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Performance of Lignin Derived Compounds as Octane Boosters

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Abstract

The performance of spark ignition engines is highly dependent on fuel anti-knock quality, which in turn is governed by autoignition chemistry. In this study, we explore this chemistry for various aromatic oxygenates (i.e., anisole, 4-methyl anisole, 4-propyl anisole, guaiacol, 4-methyl guaiacol, 4-ethyl guaiacol) that can be produced from lignin, a low value residual biomass stream that is generated in paper pulping and cellulosic ethanol plants. All compounds share the same benzene ring, but have distinct oxygen functionalities and degrees of alkylation. The objective of this study is to ascertain what the impact is of said side groups on anti-knock quality and, by proxy, on fuel economy in a modern Volvo T5 spark ignition engine. To better comprehend the variation in behavior amongst the fuels, further experiments have been conducted in a constant volume autoignition device. The results demonstrate that alkylation has a negligible impact on anti-knock quality, while the addition of functional oxygen groups manifests as a deterioration in anti-knock quality.

Keywords: Lignin, knock, constant volume autoignition, anisole, guaiacol, octane boosters

1. Introduction

1.1. Requirements

At present, the most widely adopted strategy to further improve the efficiency of spark ignition (SI) engine is a combination of downsizing and turbocharging. The associated higher engine loads, however, increase the risk of knock [1] and therefore can be pursued more aggressively with more knock resistant fuels.

7 Knock resistance has been conventionally quantified in terms of the research
8 octane number (RON) and the motor octane number (MON). RON is measured
9 at lower speed and temperature conditions relative to MON. The two tests thus
10 represent distinct engine operating regimes. An attempt to create a more generic
11 measure for anti-knock quality, Kalghatgi [2] proposed the concept of octane in-
12 dex (OI):

$$OI = (1 - K) \cdot RON + K \cdot MON = RON - K \cdot (RON - MON) = RON - K \cdot S \quad (1)$$

13 In this equation, S denotes the so-called octane sensitivity of a fuel's auto-ignition
14 chemistry to temperature. Mathematically, S is the difference between RON and
15 MON.

16 When $K = 0$ and $K = 1$, the OI is by definition equal to RON and MON,
17 respectively. The constant K is a function of unburnt gas (end gas) temperature
18 and pressure and is a property of the engine, not the fuel. A number of stud-
19 ies show that over time K values have on average become lower, consistent with
20 better intake air and cylinder cooling, as well as more efficient combustion pro-
21 cesses which reject less chemical energy as heat [1, 3–5]. Negative K values have
22 been reported for downsized, turbocharged engines, which in practice implies that
23 knock resistance as measured by the OI is greater than RON for those fuels having
24 a octane sensitivity greater than zero [3–5].

25 Aromatics are among the highest RON and S compounds found in gasoline
26 today. The past decades, however, have seen legislation come into force that curbs
27 aromatic levels in gasoline, citing concerns regarding toxicity. In the EU, aromatic
28 content is currently limited to maximum 35% [6].

29 Omission of aromatics from the mix means that other high octane and S com-

30 ponents must be used to maintain a target level of knock resistance. For high RON
31 this can be achieved by blending paraffinic compounds such as iso-octane, which
32 has a RON of 100. While solving the RON issue, iso-octane has by definition an
33 S of 0 and thus cannot elevate this value back into pre-aromatic legislation terri-
34 tory. There are nevertheless other octane boosters on the market that do possess
35 both aforementioned attributes, such as ethyl-tert-butylether (ETBE) and ethanol
36 [1, 6, 7].

37 1.2. Market premium

38 Starting from any feedstock, it makes sound economic sense to aim production
39 processes towards compounds that have good anti-knock quality. The case for this
40 becomes quite clear when reviewing the data in Table 1. Evidently, an average
41 market premium of 5-22.5 US\$/ton (Table 1, far right column) can be commanded
42 for every RON point in excess of the 95 European benchmark.

43 When not crude oil but biomass is considered as the feedstock of choice, the
44 case for producing octane boosters is even more pronounced. Biofuels typically
45 contain oxygen in their molecular structure. This oxygen is often argued to be
46 commercially detrimental, owing to the associated reduction in (lower) heating
47 value (Table 1, 2nd column). In the event a biofuel can be marketed as an octane
48 booster, however, the prevailing price becomes decoupled from the *sec* calorific
49 value (Table 1, 4th and 5th columns).

50 Combined high RON and S values have been reported for various aromatic
51 oxygenates that might in future be produced from lignin, a residual stream pro-
52 duced and burnt to generate heat and steam in paper pulping and cellulosic ethanol
53 plants [9]. Table 2 shows some of the aromatic (oxygenates) or aromatic blend-

Table 1: European spot market prices for RON95 gasoline and various octane boosters

Fuel	LHV [MJ/kg]	RON	premium [8] [\$/ton]	premium [\$/GJ]	premium ^a [\$/ton+/RON+]	premium [\$/Gal+/RON+] ^b
Gasoline	41.9	95	500.75	11.95	0	0
Ethanol ^c	27	109	816.5	30.3	22.5	0.074
MTBE	35.1	117	610.92	17.4	5.0	0.014
ETBE	36.3	119	692	18.9	8.0	0.021

^a The premium of other fuels compared to gasoline per ton per RON, e.g. for MTBE, $(610.92 - 500.75)/(117 - 95) = 5$

^b US gallon

^c The spot price of ethanol in the US (American CBOT), as of June 19 2016, is 1.66 \$/gallon or roughly 555.8 \$/ton. This translates into a RON premium of 3.90 \$/ton+/RON+, 0.018 \$/Gal+/RON+.

