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Detailed Chemical Kinetic Reaction Mechanisms for Primary Reference Fuels for Diesel Cetane Number and Spark-Ignition Octane Number

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Figure 2: (64 mm+10)x2.2 + 8	171
Figure 3: (40 mm+10)x2.2 + 12	122
Figure 4: (83 mm+10)x2.2 +15	220
Figure 5: (80 mm+10)x4.4 +20	416
Figure 6: (40 mm+10)x2.2 + 12	122
Figure 7: (42 mm+10)x2.2 +18	132
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Abstract

For the first time, a detailed chemical kinetic reaction mechanism is developed for primary reference fuel mixtures of n-hexadecane and 2,2,4,4,6,8,8-heptamethyl nonane for diesel cetane ratings. The mechanisms are constructed using existing rules for reaction pathways and rate expressions developed previously for the primary reference fuels for gasoline octane ratings, n-heptane and iso-octane. These reaction mechanisms are validated by comparisons between computed and experimental results for shock tube ignition and for oxidation under jet-stirred reactor conditions. The combined kinetic reaction mechanism contains the submechanisms for the primary reference fuels for diesel cetane ratings and submechanisms for the primary reference fuels for gasoline octane ratings, all in one integrated large kinetic reaction mechanism. Representative applications of this mechanism to two test problems are presented, one describing fuel/air autoignition variations with changes in fuel cetane numbers, and the other describing fuel combustion in a jet-stirred reactor environment with the fuel varying from pure 2,2,4,4,6,8,8-heptamethyl nonane (Cetane number of 15) to pure n-hexadecane (Cetane number of 100). The final reaction mechanism for the primary reference fuels for diesel fuel and gasoline is available on the web.

1. INTRODUCTION

Performance of reciprocating engines under normal operating conditions depends rather sensitively on fuel ignition properties. Over the years, graded scales have evolved for relative ignition rates of diesel fuels in diesel engines and knocking tendency of gasolines in spark-ignition (SI) engines. Diesel fuels are rated by their Cetane Number (CN), where fuels with higher values of CN ignite more readily than fuels with lower CN values. Gasolines are rated by their Octane Number (ON), where a higher value of ON indicates a greater resistance to autoignition and therefore lower potential to experience engine knock. While these two rating scales describe "ignitability" in the opposite order, both scales assign higher ratings for generally perceived preferred behavior, so higher CN indicates easier or earlier ignition in the diesel engine and greater knock resistance is associated with higher ON.

Each of these ignitability scales is defined in terms of a pair of specific fuels with ignition properties as widely different as possible. The following discussion summarizes a more detailed description from Obert [1]. Selection of these two pairs of specific fuels, which are termed "Primary Reference Fuels" or PRFs, reflects the fact that diesel fuels are typically much heavier than gasolines, with hydrocarbon molecules correspondingly larger in diesel fuels. Thus the PRF components assigned to diesel fuel are both C_{16} molecules, relecting the average carbon number and density of diesel fuel, while the PRF components for gasoline are a C_7 and a C_8 hydrocarbon. Both scales are similar in that each has a very easily ignited PRF n-alkane molecule, n-heptane (n-C_7H_{16}) in the case of gasoline and n-hexadecane (n-$C_{16}H_{34}$, n-cetane) in the case of diesel fuel, and each has a highly branched iso-alkane component that is difficult to ignite, specifically iso-octane (2,2,4-trimethyl pentane, i-C_8H_{18}) for gasoline and iso-cetane

(2,2,4,4,6,8,8-heptamethyl nonane, HMN, i-$C_{16}H_{34}$) for diesel fuel. By definition, iso-octane has an ON of 100, while n-heptane has an ON equal to zero. Also by definition, n-hexadecane has a CN equal to 100 while iso-cetane has a CN of 15.

For a test gasoline of arbitrary composition, its ON rating is evaluated by finding that mixture of *x* percent of iso-octane and (100-*x*) percent of n-heptane that ignites at the same compression ratio in a specific Cooperative Fuels Research (CFR) test engine as the gasoline being tested. The ON of that fuel then is, by definition, equal to x, the iso-octane fraction of the PRF mixture that best matched the ignition properties of the test fuel. A similar approach is used to determine the CN of a test diesel fuel. The formula used for mixtures of n-cetane and iso-cetane is slightly more complex than the ON scale, and CN for PRF mixtures is given by the relation CN = [F(n-cetane) + 0.15 F(iso-cetane)] x 100, in which F(n-cetane) and F(iso-cetane) are the mass fractions of these fuels and sum to unity. Thus n-cetane has a CN = 100 and iso-cetane has the value CN=15. The CN of an arbitrary diesel fuel is defined as for ON by finding a diesel PRF mixture with the same ignition behavior as the test fuel.

