Chemical Kinetics of Octane Sensitivity

in a Spark-Ignition Engine

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Abstract

This paper uses a chemical kinetic modeling approach to study the influences of fuel molecular structure on Octane Sensitivity (OS) in Spark Ignition (SI) engines. Octane Sensitivity has the potential to identify fuels that can be used in next-generation high compression, turbocharged SI engines to avoid unwanted knocking conditions and extend the range of operating conditions that can be used in such engines.

While the concept of octane numbers of different fuels has been familiar for many years, the variations of their values and their role in determining Octane Sensitivity have not been addressed previously in terms of the basic structures of the fuel molecules. In particular, the importance of electron delocalization on low temperature hydrocarbon reactivity and its role in determining OS in engine fuel is described here for the first time. The role of electron delocalization on fuel reactivity and Octane Sensitivity is illustrated for a very wide range of engine fuel types, including n-alkane, 1-olefin, n-alcohol, and n-alkyl benzenes, and the unifying features of these fuels and their common trends, using existing detailed chemical kinetic reaction mechanisms that have been collected and unified to produce an overall model with unprecedented capabilities.

INTRODUCTION

Octane ratings are widely used to measure the tendency of automotive fuels to knock in Spark Ignition (SI) engines [1]. Primary Reference Fuels (PRF) provide the scales for Research Octane Number (RON) and Motor Octane Number (MON), with the knock resistant *iso*-octane (*iso*-C₈H₁₈) defining RON=MON=100 and the very knock-prone *n*-heptane (*n*-C₇H₁₆) assigned RON=MON=0. Values of RON and MON for test fuel mixtures are then determined by comparing the autoignition of a test fuel with autoignition of PRF fuel mixtures of *iso*-octane and *n*-heptane, using a highly calibrated special CFR engine and associated testing protocols [2]. For each test, the octane number of a test fuel is defined as the volume percent of *iso*-octane in the PRF mixture that matches the behavior of the test fuel. Important differences between the RON and MON tests are that the RON test operates at (1) a slower engine speed (600 rpm vs. 900 rpm), (2) a lower intake temperature (52°C vs. 149°C), and (3) less spark advance (13°BTDC vs. 19-26°BTDC), so the two tests interrogate somewhat different reaction conditions.

RON and MON are empirical, relative quantities, measured using an established protocol, which are important because they are used to qualify fuels for public sales, but there is no real theoretical basis for their values. A related quantity, Octane Sensitivity (OS), is defined as the difference between RON and MON,

$$OS = RON - MON . \quad (1)$$

For many fuels, OS is close to zero, but for some fuels, values of OS can be as large as 10-20. Kalghatgi [3,4] has proposed other quantities related to OS, including an Octane Index (OI), defined as $OI = RON - K \cdot OS$, where K is determined experimentally in engines, and Kalghatgi has then used OS and OI to increase understanding of octane requirements of modern SI engines.

An important current trend in SI engine development is to improve engine efficiency by increasing compression ratios and implement turbocharging [4]. However, this can make knocking operation more likely for conventional fuels since engine autoignition delay times decrease rapidly as

the cylinder pressure increases, but fuels with high levels of OS may offer some solutions. Ignition delay times of high OS fuels are observed to decrease less rapidly with increasing pressure than ignition delay times of other fuels [4-6], making high OS fuels more resistant to knock and more desirable in turbocharged and high compression engines. A more predictive, less empirical understanding of factors that determine OS would therefore be very useful in design of next-generation engines and fuels.

Formally there is no other definition for OS except Eq. (1), and there has been considerable discussion of the fuel properties that might contribute to OS for different fuels. None of these studies has provided a fully satisfactory explanation why some fuels have little or no OS while other fuels have high values of OS. Empirically, OS fuels tend to react more slowly than other fuels at temperatures below about 850K and thus do not experience low temperature “cool flames”, but they then react more rapidly than other fuels at higher temperatures, so it has been suggested that OS results from some particular temperature dependence of their heat release rates and ignition delay. On the basis of the explanations described below in this paper, perhaps the best way to define octane sensitivity was given by Leppard in 1990 [7], noting “any fuel not possessing NTC behavior would have a significant octane sensitivity”. Mehl et al. [8] carried out perhaps the closest previous approach to the present study, discussing the combined effects of RON and OS in terms of low temperature reactivity, recognizing that OS fuels, olefins in their studies, reduced knocking tendencies and inhibited ignition at lower temperatures. The present work uses detailed kinetic models to identify kinetic factors in a wide variety of fuel classes that suppress low temperature NTC heat release, resulting in high OS.

Fuels and kinetic mechanisms

Modern fuels in practical SI combustion engines usually consist of complex mixtures of hydrocarbon and oxygenated hydrocarbon fuels with molecules containing as many as 8 – 10 carbon atoms. In addition to more conventional fuels derived from petroleum, bio-derived fuels including alcohols, especially ethanol and methanol, are often present in significant amounts, and new components are being constantly explored. Combustion processes, particularly involving autoignition and emissions, depend strongly on the molecular structure of the specific molecules in the fuel, so autoignition and knock sensitivity cannot be evaluated simply by studies of *iso*-octane and *n*-heptane, and engine performance and emissions also must consider the full range of fuel components.

This paper exploits a wealth of recent advances in kinetic mechanisms for the classes of practical fuel types that reflect the complexity of modern fuel composition. In addition to the present specific focus on OS, these models demonstrate that current kinetics have become realistic and valuable tools for practical, applied fuel and engine research. We have collected together, into a single chemical kinetic reaction mechanism, models for *n*-alkane fuels from methane to *n*-octane [9,10], 2-methyl alkanes from iso-butane to 2-methyl heptane [10], other branched chain hydrocarbons including the isomers of pentane and hexane [11,12] and selected isomers of heptane [13,14], and *iso*-octane [15]. In addition, recent mechanisms are included for alcohol fuels methanol, ethanol, and the isomers of propanol and butanol [16,17], as well as *n*-pentanol [18] and *iso*-pentanol [19], and mechanisms for benzene and alkyl benzenes as large as *n*-butyl benzene [15,20-23]. New mechanisms for a wide variety of olefin fuels from propene [24,25] to heptene [26] are also included, as well as cyclic paraffin fuels cyclopentane [27], cyclohexane [28] and methyl cyclohexane [29]. It would also be straightforward to add existing compatible kinetic mechanisms for many other fuel molecules [9,10,30-32] as needed for future studies. It is particularly important that these kinetic mechanisms include submechanisms to describe low temperature kinetics, specifically to temperatures as low as about 600K, since our

experience as described below show that the existence or lack of low temperature reactivity, including cool flames, is critically important in assessing OS features of different fuels. Extensions of high temperature kinetic mechanisms to lower temperature ranges have been particularly valuable, requiring extensive mechanism validation through measurements of low temperature, species-specific quantities. All of these fuel molecule kinetic mechanisms have been built upon a base mechanism for small molecules and radical species common to all fuel combustion models, consisting of a C₀ – C₄ species mechanism from Curran et al. at the National University of Ireland at Galway [33] that has been exhaustively validated. Recent theoretical breakthrough studies of alkylperoxy radical isomerization reaction pathways have been critical in refining large-scale mechanisms and improving the accuracy of their predictions [34-36]. This provides a computational modeling tool of unique capabilities, combining many fuels and fuel classes. Important submechanisms have been extensively validated and can be upgraded as newer kinetic features, such as experimental data for mechanism validation, and species submodels become available. It is also a potential source for future mechanism reductions for more efficient use in CFD modeling applications.

This combined mechanism, and the individual fuel submodels within it, must always be considered as “works in progress” and are subject to almost continuous additions and modifications as improvements in chemical theory, new experimental data for model validations, and development of models for new fuels become available. The entire current mechanism and associated thermochemistry are available as Supplemental Material and on the LLNL website [37].

Combustion Model Environments

The present kinetic simulations consider spatially homogeneous mixtures of fuel and air and are not intended to be a full engine simulation. Two sets of calculations have been carried out to examine the oxidation and autoignition of fuel/air mixtures related to OS under conditions relevant to SI engines. The most important system parameters in these studies are the fuel type and molecular structure, as well as the reaction temperature and pressure, and the time period during the engine cycle at which reaction and autoignition occur. In our previous study [38], autoignition reactions were studied computationally under Perfectly Stirred Reactor (PSR) conditions over a range of reaction temperatures in order to explore the role of temperature on reaction progress. Those PSR modeling calculations predicted time-independent overall rates of reaction and heat release for stoichiometric fuel/air mixtures as functions of reaction temperature at 15 bar pressure. Comparisons of the computed heat release rates at different temperatures indicate strongly that OS fuels have low rates of oxidation at low temperatures (i.e., below 700-800K), in contrast with non-sensitive fuels which have substantial rates of low T reactivity. Differences in reactivity were interpreted as a lack of low temperature, Negative Temperature Coefficient (NTC), “cool flame” reactivity in the OS fuels. The strength of this correlation between cool flame reactivity and low OS values was limited by the lack of corresponding simulations under more engine-relevant conditions. Most significant is the realization that octane numbers and engine autoignition are dynamic quantities, in which a fuel/air mixture is followed over its reactive cycle, while PSR simulations are time-independent quantities that do not consider the residence time of the reactive mixture at each point in the temperature/pressure/reactivity/time path that the mixture follows in the engine.

In the present study, we replace those PSR time-independent computations with simulations in an SI engine operating at conditions that are encountered in real applications. Combining both approaches, the time independent PSR reactivities and the time-varying histories of fuel/air mixtures as

they progress along an engine cycle approaches, provides a thorough test that shows how OS is related to fuel molecular structure, and we anticipate that the resulting insights can be useful in future developments of next-generation engines and fuels.

