Lube oil chemistry influences on autoignition as measured in an Ignition Quality Tester

Francis M. Haas, Rowan University
Sang Hee Won, University of South Carolina
Frederick L. Dryer, Princeton University
Cécile Pera, Infineum UK Ltd.

Available at: https://works.bepress.com/francis-haas/7/
Lube Oil Chemistry Influences on Autoignition as Measured in an Ignition Quality Tester

Francis M. Haas¹,², Sang Hee Won¹,³,*, Frederick L. Dryer¹,³, Cécile Pera⁴

¹Department of Mechanical and Aerospace Engineering, Princeton University, NJ 08544, USA
²Mechanical Engineering Department, Rowan University, NJ 08028, USA
³Department of Mechanical Engineering, University of South Carolina, SC 29208, USA
⁴Infineum UK Ltd., Abingdon, Oxfordshire OX13 6BB, United Kingdom
*Corresponding Author Email: sanghee@mailbox.sc.edu

Abstract: Derived Cetane Numbers (DCNs) of engine lubricating oil/95 Research Octane Number gasoline surrogate mixtures are measured in an Ignition Quality Tester. These measurements separately screen for effects of (1) calcium- and magnesium-based detergent additive, (2) oil degradation, and (3) base oil on mixture ignition propensity at conditions relevant to low speed pre-ignition (LSPI) in gasoline engines. Initial testing of ≤25% mass oil in the gasoline surrogate indicates a positive linear relationship between DCN and blend fraction, and also demonstrates the sensitivity of the measurement technique to mixture composition. Despite variation in Ca and Mg concentrations, DCN responses for 5, 10, and/or 25% oil-surrogate blends indicate no statistically significant effect of either Ca or Mg concentration relative to the reference oil. Similarly, neither aging of the oils nor peroxide addition yields a significant effect on measured DCNs of oil-surrogate blends. Notwithstanding these results, a distinct response is found with variation of the base oil: at 25% oil blending with gasoline surrogate, the measured DCNs range from 19.6 to 42.1.

Keywords: Low speed pre-ignition (LSPI); Derived cetane number (DCN); Lubricant oil;

1. Introduction

Downsizing has been a major trend in gasoline engine over the last decade. However, a new engine knock mode, called super-knock or low-speed pre-ignition (LSPI) has emerged for highly boosted operation, especially for direct injection at low-speed, high-load conditions. These abnormal phenomena are sporadic and can quickly result in severe engine damage. Though several hypotheses have been put forth as to the cause of LSPI, there is no consensus as to the exact mechanism(s). Several of the leading hypotheses propose either the lubricant or lubricant additive properties as key contributing factors. In particular, oil additives such as Ca-based detergents have been demonstrated to influence the frequency and the severity of LSPI events, while Mg-based detergents appear to have no effect [1]. Similarly, the properties of the base lubricant stock have been shown to play a role in the LSPI mechanism [2]. However, base oil effects remain unclear, as contradictory results are obtained with variation in engine hardware and operating conditions, as well as specific lubricant oil formulation. Since oil combustion properties seem to play a major role in LSPI, a better understanding of base oil and additive package properties related to combustion is crucial.

In this study, the autoignition behaviors of mixtures of 0-25% (by mass) lubricant oils with a multicomponent 95 RON gasoline surrogate[3] (Sur95f) are studied in an Ignition Quality Tester (IQT). The Derived Cetane Number (DCN) of each subject mixture is determined using the ASTM
D6890[4] method. In particular, the influences of Ca and Mg concentration in the additive package, oil aging, peroxide coupling, and base oil chemical properties on ignition propensity are separately screened for their effects on the observed DCN.

2. Experimental Approach

Individual reactant fractions for Sur95f [3], a gasoline surrogate previously investigated for real gasoline autoignition and combustion properties, and each oil tested (whether fresh or aged) were initially filtered according to the ASTM D6890 method [4] and stored at room temperature in amber glass bottles for later use. A stock mixture of Sur95f was then prepared gravimetrically from ≥ 99% pure reagents according to ≥ 99% pure reagents according to [3]. Notably, uninhibited cyclohexene (99%, Sigma-Aldrich, St. Louis) was used to avoid any confounding DCN-reducing effects due to antioxidants typically added to extend shelf life. To ensure subsequent degradation of the cyclohexene was not a significant factor in the present study, the DCN of the Sur95f surrogate was monitored over the duration of the research. As demonstrated in a later figure, the measured DCN of Sur95f remained within ~1 DCN unit bounds throughout the study. Mixtures of filtered oils at 5, 10, and/or 25 weight percent in Sur95f (with or without added peroxide (di-tert-butyl peroxide, DTBP, 98%, Sigma-Aldrich)) were then prepared gravimetrically from the filtered stock solutions on an as-needed basis. Each mixture was observed before use to ensure mixture homogeneity, and in no case was insolubility of oil in the gasoline surrogate detected.