We previously developed detailed chemical kinetic reaction mechanisms for the gasoline PRF components n-heptane [2] and iso-octane [3]. These mechanisms included species and reaction pathways valid over a very wide range of temperatures, including a high temperature submechanism for temperatures above 900K, that is dominated by H atom abstraction from the fuel, followed by radical thermal decomposition to smaller species. The dominant chain branching mechanisms in this temperature range include the reaction $H + O_2 = O + OH$. These detailed kinetic mechanisms for n-heptane and iso-octane also included reaction pathways important at lower temperatures, roughly between 600K and 850K, which are initiated by addition of molecular oxygen to alkyl and other radical species to produce alkylperoxy radicals, denoted as RO_2,. These RO_2 species then isomerize, then decompose or add further O_2, leading to chain branching sequences that are unique to these lower temperatures. The overall diagram of the differences between the high and low temperature mechanisms is summarized in Fig. 1. Development of these reaction mechanisms was facilitated by defining 25 classes of reactions [2,3] so that a series of reaction rate rules could be employed in a systematic way. This approach has been used widely since that time and is used again in the present development of new kinetic models for diesel PRF components. The gasoline PRF reaction mechanisms have been used many times as a surrogate for gasoline and diesel fuel. Since they represent the extremes of behavior in SI combustion, these PRF components provide a broad scale of responses that can be used in modeling engine behavior. Development of detailed chemical kinetic reaction mechanisms using the same reaction pathway and rate classes have provided kinetic tools for ignition and combustion studies of many other fuels [4-12] to study the role of fuel molecular structure on hydrocarbon ignition, and they provided a starting point to development of more general surrogate fuels for gasoline in SI engines [13] and diesel fuel in diesel engines [14].

The present study describes the development of comparable reaction mechanisms for the reference fuels for CN and diesel combustion. The resulting mechanism, combining both n-cetane and iso-cetane, is quite large, with more than 2800 chemical species and nearly 11,000 elementary reactions, but typical homogeneous ignition calculations of autoignition of these diesel PRF mixtures can be done in 5 minutes of CPU time on a laptop computer.

2. KINETIC MECHANISMS

Kinetic mechanisms have been developed recently for both n-cetane and iso-cetane combustion. Ristori et al. [15] developed a mechanism for n-hexadecane to describe their own experiments in a jet-stirred reactor. The experiments covered the high temperature regime above 1000K, and the kinetic mechanism included only the high temperature kinetic reaction pathways; for those conditions, that reaction mechanism provided very good agreement with their experimental results. Dagaut et al. [16] later used this same high temperature n-cetane kinetic model to simulate oxidation of rapeseed methyl ester (RME), which is based on a methyl ester with a carbon chain with 17 C atoms. For the most part, the n-cetane mechanism was a very successful surrogate for the RME fuel. More recently, Biet et al. [17] and Westbrook et al. [12] developed detailed kinetic mechanisms for n-alkanes up to n-hexadecane that not only included the high temperature regime but also the much more complex low temperature reaction pathways. The Biet et al. study used the EXGAS computer-generation software approach to build their kinetic model, and the Westbrook et al. study used the reaction classes of Curran et al. [2,3] to build their kinetic model. Both studies used similar experimental results to validate their mechanisms, and both mechanisms demonstrated overall good performance. However, both studies showed that there is still a serious lack of careful experimental results that can be used to test and validate detailed kinetic models for complex hydrocarbon fuels, especially in the lower temperature range, and that conclusion is reinforced by the present study.