We carried out engine experiments at Sandia National Laboratories to study the performance of a 70/30 volume mixture of gasoline and ethanol (E30) with a RON value of approximately 104 in an instrumented single-cylinder SI engine. In particular, the time-varying engine pressure is measured and recorded on a crank-angle basis. From this pressure, the time-dependent unburned gas temperature and overall heat release rates are calculated. For details of the experiment, data acquisition and processing, please refer to Ref. [39], which also include specifications for the E30 fuel used here. In our simulations, we begin with unreacted fuel and air, at a slightly fuel-rich mixture with equivalence ratio of 1.1, and then follow the measured pressure-time history from the engine measurements. Two basic engine cycles were tested in order to provide experiments as close as possible to the specialized RON and MON test procedures. One test was done at an engine speed of 600 RPM, as done in the RON test, and the second test was done at 900 RPM as in the MON test. The intake-air temperature in the RON-like cycle was 32°C, and 121°C in the MON-like cycle. This renders an intake-air temperature difference of 89°C, which is comparable to the 97°C difference in the corresponding RON and MON tests (for which the intake temperature is specified to 52°C and 149°C, respectively). To compensate for the fact that the intake temperatures were slightly lower than the baseline values of the official RON and MON tests, the intake pressure was maintained slightly below atmospheric, at 93 kPa absolute, following compensation table A4.4 in ASTM D2699-13b. Hence, these conditions are similar enough to the actual test conditions to have confidence that the experimental engine cycles feature the same families of reactions as the actual test procedures. A fairly high compression ratio of 12 was used for both the RON- and MON-like tests, matching the high resistance to autoignition of the E30 fuel. For the simulations, we do not consider the earliest times in either cycle, since virtually no reactions occur prior to our problem start

time at about 500K. The initial pressure at the beginning of each RON-like calculation is 3.1 bar and the temperature is 502K, corresponding to a time 65.3 Crank Angle Degrees before Top Dead Center(TDC) in the engine, and the initial pressure in the MON-like cycles was 2.09 bar and initial temperature of 501K, corresponding to 80.6 Crank Angle Degrees before TDC. The progress of the spark-ignited flame is included in the pressure profiles used to drive the unreacted fuel/air gas mixtures, so we are carrying out our simulations in the “end gas” in the combustion chamber. These test conditions are close to the test conditions for the standardized RON and MON tests [2], but this is not a test CFR engine. For simplicity, we use the terms ‘RON’ and ‘MON’ below to refer to the simulations for the two engine cycles, with the realization that these are only approximately RON and MON simulations. Full documentation of the experimental results, digitized and tabulated into a format convenient for numerical simulations, is available from the authors.

Each fuel/air mixture in our simulations is then compressed in time by specifying the pressure-time profiles as input for a ChemkinPro [40] simulation, using the option to specify the pressure history and let the chemical reactions determine the subsequent fuel/air combustion and its rate of heat release. These mixtures are calculated to autoignite at elapsed times close to TDC, but with a distribution of autoignition times that depend on the RON and MON of the fuel, which depend in turn on the molecular structure of the fuel, as described further below.

The pressure histories for all of the present calculations are shown in Figure 1. The progress of each simulation produced an ignition, at which time the cycle simulation is terminated. No computed information after that ignition is then used in the problem analysis. Note that the RON pressures are higher than the MON pressures after TDC.

This approach is therefore somewhat approximate, since the actual engine pressure history varies with different fuels. However, this pressure history depends largely on the compression stroke without significant heat release from the fuel until quite late in the cycle. Note that the inflection point in the pressure history in Fig. 1 occurs at about TDC, where an ON=100 fuel is expected to autoignite.

Although the specific heat of each fuel/air mixture is slightly different, using this single pressure history is still relatively accurate, and the large-scale effects we are exploring are not expected to be distorted by this approximation.

To calibrate this approach, the RON-like pressure history was used to simulate autoignition of mixtures of Primary Reference Fuels (PRF) n-heptane and iso-octane from 0 to 100, and the computed times of autoignition were plotted as functions of their mixture value of ON, with the results shown in Figure 2 as the solid line and black data points. Computed ignition times for samples of other fuel classes are also included in Fig. 2 and will be discussed below. The scatter around the calibration line can be due to uncertainties in the use of the single pressure curve, uncertainties in kinetic rate constants used in the simulations, and uncertainties in the original RON measurements [1].

As we will show below, none of these uncertainties and approximations affect the conclusions of the present analysis. The rate of flame propagation in the combustion chamber is not expected to vary strongly from one fuel to another, and much of the pressure history driving the end gases depends on piston motion, which is expected to be rather constant for all of these fuels.

Experimentally measured values of RON and MON, and therefore of OS, for a rather wide variety of fuels and fuel classes are summarized in Table I. In each of these fuel classes, with the

possible exception of the alkyl cyclohexanes, fuels have high OS values for the smaller members of each class. As the size of molecules in each class of fuels increases by lengthening attached linear -CH₂- chains, the OS value decreases steadily, so *n*-alkyl alcohols larger than *n*-butanol, alkyl benzenes larger than *n*-butyl benzene, and *n*-alkanes larger than propane, all have low values of OS. In the next portion of this paper, we will examine each of these fuel classes and determine the sources of these variations in OS values.

RESULTS FOR DIFFERENT FUEL CLASSES

n-alkanes

In our previous PSR study [38] of *n*-alkane octane sensitivity, overall reaction rates were computed for stoichiometric fuel/air mixtures at 15 bar pressure and a residence time of 50 ms, over a range of temperatures from 550 – 1100K. These results are best interpreted as “intrinsic reactivities” that do not depend on how the mixture evolved to reach these reaction conditions. The computed results for *n*-alkanes including methane, ethane, propane, *n*-butane and *n*-heptane are shown in Fig. 3.

These results show that, for these conditions, methane and ethane show virtually no reactivity at temperatures below about 850K, while the larger *n*-alkanes show increasing amounts of low temperature reactivity as the length of the *n*-alkane C chain grows. Propane shows a transitional behavior with relatively little reactivity below 850K, but with signs of a small amount of low temperature “cool flame” reactivity between 650 and 750K. Detailed examination of the computed results shows that all of the reactivity in Fig. 3 below 850K is due to alkylperoxy radical isomerization kinetics that releases a considerable amount of energy and consumes significant fractions of the initial fuel. From Table I, it is clear that the lack of cool flame kinetics correlates strongly with the high OS value of methane (OS $\approx$ 10), and ethane (OS = 16), and the substantial low temperature reactivities of *n*-butane and *n*-heptane correlate well with their small or negligible OS values. The transitional behavior of propane, with its small cool flame in Fig. 3, is reflected in an OS = 15, and we will explore this transitional behavior below.

In the discussions of fuel reactivity in this paper, we will constantly be discussing reactions that occur primarily at temperatures between about 500K and 850K and are controlled by addition of molecular oxygen O₂ to chemical radical species produced mostly from the fuel. Following addition of

O₂, the resulting RO₂ radicals then react further via internal isomerization reactions and other elementary steps that release modest amounts of heat and consume fractions of the fuel molecules into metastable compounds that result in degenerate chain branching that ultimately leads to thermal autoignition of the fuel/air mixture. This degenerate chain branching kinetics generally leads to ignition earlier than would have occurred without this low temperature reactivity. This chemical oxidation regime has been the subject of many theoretical, experimental, and kinetic modeling studies and will not be pursued here except to acknowledge its capacity of producing accelerated overall rates of fuel/air ignition. The low temperature reactivity is frequently discussed as “cool flame chemistry” and is usually observed as a distributed glow or moderate amount of heat release that first appears at the lowest end of its temperature limits and then ceases when the temperature reaches the high end of the process. The temperature limits for low temperature reactivity and “cool flames” are closely related to the lowest temperatures at which O₂ addition to hydrocarbon radical species leads to observable reactivity, at about 500K, and the high temperature limit where the R-O₂ bond primarily dissociates to R + O₂, and ending the net addition rate of O₂ to fuel radicals effectively quenches the low temperature reactivity or “cool flame”. We use both terms below, but it must be understood that the “cool flame” refers to the homogeneous region of chemical heat release via these low temperature reaction sequences and not to any type of conventional flame.

The same *n*-alkanes described above for PSR simulations were used in the present SI simulations as described above, following the RON-like pressure history and computing the kinetic evolution of the reactant end gases, and the results are summarized in Figures 4a, 4b, and 4c, showing the computed heat release rates, unburned gas temperatures, and unburned fuel mole fractions of methane, ethane, propane, *n*-butane, *n*-pentane, and *n*-heptane.

Beginning with methane, which ignites almost 25 degrees after TDC, the *n*-alkane fuels ignite at steadily earlier CA degrees as the length of the molecular C atom chain increases. The slight drop in the methane heat release curve at about 22 degrees after TDC shows that ignition is late enough that cooling due to volume expansion from piston motion after TDC actually reduces the overall rate of heating for a short time, after which the entire remaining fuel/air mix ignites. Ignition of the larger *n*-alkanes occurs in two distinct stages, shown by an early peak in the heat release rates in Fig. 4a for *n*-butane at TDC, and for *n*-pentane, and *n*-heptane. This earlier heat release peak is the “signature” of a cool flame, which occurs at lower temperatures than the subsequent, much larger heat release from the main, final ignition event. The *n*-butane, *n*-pentane, and *n*-heptane curves show increasing amounts of heat release due to cool flame reactions, with a very small cool flame heat release at TDC for *n*-butane, much larger cool flame for *n*-pentane, and even larger amounts of cool flame heat release for *n*-heptane. The corresponding fuel consumption profiles are shown by the fuel mole fractions plotted in Fig. 4b. The initial mole fractions of each fuel vary according to the molecular weight of each fuel and the fact that all these fuel/air mixtures are at the same initial equivalence ratio of 1.1. This plot shows that as the size of the fuel molecule grows from *n*-butane to *n*-heptane, a cool flame consumes progressively larger fractions of the fuel. Cool flame fuel consumption is shown by the first-stage reduction in fuel mole fraction from its initial value to a lower level in Fig. 4b. This cool flame consumes a small fraction of the fuel in *n*-butane, more of the fuel in *n*-pentane, and even more of the fuel in the *n*-heptane cool flame. Little or no first-stage, cool flame fuel consumption occurs for the small *n*-alkanes methane, ethane and propane, so that most or all of their fuel consumption occurs at a later time in the final ignition.

Ignitions for the *n*-alkanes, including the two-stage ignition events for the larger *n*-alkanes, are shown by the unburned gas temperatures in Fig. 4c. The unburned temperature for each fuel/air mixture rises steadily along a common curve, due to compressional heating from engine piston motion and flame propagation elsewhere in the engine chamber. At about 18 degrees before TDC, the most reactive fuel, *n*-heptane, reaches 750K where the first cool flame reactivity can begin, producing a rapid rise in temperature. This rapid rise slows briefly at about 950K, when the cool flame is quenched, and a final high temperature ignition completes the full ignition beginning at about 1000K. The *n*-pentane fuel/air mixture, with a slightly smaller amount of cool flame reactivity, begins its low T reaction at about 800K, slowing at about 925K, with its final ignition also at about 1000K. The *n*-butane follows, first with its cool flame reactivity beginning at about 820K and its final ignition again at about 1000K. The sequential cool flame, low temperature ignitions of these fuels occur as the most ignitable fuels, with their greatest low temperature reactivity, ignite earliest, followed in order by the progressively less reactive fuels. The overall effect of this cool flame fuel consumption is magnified by the fact that fuels with more low temperature reactivity have correspondingly less fuel to consume following their cool flames and reach a higher temperature, and thus proceed more rapidly to the final ignition step. Those fuels that do not exhibit any low temperature reactivity or cool flames are last to ignite and are the fuels with significant OS values.

