

Lignin Derivatives as Potential Octane Boosters

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ABSTRACT

Owing to environmental and health concerns, tetraethyl lead was gradually phased out from the early 1970's to mid-1990's in most developed countries. Advances in refining, leading to more aromatics (via reformat) and iso-paraffins such as iso-octane, along with the introduction of (bio) oxygenates such as MTBE, ETBE and ethanol, facilitated the removal of lead without sacrificing RON and MON. In recent years, however, legislation has been moving in the direction of curbing aromatic and olefin content in gasoline, owing to similar concerns as was the case for lead.

Meanwhile, concerns over global warming and energy security have motivated research into renewable fuels. Amongst which are those derived from biomass. The feedstock of interest in this study is lignin, which, together with hemicellulose and cellulose, is amongst the most abundant organic compounds on the planet. Contrary to (hemi-) cellulose, however, which is an important constituent of feed for livestock, lignin falls completely outside of our food chain.

This study was motivated by the need for renewable octane boosters of low toxicity, which improve both anti-knock quality and fuel economy under modern engines conditions. The goal of this study is to investigate on a Volvo T5 spark ignition engine whether or not the lignin derived aromatic oxygenates, benzyl alcohol, 2-phenyl ethanol and acetophenone, adhere to such requirements.

It was found that these aromatic oxygenates have a low toxicity and improve both knock resistance and volumetric fuel economy under modern engine operating conditions.

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INTRODUCTION

Throttle losses are largely to blame for the efficiency penalty at part load of spark ignition (SI) relative to compression ignition engines. A widely employed method to minimize these losses is to downsize the engine by means of turbo-charging. Downsizing potential, however, is constrained by engine knock. Knock may be avoided to some extent by increasing the octane rating of gasoline, for example by adding octane boosters.

Research (RON) and motor (MON) octane number are parameters that rate anti-knock quality at specific conditions by comparing them with so-called primary reference fuels (PRF's), a binary blend of iso-octane and n-heptane. The ON simplifies the complex auto-ignition chemistry by comparing a fuel to PRF. The higher the ON, requiring a higher iso-octane concentration in the PRF, the higher the resistance to auto-ignition.

When first introduced in the 1930s, the relatively high intake temperature of 149 °C for MON was representative for contemporary automobiles and a consequence of poor engine cooling and heated carburetors. Over the years, new technologies, such as direct injection, better cooling system, higher compression ratios and

boosted intake air, resulted in significantly lower intake temperature. In fact, temperatures have now fallen well below the already significantly cooler RON level of 52°C.

This prompted research into new octane rating scales, such as the Octane Index (OI: Eq.1) [1], which takes into account shifts in intake temperature relative to intake pressure via a new parameter K [2].

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

$$OI = RON - K \cdot S \quad (2)$$

$$S = RON - MON \quad (3)$$

By definition, K is 0 and 1 at RON and MON conditions, respectively. In other words, K decreases with intake temperature, relative to pressure. Accordingly, when cooling at constant pressure, as is the case for direct injection and intercooling, both common in modern SI engines, near-zero or even negative K values can be expected.

A second variable introduced in the OI equation is the fuel sensitivity S . S indicates the dependence of a fuel's auto-ignition behavior on the prevailing gas temperature. While intuitively one might expect a fuel to be more prone to auto-ignition in hotter environments, this is not the case for all hydrocarbon types. For instance, the auto-ignition tendency of most paraffin, such as the PRF's used in RON and MON tests are hardly affected at all by shifting gas temperatures in the range relevant for knock. This is due to a reaction kinetics phenomenon known as negative temperature coefficient or NTC behavior. Consequently, without going further into detail here, paraffin typically have near-zero S values. Conversely, more complex hydrocarbons such as olefins and aromatics, in the absence of NTC chemistry, behave more as one expects and ignite more readily as temperature increase, manifesting in a positive value for S .

From the OI equation follows that for a positive K , as is generally the case for older engine technology, as low an S as possible is required to achieve the highest OI. Conversely, when K becomes negative, as is the case in most contemporary engines, the higher the value for S , the higher the OI. In other words, according to the OI theory, as we travel through time from past to present to future, paraffin should gradually give way to olefins and aromatics as the fuel of choice.