54 ings from literature, which have high RON and S. From a review of earlier data on
 55 DCN for various aromatic oxygenates [10], it becomes clear that DCN increases
 56 proportionally with the number of functional oxygen groups, irrespective of group
 57 type or whether or not the ring is alkylated with C1-C3 chains (Figure 1).

58 While there have been many studies on the performance of lignin derived aro-
 59 matic oxygenates in compression ignition engines [13–18], little is known about
 60 their potential as renewable octane boosters. The goal of this paper is to determine
 61 both qualitatively and quantitatively the anti-knock quality of various members of
 62 two important families of aromatic oxygenates - anisoles and guaiacols - that are
 63 frequently subject of discussion in lignin related literature. Anti-knock quality

Table 2: Octane number of some aromatic (oxygenates)

	RON	MON	S
P-xylene [11]	116.4	109	7.4
Ethylbenzene [11]	107	97.5	9.5
2-Phenyl ethanol [12]	110	90	20
10 vol-% Benzyl alcohol with Euro95 [9]	96.9	86.6	10.3
10 vol-% Acetophenone with Euro95 [9]	96.1	86.6	9.5

64 is evaluated in a port-fuel injected turbo-charged SI engine and ignition quality
 65 tester (IQT). Distinctions found amongst the fuels are subsequently explained by
 66 means of kinetic model.

67 **2. Aromatic oxygenates**

68 Lignin, a critical component of plant cell walls, is the third most abundant
 69 natural polymer after cellulose and hemi-cellulose. Its large quantity and chemical
 70 structure make it an attractive feedstock for producing bio-aromatics [19]. As a
 71 three-dimensional amorphous polymer consisting of methoxylated phenylpropane
 72 structures, including mono-, di-, and poly-alkyl substituted phenols, benzenes and
 73 alkoxybenzenes, connected by C-O-C and C-C bonds [20], it is the largest direct
 74 source of aromatics found in nature.

75 There are three principal types of monolignols, or monomer units in lignin,
 76 namely p-coumaryl, coniferyl alcohol and sinapyl alcohol [21] (Figure 2).

77 Given that a wide variety of compounds can be produced from these units, a
 78 survey of the lignin literature has been conducted to reveal the most prevalent aro-

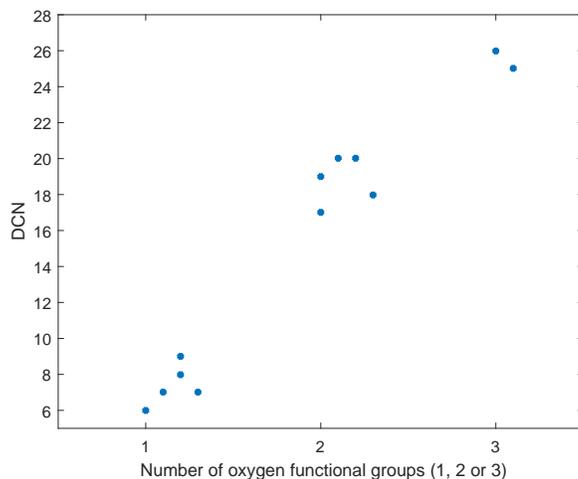


Figure 1: DCN as a function of number of functional oxygen groups for various types of oxygenated aromatics. Underlying data retrieved from [10]

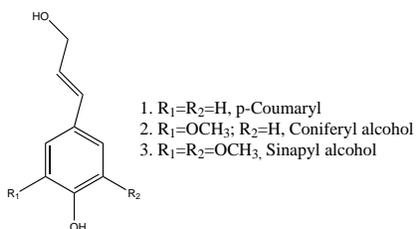


Figure 2: Lignin monolignols [22]

79 matic oxygenates that are also liquid at room temperature. Listed in Table 3, these
 80 are anisole and guaiacol, as well as the most common alkylated versions thereof,
 81 namely 4-methyl anisole (4-MA), 4-propyl anisole (4-PA), 4-methyl guaiacol (4-
 82 MG) and 4-ethyl guaiacol (4-EG). This set of compounds will allow us to analyze
 83 the impact of both alkylation and functional oxygen groups on anti-knock quality.

