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Short communication

Discovery of novel octane hyperboosting phenomenon in prenol biofuel/gasoline blends

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ABSTRACT

This work describes the first documented case of an effect defined herein as "octane hyperboosting" by an oxygenated fuel compound, 3-methyl-2-buten-1-ol (prenol). Octane hyperboosting is characterized by the Research Octane Number (RON) of a mixture (e.g. an oxygenate biofuel blended into gasoline) exceeding the RON of the individual components in that mixture. This finding counters the widely held assumption that interpolation between the RON values of a pure compound and the base fuel provides the bounds for the RON performance of the blend. This is clearly distinct from the more commonly observed synergistic blending of oxygenates with gasoline, where the RON never exceeds the performance of the highest performing component. Octane hyperboosting was observed for blends of prenol and six different gasoline fuels with varying composition. Testing of compounds chemically similar to prenol yielded no qualitatively similar instances of octane hyperboosting, which suggests that the effect may not be widespread among fuel candidates. The phenomenon suggests an unexplored aspect of autoignition kinetics research for fuel blends, and may provide a new mechanism for significantly increasing fuel octane number, which is necessary for increasing combustion efficiency in spark ignition engines. This phenomenon also increases the potential candidate list of biofuels, as compounds hitherto discounted due to their lower pure component RON may exhibit hyperboosting behavior, and thereby enhanced performance, in blends.

1. Introduction: Challenging the assumptions of fuel octane metrics

The ability to accurately predict engine performance based on an understanding of basic fuel chemistry has been a major goal of combustion science and engineering since the advent of the internal combustion engine. As mid-to-low boiling range petroleum distillates became the standard raw material to power spark ignition (SI) combustion engines, a significant quantity of SI combustion research has focused on identifying fuel additives that could increase a fuel's ability to resist autoignition, and thereby prevent a phenomenon known as engine knock [1,2]. Historically, additives such as tetra-ethyl lead (TEL) and methyl tert-butyl ether (MTBE) were used to minimize engine knock [3]. However, health and environmental risks associated with these additives resulted in each being phased out of the US market, with ethanol becoming the dominant oxygenate and octane enhancer for gasoline blending by the mid-2000s [4]. Resistance to autoignition is quantified by the octane rating, with Research Octane Number (RON) and Motor Octane Number (MON) ASTM tests having long been used as the two metrics to quantify a fuel's octane or antiknock performance [5–7]. Increasing octane number would enable several efficiency improvement technologies to be implemented in SI engines including increased compression ratio, increased turbocharging, and reduction of carbon monoxide and soot [8]. Clearly, the impact of higher octane fuels can be significant, with Chow et al reporting that if the RON of gasoline was globally raised to 98, overall greenhouse gas emissions could be 4.5–6% lower than the baseline case of lower octane gasoline [9].

Abbreviations: RON, Research Octane Number; MON, Motor Octane Number; ASTM, American Society of Testing and Materials; TEL, tetra-ethyl lead; MTBE, methyl tert-butyl ether; RBOB, Reformulated Blendstock for Oxygenated Blending; GC, Gas Chromatography

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Numerous studies have been conducted to understand the RON and MON performance of both neat compounds and blended fuels [10–13]. More recently efforts have focused on using first principles approaches, such as chemical kinetics, to predict antiknock properties, however, these have been limited to low complexity fuel surrogates and computational modeling approaches [14–17]. Despite these efforts, a detailed understanding of why certain fuel additives blend synergistically (i.e. generate higher octane number than that which would be predicted based on the relative mole fraction of the additive and a linear blending rule), while others blend antagonistically is still not well understood. This is because these phenomena intrinsically depend on chemical interactions among the numerous components of the fuel blend in the combustion cycle [14,18–20].

