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Performance of lignin derived compounds as octane boosters

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HIGHLIGHTS

- Various anisoles and guaiacols which can be derived from lingin have been evaluated as octant boosters.
- All compounds match or outperform RON 95 gasoline with respect to anti-knock quality, and showed equal or improved thermal efficiency.
- The trends of auto-ignition delay time measured in a modified IQT are in line with the engine test.

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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.

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.

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

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

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

When $K = 0$ and $K = 1$, the OI is by definition equal to RON and MON, respectively. The constant K is a function of unburnt gas (end gas) temperature and pressure and is a property of the engine, not the fuel. A number of studies show that over time K values have on average become lower, consistent with better intake air and cylinder cooling, as well as more efficient combustion processes which

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reject less chemical energy as heat [1,3–5]. Negative *K* values have been reported for downsized, turbocharged engines, which in practice implies that knock resistance as measured by the OI is greater than RON for those fuels having a octane sensitivity greater than zero [3–5].

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

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

1.2. Market premium

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

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

Combined high RON and *S* values have been reported for various aromatic oxygenates that might in future be produced from lignin, a residual stream produced and burnt to generate heat and steam in paper pulping and cellulosic ethanol plants [9]. Table 2 shows some of the aromatic (oxygenates) or aromatic blendings from literature, which have high RON and S. From a review of earlier data on DCN for various aromatic oxygenates [10], it becomes clear that DCN increases proportionally with the number of functional oxygen groups, irrespective of group type or whether or not the ring is alkylated with C1-C3 chains (Fig. 1).

While there have been many studies on the performance of lignin derived aromatic oxygenates in compression ignition engines [13–18], little is known about their potential as renewable octane boosters. The goal of this paper is to determine both qualitatively and quantitatively the anti-knock quality of various members of two important families of aromatic oxygenates - anisoles and guaiacols - that are frequently subject of discussion in lignin related literature. Anti-knock quality is evaluated in a port-fuel injected turbo-charged SI engine and ignition quality tester (IQT). Distinctions found amongst the fuels are subsequently explained by means of kinetic model.

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

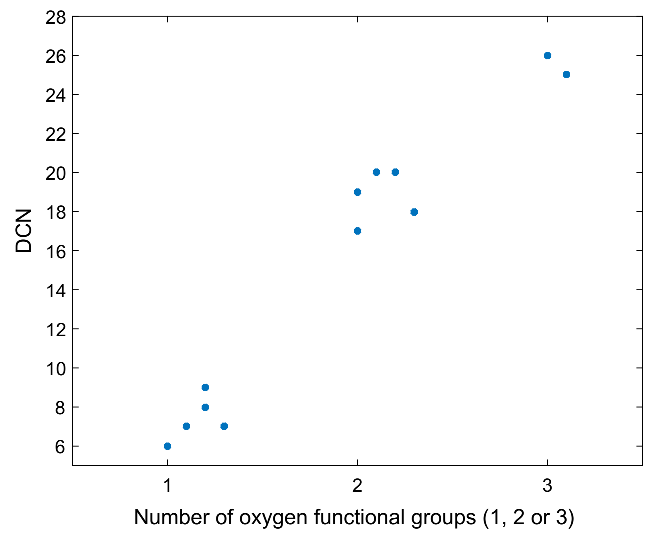

Fig. 1. DCN as a function of number of functional oxygen groups for various types of oxygenated aromatics. Underlying data retrieved from [10].

2. Aromatic oxygenates

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

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

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+.