Dagaut and Hadj-Ali [18] studied iso-cetane combustion in a jet-stirred reactor. Their experiments covered a temperature range from 770K to 1070K and used a lumped high temperature kinetic mechanism from Agosta et al. [19] and another lumped mechanism from Battin-Leclerc et al. [20] to analyze their experimental results. Subsequent kinetic modeling by Ranzi et al. [21] refined the mechanisms and added a lumped approach for the low temperature kinetic regime. In another high temperature study, Oehlschlaeger et al. [22] carried out high temperature shock tube ignition delay experiments and used a detailed kinetic mechanism to analyze their results, with very good agreement between experiments and kinetic modeling results. To our knowledge, the present kinetic mechanism for iso-cetane is the first model that includes both high and low temperature regimes without lumping assumptions.

The present reaction mechanisms for n-cetane and iso-cetane were produced using the same reaction rate rules and approach used by Curran et al. [2,3] for n-heptane and iso-octane. While some of the reaction classes and rate rules are somewhat simplified and improvements and additional detail could be made, the same level of approximation has been extremely productive in the cases of n-heptane and iso-octane, and we have chosen to retain the same level of approximation in the present mechanisms. Examples of improvements that will be included in the future include recent work of Taatjes et al. [23] on alternative reaction pathways for reactions of alkyl radicals and O_2 to directly produce olefins via a concerted molecular elimination pathway will be implemented, and site-specific reactions of olefins can be improved following recent studies of Mehl et al. [24] and VanHove et al. [25].

The implementation of the reaction pathway analysis and reaction rate rules are straightforward and can be examined in the accompanying supporting material, which reproduces the entire detailed chemical kinetic reaction mechanism and thermochemical data in a common format. The n-alkane fuel n-hexadecane is best understood as structurally the same as n-heptane, but with additional CH_2 groups present in the C chain, as seen in Fig. 2. Therefore, all of the reaction pathway and reaction rate rules are taken directly from the n-heptane mechanism. Our previous paper on n-alkanes [12] showed that most of the combustion properties of n-hexadecane are virtually identical to those for n-heptane, especially those associated with ignition. All of the low temperature reaction pathways for n-cetane already occur in n-heptane, and the only change is that there are more opportunities for those reaction pathways in n-hexadecane.

The structure of iso-cetane, also shown in Figure 2, can be seen to be closely related to the structure of iso-octane. Breaking the central C - C bond in iso-cetane produces two C_8H_{17} radicals, both of which are octyl radicals produced in iso-octane combustion. As a result, the ignition and combustion of iso-cetane are very similar to those of iso-octane, especially the high levels of iso-butane that are the primary intermediates in the combustion of both fuels. However, by coupling the two iso-octyl radicals together, the resulting iso-cetane molecule has 6 secondary C-H bonds while iso-octane has only 2; both fuels have one tertiary C - H bond. The existence of multiple secondary C - H sites in iso-cetane makes it considerably easier for intramolecular RO_2 isomerization reactions to occur at significant rates, while there are no comparable reaction pathways available in iso-octane [3]. These factors combine to make iso-cetane somewhat more reactive than iso-octane, especially in the low temperature regime, although since iso-cetane has such a high fraction of primary C - H bonds, it is still relatively unreactive at low temperatures. As shown below, iso-cetane autoignition falls between the ignition rates of iso-octane and the n-alkanes, consistent with this simplified analysis.

The mechanism for n-heptane is a subset of the mechanism for n-cetane, and the mechanism for iso-octane is a subset of that for iso-cetane, so the present kinetic mechanism includes the kinetic reaction mechanisms for the ON primary reference fuels, and the entire mechanism thus includes the PRF mechanisms for both gasoline and diesel fuels.

3. Mechanism validations

A wide variety of mechanism validations for n-hexadecane were included in our previous study of n-alkane fuel mechanisms [12]. Perhaps most interesting, that study indicated that the ignition rates of all of the n-alkanes from n-C_7H_{16} to n-$C_{16}H_{34}$ are almost identical, at least for stoichiometric mixtures of each n-alkane in air at pressures of 13.5 and 40 bar pressure. This is illustrated in Fig. 3, showing experimental shock tube ignition delay results from Ciezki et al. [26] at 13.5 bar pressure for stoichiometric mixtures of n-heptane and air as filled triangles. Similar experiments using n-decane as the fuel [27] produced ignition delay times very close to the n-heptane values in Fig. 3. Computed ignition delay times for n-heptane and n-cetane are shown in Fig. 3, showing the very close agreement between them and excellent agreement with the experimental results. Recent experimental shock tube results of Shen et al. [28], using n-heptane, n-decane, n-dodecane and n-tetradecane strongly support the model prediction that the ignition rates of all these n-alkanes are very similar.

