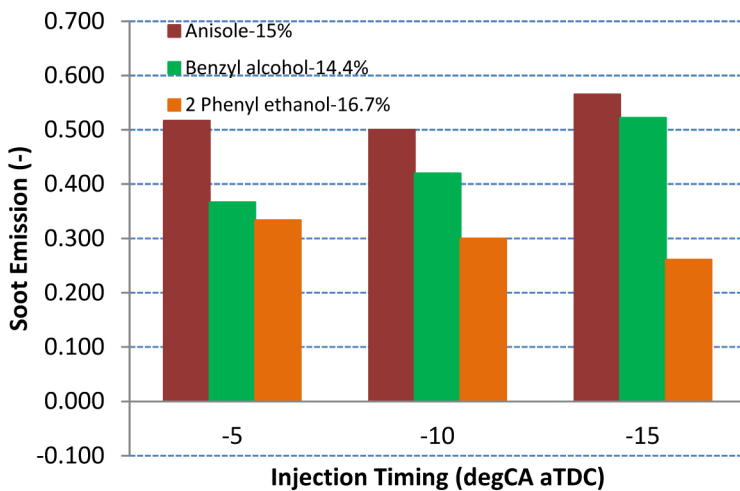


Fig.7. Normalized Soot Emission (Soot emission of pure diesel=1.0) at 12 bar gross IMEP, no EGR, and $\lambda=1.60$, for Anisole-15% (red bars), Benzyl alcohol-14.4% (green bars) and 2-Phenyl ethanol 16.7% (orange bars)

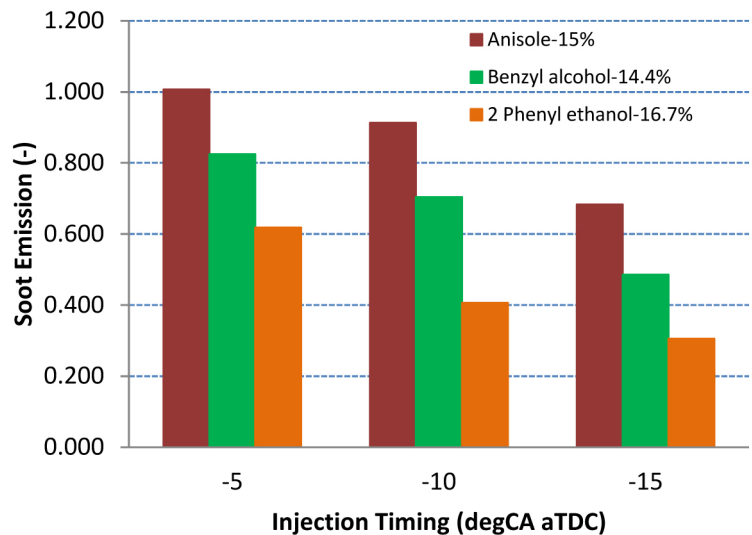


Fig.9. Normalized Soot Emission (Soot emission of pure diesel=1.0) at 12 bar gross IMEP, 30 wt% EGR, and $\lambda=1.15$, for Anisole-15% (red bars), Benzyl alcohol-14.4% (green bars) and 2-Phenyl ethanol 16.7% (orange bars)