Table 3: Aromatic oxygenates frequently cited in lignin studies

Compound	References
anisole	[10, 23–29]
4-MA	[10, 26, 28–32]
4-PA	[10, 29, 33]
guaiacol	[10, 23, 24, 26, 34–50]
4-MG	[10, 32, 38, 39, 42, 43, 45, 49–53]
4-EG	[10, 25, 32, 39, 42, 43, 45, 51–56]

84 **3. Methodology**

85 *3.1. Fuel matrix*

86 *3.1.1. Base fuel*

87 Detailed hydrocarbon analysis of the Euro95 base fuel has been conducted in
 88 accordance with ASTM method D6729 [57] (Table 4). The results indicate that
 89 this commercial gasoline used in the Netherlands has a relatively high aromatic
 90 content, notably toluene (14-vol%). The following oxygenates were also iden-
 91 tified in the base fuel: methanol, ethanol and MTBE at 0.4%, 3.9%, 3.1% by
 92 volume, respectively.

93 *3.1.2. Oxygenates*

94 The molecular structures of the oxygenated aromatics investigated in this study
 95 are shown in Figure 3. Associated physiochemical properties are tabulated in Ta-
 96 ble 5.

97 Measurement of octane numbers for pure components with high boiling points

Table 4: Components of Euro95

Component	vol.-%
Paraffin	48.90
Aromatics	31.58
Olefins	6.62
Oxygentates	7.44
Naphthenes	4.60
Others	0.86
Average molecular weight	87.53
Empirical formula	$C_{6.11}H_{11.51}O_{0.12}$

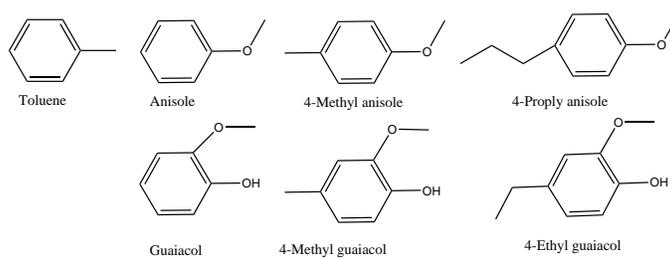


Figure 3: Molecular structures of selected aromatic oxygenates

Table 5: Physiochemical properties of neat compounds

Fuel	Formula	Density g/L	BP ^a °C	Viscosity ^b cP	LHV ^c MJ/L	DCN ^c	RON	MON
Toluene	C_7H_8	0.865	110	0.557	35.27	3	116 ^d	102 ^d
Anisole	C_7H_8O	0.995	154	1.00	33.19	6.4	103 ^e	92 ^e
4-MA	$C_8H_{10}O$	0.941	174	1.08	33.38	7.4	104 ^e	92 ^e
4-PA	$C_{10}H_{14}O$	0.941	215	1.64	34.22	7.5	–	–
Guaiacol	$C_7H_8O_2$	1.129	205	6.01	31.06	19.3	–	–
4-MG	$C_8H_{10}O_2$	1.092	221	7.70	31.57	19.8	–	–
4-EG	$C_9H_{12}O_2$	1.063	234	6.50	30.48	19.6	–	–

^a Boiling point

^b @ 25°C.

^c Toluene [58]; aromatic oxygenates [10]

^d [59]

^e ASTM method D2699 (RON) and D2700 (MON)

98 is challenging and was not attempted in this study. However, derived cetane num-
99 ber (DCN) is a measure of autoignition tendency that is inversely proportional
100 to octane number but is easily measured for pure compounds with high boiling
101 points [58]. Therefore, DCNs from McCormick et al. [10] were used (Table 5). A
102 further observation is that the boiling points of 4-PA, guaiacol, 4-MG and 4-EG
103 are relatively high in comparison to the ASTM D4814, distillation temperature
104 T90 and final boiling point limits of 190 and 225°C, respectively.

105 *3.1.3. Blends*

106 Compared to the RON95 base fuel (Euro95), all blends with 10 vol-% aro-
 107 matic oxygenates yield a similar or modestly higher volumetric LHV, an ele-
 108 vated oxygen content notwithstanding (Table 6). The RON and MON of Euro
 109 95, anisole and guaiacol blends were measured, anisole blend shows higher RON
 110 than Euro95, while guaiacol blend has same RON and slightly less MON.

Table 6: Properties of fuel blends

Fuel	Density g/L	O content [wt.-%]	LHV ^a MJ/kg	LHV ^a MJ/L	Viscosity ^b cP	RON	MON
Euro 95	0.74	2.24	41.91	31.01	0.31	95.0 ^c	85.6 ^c
10% Toluene	0.756	2.02	41.78	31.58	0.38	–	–
10% Anisole	0.764	3.46	40.79	31.15	0.33	97.4 ^c	86.8 ^c
10% 4-MA	0.766	3.26	40.96	31.37	0.35	–	–
10% 4-PA	0.764	3.00	41.22	31.51	0.35	–	–
10% Guaiacol	0.785	4.86	39.82	31.24	0.37	95.0 ^c	84.1 ^c
10% 4-MG	0.778	4.49	40.07	31.18	0.40	–	–
10% 4-EG	0.777	4.20	40.08	31.15	0.40	–	–

^a Values computed with molar blending rule

^b Blend viscosity were calculated using the Refutas equation [60]

^c Measured using ASTM method D2699 (RON) and D2700 (MON) by ASG Analytik-Service Gesellschaft mbH

111 3.2. *Engine experiments*

112 A 2.5L 5-cylinder Volvo T5 port-fuel injected turbocharged gasoline engine
113 was used in this study (Table 7). The test rig is equipped with a water-cooled
114 Schenck E2330 eddy current brake. A Kistler piezoelectric pressure sensor with a
115 resolution of 3600 samples per crank shaft rotation has been installed into one of
116 the cylinders for pressure analysis.