Oils have been aged through an oxidation process following the method GFC LU-43-A-11-ind2 [5] with the aim to simulate the oxidation of motor oil submitted to fuel dilution and running in severe (high load/speed and “hot” crankcase) conditions. In this oxidative aging process, the oil is maintained 144 hours at high temperature in the presence of an iron salt catalyst, under a constant air flow and with addition of fuel. Finally, and to be expected with lubricating oils, many samples had a strong affinity for forming a film on the surfaces of the preparation and testing apparatus. Therefore, specific efforts were made to eliminate cross-contamination effects among fuel/blend samples, both in their preparation as well as during IQT testing. Care in contamination control is particularly important when considering that certain anti-wear and anti-corrosion additives in fully-formulated engine lubricants act on wetted surfaces, leading to the potential for delayed desorption of these additives into subsequently-tested samples that may have different levels of such additives. After test of a particular oil/Sur95f blend condition, DCN measurements of a previously used common service station diesel or certified cetane number check fuel were repeated until values were observed to return to those obtained prior to the oil/Sur95f blend tests. This procedure assured the fidelity of each oil/Sur95f blend result.

DCNs for the Sur95f gasoline surrogate, its blends with oils, and a pure oil (in one case) were measured in an IQT (Advanced Engine Technology, Ottawa) according to the ASTM D6890 method. The use of the IQT to assess gasoline-like base fuels as well as engine lubricants is distinctly outside of the narrowly-defined use of the IQT for DCN rating of middle distillate fuels according to ASTM D6890. However, there is a large and growing body of literature applying the IQT testing platform for “off-label” uses [6-14]. Accordingly, the present DCN measurements can be meaningfully interpreted, as will be subsequently discussed. A single DCN measurement is based on ignition delay time statistics for 32 sequential IQT ignition events, which permits determination of both a mean DCN

<table>
<thead>
<tr>
<th>Oil Identification</th>
<th>SAE Grade</th>
<th>Ca Level</th>
<th>Ca:Mg Ratio</th>
<th>HTHS Viscosity [mPa.s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil A</td>
<td>0W30</td>
<td>+</td>
<td>100:0</td>
<td>2.9</td>
</tr>
<tr>
<td>Oil C</td>
<td>0W30</td>
<td>-</td>
<td>100:0</td>
<td>2.9</td>
</tr>
<tr>
<td>Oil D</td>
<td>0W30</td>
<td>++</td>
<td>100:0</td>
<td>2.9</td>
</tr>
<tr>
<td>Oil E</td>
<td>0W30</td>
<td>+++</td>
<td>100:0</td>
<td>2.9</td>
</tr>
<tr>
<td>Oil J</td>
<td>0W30</td>
<td>+</td>
<td>50:50</td>
<td>2.9</td>
</tr>
<tr>
<td>Oil K</td>
<td>0W30</td>
<td>+</td>
<td>0:100</td>
<td>2.9</td>
</tr>
<tr>
<td>Oil M</td>
<td>0W30</td>
<td>-</td>
<td>100:0</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table 1. Characteristics of Oils Tested
value and its standard deviation. Each nominal DCN measurement reported below is an average of at least three individual mean DCN measurements. Unless otherwise indicated, the associated error bars presented are representative uncertainties defined by extremal values of each mean DCN offset by its corresponding standard deviation. A reference oil (Oil A) having key properties (Table 1) was initially tested in the IQT to both quantify its DCN and to determine suitability of the IQT for neat lubricant oil testing. Though on-calibration ASTM D6890 DCNs were obtained for this pure oil, measurements led to significant coking and eventual clogging of the IQT exhaust valve. Consequently, the very high, pure oil DCN (93.2 units) and the present interest in a phenomenon involving potential mixtures of gasoline and lubricating oil, further testing of pure oils was not pursued. Instead, homogeneous blends of up to 25% by mass of oil in Sur95f gasoline surrogate were measured for ignition response to detergent concentration and identity, oil degradation, and oil Group type. The 95 RON, six component Sur95f gasoline surrogate described in [3], was used as a gasoline-like performance baseline. Compared to fewer-component surrogates [14], Sur95f is intended to more closely emulate gasoline-like behaviors and properties such as multicomponent distillation, chemical class distributions, oxygenate content, overall C/H/O atomic ratios, average molecular weight, mass density, presence of octane number sensitivity, etc.