A recent shock tube study of ignition and soot production in combustion of iso-cetane has been reported by Mathieu et al. [29], but no kinetic modeling was included. Another recent study of shock tube ignition of iso-cetane, at the same conditions as those shown in Fig. 3, by Oehlschlaeger et al. [22] included kinetic analysis using the present mechanism, and these experimental (filled diamonds) and kinetic modeling results are included in Fig. 3, showing excellent agreement. However, those experiments were limited to a temperature range from 879K to 1347K and no low temperature phenomena were observed. To illustrate the influence of low temperature kinetic reaction pathways on iso-cetane ignition, the model predictions are extended to lower temperatures in Fig. 3, showing a modest negative temperature coefficient behavior over temperatures from about 700K to 900K. Also shown for comparison is a curve showing comparable computational results for iso-octane. Experimental results for the same conditions for iso-octane by Fieweger et al. [30] are shown as filled circles in the figure and agree very well with the mechanism results but are available only for the higher temperature regime. It is clear from Fig. 3 that all of these n-alkane and branched alkane fuels have very similar ignition delays for high temperatures, above about 950K, and quite similar ignition delays at temperatures below about 700K, but they differ considerably within the NTC temperature range. The n-alkane fuels have extremely similar ignition delays for all temperatures, and within the NTC region iso-cetane ignites more slowly than the n-alkanes but faster than iso-octane. We interpret these results to suggest that all of the kinetic factors influencing differences in octane and cetane ratings of saturated hydrocarbon fuels must be attributed to differences in their kinetic behavior within this rather narrow temperature range. Further kinetic analysis is needed to extend this conclusion to other classes of hydrocarbon fuels such as those with aromatic rings and double bonds, but recent studies of alkyl ester fuels such as those in biodiesel fuels [11] show very similar ignition behavior as that observed for the n-alkanes shown in Fig. 3.

We have used recent experimental results from Dagaut et al. [15,18] from a jet-stirred reactor, with both n-hexadecane and iso-cetane (heptamethyl nonane) as fuels, to provide further validation of the kinetic reaction mechanisms. Mechanism validation results for n-cetane were summarized in Ref. [12], and results for iso-cetane are shown in Figure 4, comparing representative experimental and computed species concentrations for stoichiometric mixtures of iso-cetane and oxygen at 10 atm, diluted by nitrogen. Previous simulations used reaction mechanisms that are somewhat lumped or are limited to high temperature conditions [15,18].

The major species CO and CO_2 show excellent agreement with experiments, and other major intermediate species formaldehyde, iso-butene and propene also show very good agreement. Many other species also show very good agreement, while a few such as 1,3-butadiene are underpredicted by factors of about 5. While the experiments used for mechanism validation did not show any low temperature kinetic features, we used the kinetic model to examine the lower temperature regime. Our computed analysis extended the operating temperature of the experiments in Fig. 4 down to 500K, and the computed iso-cetane fuel profile in Fig. 5 shows a very pronounced NTC region from 600K to 700K.

While there are a considerable number of experimental results for mechanism validation of the gasoline primary reference fuels n-heptane and iso-octane, there are only limited results suitable for validating kinetic mechanisms for n-cetane and iso-cetane. In the examples below, we have used the existing mechanisms knowing that future improvements are likely when new validation studies appear. The fact that the same reaction pathways and reaction rate rules have been used in their development, and those rules have been extremely productive in other kinetic studies, gives us some confidence that the general features of these mechanisms will provide considerable kinetic insights and useful combustion predictions.

5. Primary reference fuel mechanism calculations

In this section, we use the combined PRF mechanisms to illustrate the capabilities of this approach and model. In Fig. 3, we used experimental results [26,27] for stoichiometric fuel/air mixtures at 13.5 bar pressure to validate the present reaction mechanisms. The experiments demonstrated that for both the diesel and gasoline PRFs, below 650K and above 900K, the branched iso-alkane fuels show ignition delay times very close to those of the n-alkane fuels. This agrees with past shock tube ignition delay experiments of Smith et al. [31] and computed results of Westbrook et al. [8,9] that showed that the ignition delay times for all of the heptane isomers, whose octane numbers range from 0 to 112, have nearly identical ignition delay times at high temperatures. The differences in ON for these isomers do not produce different ignition delay times at high temperatures. Many other similar studies of high temperature ignition delays for other hydrocarbons, including iso-cetane [22], confirm this conclusion. At temperatures between 650K and 900K, however, iso-cetane and iso-octane ignition is significantly slower to ignite than the n-alkanes. This means that the kinetic factors that cause differences in ON and CN for hydrocarbon fuels are particularly important in this rather narrow temperature range between about 650K and 900K, where alkylperoxy radical isomerization reaction pathways are most important.