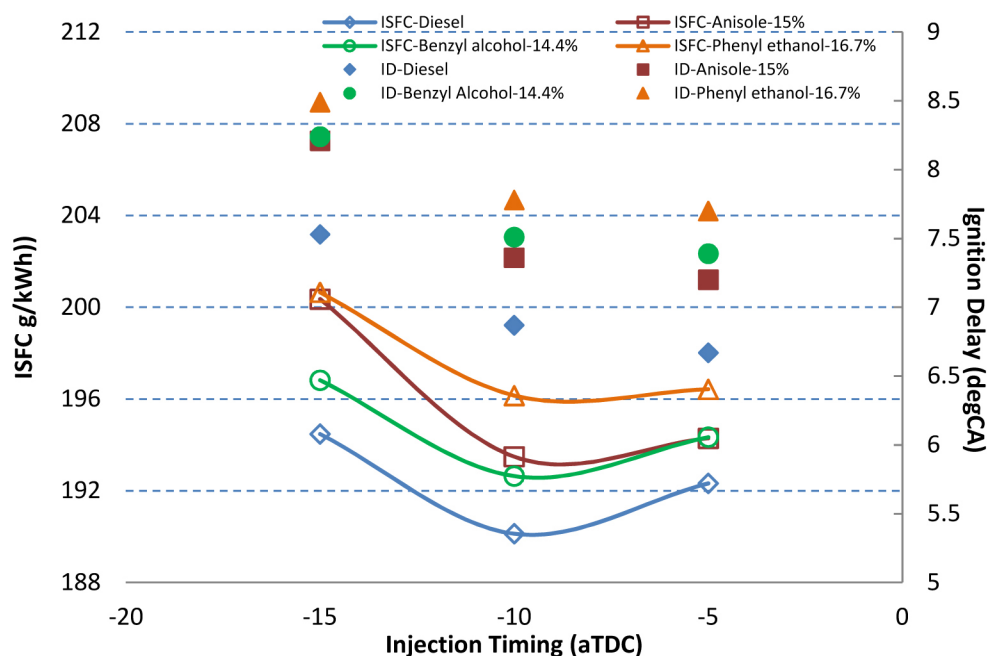


Figure 10. Fuel consumption (open symbols) and ignition delay (solid symbols) at 7.5 bar gross IMEP, no EGR, and $\lambda=1.45$, for diesel (blue diamonds), Anisole-15% (red squares), Benzyl alcohol-14.4% (green circles) and 2-Phenyl ethanol 16.7% (orange triangles)

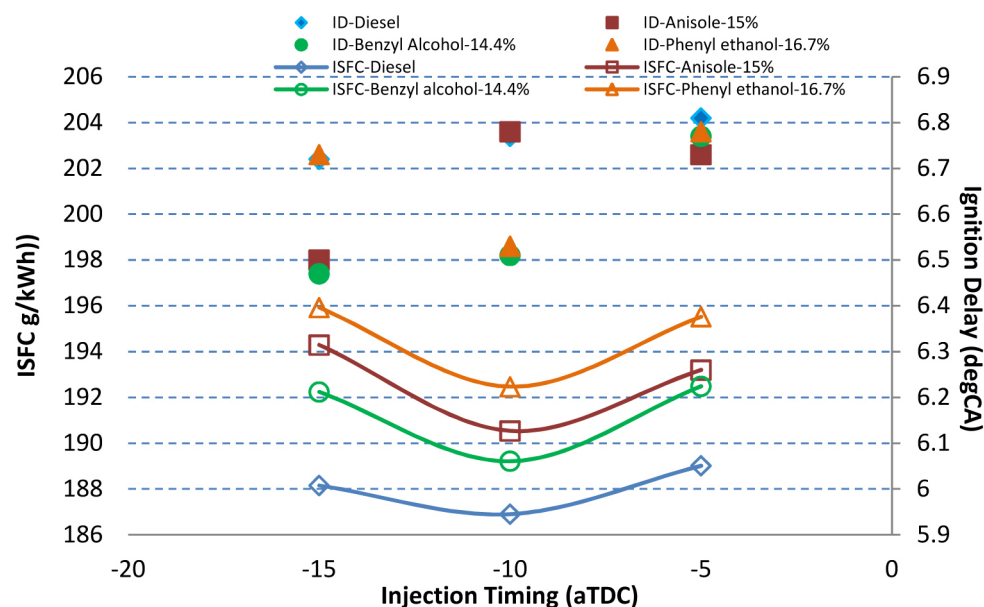


Figure 11. Fuel consumption (open symbols) and ignition delay (solid symbols) at 12 bar gross IMEP, no EGR, and $\lambda=1.60$, for diesel (blue diamonds), Anisole-15% (red squares), Benzyl alcohol-14.4% (green circles) and 2-Phenyl ethanol 16.7% (orange triangles)

ISFC In Terms Of Mass and Ignition Delays

Ideally, an improvement in the soot-NO_x trade-off should be realized at no expense of fuel economy. As could be expected in light of the presence of oxygen, this is not the

case for the aromatic oxygenates (Figures 10, 11, 12, 13). A compounding adverse factor intrinsic to aromatics is their relatively low H/C-ratio due to the aromatic carbon-carbon bonds.

Compared to the base fuel, the studied oxygenated blends have a reduced gravimetric lower heating value (LHV) of