Owing to environmental and health concerns, tetraethyl lead, in the past the most widespread octane booster of choice since the 1920's, was gradually phased out from the early 1970's to mid-1990's in most developed countries. Advances in refining, leading to more aromatics (via reformat) and iso-paraffins such as iso-octane, along with the introduction of (bio) oxygenates such as MTBE, ETBE and ethanol, facilitated the removal of lead without sacrificing RON and MON. In recent years, however, legislation has been moving in the direction of curbing aromatic and olefin content in gasoline, owing to similar concerns as was the case for lead. Effectively, this is making gasoline more paraffinic and thus low S . As argued earlier, this is the wrong direction when considering ideal fuel requirements for modern engines.

Meanwhile, concerns over global warming and energy security have motivated research into renewable fuels. Amongst which are those derived from biomass. The feedstock of interest in this study is lignin, which, together with hemicellulose and cellulose, is amongst the most abundant organic compounds on the planet. Contrary to (hemi-) cellulose, however, which is an important constituent of feed for livestock, lignin falls completely outside of our food chain.

Etymologically speaking, lignin is derived from the Latin word for wood, *lignum*. On a molecular level, it is a complex, amorphous polymer of various mono-aromatic oxygenates, linked via a variety of short side chains. Lignin is currently being produced as a side stream in the paper- and cellulosic ethanol industry. Its fate, in most instances, is to be burnt for process heat and electricity generation; both low value applications. Accordingly, conversion of lignin to higher value transport fuels might help improve the bottom line of biorefineries.

In earlier work, Boot et al. [3] measured the octane number and heating value of various oxygenated mono-aromatics. These compounds were found to have both a higher octane number and

(volumetric) heating value compared to gasoline. From literature it is known that at least three such compounds, namely acetophenone [4,5], 2-phenylethanol [6,7] and benzyl alcohol [5] can be derived from lignin. Interestingly, all three happen to be approved food ingredients [8] and can therefore be considered of relatively low toxicity compared to the aromatics conventionally found in gasoline, such as benzene, toluene and xylene.

Accordingly, such aromatic oxygenates would not only be renewable, but would also to break from the antagonistic behavior found in conventional gasoline aromatics, namely curbing CO_2 by improving anti-knock quality, while at the same time being highly toxic. The goal of this study is to investigate if aromatic oxygenates improve anti-knock quality and fuel economy under modern engines conditions.

METHODOLOGY

Experimental Setup and Operating Conditions

A 2.5L 5-cylinder Volvo T5 port fuel injection turbocharged gasoline engine was used. The experiments were conducted at stoichiometric condition, with changing throttles and spark timing. The engine-out coolant and oil temperatures were 91°C. The detail engine parameters are listed in Table 1. The setup is equipped with a water-cooled Schenck E2-330 eddy current brake; a Kistler piezoelectric pressure sensor is installed into one of the cylinders at 3600 samples per resolution.

Experiments are conducted at a constant engine speed of 1500 RPM and fixed throttle valve position for two load points, namely wide open throttle (WOT) and 190 Nm. The latter load holds for neat gasoline at the stock spark timing of 22.5 degrees before top dead center or bTDC. Remaining engine settings are also kept at their stock values with the exception of intake air temperature which is regulated by an external heat exchanger at roughly 25 °C.

Table 1. 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	95-98 RON
Max output, [kW]/(HP)/RPM	[147]/(200)/4800
Max torque, [Nm]/rpm	[300]/1500-4500
Maximum boost pressure [bar]	1.38



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Fuel Matrix

All oxygenates were blended at 10 vol.-% to commercial (Dutch) Euro 95 gasoline. The physicochemical properties of the neat oxygenates and blends with Euro 95 are listed in [Table 2](#) and [Table 3](#), respectively. Note that the relatively high oxygen concentration and fuel sensitivity reported for Euro 95.