We have included horizontal grid lines in Fig. 4c to emphasize the role of the temperature in determining the times at which the cool flames begin and end, as well as the observation that the second and effectively final stage in fuel/air autoignition occurs at about the same temperature in every fuel/air mixture. As we will demonstrate for other fuel classes below, this common final ignition

temperature applies to all of the fuel classes studied. This pattern has been described previously [43] as being determined by the activation energy of the reaction

which produces rapid decomposition of hydrogen peroxide at about 950 - 1000K, with the resulting degenerate chain branching from OH radical production triggering the autoignition. Each class of fuels discussed below has specific class members which we will identify as OS fuels that avoid low temperature, cool flame reactivity by producing metastable intermediates. These intermediates, rather than reacting vigorously and releasing substantial amounts of heat in cool flames at lower temperatures (i.e., < 850K), remain unreactive in a variety of metastable molecular forms that do not react further until they reach significantly higher temperatures where, like H_2O_2 , they decompose and add to the degenerate chain branching that completes the full fuel/air autoignition. Each class of OS fuels produces its own variety of stable intermediates, and we will illustrate each class of OS fuels and the intermediate species they produce in the discussions below. In conclusion for the family of *n*-alkane fuels, only the smallest *n*-alkane molecules, methane, ethane and propane, have appreciable OS values and are shown above as the only *n*-alkanes that do not produce low temperature cool flames under engine timescales. They do not produce cool flames because the molecules are too small to enable the alkylperoxy radical isomerization reactions on the timescales that are necessary to produce cool flames. As a side note, propane is known to produce cool flames [44] but only at time scales too long to be observable in an engine.

Linear Olefin Fuels and Octane Sensitivity

Introduction of a C=C double bond into a chain of saturated carbon atoms removes two H atoms and produces two very strongly bonded vinylic H atoms (indicated below by 'v' in Fig. 3) and four very weakly bonded allylic H atoms (indicated by 'a'). Another effect, not visible here, is a rearrangement of the bonding electron density in the vicinity of the C=C double bond.

This rearrangement, termed “electron delocalization”, is responsible for the strength of the C=C double bond, as well as the strength of the two C-H vinylic bonds, and perhaps less intuitively, for the weakness of the four C-H allylic bonds. Electron delocalization due to the C=C double bond above moves electron density away from the neighboring C atoms towards the double bond, electron density which would otherwise contribute to the strength of the neighboring secondary C-H bonds. The result is a weak allylic secondary C-H bond strength of about 85.5 kcal/mol, significantly less than the 98 kcal/mol strength of a conventional secondary C-H bond, and this difference in C-H bond energy makes it dramatically easier for reactive radical species to abstract one of these secondary allylic H atoms denoted as R_{as} . We will use the term R_a to represent general allylic radicals in the discussions below. For example, at conditions in an engine prior to end gas autoignition, the rate of H atom abstraction by OH radicals from the ‘a’ locations in the molecule above is twice that of abstraction of the

conventional, neighboring conventional secondary H atoms, with even more dramatic abstraction rate enhancements noted below for other OS fuels.

Equally important, the allylic radical species R_a shown above is much more thermally stable than a corresponding conventional alkyl radical and resists thermal decomposition or addition of molecular O_2 , both reaction pathways that dominate the oxidation of conventional alkyl radicals. Specifically, the

activation energy for the decomposition of a typical allylic alkenyl radical, the $\text{aC}_5\text{H}_9\text{-c}$ radical from 2-methyl 2-butene, is more than 50 kcal/mol, while a typical alkyl radical decomposition reaction has an activation of about 35 kcal/mol [5]. Instead, at lower combustion temperatures, allylic radicals most frequently add with HO_2 radicals [5,45] to produce metastable allyl hydroperoxide species, R_aOOH , which then remain unreactive until the end gas reaches temperatures high enough to break the O-O bond at about 950 – 1000K. This is a familiar degenerate chain branching process, similar in its effect to the low temperature production and decomposition of H_2O_2 discussed above, as well as the formation of ketohydroperoxide intermediate species in cool flame reaction pathways, and all three families of products, the allyl hydroperoxide, ketohydroperoxide, and hydrogen peroxide species, decompose thermally at approximately the same temperature of 950 - 1000K, since it is an O-O that is broken in all three decomposition reactions, and the activation energies for decomposition of all of these hydroperoxide molecules are the same at about 50 kcal/mol. Olefin fuels are unique because the allylic H atoms are preferentially abstracted at low temperatures, which focuses a large fraction of the reaction flux through those pathways which lead immediately to a shutdown in the reaction progress towards ignition, due to the degenerate chain branching production of metastable allylic hydroperoxides R_aOOH .

The example above describes the case where the C=C double bond is interior to a carbon chain, so there are four allylic C-H bonds available for H atom abstraction. Two other situations are also possible, one in which the C=C double bond is at the '1' location and the second with the double bond at the '2' location. For the 1-olefin, there are only two allylic C-H bonds, since the terminal C atom has two primary vinylic C-H bonds that are not easily abstractable, so the overall influence of the C=C double bond at the '1' location is only half the effect of the interior C=C double bond depicted above. The 2-olefin has a somewhat intermediate effect, since it has three primary allylic C-H bonds in addition to the two secondary allylic C-H bonds as in the 1-olefin. The primary allylic C-H bond strength is 87.9 kcal/mole, stronger than the secondary allylic C-H bonds but also much weaker than conventional

primary C-H bonds (101.2 kcal/mole), and the overall impact of the 2-olefin is stronger than the 1-olefin and weaker than the olefin with the interior C=C double bond. We will next illustrate these effects with kinetic model RON ignition simulations for the linear isomers of hexene, C₆H₁₂.

Example of the linear hexene isomers

All three linear isomers of hexene show substantial amounts of OS, as shown in Table 1. Kinetic modeling of these three molecules has been studied extensively [46-48] and we have

included the Mehl et al. [47] mechanism in the present model. Autoignition of these olefin fuels and the related saturated *n*-alkane, *n*-hexane, were computed for the present RON end gas engine cycle, and the results are summarized in Figs. 5a, 5b, and 5c.

The saturated *n*-hexane shows a strong cool flame at about 17-18 degrees before TDC, 1-hexene shows only a trace of a cool flame at 10 degrees before TDC, and the other two olefins show no cool flame.

The temperature history for *n*-hexane shows the two-stage ignition that is characteristic of larger *n*-alkanes with cool flames and significant low temperature reactivity. The temperature history of 1-hexene shows an early rise in temperature at about 800K and a small inflection at about 875K indicating an end to its low temperature reactivity, followed by a conventional ignition at about 950K. The two

other hexene isomers do not show any low temperature reactivity and also ignite at about 950K. The fuel consumption plots in Fig. 5c show that the cool flame consumes more than half of the *n*-hexane fuel. The temperature plot for 1-hexene is not as distinct as that for *n*-hexane, but it appears that the small cool flame for 1-hexene has consumed perhaps a third of the fuel.

These fuels illustrate most of the important characteristics of Octane Sensitivity for many families of molecules that will be illustrated below. The low temperature reactivity or “cool flame” that was quite strong in the saturated fuel *n*-hexane is effectively quenched in all three olefin isomers. The degenerate

chain branching from the allylic hexenyl radicals R_a have quenched enough of the reaction pathways from the fuel that the overall rate of low temperature chain branching cannot produce a significant level of cool flame heat release. The almost total absence of low temperature cool flame reactivity in all three hexene isomers is reflected in the relatively substantial OS values of 13.0, 11.9, and 13.9 for these hexenes as shown in Table 1. The strength of this argument suggests that either the 1-hexene OS of 13.0 or the OS for 2-hexene of 11.9 could be incorrect, since the kinetic modeling trends indicate that the location of the C=C double bond ought to be reflected in a monotonic variation in their OS values. A closer experimental examination of the RON and MON values for 1-hexene could resolve this question.

The slightly greater low temperature reactivity of 1-hexene, compared to the 2- and 3-hexene, is unmistakable from the present computed results, and it illustrates a very important feature of the transitions from high OS fuels to low OS fuels within this and other fuel classes. In the C_6 linear olefins shown above in (4), only the 1-hexene molecule has a continuous, uninterrupted length of saturated carbon atoms as long as three – CH_2 - units. In this molecule, the weak allylic bond at the ‘3’ site preferentially produces the ‘3’ hexenyl allylic radical, and while addition of HO_2 as discussed above

dominates the reactions of the allylic radical, molecular oxygen O_2 can also add to this site to produce an R_aO_2 radical. This reaction is important, even though alkyl radical addition to O_2 is significantly slower than addition of allylic radicals to O_2 , and the R_a-O_2 bond is weaker than the same bond with a conventional alkyl radical, making the lifetime of the allylic peroxy radical shorter than that of the conventional alkylperoxy radical. This R_aO_2 radical can abstract an H atom from within the same R_aO_2 radical via a 6-membered transition state ring with the secondary-bonded H atoms at the '5' site, or a 7-membered transition state ring with the primary-bonded H atoms at the '6' site, to produce an allylic hydroperoxy alkyl radical QOOH. Both of these isomerizations are quite rapid [34-36] and provide low temperature chain branching and accelerate progress toward ignition. The molecular geometry of 1-hexene is therefore capable of sustaining modest levels of cool flame, low temperature reactivity, which is exactly what is seen in Fig. 5. Rates of low temperature R_aO_2 isomerization reactions are much smaller for the similar but smaller R_aO_2 transition state rings based at the '4' site in 2-hexene because transition state rings of R_aO_2 in 2-hexene are smaller than those in the R_aO_2 species in 1-hexene. The lower rates are due to the much greater ring strain energy barrier in the smaller transition state rings, so much less analogous low temperature reactivity occurs in the 2-hexene isomer, and the 3-hexene geometry is even less conducive to low temperature chain branching reactivity. The overall low temperature reactivity in 1-hexene is still considerably less than in *n*-hexane because only the '3' site in 1-hexene can support substantial cool flames, while *n*-hexane supports rapid, low ring strain energy barrier RO_2 isomerization reaction pathways from all four secondary radical sites and from the primary radical sites in *n*-hexane. Larger linear olefin fuels, such as 1-heptene, 1-octene, and larger 1-olefins can provide a much more extended continuous saturated region and therefore more vigorous cool flame, low temperature reactivity and heat release than any of the hexene isomers, and the OS values for these larger 1-olefins are very small due to this significant low temperature reactivity. For linear olefins with interior C=C double bonds, as the fuel molecule grows in length, significant extents of saturated carbon

chains are possible and will similarly support low temperature reactivity and cool flames and have minimal OS values. For example, 8-hexadecene or 6-dodecene would be expected to have very small OS values because they would have many sources of low temperature reactivity, in spite of the centrally-located C=C double bond. Other intriguing implication of these features can occur, such as unexpected trends that are possible for low temperature reactivity in larger olefins. For example, the low temperature reactivity of 4-octene is likely to be considerably lower, with higher OS, than 2-octene or 3-octene, since the centrally located C=C double bond of 4-octene will yield very small levels of low temperature reactivity, about twice that of 1-hexene, while the 2- and 3-octene fuels would have many more, longer, uninterrupted, saturated carbon chains to support more vigorous cool flames than are possible in 2- and 3-octene.