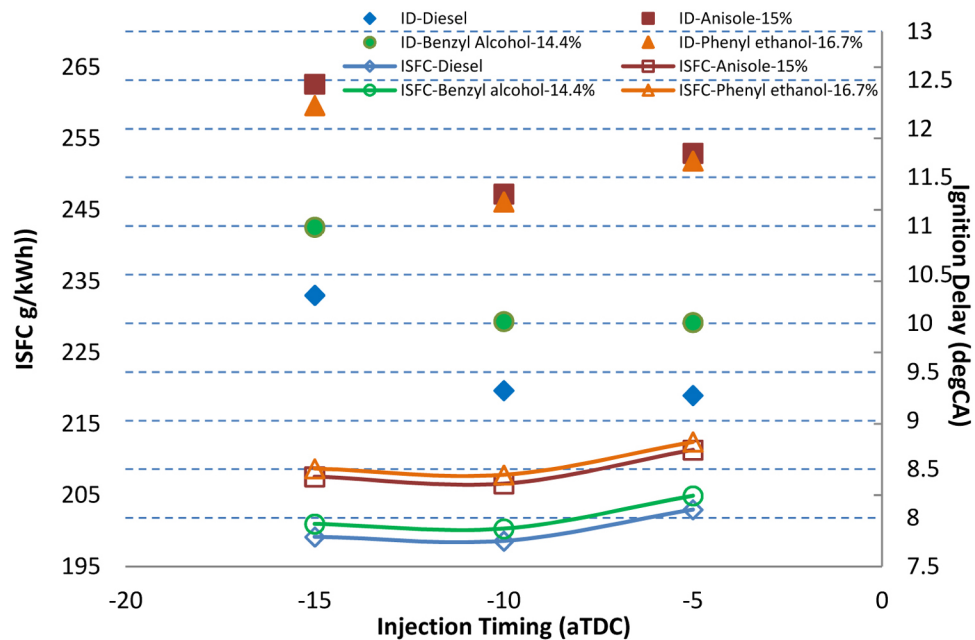


Figure.12. Fuel consumption (open symbols) and ignition delay (solid symbols) at 7.5 bar gross IMEP, 30 wt% EGR, and $\lambda=1.00$, for diesel (blue diamonds), Anisole-15% (red squares), Benzyl alcohol-14.4% (green circles) and 2-Phenyl ethanol 16.7% (orange triangles)

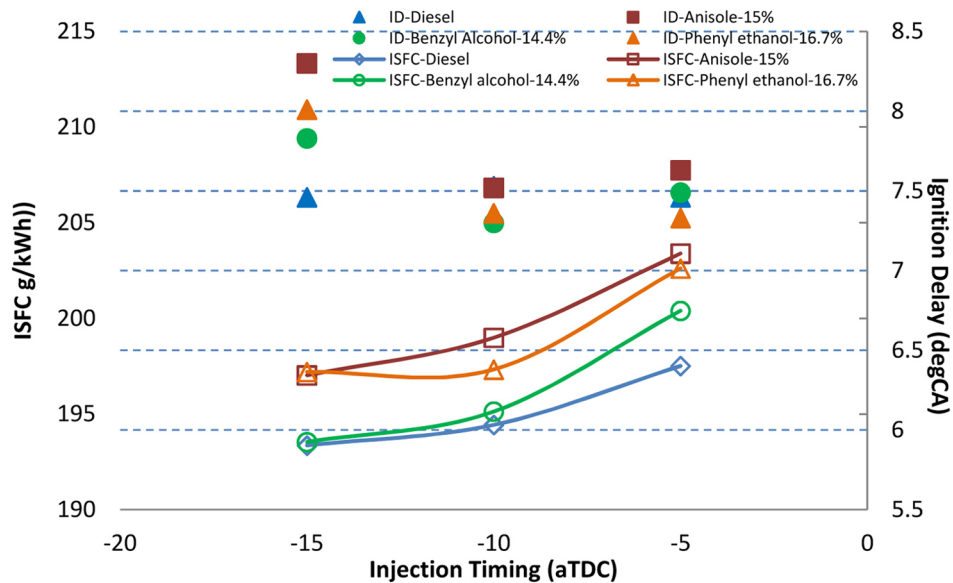


Figure.13. Fuel consumption (open symbols) and ignition delay (solid symbols) at 12 bar gross IMEP, 30 wt% EGR, and $\lambda=1.15$, for diesel (blue diamonds), Anisole-15% (red squares), Benzyl alcohol-14.4% (green circles) and 2-Phenyl ethanol 16.7% (orange triangles)

6.0%, 6.5% and 5.5%, respectively (Table.3). Based on this decrease in LHV, penalties in indicated specific fuel consumption (ISFC) could be expected in the order of 7-9, 8-10 and 7-9 g/kWh for anisole, benzyl alcohol and 2-phenyl ethanol, respectively.

However, from Figures 10,11,12,13, it becomes clear that the penalty in fuel consumption incurred with the aromatic

oxygenates is in all cases lower than could be expected based solely on the difference in LHV. It will be argued later in this paper that this might be linked to a more rapid combustion event.

While all oxygenates have consistently longer ignition delays than diesel fuel, the delays are not equal for all oxygenates, an equal (calculated) CN, notwithstanding