In previous efforts to identify new fuel additives for increasing engine efficiency, hundreds of biofuel molecules have been evaluated for neat RON and MON to establish suitability as an octane boosting or antiknock agent, as the neat octane of fuels is commonly used to interpolate the RON of mixtures under the assumption that the RON of a mixture will never exceed the bounds of the RON values for the base fuel of the bioblendstock [13,21–23]. This has held true in all known studies published to date, with recent efforts using the neat RON as a means to screen potential renewable fuel candidates [23]. The work presented here provides new data that question the implicit bounds of the RON interpolation assumption, documented for the case of a potential biobased fuel candidate, 3-methyl-2-buten-1-ol, also known as prenol.

2. Experimental methodology and materials

2.1. General approach and octane number testing

Prenol was blended volumetrically into five different gasoline blendstocks, referred to as Reformulated Blendstocks for Oxygenated Blending (RBOBs). We denote these five RBOBs as RBOB 1, 2, 3, 4 & 5. The composition of the RBOB samples, where available, is provided in Appendix A. Prenol was also blended into a simplified surrogate gasoline consisting of iso-octane (55 vol%), *n*-heptane (15 vol%), toluene (25 vol%), and 1-hexene (5 vol%) that has been used as a base fuel for comparing blending octane numbers for a wide range of potential high-octane gasoline blendstocks [23,26,27]. Finally, prenol was blended into 10% ethanol blends of this surrogate and RBOB5. The RON and MON of these mixtures in different blend ratios were measured. RON and MON were determined via ASTM D2699 and ASTM D2700 respectively. More than one RON and MON testing laboratory was used to ensure robust data quality and reproducibility. Volumetric blending and RON & MON measurements of prenol from 0 to 30% v/v into RBOB 1, RBOB 2, RBOB 3, and RBOB 4 was done at Intertek Inc., Benecia, CA. RON and MON measurements of neat prenol, prenol blends from 0 to 30% v/v into the surrogate fuel, 0 to 100% v/v into RBOB 5 and the E10 samples were made at Southwest Research Institute (SwRI) in San Antonio, TX. The detailed hydrocarbon analysis of RBOB 4, RBOB 5, and the surrogate fuel was measured and is shown in A-1. One of the operating conditions of both the RON and MON tests is that the fuel level in the vertical jet, at maximum knock intensity, must be between 1.78 and 4.32 cm below the center line of the venturi. Due to the lower stoichiometric air/fuel mass ratio of the high prenol containing samples, the jet size was increased to allow for the higher fuel flow needed to maintain the required fuel level [24].

2.2. Confirmation of sample volume fractions

Concentrations of prenol in blends were measured by gas chromatography (GC). Details on equipment and the specific method used can be found in Appendix E. Instrument response was calibrated with a gravimetrically prepared mixture of prenol at five calibration points, in the region corresponding to the expected concentration of the blends. Calibration curves were found to have R^2 values of 0.998 or greater for all compounds [23].

2.3. Chemicals and purities used for RON testing

Sigma-Aldrich was used as the vendor for all the chemicals investigated. High purity samples (> 98%) were purchased to ensure data reproducibility. The exact product number and associated purity can be seen in the Appendix in Table B-2. Samples were used for testing immediately after the containers were opened to avoid sample degradation.

2.4. Removal of polar contaminants from prenol samples

Potential polar contaminants, such as peroxides and hydrates, were removed from the neat prenol sample using a silica column following the protocol outlined by Mueller et al. [25] RON testing of this sample was carried out to confirm that these contaminants were not affecting the RON measurement. The sample containers were stored at 85% capacity and sealed with parafilm to limit exposure to air and peroxide formation after the silica column treatment; testing was performed within 10 days of the treatment.

2.5. Determination of prenol sample purity

The peroxide number of the silica column treated sample (sample processed as described in Section 2.4) was tested by the ASTM D3703 method at the Southwest Research Institute in San Antonio, TX. This method quantifies the concentration of hydroperoxides in a sample within the range of 0–50 mg/kg (ppm). To further validate the > 98% purity of the prenol used for RON and MON testing, samples were analyzed for contaminants via GC–MS with only trace contaminants found as shown in the Appendix in Table B-2.