Octane sensitivity of linear olefin fuels is produced by electron delocalization due to the C=C double bond that characterizes an olefin fuel. Weak allylic C-H bonds result from that electron delocalization and makes them very easily abstracted from the fuel and makes the resulting allylic radical R_a unable to decompose or support cool flame reactivity, in contrast with conventional alkyl radicals. This forces a large fraction of the reaction flux at low temperatures to become accumulated as relatively unreactive allyl hydroperoxide species, not reacting further until higher temperatures are reached. These metastable intermediate species do not react further until temperatures of 950 – 1000K are reached, when they and other hydroperoxide intermediate species decompose via O-O bond fission and produce the final overall autoignition.

We will see the same effects for other classes of fuels, in addition to the linear olefins, where growth in the length of a saturated continuous chain of carbon atoms similarly begins to produce significant low temperature reactivity and cool flames and quench the OS qualities that are observed in smaller versions of a fuel class. This will be shown explicitly next for alcohol and alkyl benzene fuels, and it occurs in other types of fuels as well. This critical number of continuous saturated carbon atoms is

responsible for the relatively weak cool flame discussed above (Fig. 3) for propane low temperature reactivity and has the same origin as the minor cool flame for 1-hexene in Fig. 5b and will be discussed as transitional cases in the low temperature reactivities of the related 1-alcohols and n-alkyl benzenes below.

Alcohol Fuels and Octane Sensitivity

There are many similarities between the low temperature reactivity of alcohol and olefin fuels and their effects on Octane Sensitivity. Many smaller alcohol species have considerable OS values as shown in Table 1, and like the *n*-alkanes and olefins, the large OS levels for smaller molecules decline steadily as linear chains of saturated carbon atoms are incorporated into the alcohol molecule. Note that the OS values for methanol and ethanol are very large (i.e., 20 and 19, respectively) but have almost completely vanished for 1-hexanol and 1-octanol.

A “typical” 1-alcohol and its major radical due to H atom abstraction can be written

H atoms bonded to the C adjacent to the OH group, signified as ‘ α ’ in (5), usually denoted as the α -site, have a smaller C-H bond energy than the others in the molecule. For example, Black et al. [49] observed a faster abstraction of these α -site H atoms than others in *n*-butanol by a factor of 9 at combustion temperatures. This is due to the effects of the O-H group on the molecule, which is a form of electron delocalization as noted previously for C=C double bonds in olefin fuels. Specifically, the electron density that ordinarily provides strong secondary C-H bonding at the α -site is instead drawn away by the O–H group, reducing the α -site C-H bond energy, as noted above for allylic sites in olefin fuels. Following this H atom abstraction, molecular oxygen O_2 then adds to the α -site, producing an $\text{R}_\alpha\text{O}_2$ radical, using 1-butanol for illustration in Eq. 6. Recent theoretical studies of reactions of this $\text{R}_\alpha\text{O}_2$ species [17,50,51] have studied an important reaction of this radical in which the H atom in the OH group combines with the O–O• and are eliminated directly, avoiding the high energy barrier of an actual H atom shift,

so effectively instantaneously, C-O bond fission produces propionaldehyde in this example and HO₂ as final products. In 1-alcohols of different sizes, different aldehydes are produced in place of propionaldehyde, but in each case stable a stable oxygenated product results from this reaction pathway. For the present study, the importance of this step is that the oxygenated product is quite stable at low temperatures and provides another example of degenerate chain branching which is not completed until higher temperatures are reached. In this sense, formation of the aldehyde is functionally equivalent to the production of the metastable allyl hydroperoxide species in low temperature olefin oxidation, delaying autoignition until higher temperatures and quenching low temperature reactivity and any possible resulting cool flame activity. Examination of other alcohol fuels in which the OH group is found at a site interior to the carbon chain shows that the oxygenated metastable product is usually a ketone species rather than an aldehyde, but the functionality of this product is still the same, eliminating sources of subsequent low temperature chain branching and cool flame reactivity. The metastable oxygenated product remains largely unreacted until about the same temperatures at which the hydroperoxide species decompose, so the final autoignition event at about 950 – 1000K will also occur for the OS alcohols.

Kinetic mechanisms for the *n*-alcohol species from methanol to *n*-butanol were included in our overall model from earlier studies of ethanol through pentanol [16,17,52-56], and the mechanism for *n*-

pentanol was included from a mechanism of Heufer et al. [18]. The computed results for the heat release of the 1-alcohols during the end gas simulation cycle are summarized in Fig. 6a, 6b and 6c.

Of the *n*-alcohols shown in Fig. 6, only the *n*-C₅H₁₁OH fuel shows significant amounts of low temperature heat release and cool flame reactivity, with a distinct cool flame, heat release region, beginning at about 9 degrees before TDC and ending at about 3 degrees before TDC. The remaining 1-alcohols react much later, with the 1-butanol igniting at a slightly earlier time than the C₁, C₂, and C₃ 1-alcohols. The corresponding computed end gas temperatures are shown in Fig. 6b, in which only the 1-pentanol fuel begins to react and its temperature rises much earlier than the other alcohols and showing a two-stage autoignition, with the first stage beginning at about 780K and the second stage occurring at about 950K. Single-stage ignitions of all the other, smaller 1-alcohols begin at the same temperature of about 950K. Computed fuel mole fractions (not shown) have a two-stage consumption pattern only for 1-pentanol, with about one-third of the fuel being consumed in its cool flame, very similar to the fuel consumption of the hexene isomers in Fig. 5c.

The ignition of 1-butanol occurs slightly earlier than for the smaller alcohols and is a result of the structure of the 1-butanol molecule, seen in (5,6) above. Although most of the reaction of the C₄H₈OH- α O₂ shown in the left-hand-side of (6) proceeds via internal abstraction of the H atom from the OH site, the same radical can also abstract H atoms from the *n*-propyl radical on the opposite side of the radical species. This part of the *n*-butanol fuel “geometry” is exactly the same as that discussed earlier for propane and 1-hexene, and their limited RO₂ internal H atom abstraction reactions proceed via the same 6- and 7-membered transition state rings. From comparisons of Fig. 5 and Fig. 6, it appears that the very same minimal cool flame kinetic reaction paths in 1-hexene make a somewhat greater contribution to

the low temperature reactivity of 1-hexene than the very same reactions contribute to the low temperature reactivity of 1-butanol. These reactions take place at about 2 degrees after TDC for both fuels, as shown by comparing Figs. 5a and 6a. Detailed examination of the same regimes for 1-hexene and 1-butanol show that the alternative chain termination reaction in 1-butanol, producing propionaldehyde, that competes with its cool flame reactions is proportionately slightly more effective than the comparable reaction in 1-hexene that produces allyl hydroperoxides.

Recent kinetic modeling studies [57-60] have extended modeling capabilities to 1-alcohol molecules as large as 1-octanol, many of which are derived from biomass. The present analysis above implies that 1-alcohols larger than n-butanol should react with considerable levels of NTC, cool flame behavior, and have very little OS functionality. Cai et al. [60] observed considerable levels of NTC behavior with 1-octanol and concluded very sensibly that it was a better candidate for use as a diesel fuel than as an SI engine fuel, and the present analysis would predict little or no OS in the autoignition of 1-octanol. Experiments and kinetic modeling of 1-pentanol and 1-hexanol show considerable amounts of NTC behavior [56,57], although Rodriguez et al. [57] did not observe NTC behavior in low temperature PSR oxidation of 1-hexanol. Rodriguez et al. [57] recognized this disagreement and suggested that the very high levels of dilution required by their PSR experiments may have obscured any possible NTC behavior by emphasizing radical R_α decomposition, and other agreements between their results and those from other studies [58,59] showed more agreement than disagreement. Resolution of this disagreement about NTC behavior is important because significant cool flame, NTC behavior of 1-hexanol, as predicted by the present kinetic analysis and most other studies would make these C_5 and C_6 1-alcohol fuels low OS fuels unsuitable for high compression ratio and turbocharged engines, but it could make them better options for diesel engine fuels, as concluded by Cai et al. for 1-octanol.

Alkyl benzene fuels and Octane Sensitivity

A further class of hydrocarbon fuels that has seen important recent development of detailed chemical kinetic reaction mechanisms, for both high and low temperature regimes, is that of benzene and *n*-alkyl benzenes. Kinetic modeling studies of benzene and *n*-alkyl benzenes as large as *n*-decyl benzene [61-69] have appeared, although experimental data for testing these kinetic mechanisms is still quite limited primarily to *n*-butyl benzene with a single study of measurements for oxidation of *n*-hexyl benzene in a JSR [61].

The *n*-alkyl benzenes have a very large source of electron delocalization, consisting of the entire benzene ring with its highly aromatic structure. In the case of alkyl benzenes, this electron delocalization results in a weakening of the “benzylic” C-H bonds for the H atoms bonded to a C atom immediately adjacent to the aromatic ring.

Insert diagram (7)

The aromatic benzylic radical produced in *n*-propyl benzene is shown in (7) at the left and that in *n*-hexyl benzene at the right. These secondary benzylic C-H bonds are very weak, at 86.5 kcal/mole, nearly the same as the secondary allylic C-H bonds discussed previously for the linear olefin fuel molecules, and the selectivity for abstracting these benzylic H atoms is similarly very high. Like allylic radicals, benzylic radicals do not decompose, and the dominant reaction sequences, all of which take place within the *n*-alkyl chain and do not involve the aromatic ring. The reactions in the side chain eventually produce stable structures within the chain and which then remain unreactive until the end gases reach higher temperatures. These reaction sequences all begin by abstraction of a benzylic H atom and are then followed by addition of molecular oxygen O₂, addition of HO₂, or addition of OH, all to the benzylic radical site. Further reactions within the side chain then occur, and all lead eventually to stable structures within the side chain and do not include cool flame reactivity at low temperatures. Among

the species produced in the side chain at reaction temperatures below 1000K are benzaldehyde and unsaturated other hydrocarbon fragments that stabilize the chain, fragments including allyl, propargyl, vinyl and other similar structures. The stability of these aromatic rings with unsaturated carbon chains are such that they do not react further until much higher temperatures are reached, very much like the histories of the low temperature intermediates produced from olefin and alcohol species. The resistance of these smaller *n*-alkyl benzenes to low temperature reactivity and the absence of any significant low temperature heat release result in the high OS values for these fuels.

We incorporated alkyl benzene mechanisms from Darcy et al. [21-23] and Mehl et al. [15] and carried out end gas autoignition engine cycle simulations for toluene, ethyl benzene, *n*-propyl benzene, and *n*-butyl benzene. The computed results for the rates of heat release and temperature for these fuels are shown in Figs. 7a and 7b.