Table 7: Engine specifications

Engine	2.5T (B5254T6)
Type	In-line 5-cylinder LPT
Displacement [cm ³]	2521
Bore [mm]	83
Stroke [mm]	93.2
Combustion chamber type	Pent-roof
Compression ratio [-]	9.0:1
Valves per cylinder	4
Ignition sequence	1-2-4-5-3
Fuel, octane requirement [RON]	95-98
Max. output [kW(HP)@RPM]	147(200)@4800
Max. torque [Nm@RPM]	300@1500-4500
Max. boost pressure [bar]	1.38

117 Engine experiments were conducted at stoichiometric conditions, wide open
118 throttle (WOT) and low speed (1500 RPM). Spark timing was advanced until the
119 onset of knock, the definition of which will be presented later on. The spark tim-

120 ing and boost pressure used for the baseline gasoline measurements was 12 crank
121 angle degrees before top dead center ($^{\circ}\text{CA}$ bTDC) and 1.26 bar, respectively. In-
122 take air temperature was regulated by means of an external heat exchanger and
123 kept constant at roughly 20°C . Engine-out coolant and oil temperatures were kept
124 constant at approximately 91°C . All remaining engine settings were kept at their
125 stock values.

126 Knock intensity (KI) was quantified by means of the maximum amplitude
127 pressure - peak-to-peak - oscillation (MAPO) method [61]. The MAPO value is
128 obtained by filtering the in-cylinder pressure profile with a 6-25 kHz bandpass
129 filter. The knock threshold is met when the knock intensity (KI), as expressed by
130 MAPO, equals 0.25 bar. The spark timing at which this event occurs is referred
131 to as the knock limited spark advance (KLSA). Besides cycle-by-cycle variation,
132 the engine experiments will also vary day to day, so the day-to-day variation of
133 the base gasoline was recorded during the measurement (four different days), the
134 standard deviation of these measurement are shown as error bars in the engine
135 performance results. Limited by the amount of fuels purchased, the other fuels
136 have only tested in one day, so no day-to-day variation shows here.

137 *3.3. Constant volume autoignition experiments*

138 A modified ignition quality tester (IQT) was used to study the temperature
139 dependency of autoignition for the oxygenates. The IQT is a constant volume
140 combustion chamber, equipped with a fuel injection system in accordance with
141 the ASTM method D6890 for measuring DCN [62]. ID is defined here as the
142 duration between the start of injection and the time at which the pressure reaches
143 the so-called pressure recovery point of 138 kPa above the value prior to fuel

144 injection.

145 However, the ASTM D6890 method is known to produce a heterogeneous
146 fuel-air mixture such that the ignition delay time measured is a combination of
147 physical and chemical kinetic factors. Bogin et al. have modified the IQT con-
148 trols and operating parameters for use in more fundamental ignition delay and
149 kinetic mechanism validation studies [63–65]. The authors observed that for a
150 sufficiently long auto-ignition delay time (ID) (e.g., > 40 ms), the mixture condi-
151 tions are nearly homogeneous in nature. In such an environment, chemical kinet-
152 ics dominated the auto-ignition process. Fluid dynamical effects associated with
153 injection phenomena such as spray break and evaporation can be ignored under
154 these circumstances.

155 Temperature sweeps of the neat oxygenates were performed in the modified
156 IQT at a pressure of 10 bar. This specific pressure was selected because it was
157 required to obtain ignition delay times in excess of aforementioned 40 ms, while
158 still being representative of the end-gas pressure for SI engine operation. Accord-
159 ingly, we assume SI engine-like pseudo-homogeneous mixtures exist for most of
160 the data.

161 The IQT chamber was pressurized with air (21% O_2 in N_2) and heated to the
162 highest temperature in the sweep (e.g., 980 K). For lower temperatures, down to
163 700 K, the heaters were turned off while fuel was injected at regular intervals as
164 the chamber cooled down. To produce an equivalence ratio of 1 at 900 K, the mass
165 of injected fuel was adjusted to accommodate the distinct densities and molecular
166 formulas of the various fuels by using the variable volume injection pump. The
167 volume of the fuel injected can be changed by using metal shims with different
168 thickness, which will change the relative position of the fuel plunger of the in-

169 jection pump (more detailed description of how to choose the shim thickness are
170 in Appendix A). The mass of fuel injected was then held constant for each tem-
171 perature sweep, and consequently the equivalence ratio of the combustion events
172 decreased as the combustion chamber cooled. Other studies comparing constant
173 mass to constant equivalence ratio temperature sweeps have shown that the effects
174 of this change in equivalence ratio on ID measurements are small [64–66].