Oils in Table 1 were blended into Sur95f for the effects of Ca and Mg concentration, oil aging, peroxide coupling, and base oil Group type on ignition. Neat Oil A (with no aging or peroxide additive) served as a reference for detergent concentration screening. Oils C, D, and E relate to reference Oil A through variation in Ca concentration, while Oils J and K similarly relate through variation in Mg concentration (with a constant level of global detergency Ca/Mg concentration). Oil M is a variant of low Ca-containing Oil C with a higher high temperature high shear (HTHS) viscosity. All the oils are non-commercial products. Aged variants of Oils A and C were generated as described above and tested in Sur95f blends to compare ignition performance against the corresponding fresh oils. Simultaneous comparison among Oil A (fresh/aged) and Oil C (fresh/aged) also permitted screening for synergy between Ca concentration and aging effects. Similarly, 1% mass DTBP-treated variants of fresh and aged Oils A and C were generated and tested in Sur95f blends. The DCN measurements for these mixtures further screened for synergy between Ca concentration and aging effect, plus additional binary synergies for Ca and peroxide effect or aging and peroxide effect, as well as ternary synergy among Ca, aging, and peroxide effects. A separate sequence of DCN determinations involving additive package-free base oils unrelated to those identified in Table 1 was also conducted to examine the effect of lubricant oil organic characteristics (as characterized by API Group number) on DCN.

3. Results and Discussion

**Fuel-Oil Mixture Trends in DCN and RON**

Measured DCNs of blends of 0-25 mass% reference Oil A in Sur95f are presented below in Figure 2. DCN variation follows an essentially linear trend with mass fraction of oil blended. The DCN measured for neat Oil A is 93.2, indicating that,

![Figure 1. Experimental design matrix for oil tested](image1)

![Figure 2. Variation of measured DCN and estimated RON as a function of mass fraction of reference Oil A blended into Sur95f](image2)
under the reasonable assumption of monotonic behavior, only modest curvature in the trend exists even at higher blend fractions. Importantly, the behavior of DCN versus oil blend fraction indicates that the test method employed is sufficiently sensitive to resolve DCN changes due to small amounts of oil dissolved into fuel, as well as small amounts of fuel dissolved into oil. This is relevant to pre-ignition chemistry in gasoline engines as droplets anywhere along the fuel-oil mixture fraction continuum may act as unwanted ignition kernels.

Figure 2 also presents RON values for the same mixtures estimated from a DCN→RON quantitative property-property relation (QPPR) developed and described in [11]. The measured 20.7 DCN average of pure Sur95f corresponds to a RON of 94.3 compared to a theoretical value of 95 [3]. Over the range of 0-25 mass% reference Oil A blended into Sur95f, the RON variation follows an apparently linear trend with mass fraction of oil blended, and similarly to DCN, also demonstrates sufficient sensitivity to resolve RON changes due to variations in oil/fuel blend fractions. Figure 2 demonstrates that present DCN tests can be interpreted on a RON scale even if all results in this article are presented in measured DCN.

**Effects of Calcium/Magnesium and Oil Degradation**

Figure 3 compares DCN measurements for Sur95f mixtures with six oils in Table 1. The similarity between the DCN results presented in Figure 3a and Figure 2 is remarkable: reasonable variations in Ca and Mg levels (separately) appear to have no significant effect on mixture ignition propensity at up to 25% oil blend levels. The lack of significance is informally judged relative to the maximal and minimal DCN values recorded for Sur95f (Figure 3b). The ~1 DCN unit repeatability for the Sur95f base fuel exceeds test mixture deviations relative to reference Oil A in all cases. These observations are in part at odds with recent engine test results [1], implicating Ca-based detergent in oil as a promoter of LSPI and Mg to be neutral. As the mechanism(s) leading to LSPI remain(s) poorly understood, the cause of this discrepancy in Ca is unclear. However, there may be mechanisms through which detergent-ignition interactions occur that are not fully encompassed by the injection/mixing processes affecting ignition under DCN measurement conditions. Another explanation for the discrepancy could be that Ca needs a heterogeneous phase to catalyze ignition.