The ethyl, *n*-propyl, and *n*-butyl benzenes all react early at very similar low rates, with no appreciable low temperature or cool flame reactivity, consistent with their high OS values of 10, 12, and 13 as seen in Table I. Toluene begins at the same time as the larger fuels, but it continues to slowly release heat long after TDC. The *n*-butyl benzene starts to react earlier than the other fuels but it does not have the familiar shape of cool flame heat release seen in other reaction classes. The computed end gas temperatures in these simulations are shown in Fig. 7b, showing that the toluene ignites at very late times and that all of these fuels have only a very small amount of heat release (which is impossible to see in Fig. 7b), even in the *n*-butyl benzene, at temperatures below 1000K. For all four fuels, it appears that the ignition is a single-step high temperature event. Examination of the detailed kinetics shows that only the *n*-butyl benzene produces a very small amount of peroxy radical isomerization, cool flame kinetics, all within the side chain, consisting of the same transitional behavior seen in carbon chains with

three saturated carbon atoms that we have seen in 1-hexene and *n*-butyl alcohol. Just as seen for the other fuel classes, addition of O₂ to the benzylic site in *n*-butyl benzene produces the same smallest chain that can produce a small amount of cool flame behavior, but the amounts of the heat release are small and have only a very small effect on the OS value of 10 for *n*-butyl benzene.

Battin-Leclerc et al. [61] developed kinetic mechanisms for *n*-alkyl benzenes for alkyl chains from toluene to *n*-decyl benzene. Although most of these mechanisms could not be independently validated due to lack of suitable experimental results for some of those fuels, they did carry out some JSR experiments for *n*-hexyl benzene that helped validate the rest of their family of mechanisms. Using this model, their computed results under JSR conditions confirmed that *n*-butyl benzene is indeed a transitional alkyl benzene molecule, and that all such fuels with side chains larger than 4 C atoms show very significant low temperature reactivity and thus have minimal OS values, consistent with the present modeling results and analysis.

Cycloparaffin fuels and Octane Sensitivity

As noted in Table I above, the small number of cycloparaffin fuels for which RON and MON are well established [1] predict that their OS values should be very small. Based on the above discussions for many other classes of hydrocarbon fuels, no OS should be expected since no electron delocalization is seen in this class of fuels. Recent detailed kinetic modeling for these fuels at low temperature reactivity [28,29,70] show considerable levels of alkylperoxy radical isomerization reactions and overall cool flame behavior for both cyclohexane and methyl cyclohexane. A number of fairly recent experimental studies [29,71] show this low temperature reactivity regime very clearly. However, Lemaire et al. also showed [71] that unsaturated cyclic hydrocarbon such as cyclohexene and cyclohexadiene behave much like olefin relatives of conventional hydrocarbons by strongly quenching

low temperature reactivity, and the C=C double bonds in these unsaturated naphthenes and the resulting electron delocalization should be expected to produce OS behavior in these unsaturated species. However, kinetic modeling of these unsaturated cyclic species is not very well established, and further experimental and kinetic modeling work is needed here.

Using RON and MON values from Lovell [1], cyclopentanes and branched cyclopentanes ought to have high values of OS. For example, for methyl cyclopentane, RON=91 and MON=80, with OS of 11, with comparable values for other branched cyclopentanes. In contrast, various methyl-, ethyl-, and dimethyl-cyclohexanes have very nearly equal values of RON and MON, so they don't appear to have much OS. But cyclo-hexene has OS = 21 (RON = 84, MON=63) and the few other unsaturated naphthenes for which RON and MON have been reported also have high predicted OS values. Kinetic models for all of these species are still not available for most of the fuels in this overall class, so much more kinetic model development is needed.

A very interesting, recent study by Herbinet et al. [64] has studied oxidation of a family of alkyl cyclohexane fuels with comparable alkyl benzene fuels in new experiments, drawing thought-provoking conclusions and inferences about their major reaction pathways. Very consistent with kinetic modeling results shown above for *n*-alkyl benzene fuels, Herbinet et al. find that vigorous low temperature reactivity begins in the *n*-alkyl benzenes when the alkyl chain reaches a length of 5 carbon atoms, with *n*-butyl benzene being a somewhat intermediate or transitional fuel with respect to cool flame production, consistent with our conclusions about the effects of carbon chain length and OS behavior. Herbinet et al. also show substantial low temperature cool flame behavior for cyclic alkanes with side carbon chains of all lengths, including those with no side carbon chain. RCM experimental studies of alkyl benzenes by Roubaud et al. [62,63] describe low temperature reactions of *n*-alkyl benzenes and show the same sort of transition region between *n*-propyl benzene, with no NTC behavior, and *n*-butyl benzene with considerable NTC behavior.

Alkyl ester fuels and Octane Sensitivity

Alkyl ester fuels include smaller examples in which the alkyl radical consists of propyl, *n*-butyl and other smaller alkyl radicals as large as 8 – 10 C atoms have been the subject of numerous experimental and kinetic modeling studies. At the larger end of the size spectrum for fuels, biodiesel fuels, some of which are in practical use today, are being made from soy and rapeseed oils and consist of very large saturated and unsaturated methyl esters. Recent kinetic models of combustion of these biodiesel fuel molecules [31], which consist of mixtures of C₁₈ and C₁₆ saturated and unsaturated methyl esters, as well as kinetic models of methyl ester fuels of intermediate size such as methyl decanoate [32] and its unsaturated version methyl decenoate [72], all have shown that methyl ester fuels are complex and interesting mixtures of molecules with multiple sources of electron delocalization. Specifically, biodiesel molecules like methyl linoleate and methyl linolenate contain both a methyl ester moiety that has considerable electron delocalization from the – (C=O) – O – CH₃ methyl ester group, as well as multiple C=C double bonds in their long carbon chains, with their contributions due to that source of electron delocalization. However, while autoignition of biodiesel fuels is a kinetically challenging problem which may benefit from engine octane studies of other, smaller methyl ester fuels, actual biodiesel fuels are outside the practical limits of molecule size for use in SI engines and thus outside the subject area of this paper.

Smaller alkyl ester fuels have potential as SI engine fuels when the total molecule size is within the useful range for such engines, and kinetic mechanisms for some of these fuels have been developed. Boehman et al. [73,74] in particular have explored their uses in HCCI engines, but there are still unresolved kinetic modeling questions remaining to be resolved and their properties as engine fuels are still being probed. Methyl and ethyl ester fuels with chains of as many as 4 – 8 carbon atoms in the linear chain certainly have the same order of magnitude contributions from electron delocalization as we have seen above for the 1-alcohols in particular. The same sort of α -site CH₂ groups are found in

1 methyl esters as in 1-alcohols, with some modifications required because the familiar - CH₂ – O – H
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4 structure in 1-alcohols is sufficiently different in details from the methyl ester group. At this time,
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7 probably the best estimate that can be made is that small methyl esters probably have the same degree
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10 of OS as the 1-alcohols of similar molecular size. The incorporation of C=C double bonds and their
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13 effects on autoignition rates and their OS levels for unsaturated alkyl ester fuels will require new
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16 experimental and kinetic modeling attention.
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19 Current research and development of automotive fuels from many new sources, many of them
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21 derived from biomass sources, are being developed, and kinetic modeling is trailing these new fuel
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23 development efforts. In addition, even when novel fuels are being tested in engines, traditional
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25 parameters such as RON or MON seem to largely be overlooked in the momentum to carry out more
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27 practical engine studies. In the longer term, it seems possible, if not likely, that kinetic modeling studies
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29 of such novel fuels might be more profitably carried out first by numerical simulations to evaluate those
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31 fuels before expensive and time-consuming development projects are engaged.
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38 **Octane Sensitivity of Branched Fuels**

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41 Computations for both RON and MON cycles were also carried out for branched hydrocarbon
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43 and alcohol fuels shown in Table I, and the overall results were very consistent with the results for the
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45 primarily straight chain molecules discussed above. We will defer those discussions to a future report in
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47 the interests of keeping this paper modest in length and more focused on those fuels where the most is
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49 known about their autoignition metrics. For branched- as well as for straight-chain hydrocarbon fuels,
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51 until those fuel molecules grow in size to include continuous saturated carbon chains of length three or
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53 more, low temperature reactivity is generally suppressed and such molecules are found to have
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55 relatively large OS values. The number and variety of existing detailed kinetic reaction mechanisms,
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with both high and low temperature kinetic treatments, are less common for branched molecules than for straight chain molecules. We will continue to explore OS issues for such fuels and extend present capabilities to predict OS values and a priori estimates of RON and MON, based on detailed kinetic approaches, but more experimental studies with species-specific measurements for kinetic model validation will be necessary, as well as experimental determinations of RON and MON values for many non-traditional fuels for which RON and MON have not been measured.

Octane Sensitivity and MON

In the above discussions, we have analyzed the RON performance of fuels and focused on the role of low temperature reaction rates and heat release on autoignition during the RON test cycle. The overall conclusion has been that high OS fuels do not have significant reactivity during the low temperature regions in the RON cycle, while fuels with little or no OS have considerable levels of cool flame and other low temperature reactivity and heat release. But OS is defined as the difference between RON and MON, so it is necessary to examine the MON cycle reactivity of fuels to be able to draw conclusions about the origin of Octane Sensitivity.

A common “trademark” of OS is often presented as shown in Fig. 8, where the PSR oxidation of a high OS fuel, 2-methyl 2-butene (2M2B), with OS = 12.6, is compared with the oxidation of a low OS fuel, PRF90, with OS = 0. These PSR computations were carried out for stoichiometric fuel/air mixtures at 10 bar pressure and a residence time of 0.05s. The 2M2B has RON=97 and MON=84, while the PRF fuel has both RON and MON equal to 90. These heat release curves cross twice, once at low temperature and again at a higher temperature. The late rise in reactivity above 650K for the OS fuel is a reflection of the lack of cool flame reactivity discussed above and the high RON for the 2M2B, while the prominent

heat release peak for the low OS PRF fuel at 675K indicates considerable cool flame activity. The higher reactivity of the OS fuel between 700 and 850K is responsible for its relatively low MON value of 84, much less than the reactivity of the PRF fuel mixture with its higher MON value. It is important to recall that the RON cycle test begins at a much lower temperature than the MON test (52°C vs. 149°C, or 325K vs. 422K), which when combined with the higher engine speed of the MON test cycle results in much less residence time at low temperatures for the MON test.

To illustrate the very different behaviors of OS and low OS fuels in the MON test, compared to their reactivity in the RON test, several comparison computations were made, using the MON cycle shown in Fig. 1. In Figure 9, PRF95 fuel mixture autoignition is shown under both RON and MON conditions, showing that the fuel ignites earlier in the RON cycle, and only the RON cycle shows any evidence of low temperature cool flame reactivity. The same PRF95 fuel is used in both engine cycles, and the MON heat release profile shows absolutely no cool flame, NTC behavior for PRF95 fuel.