175 **4. Results & discussion**

176 *4.1. Engine experiments*

177 *4.1.1. Knock intensity and knock limited spark advance*

178 Knock intensity, expressed here as MAPO, increases for all fuels with ad-
179 vancing spark timing (Figure 4). As might be expected from the ON and DCN
180 data presented earlier (Table 5 and 6), the toluene blend shows the greatest knock
181 resistance by allowing the most spark advance before reaching KLSA, with the
182 (alkylated) anisoles trailing close behind (Figure 4). The (alkylated) guaiacols
183 blends, which have ON similar to the base fuel, are more reactive fuels com-
184 pared to anisoles and toluene, as indicated by the less amounts of possible spark
185 advance. These effects are quantified in Table 8. Evidently, the benzene ring im-
186 parts low reactivity to all the oxygenated compounds. Nevertheless, the type and
187 number of functional groups, exert a strong influence on the anti-knock quality.

188 Based on the RON, MON and the KLSA of the blends, the OI equation (Equa-
189 tion (1)) gives $K=-1.28$ for this engine at this working condition. This is consistent
190 with results from literature [2, 7], and indicating that fuels with high octane sen-
191 sitivity are preferred.

Table 8: Knock limited spark advance for all fuels at WOT and 1500 RPM^a

Fuel	KLSA CA bTDC	KLIMEP bar	KLEfficiency %	KLFuel consumption ml/kWh
Euro 95	10.5	14.1	37.3	311.2
10% Toluene	13.9	14.4	38.3	297.8
10% Anisole	12.7	14.3	38.1	303.3
10% 4-MA	13.1	14.3	38.1	301.1
10% 4-PA	13	14.3	37.0	308.7
10% Guaiacol	11.3	14.1	36.9	312.5
10% 4-MG	10.9	14.2	36.9	312.7
10% 4-EG	11.5	14.1	36.5	316.6

^a All values in this table are taken at the knock limited (KL) spark timing

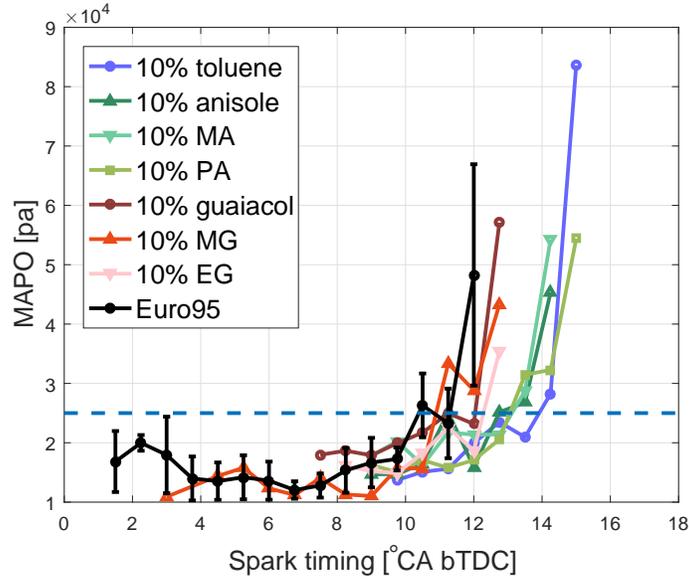


Figure 4: MAPO for all fuels at WOT and 1500 RPM, the dashed line represents the threshold for knock

192 *4.1.2. Efficiency*

193 It can be seen from Figure 5 that when advancing the spark timing, the IMEP
 194 is increasing for all the fuels. Fuels with better anti-knock quality allow more
 195 advanced spark timings, and thus can achieve higher IMEP. While none of them
 196 reached the maximum IMEP due to the knock limitation. This again indicates the
 197 importance of having a high anti-knock quality fuel.

198 More advanced KLSA yields dividends in terms of the engine performance,
 199 i.e., IMEP, efficiency and fuel consumption. Among these parameters, fuel con-
 200 version efficiency is calculated by Equation 2, where P is power, m is the mass of
 201 fuel inducted per cycle.

$$\eta_f = \frac{P}{LHV \times m} \quad (2)$$

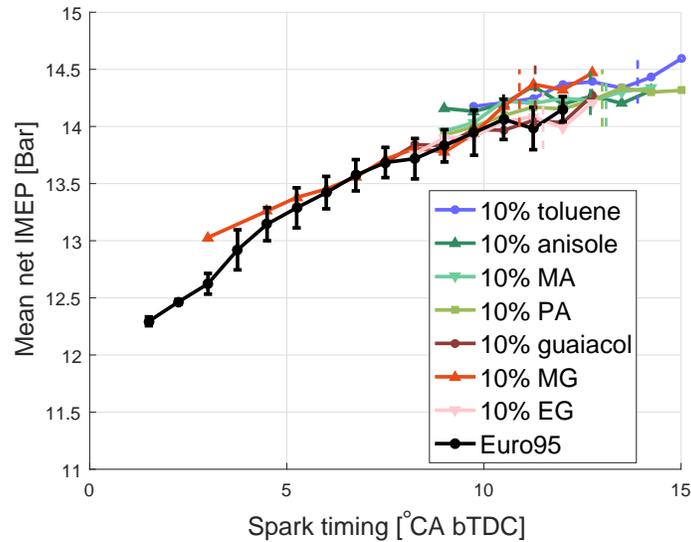


Figure 5: Net IMEP as a function of spark timing for all fuels at WOT and 1500 RPM. Fuel specific KLSA is indicated by dashed bars in the same color

202 However, The 4-PA and guaiacols blends show a penalty in efficiency relative to
 203 the base fuel, a slightly more favorable KLSA (Figure 6) notwithstanding. How-
 204 ever, the day-to-day variance has a similar discrepancy to the efficiency difference,
 205 therefore, based on our tests, the blends composition has a negligible impact on
 206 fuel efficiency.