2.6. Uncertainties

For fuels in the 90–100 RON range, the method reproducibility is ± 0.7 ON (repeated tests would differ by more than 0.7 ON, no more than 5% of the time) [5]. The absolute value of the average error from the target volume range for the samples that were determined was 1.39 vol% so the samples that were not quantified by GC can be expected to have a similar blending volume error. Multiple gasoline samples were used to address variability in materials.

3. Results and discussion

3.1. Octane hyperboosting phenomena

RON values of neat prenol and blends into different gasoline RBOBs as well as a fuel surrogate were measured by SwRI and Intertek as outlined in Section 2.1. The neat RON value of prenol is reported as 93.6 and is the average of four independent measurements with a standard deviation of 0.55 which is within the accepted error of the test (± 0.7). The RBOBs used cover a wide range of starting RON values and each has a unique hydrocarbon composition.

Fig. 1 shows the results from the RON tests of neat prenol and each of the blends investigated. It was observed that the RON of the prenol containing fuel blends can exceed the RON of both neat prenol and the base fuels at some blending level. We refer to this effect as octane hyperboosting to distinguish it from synergistic blending or RON boosting commonly used to describe non-linear RON blending. RON testing of prenol in the surrogate fuel with 10% by volume ethanol was also carried out and is discussed in detail in Section 3.3. The octane hyperboosting effect was observed at the 20% v/v prenol blend level and higher in all base fuels, with RBOB 2 and the surrogate showing the hyperboosting effect by 10% v/v prenol. The range of the observed

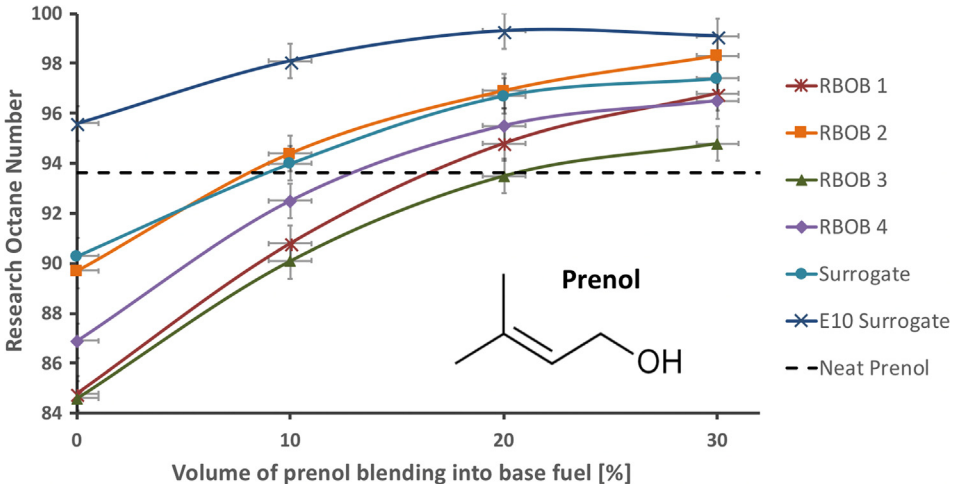

Fig. 1. This figure shows the RON of prenol blended into six different gasoline mixtures along with the structure of prenol. Each of the mixtures shows blended RON values greater than the neat RON of prenol by the 20% volume fraction, with the surrogate and RBOB 2 showing hyperboosting at just 10% by volume. The highest blended RON that was achieved was 98.3, which is 4.8 RON points higher than prenol's neat RON value. The ordinate error bars represent the ± 0.7 ON reproducibility within this range of the RON test [5] and the abscissa error bars represent ± 1.4% volume error.