The temperature profiles (not shown) for these same two engine cycles also show no NTC behavior of any sort in the MON cycle. With the low temperature reactivity contributing more in the RON simulation, the fuel mixture ignites much earlier (by about 10 CAD) in the RON cycle than in the MON cycle. The differences in reactivity between the two engine cycles gives the low temperature reactivity in the RON cycle the opportunity to advance the time of ignition by some amount, in addition to the advance caused by the differences in engine speed. It is necessary to repeat this RON vs. MON test,

using a fuel with no low temperature reactivity, to separate out the amounts of ignition advance caused by the engine speeds from that due to low temperature reactivity.

So to provide this contrast, computed results for a strongly OS fuel, 3-hexene (RON=94, MON=80, OS=14) autoignition, using both the RON and MON engine cycles, were carried out and show that ignition occurs only about 5 CAD earlier in the RON cycle, as shown in Fig. 10. For this high OS fuel, neither cycle shows any evidence of low temperature, cool flame heat release, with the fuel/air mixtures in both engine cycles experiencing a single-stage autoignition that (not shown) occurs at 950 – 1000K, as noted above in Fig. 5 for the RON cycle. We conclude that 5 CAD difference in ignition time for 3-hexene can be attributed solely to the differences in the two ON tests. We then assume that the same 5 CAD of the difference between the ignition delay times in RON and MON tests for PRF95 is again due to the different tests and the remaining difference of another 5 CAD can be attributed to low temperature reactivity (i.e., the lack of OS for the PRF95 fuel).

A final example of RON and MON cycle autoignition is shown in Fig. 11, for a high OS fuel, 3-hexene, and a zero-OS fuel, PRF80, both of which have MON = 80. Figure 11 shows that both ignite in the MON cycle (9.5 CAD ATDC) at the same time, as expected, although the PRF80 fuel shows a modest NTC low temperature heat release in the MON test, while the 3-hexene, as noted above in Fig. 10, has no low temperature heat release. Comparison of the PRF fuels in Figs. 9 and 11 for MON test conditions shows that the higher level of *n*-heptane in PRF80 in Fig. 11 leads to a small amount of cool flame reactivity that is not seen in the computed heat release curve for PRF95 in Fig. 9.

The lighter curves in Fig. 11 show the same fuels, PRF80 and 3-hexene, in the RON engine cycle, and both fuels ignite at earlier CAD values in the slower engine speed RON cycle. There is a large amount

of cool flame heat release from the PRF80 fuel for the RON cycle, ten times greater in the RON cycle (1.5E+10 W/m³ maximum cool flame HRR) than the peak value of 1.5E+09 W/m³ in the MON cycle.

Two factors discussed earlier combine for this dramatically different amount of low temperature reactivity of the PRF fuel in RON conditions. The RON cycle begins at a lower intake temperature

and has a slower cycle (600 vs. 900 RPM) than the MON cycle, so a much longer amount of time is spent in the low temperature region in the RON cycle where the cool flame originates.

The simulated PRF80 fuel ignition is earlier in the RON cycle by about 10.5 CAD earlier than its ignition time in the MON cycle, while the 3-hexene ignition is earlier in the RON cycle by about 5.5 CAD. We can therefore attribute about 5.5 CAD of the ignition difference between 3-hexene and PRF80 to the differences in engine speed and initial cycle temperatures that are common to both fuels, and the rest, approximately 5 CAD, must be due to differences in reactivity of the two fuels due to the RON cycle conditions, specifically to the low temperature reactivity that is clearly absent from the 3-hexene fuel reactivity. The plot of Ignition Delay Time vs. RON curve for PRF and other fuels in Fig. 2 shows that RON changes by about 10 points for a difference of 5 CAD in ignition delay time. Therefore, the difference in ignition delay of 5 CAD for 3-hexene that is due to the absence of a cool flame, low temperature heat release shown in Fig. 11 can be estimated to cause a RON difference of approximately 10 points in the RON scale. This extra resistance to autoignition for the high OS fuel 3-hexene, relative to the comparable zero-OS fuel PRF80, with its “functional extra octane rating” of 10 octane numbers, is responsible for the attractiveness of high OS fuels for knock avoidance in modern high compression ratio SI engines [3,6,75]. In other words, the lack of low temperature reactivity and the corresponding high

value of Octane Sensitivity increases the knock resistance of 3-hexene by about 10 Octane numbers, compared to a PRF fuel with Octane numbers in the range of 80 – 95. The reason high sensitivity fuel is desired when an engine is boosted, the compression ratio is raised, and intake temperature is increased is that low temperature reactivity does not emerge and cause excessive end-gas autoignition, features that are seen in the MON-like cycle results in Fig. 11, in contrast to the behavior shown by the RON-like results in Fig. 11.

CONCLUSIONS

The overall behaviors of low temperature autoignition of 1-alcohols, linear olefins, and *n*-alkyl benzenes are very similar to each other. All of the *n*-alkanes, linear olefins, *n*-alkyl benzenes, and 1-alcohols with significant OS have been determined from our modeling calculations to have negligible low temperature reactivity. In each of these classes of fuel molecules, we have been able to identify and characterize the specific low temperature reaction pathways of the OS fuels that avoid or quench low temperature reactivity so that such cool flames cannot occur. These modeling calculations have shown that the specific kinetic mechanisms that limit low temperature reactivity and heat release are uniquely different for each class of fuels, although the fundamental, uniting principle of these limiting mechanism can be traced to the concept of electron delocalization that takes different forms in each class of high OS fuel. Exceptions to this general view include very small molecules such as methane, ethane, methanol, and ethanol, which have high OS values and negligible low temperature reactivity because their small size makes it impossible for them to support the radical isomerization reactions that produce low temperature reactivity. Other exceptions can be seen as well; cyclopentane (OS = 13) and methyl cyclopentane (OS = 11) do not have significant levels of low temperature reactivity, but kinetic factors responsible have not yet been established. We have also been able to establish a kinetic boundary between OS and non-OS fuels within each fuel class and the features of the transitional regime that exists between these limiting behaviors. Those transitional regimes are extremely consistent for the 1-alcohols, *n*-alkanes, *n*-alkyl benzenes, and linear olefins. We have shown that as straight-chain carbon features in these transitional fuels appear and grow in length, the transitions from “no low temperature reactivity” to “marginal low temperature reactivity” and then to “robust low temperature reactivity” result from the appearance first of a marginal degree of alkyl peroxy radical isomerization from 6-membered secondary and 7-membered primary RO₂ isomerizations within a linear carbon chain. We have speculated about and intend to pursue extensions of this approach to alkyl ester fuels and begin to

examine additional classes of fuels such as furans, mixed aromatic/aliphatic multi-ring fuel types, and others that might contribute to next-generation SI engine fuels. This kinetic modeling study provides fundamental insights into the basic chemistry that controls important phenomena of fuel autoignition and should assist in development of future engines and fuels.

Within the discipline of chemical kinetic detailed reaction mechanisms, the present model represents an unprecedentedly varied and unusually robust set of coupled kinetic models for many representatives of practical fuel classes. Past kinetic modeling studies have most often considered only one class of fuels in a given reaction mechanism, even when the fuel molecules being addressed are large and complex, such as for *n*-alkyl benzenes or isomers of butanol. The present kinetic mechanism, following an earlier, similar version by many of the same authors [15], has combined together kinetic mechanisms for large *n*-alkanes, linear olefins, alcohols, alkyl benzenes, cyclohexanes and cyclopentanes, and gasoline Primary Reference Fuels, each of which has conventionally been presented as a separate reaction mechanism. As such, it already represents a valuable analysis tool that can be used to study many features of practical engines for both idealized studies and addressing practical engine and fuel design questions. We intend to continue to build on this existing model in several ways. We are currently adding a wide range of branched alkane, branched olefin, and branched alcohol fuels to this large mechanism, as well as a variety of alkyl ester fuels from methyl butanoate to methyl decanoate. As new theory and experimental results become available, we will continue to refine the present kinetic mechanisms. We are pursuing especially detailed analyses with many model validation tests, and these will also lead to model refinements and improvements. Finally, we intend to add models to describe significantly larger fuel modules for aircraft gas turbine engine studies and then for diesel engine studies, both of which will require fuels with 15 to 20 or more carbon atoms. The most significant feature of this and other future mechanisms is the capacity and variety of molecules to describe realistic fuels developed from both petroleum and biomass, fuels which contain many different

classes of fuel components, so that interactions between different fuel components, both positive and negative, can be described in future modeling studies.

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FIGURE CAPTIONS

Figure 1. Pressures used for engine cycle simulations for simulations similar to RON and MON cycles

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Fig. 3. Computed PSR reactivities for selected n-alkanes, residence time 50ms, pressure 15 bar

Fig. 4a. Computed heat release rates for n-alkanes in RON-like cycle simulations.

Fig. 4b. Computed fuel mole fractions for n-alkane fuels in RON-like cycle simulations

Fig. 4c. Computed unburned gas temperatures in n-alkane RON-like cycle simulations.

Fig. 5a. Computed rates of heat release during end gas RON-like cycle simulations

Fig. 5b. Computed end gas temperatures for *n*-hexane and hexene isomers in RON-like cycle simulations

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Fig. 7a. Computed heat release rates for alkyl benzenes during RON-like cycle simulations

Fig. 7b. Computed end gas temperatures in n-alkyl benzenes during RON-like cycle simulations

Fig. 8. Computed PSR computations of 2-methyl 2-butene (OS=12.6) and PRF90 (OS = 0), for stoichiometric fuel/air mixtures at residence time of 0.05 s and 10 bar pressure

Fig. 9. Computed heat release in both RON and MON cycles, with PRF95 as the fuel.

Fig. 10. Computed autoignition of 3-hexene in both RON and MON engine cycles.

Fig. 11. Computed autoignition of PRF80 and 3-hexene under RON (red lines) and MON (black lines) cycle conditions.

TABLE CAPTION

Table I. Selected values of RON, MON and OS [1,41,42]

References

1. W.G. Lovell, Knocking Characteristics of Hydrocarbons, *Indust. Eng. Chem.* 40 (12) (1948) 2388-2438.
2. American Society of Testing Materials. D-2699 and D-2700. ASTM Research Method ASTM D 908 – 56 and ASTM Motor Method ASTM D 357 – 56, 1956.
3. G.T. Kalghatgi, The outlook for fuels for internal combustion engines, *Int. J. Engine Res.* 15 (4) (2014) 383-398.
4. G.T. Kalghatgi, *Fuel/engine interactions*, SAE International, Warrendale, PA, 2013.
5. C.K. Westbrook, W.J. Pitz, M. Mehl, P.-A. Glaude, O. Herbinet, S. Bax, F. Battin-Leclerc, O. Mathieu, E.L. Petersen, J. Bugler, H.J. Curran, Experimental and Kinetic Modeling Study of 2-Methyl 2-Butene: Allylic Hydrocarbon Kinetics, *J. Phys. Chem. A* 119 (2015) 7462-7480.
6. A. Amer, H. Babiker, J. Chang, et al., Fuel effects on knock in a highly boosted direct injection spark ignition engine, *SAE Int. J. Fuels Lubr.* 5 (2015) 1048-1065.
7. W.R. Leppard, The chemical origin of fuel octane sensitivity, SAE paper SAE-902137, 1990.
8. M. Mehl, T. Faravelli, F. Giavazzi, E. Ranzi, P. Scorletti, A. Tardani, D. Terna, Detailed Chemistry Promotes Understanding of Octane Numbers and Gasoline Sensitivity, *Energy Fuels* 20 (2006) 2391-2398.
9. C.K. Westbrook, W.J. Pitz, O. Herbinet, H.J. Curran, E.J. Silke, A Comprehensive Detailed Chemical Kinetic Reaction Mechanism for Combustion of n-Alkane Hydrocarbon Fuels from n-Octane to n-Hexadecane, *Combust. Flame* 156 (2009) 181-199.
10. S.M. Sarathy, C.K. Westbrook, W.J. Pitz, M. Mehl, C. Togbe, P. Dagaut, H. Wang, M.A. Oehlschlaeger, U. Niemann, K. Seshadri, P.S. Veloo, F.N. Egolfopoulos, T. Lu, Comprehensive chemical kinetic modeling of the oxidation of 2-methyl alkanes from C₇ to C₂₀, *Combust. Flame* 158 (2011) 2338-2357.