207 4.1.3. Fuel consumption

208 As is true by definition for any oxygenated fuel, the presence of oxygen in
 209 the molecular structure has a negative impact on the gravimetric fuel consumption
 210 (Figure 7). Notably the guaiacols, having two functional oxygen groups, perform
 211 poorly by this measure.

212 In practice, however, consumers do not pay for mass, they pay for volume and
 213 aromatics have high densities relative to gasoline (Table 5). Moreover, as density

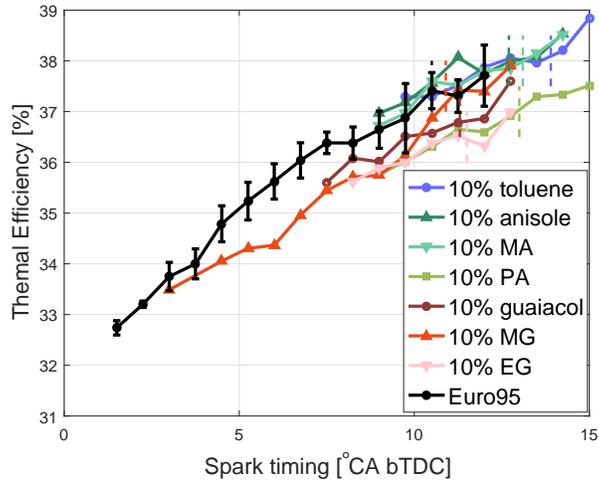


Figure 6: Fuel conversion efficiency as a function of spark timing for all fuels at WOT and 1500 RPM. Fuel specific KLSA is indicated by dashed bars in the same color

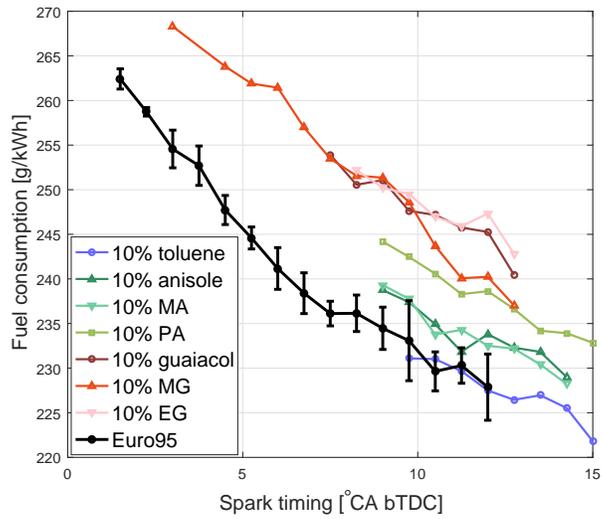


Figure 7: Indicated specific *gravimetric* fuel consumption as a function of spark timing for all fuels at WOT and 1500 RPM. Fuel specific KLSA is indicated by dashed bars in the same color

214 rises with degree of oxygenation, the spread in volumetric fuel economy is far
215 less pronounced (Figure 8). In fact, the (alkylated) anisole blends yield better fuel
216 consumption than gasoline.

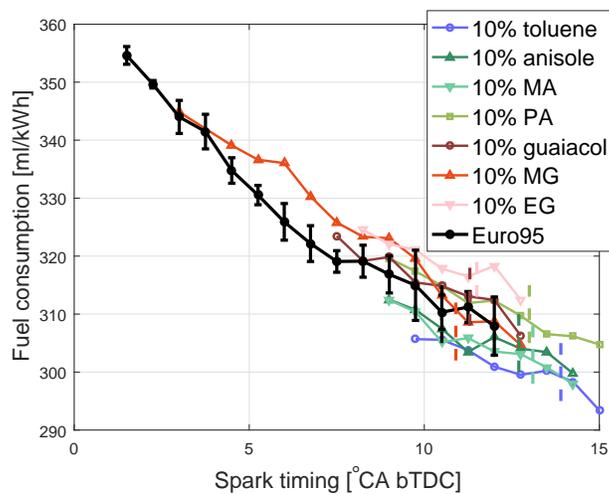


Figure 8: Indicated specific *volumetric* fuel consumption as a function of spark timing for all fuels at WOT and 1500 RPM. Fuel specific KLSA is indicated by dashed bars in the same color

217 4.2. Constant volume autoignition experiments

218 Auto-ignition chemistry is quite important for SI engines, since knock is caused
219 by the auto-ignition of the end-gas in the chamber. Therefore, constant volume
220 auto-ignition experiments were conducted for all the oxygenates and toluene.