RON hyperboosting effect at 30% v/v varied from 1.3 to 4.8 ON, which is well outside of the experimental variability (± 0.7 ON) of the test over this range. To the authors' knowledge, whilst a study by Foong et al., showed a similar effect under MON conditions in simple surrogates of two or three components, RON hyperboosting in complex fuel mixtures outside the expected error of the tests has not been documented to-date [28]. Westbrook et al., modelled similar systems and found that adding species such as toluene to the binary surrogate reduced the effect [29]. The same study referenced by Foong et al., reported the RON of an iso-octane/ethanol blend to be as high as 110.2, which is above the RON of both iso-octane (100) and ethanol (108.5). However, method reproducibility of the RON test for values from 104 to 108 is ± 3.5 octane numbers [5] and error has not been quantified for higher values bringing into question if the value of 110.2 is significantly different from that for pure ethanol [10].

Motor Octane Numbers were also measured for each blend. Prenol has a MON of 74.2 as a neat fuel which is lower than the MON of gasoline mixtures, or any of the gasoline blendstocks examined here. Adding prenol up to 30 vol% had only a small effect on MON with the results showing a small increase in some cases or a weak decreasing trend in others. These data are shown the Appendix as Fig. D-1.

As stated, the purity of the prenol sample evaluated was always > 98%. It has been previously shown that impurities such as peroxides can have large impacts on the cetane values for diesel fuels because these impurities can be a trigger to an already auto-ignition sensitive fuel. Since high octane fuels quench radical pool-building reactions, the impurities previously listed would likely require significant loadings to cause a meaningful effect. To fully validate impact of polar impurities such as peroxides on the neat RON measurement of prenol, a sample was processed to remove possible polar contaminants as demonstrated by Wallace et al. [30] and Mueller et al. [25] and described in detail in Section 2.2. The outcome from the ASTM D3703 test for hydroperoxides on this processed sample showed "non-detect", with a testing range of 0–50 mg/kg. The neat RON of the treated prenol sample was measured as 94.6, indicating that polar impurities may have been depressing the neat RON measurement slightly, but not to a level that would question the nature of the octane hyperboosting phenomenon, given the uncertainty ranges in the tests. The list of the five most abundant impurities in the prenol sample used as determined by GC–MS are shown in Table B-1. Further blending and octane testing was carried out beyond the 10, 20 and 30% blend levels to determine the blending volume where the octane hyperboosting effect was no longer observed and the RON was reduced to that of neat prenol. Blending was done at 10% v/v increments up to 90% to eliminate the possibility that additional nonlinearities were present at other blending ratios. In addition, a closely related isomer (3-methyl-3-buten-1-ol, or isoprenol), which has significantly higher RON, was tested to determine if it also showed the hyperboosting behavior. The RBOB used for the full blend range had a low octane, so it represents a lower bound for the hyperboosting effect, as additional boosting would need to occur to exceed the neat RON of prenol. The full blending range for prenol and isoprenol is shown in Fig. 2. When blended from 0 to 100% in RBOB 5 the octane hyperboosting effect was seen at every data point between 30% and 90% v/v for prenol. No octane hyperboosting was observed for isoprenol, suggesting that the underlying chemical basis for octane hyperboosting is present in prenol but not isoprenol. The octane hyperboosting effect for RBOB 5 is the least extreme case of octane hyperboosting among all the gasoline blendstocks investigated. The largest difference between a blended RON value and the neat RON of prenol is just 2 RON points and was observed at the 80% blend, while the hyperboosting effect was not noticed until beyond 20% v/v.

To further investigate if octane hyperboosting is unique to prenol, three additional compounds with structural similarities to prenol (2-methyl-1-butanol, 3-methyl-1-butanol (isopentanol), and 2-methyl-3-buten-2-ol) were evaluated, despite previous investigations not revealing octane hyperboosting for these compounds [21,23,31]. The structures for these molecules, including isoprenol, are shown in Fig. 3. Blending of 2-methyl-1-butanol, isopentanol, and 2-methyl-3-buten-2-ol was done into the RBOB 4 sample, while isoprenol was blended into the RBOB 5 sample as previously described. The RON testing of these compounds is shown in Fig. 4 and shows that none of these compounds demonstrate octane hyperboosting.