11. J. Bugler, K.P. Somers, E.J. Silke, H.J. Curran, Revisiting the Kinetics and Thermodynamics of the Low-Temperature Oxidation Pathways of Alkanes: A Case Study of the Three Pentane Isomers, *J. Phys. Chem. A* 119 (28) (2015) 7510-7527.
12. J. Bugler, B. Marks, O. Mathieu, R. Archuleta, A. Camou, C. Gregoire, K.A. Heufer, E.L. Petersen, H.J. Curran, An ignition delay time and chemical kinetic modeling study of the pentane isomers, *Combust. Flame* 163 (2016) 138-156.
13. C.K. Westbrook, W.J. Pitz, H.C. Curran, J. Boercker, E. Kunrath, A Detailed Chemical Kinetic Modeling Study of the Shock Tube Ignition of Isomers of Heptane, *Int. J. Chem. Kinet.* 33 (2001) 868-877.
14. C.K. Westbrook, W.J. Pitz, J. Boercker, H.C. Curran, J.F. Griffiths, C. Mohamed, M. Ribaucour, Detailed Chemical Kinetic Reaction Mechanisms for Autoignition of Isomers of Heptane Under Rapid Compression, *Proc. Combust. Inst.* 29 (2002) 1311-1318.
15. M. Mehl, W.J. Pitz, C.K. Westbrook, H.J. Curran, Kinetic modeling of gasoline surrogate components and mixtures under engine conditions, *Proc. Combust. Inst.* 33 (2011) 193-200.
16. S.M. Sarathy, S. Vranckx, K. Yasunaga, M. Mehl, P. Osswald, W.K. Metcalfe, C.K. Westbrook, W.J. Pitz, K. Kohse-Hoinghaus, R.X. Fernandes, H.J. Curran, A comprehensive chemical kinetic model for the four butanol isomers, *Combust. Flame* 159 (2012) 2028-2055.
17. S.M. Sarathy, P. Oßwald, N. Hansen, K. Kohse-Höinghaus, Alcohol combustion chemistry, *Prog. Energy Combust. Sci.* 44 (2014) 40-102.
18. K.A. Heufer, S.M. Sarathy, H.J. Curran, A.C. Davis, C.K. Westbrook, W.J. Pitz, Kinetic Modeling Study of n-Pentanol Oxidation, *Energy Fuels* 26 (2012) 6678-6685.
19. S.M. Sarathy, S. Park, B.W. Weber, W. Wang, P.S. Veloo, A.C. Davis, C. Togbe, C.K. Westbrook, O. Park, G. Dayma, Z. Luo, M.A. Oehlschlaeger, F.N. Egolfopoulos, T. Lu, W.J. Pitz, C.J. Sung, P. Dagaut, A comprehensive experimental and modeling study of iso-pentanol combustion, *Combust. Flame* 160 (2013) 2712-2728.

20. R. Bounaceur, I. Da Costa, R. Fournet, F. Billaud, F. Battin-Leclerc, Experimental and Modeling Study of the Oxidation of Toluene, *Int. J. Chem. Kinet.* 37 (2005) 25-49.
21. D. Darcy, H. Nakamura, C.J. Tobin, M. Mehl, W.K. Metcalfe, W.J. Pitz, C.K. Westbrook, H.J. Curran, A high-pressure rapid compression machine study of *n*-propylbenzene ignition, *Combust. Flame* 161 (2014) 65-74.
22. H. Nakamura, D. Darcy, M. Mehl, C.J. Tobin, W.K. Metcalfe, W.J. Pitz, C.K. Westbrook, H.J. Curran, An experimental and modeling study of shock tube and rapid compression machine ignition of *n*-butylbenzene/air mixtures, *Combust. Flame* 161 (2014) 49-64.
23. D. Darcy, H. Nakamura, C.J. Tobin, M. Mehl, W.K. Metcalfe, W.J. Pitz, C.K. Westbrook, H.J. Curran, An experimental and modeling study of surrogate mixtures of *n*-propyl- and *n*-butylbenzene to simulate *n*-decylbenzene ignition, *Combust. Flame* 161 (2014) 1460-1473.
24. S.M. Burke, W. Metcalfe, O. Herbinet, F. Battin-Leclerc, F.M. Haas, J. Santner, F.L. Dryer, H.J. Curran, An experimental and modeling study of propene oxidation. Part 1: Speciation measurements in jet-stirred and flow reactors, *Combust. Flame* 161 (2014) 2765-2784.
25. S.M. Burke, U. Burke, R. McDonagh, O. Mathieu, I. Osorio, C. Keese, A. Morones, E.L. Petersen, W. Wang, T.A. DeVerter, M.A. Oehlschlaeger, B. Rhodes, R.K. Hanson, D.F. Davidson, B.W. Weber, C.-J. Sung, J. Santner, Y. Ju, F.M. Haas, F.L. Dryer, E.N. Volkov, E.J.K. Nilsson, A.A. Konnov, M. Alrefae, F. Khaled, A. Farooq, P. Dirrenberger, P.-A. Glaude, F. Battin-Leclerc, H.J. Curran, An experimental and modeling study of propene oxidation. Part 2: Ignition delay time and flame speed measurements, *Combust. Flame* 162 (2015) 296-314.
26. D. Karwat, S. Wagnon, M. Wooldridge, C.K. Westbrook, Low-Temperature Chemical Kinetic and Speciation Studies of *n*-Heptane, *Combust. Flame* 160 (2013) 2693-2706.
27. M. El Rachidi, Chemical kinetic modeling of cyclopentane, private communication (2016).

28. E.J. Silke, W.J. Pitz, C.K. Westbrook, M. Ribaucour, Detailed Chemical Kinetic Modeling of Cyclohexane Oxidation, *J. Phys. Chem. A* 111 (2007) 3761-3775.
29. W.J. Pitz, C.V. Naik, T.N. Mhaolduin, H.J. Curran, J.P. Orme, J.M. Simmie, Modeling and Experimental Investigation of Methylcyclohexane Ignition in a Rapid Compression Machine, *Proc. Combust. Inst.* 31 (2007) 267-275.
30. M.A. Oehlschlaeger, J. Steinberg, C.K. Westbrook, W.J. Pitz, The Autoignition of iso-Cetane at High to Moderate Temperatures and Elevated Pressures, *Combust. Flame* 156 (2009) 2165-2172.
31. C.K. Westbrook, C.V. Naik, O. Herbinet, W.J. Pitz, M. Mehl, S.M. Sarathy, H.J. Curran, Detailed chemical kinetic reaction mechanisms for soy and rapeseed biodiesel fuels, *Combust. Flame* 158 (2011) 742-755.
32. O. Herbinet, W.J. Pitz, C.K. Westbrook, Detailed Chemical Kinetic Oxidation Mechanism for a Biodiesel Surrogate, *Combust. Flame* 154 (2008) 507-528.
33. W.K. Metcalfe, S.M. Burke, S.S. Ahmed, H.J. Curran, A Hierarchical and Comparative Kinetic Modeling Study of C1-C2 Hydrocarbon and Oxygenated Fuels, *Int. J. Chem. Kinet.* 45 (2013) 638-675.
34. S.M. Villano, L.K. Huynh, H.-H. Carstensen, A.M. Dean, High-Pressure Rate Rules for Alkyl+O₂ Reactions. 1. The Dissociation, Concerted Elimination, and Isomerization Channels of the Alkyl Peroxy Radical, *J. Phys. Chem. A* 115 (2011) 13425-13442, and High-Pressure Rate Rules for Alkyl+O₂ Reactions. 2. The Isomerization, Cyclic Ether Formation, and β -Scission Reactions of Hydroperoxy Alkyl Radicals, *J. Phys. Chem. A* 116 (2012) 5068-5089.
35. S. Sharma, S. Raman, W.H. Green, Intramolecular Hydrogen Migration in Alkylperoxy and Hydroperoxyalkylperoxy Radicals: Accurate Treatment of Hindered Rotors, *J. Phys. Chem. A* 114 (2010) 5689-5701.

36. A. Miyoshi, Systematic Computational Study on the Unimolecular Reactions of Alkylperoxy (RO₂)m Hydroperoxyalkyl (QOOH), and Hydroperoxyalkylperoxy (O₂QOOH) Radicals, J. Phys. Chem. A 115 (2011) 3301-3325.
37. <https://combustion.llnl.gov/>
38. C.K. Westbrook, W.J. Pitz, M. Mehl, J. Bugler, H.J. Curran, P.-A. Glaude, O. Herbinet, F. Battin-Leclerc, E. Petersen, O. Mathieu, S.M. Sarathy, Chemical Kinetic Origins of Octane Sensitivity, submitted for publication (2016).
39. M. Sjöberg, W. Zeng, Combined Effects of Fuel and Dilution Type on Efficiency Gains of Lean Well-Mixed DISI Engine Operation with Enhanced Ignition and Intake Heating for Enabling Mixed-Mode Combustion, SAE Int. J. Engines 9 (2);2016, doi: 10.4271/2016-01-0689.
40. CHEMKIN-Pro, ver. 5, Reaction Design Inc., San Diego, CA, 2011.
41. E.F. Obert, Internal Combustion Engines and Air Pollution, Harper & Row, New York, 1973.
42. ASTM Special Technical Publication No. 225, "Knocking Characteristics of Pure Hydrocarbons", Amer. Petrol. Inst. Res. Proj. 45, 1958.
43. C.K. Westbrook, Chemical Kinetics of Hydrocarbon Ignition in Practical Combustion Systems, Proc. Combust. Inst. 28 (2000) 1563-1577.
44. B.H. Bonner, C.F.H. Tipper, Cool flame combustion of hydrocarbons. 2. Propane and *n*-heptane, Combust. Flame 9 (4) (1965) 387-392.
45. C.F. Goldsmith, S.J. Klippenstein, W.H. Green, Theoretical rate coefficients for allyl + HO₂ and allyloxy decomposition, Proc. Combust. Inst. 33 (2011) 273-282.
46. M. Mehl, G. Vanhove, W.J. Pitz, E. Ranzi, Oxidation and combustion of the *n*-hexene isomers: A wide range kinetic modeling study, Combust. Flame 155 (2008) 756-772.
47. G. Vanhove, M. Ribaucour, R. Minetti, On the influence of the position of the double bond on the low-temperature chemistry of hexenes, Proc. Combust. Inst. 30 (2005) 1065-1072.