221 The temperature dependent autoignition behavior for all studied aromatics at
222 10 bar, 720-950 K is shown in Figure 9, with iso-octane as a comparison, which
223 has same RON and MON of 100 [64]. As discussed earlier, when the ID is in
224 excess of 40 ms, the ignition process can be assumed to be controlled primarily
225 by chemical kinetics, as opposed to spray physics.

226 The first thing to note from Figure 9 is that none of these aromatics exhib-
227 ited any low temperature heat release (LTHR) or negative temperature coefficient
228 (NTC) behavior, in contrast to iso-octane. Analysis of the pressure traces for these
229 compounds confirms the absence of low temperature heat release (Figure 10), there-
230 fore the use of the conventional ASTM D6890 definition for start of ignition (i.e.,
a fixed 138 kPa above the chamber pressure recovery point) is valid [66].

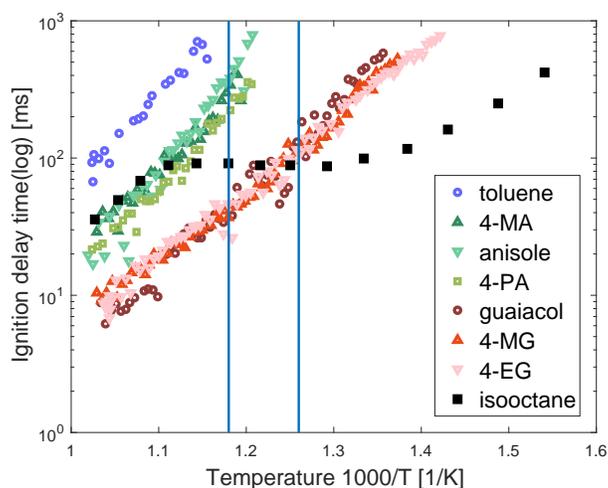


Figure 9: IQT data for all neat aromatics at 10 bar, with iso-octane as a reference from Bogin et al. [64]. The two vertical lines represent the DCN test temperature (818.13 ± 30 K) [62], although, the DCN test pressure is set at 21.4 bar, which is much higher than our test condition.

231

232 It can be seen that as expected from the DCN and RON data, toluene has the
233 longest IDs over the entire temperature range studied. Anisole and 4-MA have
234 similar reactivity, however the longer alkyl chain of 4-PA appears to slightly in-
235 crease its reactivity. The increase in reactivity is stronger upon adding another
236 oxygen functional group to the benzene ring. Guaiacol and its alkylated deriva-
237 tives have the shortest ID. Note that data from $T > 800$ K can not be assumed as

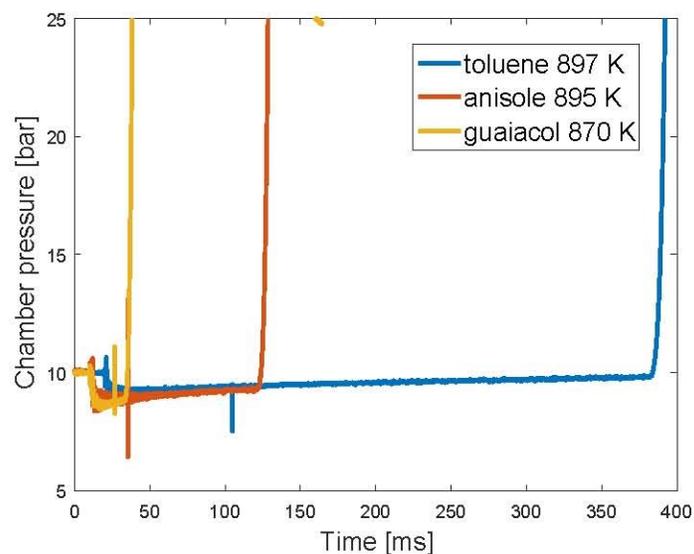


Figure 10: Pressure trace of toluene, anisole and guaiacol at specific temperature in modified IQT at 10 bar

238 homogeneous auto-ignition for guaiacols

239 All aromatics are clustered and ranked in accordance with number of functional
 240 oxygen groups, irrespective of degree of alkylation (Figure 9).

241 A fuel's octane number is a measure of its anti-knock rating, and this parame-
 242 ter is dominated by auto-ignition chemistry at the ON test conditions. Badra et al.
 243 found that 850 K and 50 atm has the best fit with the RON operating conditions.
 244 For MON, this is 980 K and 45 atm [67]. Mehl et al. predicted the ON by using
 245 detailed chemistry and a simplified two-zone SI engine model [68].

246 The IDs for iso-octane, as shown in Figure 9 can also show us some qualitative
 247 comparison of ON and this IQT test condition. The auto-ignition of iso-octane
 248 is faster than toluene for the whole test range, and it is similar to anisole when
 249 $T > 900$ K, from which point on, anisoles yield longer IDs. Compared to iso-

250 octane, guaiacol is slower when $T < 800$ K, but becomes faster when temperature
251 increases above 800 K. According to the blending RON and MON of anisole and
252 guaiacol, it is expected that anisole will have a higher RON than Euro95, while
253 guaiacol has a RON similar to Euro95, which is slightly lower than the iso-octane
254 data. The left vertical line, which is the upper limit of the DCN temperature
255 requirement, fits for the RON indication. Bogin et al. also found that the ID at
256 higher temperature was more representative of MON conditions [66]. However,
257 more experiments are needed to study this topic further.