The fact that prenol is the only compound to demonstrate this behavior despite being only subtly structurally different from the other compounds investigated should be explored further and other compounds that share structural similarities or similar reaction intermediates should be investigated. Work is currently underway to understand this unique behavior via targeted experiments and kinetic modeling. If fully understood, octane hyperboosting could have significant impacts on how fuels are blended, the way the RON and MON tests are used, and could be leveraged for design of new biofuel/bioblendstocks for maximum antiknock performance.

3.2. Evaluation of prenol as a fuel additive

Table 1 provides many relevant fuel properties for prenol and other octane boosting biofuels that have been extensively investigated for use as additives to gasoline. It also highlights the high octane sensitivity of prenol, which is defined as the difference between the RON and MON measurements. Recent studies have suggested that high octane sensitivity may be critical to limiting engine knock and improving efficiency in modern downsized turbocharged engines as well as in advanced

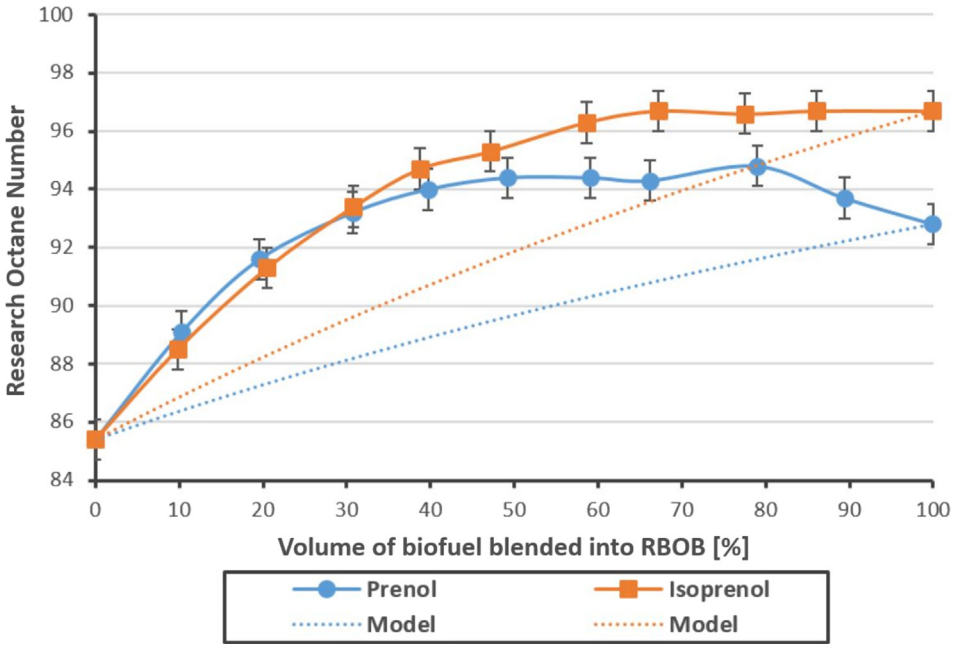

Fig. 2. Full blending profile of prenol and isoprenol in RBOB 5 gasoline sample. Isoprenol reaches its neat RON value between 50% and 60% by volume but never exceeds it. Dashed lines represent the theoretical "linear" blending curve when blended as a function of blending molar fraction.

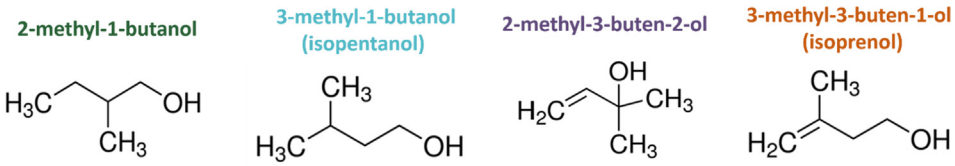

Fig. 3. Structures of the compounds similar to prenol investigated in this study. Each compound explored contains five carbons and an alcohol functional group.