48. R. Bounacour, V. Warth, B. Sirjean, P.-A. Glaude, R. Fournet, F. Battin-Leclerc, Influence of the position of the double bond on the autoignition of linear alkenes at low temperature, *Proc. Combust. Inst.* 32 (2009) 387-394.
49. G. Black, H.J. Curran, S. Pichon, J.M. Simmie, V. Zhukov, Bio-butanol: Combustion properties and detailed chemical kinetic model, *Combust. Flame* 157 (2010) 363-373.
50. J. Zador, R.X. Fernandes, Y. Georgievskii, G. Meloni, C.A. Taatjes, J.A. Miller, The reaction of hydroxyethyl radicals with O₂: A theoretical analysis and experimental product study, *Proc. Combust. Inst.* 32 (2009) 271-277.
51. G. da Silva, J.W. Bozzelli, L. Liang, J.T. Farrell, Ethanol Oxidation: Kinetics of the α -hydroxyethyl Radical + O₂ Reaction, *J. Phys. Chem. A* 113 (2009) 8923-8933.
52. P. Dagaut, C. Togbe, Experimental and modeling study of the kinetics of oxidation of ethanol-n-heptane mixtures in a jet-stirred reactor, *Fuel* 89 (2010) 280-286.
53. P. Dagaut, S.M. Sarathy, M.J. Thomson, A chemical kinetic study of n-butanol oxidation at elevated pressure in a jet-stirred reactor, *Proc. Combust. Inst.* 32 (2009) 229-237.
54. C. Togbe, A. Mze-Ahmed, P. Dagaut, Kinetics of Oxidation of 2-butanol and iso-butanol in a Jet-Stirred Reactor: Experimental Study and Modeling Investigation, *Energy Fuels* 24 (2010) 5244-5256.
55. J.T. Moss, A.M. Berkowitz, M.A. Oehlschlaeger, J. Biet, V. Warth, P.-A. Glaude, F. Battin-Leclerc, An Experimental and Kinetic Modeling Study of the Oxidation of the Four Isomers of Butanol, *J. Phys. Chem. A* 112 (2008) 10843-10855.
56. Z. Serinyel, C. Togbe, G. Dayma, P. Dagaut, An experimental and modeling study of 2-methyl-1-butanol oxidation in a jet-stirred reactor, *Combust. Flame* 161 (12) (2014) 3003-3013.
57. A. Rodriguez, O. Herbinet, F. Battin-Leclerc, Experimental investigation of the oxidation of a long-chain alcohol: 1-hexanol, *Euro. Combust. Mtg.*, 2015

58. K.A. Heufer, J. Bugler, H.J. Curran, A comparison of longer alkane and alcohol ignition including new experimental results for n-pentanol and n-hexanol, *Proc. Combust. Inst.* 34 (2013) 511-518.
59. C. Togbe, P. Dagaut, A. Mze-Ahmed, P. Dievart, F. Halter, F. Foucher, Experimental and Detailed Kinetic Modeling Study of 1-Hexanol Oxidation in a Pressurized Jet-Stirred Reactor and a Combustion Bomb, *Energy Fuels* 24 (2010) 5859-5875.
60. L. Cai, Y. Uygun, C. Togbe, H. Pitsch, H. Olivier, P. Dagaut, S.M. Sarathy, An experimental and modeling study of n-octanol combustion, *Proc. Combust. Inst.* 35 (2015) 419-427.
61. F. Battin-Leclerc, V. Warth, R. Bounaceur, B. Husson, O. Herbinet, P.-A. Glaude, The oxidation of large alkylbenzenes: An experimental and modeling study, *Proc. Combust. Inst.* 35 (2015) 349-356.
62. A. Roubaud, R. Minetti, L.R. Sochet, Oxidation and Combustion of Low Alkylbenzenes at High Pressure: Comparative Reactivity and Auto-Ignition, *Combust. Flame* 121 (2000) 535-541.
63. A. Roubaud, O. Lemaire, R. Minetti, L.R. Sochet, High Pressure Auto-ignition and Oxidation Mechanisms of o-xylene, o-ethyltoluene, and n-butylbenzene between 600 and 900K, *Combust. Flame* 123 (2000) 561-571.
64. O. Herbinet, B. Husson, H. Le Gall, F. Battin-Leclerc, Comparison study of the gas-phase oxidation of alkylbenzenes and alkylcyclohexanes, *Chem. Eng. Sci.* 131 (2015) 49-62.
65. O. Herbinet, B. Husson, M. Ferrari, P.-A. Glaude, F. Battin-Leclerc, Low temperature oxidation of benzene and toluene in mixtures with n-decane, *Proc. Combust. Inst.* 34 (2013) 297-305.
66. M. Ribaucour, A. Roubaud, R. Minetti, L.R. Sochet, The low-temperature autoignition of alkylaromatics: Experimental study and modeling of the oxidation of n-butylbenzene, *Proc. Combust. Symp.* 28 (2000) 1701-1707.
67. P. Dagaut, A. Ristori, A. El Bakali, M. Cathonnet, Experimental and kinetic modeling study of the oxidation of n-propylbenzene, *Fuel* 81 (2002) 173-184.

68. B. Husson, R. Bounaceur, K. Tanaka, M. Ferrari, O. Herbinet, P.-A. Glaude, R. Fournet, F. Battin-Leclerc, M. Crochet, G. Vanhove, R. Minetti, C.J. Tobin, K. Yasunaga, J.M. Simmie, H.J Curran, T. Niass, O. Mathieu, S.S. Ahmed, Experimental and modeling study of the oxidation of n-butylbenzene, *Combust. Flame* 159 (2012) 1399-1416.
69. P. Dievart, P. Dagaut, The oxidation of n-butylbenzene: Experimental study in a JSR and 10 atm and detailed chemical kinetic modeling, *Proc. Combust. Inst.* 33 (2011) 209-216.
70. C. Cavallotti, R. Rota, T. Faravelli, E. Ranzi, *Ab initio* evaluation of primary *cyclo*-hexane oxidation reaction rates, *Proc. Combust. Inst.* 31 (2007) 201-209.
71. O. Lemaire, M. Ribaucour, M. Carlier, R. Minetti, The Production of Benzene in the Low-Temperature Oxidation of Cyclohexane, Cyclohexene, and Cyclohexa-1,3-diene, *Combust. Flame* 127 (2001) 1971-1980.
72. O. Herbinet, W.J. Pitz, C.K. Westbrook, Detailed chemical kinetic mechanism for the oxidation of biodiesel fuels blend surrogate, *Combust. Flame* 157 (2010) 893-908.
73. Y. Zhang, Y. Yang, A.L. Boehman, Premixed Ignition Behavior of C9 Fatty Acid Esters: A Motored Engine Study, *Combust. Flame* 156 (2009) 1202-1213.
74. Y. Zhang, A.L. Boehman, Autoignition of binary fuel blends of n-heptane and C7 esters in a motored engine, *Combust. Flame* 159 (2012) 1619-1630.
75. V. Mittal, J.B. Heywood, W.H. Green, The underlying physics and chemistry behind fuel sensitivity, SAE paper 2010-01-0617, 2010.

Table I. Selected values of RON, MON and OS [1,41,42]

	RON	MON	OS
olefins			
1-butene	97.4	81.7	15.7
2-butene	99.6	86.5	13.1
1-pentene	90.0	77.1	12.9
1-hexene	76.4	63.4	13.0
2-hexene	92.7	80.8	11.9
3-hexene	94.0	80.1	13.9
2-methyl 2-butene	97.3	84.7	12.6
2-ethyl 1-butene	98.3	79.4	18.9
alcohols			
methanol	109	89	20
ethanol	109	90	19
<i>n</i> -propanol	105	88	17
iso-propanol	112	97	15
<i>n</i> -butanol	98	85	13
iso-butanol	113	94	19
<i>t</i> -butanol	105	89	16
<i>n</i> -pentanol	80	74	6
iso-pentanol	99	66	22
alkyl benzenes			
toluene	120	103	17
ethyl benzene	111	98	13
<i>n</i> -propyl benzene	111	99	12
<i>n</i> -butyl benzene	104	94	10
cycloalkanes			
cyclohexane	83	77	6
methyl cyclohexane	75	71	4
alkanes			
methane	130	120	10
ethane	115	99	16
propane	112	97	15
<i>n</i> -butane	94	90	4
<i>n</i> -heptane	0	0	0

Figure 1

Figure 1. Pressures used for engine cycle simulations for simulations similar to RON and MON cycles

Figure 2

Figure 2. Computed autoignition times for selected fuel classes. Calibration points from PRF fuel mixtures are shown as the solid line and black points.

Figure 3

Fig. 3. Computed PSR reactivities for selected n-alkanes, residence time 50ms, pressure 15 bar

Fig. 4a. Computed heat release rates for n-alkanes in RON-like cycle simulations.

Fig. 4b. Computed fuel mole fractions for n-alkane fuels in RON-like cycle simulations

Fig. 4c. Computed unburned gas temperatures in n-alkane RON-like cycle simulations.

Fig. 5a. Computed rates of heat release during end gas RON-like cycle simulations

Fig. 5b. Computed end gas temperatures for *n*-hexane and hexene isomers in RON-like cycle simulations

Fig. 5c. Computed fuel mole fractions of *n*-hexane and hexene isomers in RON-like cycle simulations

Fig. 6a. Computed heat release rates for 1-alcohol fuels in RON-like cycle simulations

Fig. 6b. Computed end gas temperatures for 1-alcohol fuels in RON-like cycle simulations

Fig. 7a. Computed heat release rates for alkyl benzenes during RON-like cycle simulations

Fig. 7b. Computed end gas temperatures in n-alkyl benzenes during RON-like cycle simulations

Fig. 8. Computed PSR computations of 2-methyl 2-butene (OS=12.6) and PRF90 (OS = 0), for stoichiometric fuel/air mixtures at residence time of 0.05 s and 10 bar pressure

Fig. 9. Computed heat release in both RON and MON cycles, with PRF95 as the fuel.

Fig. 10. Computed autoignition of 3-hexene in both RON and MON engine cycles.

Fig. 11. Computed autoignition of PRF80 and 3-hexene under RON (red lines) and MON (black lines) cycle conditions.

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