258 **5. Conclusions**

259 The goal of this paper was to determine both qualitatively and quantitatively
260 the anti-knock quality of various members of two important families of aromatic
261 oxygenates - anisoles and guaiacols - that are frequent subjects of discussion in
262 lignin related literature. Benchmarked against toluene, the anti-knock quality of
263 these compounds has been evaluated in a port-fuel injected turbo-charged SI en-
264 gine and a constant volume autoignition experiment. Based on the results of this
265 study, several conclusions may be drawn:

266 *5.1. Fuel properties*

- 267 • Addition of 10 vol.-% anisole increases the octane number of the RON95
268 base fuel, but is not as effective as toluene at an equal blend ratio.
- 269 • Addition of 10 vol.-% guaiacol has a negligible impact on the octane num-
270 ber of the RON95 base fuel.
- 271 • Alkylation of either anisole or guaiacol leads to a modest reduction in RON.

272 • Gravimetric heating values of the aromatic oxygenates blends are modestly
273 lower than for the RON 95 base fuel.

274 • Owing to a higher density, volumetric heating values of the aromatic oxy-
275 genates blends are modestly higher than for the RON 95 base fuel.

276 5.2. *Engine experiments*

277 • All oxygenated blends made it possible to operate the engine with an earlier
278 knock limited spark advance (KLSA)

279 • No significant differences in thermal efficiency were observed amongst the
280 tested fuels.

281 • Modest improvements in volumetric fuel economy were observed for the
282 anisole blends.

283 • Slight penalties in volumetric fuel economy were measured for the guaiacol
284 blends.

285 • In general, functionalization by means of oxygenation and to a lesser extent
286 alkylation has a negative impact on anti-knock quality and, by proxy, overall
287 engine performance.

288 5.3. *Constant volume autoignition experiments*

289 • Ignition delay (ID) trends amongst the fuels are in-line with both RON and
290 KLSA data, with the least reactive fuels consistently yielding the longest
291 ID.

- 292 • Alkylation generally has a modest impact on ID, with the exception of long
293 side chains at low temperature. In all cases, alkylation leads to a shorter ID.
- 294 • Oxygenation has a strong impact on ID, with the ID becoming shorter and
295 shorter as more functional oxygen groups are added to the ring.

296 In short, the anti-knock quality of aromatic oxygenates suffers from function-
297 alization, whereby oxygenation appears to be far more detrimental than alkylation.
298 Lignin conversion stakeholders should take this into account in their cost-benefit
299 analysis.

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541 **Appendices**

542 **A. Appendix A**

543 Gravimetric fuel consumption is calculated by using the measured mole count
544 of air in the combustion vessel at a given pressure and temperature. First, this
545 data is used to calculate how much fuel is required for the stoichiometric case.
546 Subsequently, the shim thickness, which is related to the amount of the injected
547 fuel, is calculated by using linear calibration of the injected amount of fuel and the
548 required shim thickness in the fuel injection pump. The amount of fuel injected is
549 controlled using the method outlined in the IQT operating manual.

550 Viscosity is an important parameter for injection at room temperature and at-
551 mospheric conditions. Three reference fuels, n-heptane, decane and hexadecane,

552 each having a distinct viscosity, were tested in order to derive a correlation be-
553 tween shim thickness and the injected fuel mass. Figure 11 shows the calibration
554 results of this relationship.

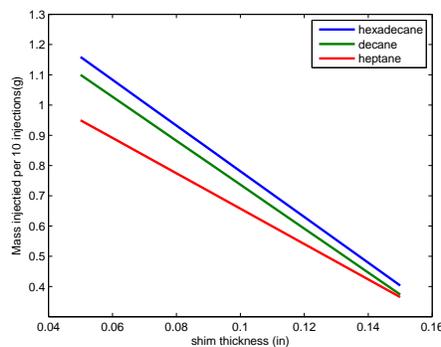


Figure 11: Calibration of injected mass for various model fuels

555 The viscosity of hexadecane at $3 \times 10^{-3} Pa \cdot s$ is roughly half that of guaiacol.
556 Nevertheless, it is the best proxy for guaiacol amongst the reference fuels, so its
557 data is used for calculating the shim thickness for the guaiacols.

558 Anisole and toluene have a viscosity of $1 \times 10^{-3} Pa \cdot s$ and $0.56 \times 10^{-3} Pa \cdot s$,
559 respectively. Both values are close to that of decane ($0.93 \times 10^{-3} Pa \cdot s$). Decane
560 data is therefore used to calculate the shim thickness for the anisoles (and toluene).

561 The figure shows that, as the shim becomes thicker, the differences between
562 the different fuels become smaller. For the aromatic fuels considered in this study,
563 the shim is always $> 0.09in$, which means the impact of viscosity is not significant
564 here.