The PRF mechanism for octane ratings is imbedded within the PRF mechanism for cetane ratings, as noted above, and this mechanism was used to examine the ignition delay times for mixtures of n-heptane and iso-octane and illustrate some of the properties of these fuel mixtures. These computations were carried out for stoichiometric fuel/air mixtures with ON values of 0, 60, 80 and 100, all at 40 bar pressure. These results are compared with experimental measurements for the same conditions and PRF mixtures by Fieweger et al. [30] in Fig. 6, in which the experimental results are shown as symbols and the computed results as lines. The computed and experimental results agree extremely well for all of the fuel mixtures, thereby adding confidence to the kinetic mechanisms for both of the reference fuels. All of the fuels show some NTC behavior, and the curves shift towards longer ignition delay times as the ON increases, as expected. At the same time, the local minimum in the ignition delay time moves to lower temperatures at ON increases. Extension of these results to SI engines would suggest that, not only would higher ON fuels resist the autoignition leading to knock more than lower ON fuels, but the different fuels would exhibit local maxima in their rate of heat release at different gas temperatures and likely at different times during an engine cycle. Similar to the observations from Fig. 3, the different fuels have different ignition delay times only for temperatures within a narrow temperature range between about 700K AND 950K. Such information could assist engine and fuel design for SI engines in important ways.

In Fig. 7, we repeat the same type of autoignition calculation for a range of diesel PRF mixtures at values of CN of 15, 50, 75 and 100. These results show that the kinetic mechanisms for these diesel PRF mixtures produce different ignition delays only at temperatures in the same narrow range of initial temperatures, as observed for the ON reference fuel mixtures. These kinetic predictions should be useful in motivating future fuel studies of ignition behaviors of diesel fuels. One cannot forget that the cetane number tests, like actual diesel ignition in engines, depend on many factors in addition to gas phase kinetics of ignition. Liquid fuel jet penetration and vaporization, mixing with residual gases and fresh air and heating of the combustion fuel/air mixture by the hot residuals and by piston motion, are also very significant factors in diesel ignition. However, most of these other processes do not vary a great deal as the fuel composition changes over the range of conventional diesel fuels, so the variations in kinetic properties shown in Fig. 7 are certain to play an important role in diesel ignition and variations in CN.

We carried out another series of numerical experiments to illustrate the capabilities of the present diesel PRF reaction mechanisms and perhaps motivate further experimental studies. We repeated the kinetic simulation above for the oxidation of both cetane PRFs in the jet-stirred reactor, based on the experiments of Dagaut and Hadj-Ali [18], including three different fuel mixtures, one consisting of only n-cetane (CN=100), a second consisting only of n-cetane (CN=15) and a mixture with a CN of 50.

Several examples of computed species profiles as functions of reactor temperature are shown in Fig. 5. One conclusion of the simulations is that a considerable amount of reactivity takes place at temperatures between 500K and 700K, and these results may have significant impacts on distinctions related to variations in cetane numbers. All three mixtures produce significant amounts of NTC behavior in the numerical jet-stirred reactor simulations, resulting in two major regions of considerable reactivity, first at about 600K and the second beginning at about 775K. This can be seen in the results for fuel concentrations, showing that during the 1 second residence time in these examples, 85% of the n-cetane is consumed at 600K, while about 60% of the fuel is consumed when the fuel is iso-cetane. In Fig. 5, the computed CO concentrations are overall very similar for the three fuel mixtures, with the only significant relative differences seen in the low temperature reaction zone at about 600K. A significant trend can be seen in the computed profiles for iso-butene, which are highest in the case where the fuel is iso-cetane, and the lowest in the case where the fuel is n-cetane. This is a result of the fact that iso-cetane, which reacts very much like iso-octane, reacts slowly specifically because it produces large amounts of iso-butene, which is quite stable. Other low CN fuels might not produce significant amounts of iso-butene but ignite slowly because they produce other stable intermediates. One result of these "computational experiments" suggest that it would be very interesting to extend the actual experiments of Dagaut and Hadj-Ali, on which the computations are based, down to 500K to fully explore the low temperature kinetic regime.