The effects of oil degradation are presented in Figure 4 for two oils of differing Ca content. The qualitative difference between the clear, golden fresh oil and opaque, brown aged oil is a readily apparent indicator of the thermal and oxidative stresses. However, there is no discernible quantitative difference between measured DCNs at either level of calcium loading or with 1% di-tert-butyl peroxide (DTBP) added to the fuel-oil...
mixtures to (roughly) simulate in-cylinder absorption of metastable combustion products into the lube oil. Though ignition enhancement was observed and expected for mixtures containing 1% DTBP, no significant difference in ignition behavior was measured among fresh and aged fuels at either Ca level.

**DCN Response to Base Oil Class**

Though no significant influence observed in the previous test matrix, Figure 5 indicates that base oil Group classification does affect DCN. Evidently, homogeneous ignition propensity of the fuel-oil blends is primarily controlled by the chemical organic composition of the base oils. This observation is in good agreement with [14]. The monotonically increasing DCN trend with increasing Group number (I to IV) merits additional consideration. Interpretation of the American Petroleum Institute (API) Group classification suggests that lubricant oils in Groups I, II, and III derived from the same putative crude oil will be successively more saturated and more paraffinic (less naphthenic and aromatic) with increasing Group Number. This trend qualitatively corresponds to an increasing DCN provided the average hydrocarbon backbone of the base oil does not otherwise vary significantly among the Groups. Oils in Group IV are composed of synthetically-derived polyalphaolefins, which are fully saturated and fully paraffinic. These oils represent, in essence, a limit to the successive degrees of refining applied to Group I-III base oils, and therefore would be expected to have the highest DCN within this framework. Group V oils are of miscellaneous chemical compositions that fall outside of the Group I-IV trend, and are reasonably excluded from this notional behavior. However, it is remarkable that one of the Group V oils tested reduces DCN (enhances RON) at 25% blending.

The DCN measurements (Figure 5), as well as some less systematic evidence from [14], appear to support the preceding reasoning; however, the presently tested oils of Groups I, II, and III are not necessarily from the same crude feedstock and no detailed chemical analyses have been performed. Accordingly, the nature of the oil hydrocarbon structure versus ignition propensity trend remains speculative, though present results more clearly support the somewhat less specific conclusion that the base oil hydrocarbon fraction is principally responsible for enhancing the gasoline ignitability of lower ignition propensity.

### 4. Conclusions

Ejection and subsequent ignition of oil-in-fuel or fuel-in-oil droplets into the cylinder is one of several competing hypotheses for the phenomena responsible for LSPI. To gain insight into ignition processes affected by such phenomena, Ignition Quality Tester (IQT)-measured Derived Cetane Numbers (DCNs) of oil-in-gasoline surrogate blends were acquired. A test matrix for oil composition was developed for the effects of Ca- and Mg-based detergent concentration, oil aging and metastable combustion byproduct accumulation, and base oil API Group number on ignition. Preliminary tests using a neat lubricating oil (Oil A) indicated that such oils have very high DCN (93.2 units). Subsequent tests using Sur95f, a 95 RON gasoline surrogate, as a base for blending of 5, 10, or 25% mass oil were successful with regard to on-calibration determination of DCN values. A positive (negative) linear relationship between DCN (RON) and oil blend fraction demonstrates the sensitivity of the measurement technique to mixture composition and the potential to further study oil-in-fuel mixture effects relevant to gasoline engine applications.
Separate variation in Ca and Mg additive package levels, indicated no statistically significant ignition effect. Similarly, neither aging of the oils nor peroxide addition yielded a significant effect on measured DCNs of oil-surrogate blends. Considering that some of these tests also screened for binary and ternary synergies among compositional factors, many of the present results indicate a general insensitivity of homogeneous ignition to oil/additive formulations for the base oil currently investigated. However, DCN-indicated ignition does significantly respond to base oil organic composition characteristics classified by API Group number. The measured DCNs range from 19.6 to 42.1 and monotonically increase as Group number increases from I→IV. Notably, one Group V oil reduced DCN at the 25% blend level. The present screening results indicate that, at ASTM D6890 DCN test conditions, the bulk hydrocarbon chemistry governs ignition and renders secondary any effects of reasonable levels of Ca and Mg detergent, oil degradation by aging, or absorption of metastable combustion byproducts.

5. Acknowledgements
The authors gratefully acknowledge the financial support of Infineum.

6. References