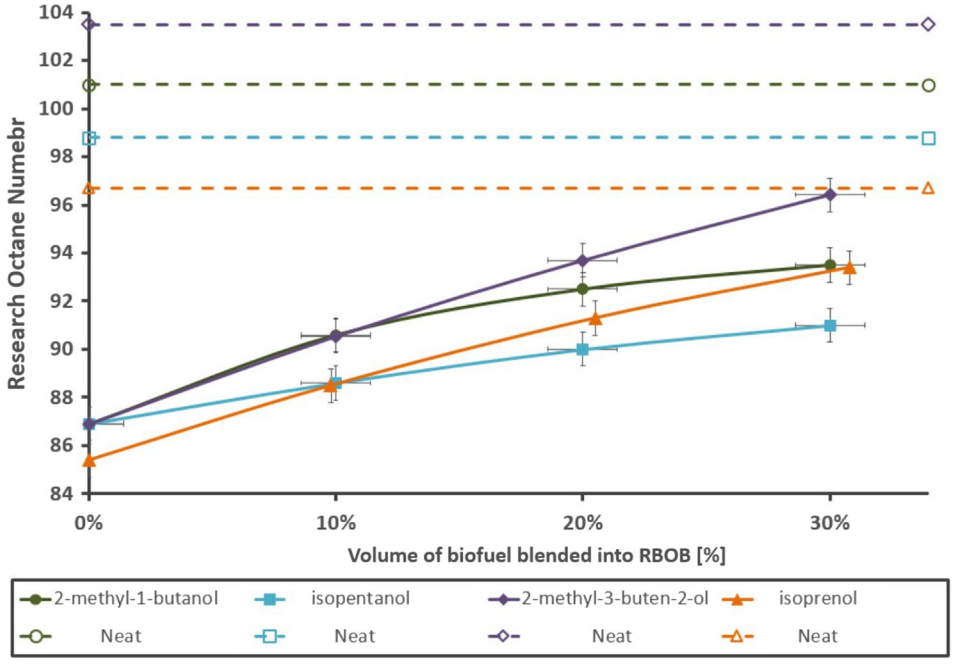

Fig. 4. Investigation of additional C5 alcohol candidates for octane hyperboosting. 2-methyl-1-butanol, Isopentanol, and 2-methyl-3-buten-2-ol were blended into RBOB 4 (starting RON 86.9) while isoprenol was blended into RBOB 5 (starting RON 85.4). The solid lines represent the experimental RON data of the blends while the dotted lines represent the neat RON measurement for each of the compounds investigated.

combustion strategies currently in development [1,32]. Sensitivity values for all the blends of prenol examined in this study can be seen in Appendix D. Additionally, many of prenol's physical properties such as molecular weight, density, lower heating value, and others are very similar to those of traditional gasoline components, while features such as low water solubility should lead to enhanced infrastructure compatibility compared to existing biofuels such as ethanol. The reasonably high boiling point of prenol may lead to issues under certain engine conditions for higher prenol blends. Investigation of these effects were outside the scope of this work but should be carried out.

Table 1
Relevant fuel properties for a selection of industrially used and promising octane boosting biofuels. Each of the properties listed is anticipated to have some contribution to the octane performance of the molecule or is important from an infrastructure compatibility perspective. All values shown are experimental values sourced from the US-DOE Co-optima fuel property database [33]. [+]Measured at 25 °C.