Table 2. Physicochemical properties of the neat oxygenates

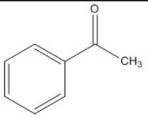
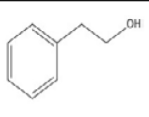
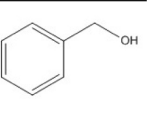
Property	Acetophenone	Phenyl ethanol	Benzyl alcohol
Structure			
Formula	C ₈ H ₈ O	C ₈ H ₁₀ O	C ₇ H ₈ O
Density [kg/m ³]	1028	1222	1081
Boiling point [K]	475	493	478
Molar mass [g/mol]	120.15	122.16	108.14
Heat of vaporization [kJ/kg]	438.62	564.83	582.58
LHV [MJ/kg]	33.2	34.3	33.1
LHV [MJ/L]	34.2	34.8	34.5

Table 3. Physicochemical properties of the oxygenate blends

Property	Euro95	10 vol.-% Phenyl Ethanol	10 vol.-% Benzyl Alcohol	10 vol.-% Acetophenone
Base fuel [vol.-%]	100	90	90	90
Oxygenate [vol.-%]	0	10	10	10
Density [kg/m ³]	740	767.7	770.5	768.8
Fuel oxygen [wt.-%]	2.70	4.41	4.85	4.5
RON	95.0	96.9	96.9	96.1
MON	85.6	86.1	86.6	86.6
Sensitivity	9.4	10.8	10.3	9.5
LHV [MJ/kg]	41.9	40.9	40.7	40.8
LHV [MJ/L]	31.0	31.4	31.4	31.3

Definition and Measurement of Knock

There are various methods to detect both knock onset and knock intensity (KI). These include analysis via in-cylinder pressure, block vibration and audible noise. In this study, in-cylinder pressure is used as the principal input for knock analysis. Burgdorf [9] reviewed such pressure-based methods and made a comparison.

Peak Cylinder Pressure

At fixed operating conditions, the maximum in-cylinder pressure is higher in a knock cycle than in a non-knock cycle. However, for a different engine speed or load, the pressure trace changes significantly, besides, because of the cycle-to-cycle variation, some cycles have high pressures even without knock. Conversely, some have knock, but with at relatively low pressures. Overall, though easy to use, this measure is not considered accurate enough for a quantitative analysis.

Peak Rates of Pressure Rise (1st Derivative)

The first pressure derivative is used to allocate the onset of knock, which is defined as the maximum value over a cycle. The onset, however, is not easy to detect when weak knock happens [10].

Third Time Derivative of the Pressure Signal

Knock onset is defined here for a certain threshold [11] or the first sharp increase of the third time derivative of the pressure signal. KI is defined as the signal energy. When the data acquisition frequency is relatively low, this method will yield reliable knock information [12].

Maximum of Oscillation or the Energy of Pressure Signal Filtered with Band Pass Filter

The maximum amplitude pressure oscillation or MAPO is the peak-to-peak amplitude of the pressure oscillation ([Figure 1](#)), which is used quite often with different band pass frequency. MAPO has been successfully used in several studies [13, 14] to quantify the knock intensity. In-cylinder pressure is filtered in these papers by a band pass filter with a frequency of 5-32 kHz and 5-27 kHz, respectively. Knock intensity is defined differently in different studies. For example, Kalghatgi [2] used an average knock amplitude of 1 Volt, which corresponds to a peak-to-peak pressure amplitude of 1.064 bar.

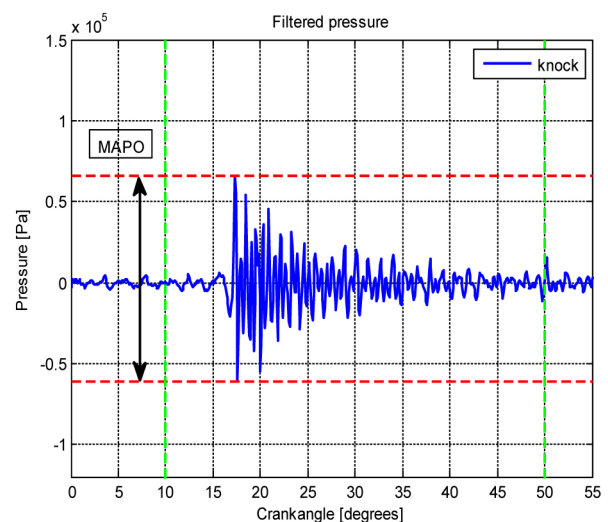


Figure 1. Filtered pressure signal for a cycle with knock

In this paper, MAPO will be used to quantify knock intensity (KI). The threshold for knock is determined based on the spark timing and the KI in the KI versus spark timing figure. As shown in [Figure 2](#) and [Figure 3](#), the knock intensity (KI) is defined as the peak-to-peak pressure amplitude of the filtered pressure signal.