Compound	Neat RON	Neat MON	Octane Sensitivity (RON-MON)	Heat of Vaporization [kJ/kg][+]	Water Solubility [g/L][+]	Boiling Point [°C]	Lower Heating Value [MJ/L]
ethanol	109	90	19	919	1000	78.5	20.2
n-propanol	104	89	15	789	1000	97.2	24.7
isopropanol	112.5	96.7	15.8	744	1000	82.5	24.1
isobutanol	105	90	15	685	85	107.9	26.6
diisobutylene	106	87	19	318	4	101.4	31.7
cyclopentanone	101	89	12	504	61	130.6	30.2
prenol	93.5	74.2	19.3	512	41	140.0	29.6

Table 2
Antiknock metrics of prenol blended in base fuels with 10% by volume ethanol added (E10 fuels). Blends were tested for the 4-component surrogate and RBOB 5.

Measurement	Base Fuel	Volume % Prenol Added			
		0	10	20	30
RON	Surr. E10	95.6	98.1	99.3	99.1
	RBOB 5 E10	91.2	94.2	95.3	96.3
MON	Surr. E10	88.3	87.2	85.6	84.5
	RBOB 5 E10	83.5	82.4	81.9	81.5
Sensitivity	Surr. E10	7.3	10.9	13.7	14.6
	RBOB 5 E10	7.7	11.8	13.4	14.8

3.3. Prenol in combination with ethanol

To assess the impact of ethanol on prenol's blending behavior, prenol was blended into two gasoline base fuels containing 10% by volume ethanol (referred to as E10 fuels). These results are shown in Table 2 and demonstrate that prenol/ethanol blends have elevated RON and sensitivity values that are beyond what each component can provide individually. This is clearly shown for the 20% volume addition of prenol into the surrogate E10 (30% by volume total biofuel) which has a high RON of 99.3 and a sensitivity value of 13.7, which is significantly higher than the sensitivity value of 30% ethanol in the surrogate, as reported by McCormick et al to be 11.4 [21]. The potential for optimized blends of ethanol/prenol may allow for improved engine efficiency as well as the opportunity to bypass the ethanol "blend wall" which would allow for increased biofuel use and reduced carbon emissions.

3.4. Production routes to prenol

Due to the promising octane boosting behavior of prenol and its potential as a biofuel, a review of strategies for large scale production of prenol was carried out. Prenol is produced industrially via a catalytic route as an intermediate in the production of citral [34], with other patents and publications focusing on catalyst development and reaction conditions [35,36]. Additionally, significant work has been done around biological production of prenol by dephosphorylation of metabolic intermediates of the isoprenoid biosynthetic pathways, isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP), via the expression of a promiscuous phosphatase enzyme [37,38]. While the most successful engineering strategies reported to date have primarily demonstrated the production of isoprenol (~2.5 g/L), there are reports that suggest that it is possible to selectively produce prenol using enzymes that preferentially dephosphorylate DMAPP [39], suggesting potential for prenol as an industrially relevant biofuel.

4. Summary and impact of results

A promising means to significantly increase the efficiency of the gasoline engine fleet is to increase the compression ratio, which would be enabled by the use of higher octane fuels. This work describes the first documented case of an effect described as octane hyperboosting by an oxygenated fuel compound, prenol, as characterized by the RON of a mixture exceeding the RON of both the neat blending agent and the blendstock. This finding counters the widely held assumption that interpolation between the RON values of a pure compound and the base fuel provides the bounds of the RON performance of the blend. This is clearly distinct from synergistic blending of oxygenates with gasoline that has been observed to-date. Octane hyperboosting was observed for blends of prenol into a variety of gasoline mixtures and tested by multiple commercial laboratories. Testing of structurally similar molecules showed prenol to be unique in its octane hyperboosting effect. This phenomenon suggests an unexplored area for combustion research by potentially providing a new approach for improving SI combustion efficiency and enabling identification of previously overlooked fuels based on presumed limitations of their anti-knock performance. Prenol itself has promising properties as a biofuel such as extremely high octane sensitivity, low water solubility, and energy density close to that of gasoline; the hyperboosting effect means that prenol could outperform biofuels currently in the market if used in a correctly formulated blendstock.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2018.11.046.

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