One species concentration that varied most with CN is hydrogen peroxide (H_2O_2) shown in Fig. 5, with high CN fuels producing considerably more H_2O_2 than lower CN fuels. Largest production of H_2O_2 is seen in the low temperature region between 600K and 700K. In an engine, H_2O_2 produced at low temperatures decomposes at higher temperatures [32], producing two OH radicals which promote ignition. Thus production of high levels of H_2O_2 leads to high fuel reactivity and high Cetane numbers.

6. CONCLUSIONS

The present work describes a new reaction mechanism that the primary reference fuels for both gasoline (octane ratings) and diesel fuel (cetane ratings), in a single model. This development has been made possible by growth in computer simulation capabilities and was carried out using established kinetic principles that apply existing rules for reaction pathways and rates for numerous classes of elementary reactions. In the present work, we have only briefly addressed the uses of the mechanism for octane ratings, since the ON PRF mechanisms have existed for several years and many such applications have previously been carried out.

The cetane number PRF mechanisms are new and have not previously been combined together to make a single model. Further refinement of the diesel PRF portion of the model will become possible as more experimental validation data become available. The PRf model provides a computational tool to apply to a wide variety of combustion chemistry problems related primarily to diesel fuels, including a capability to suggest experiments that might be especially valuable for understanding important kinetic phenomena related to fuel chemistry. They also are a basis for systematic mechanism reduction to provide a computationally efficient diesel combustion reaction mechanism for use in multidimensional CFD simulations.

The entire kinetic mechanism will be available as supplemental material and will also be available on the LLNL combustion chemistry web page at https://www-pls.llnl.gov/?url=science_and_technology-chemistry-combustion.

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Figure captions

1. Reaction pathways at high and low temperatures.
2. Primary reference fuels for gasoline and diesel fuel
3. Computed (lines) and experimental (symbols) ignition delay times for primary reference fuels
4. Computed (lines) and experimental (symbols) for stoichiometric iso-cetane oxidation in jet-stirred reactor at 10 atm [18]
5. Computed fuel and intermediate species concentrations for selected PRF mixtures. CN number of each fuel mixture indicated on each frame.
6. Computed (lines) and experimental (symbols) for PRF mixtures at indicated ON values. Data from [30] at 40 bar pressure.
7. Computed ignition delay times for indicated CN mixtures at 13.5 bar pressure

FIGURES

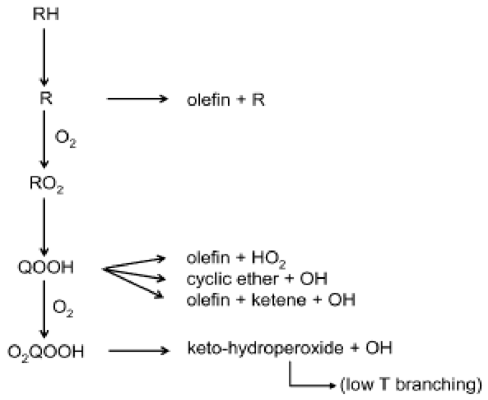
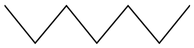


Figure 1

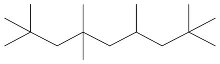
Figure 2

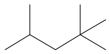
n-heptane



n-hexadecane

iso-cetane





iso-octane

Figure 3

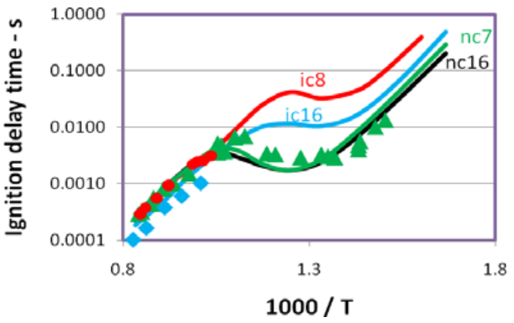
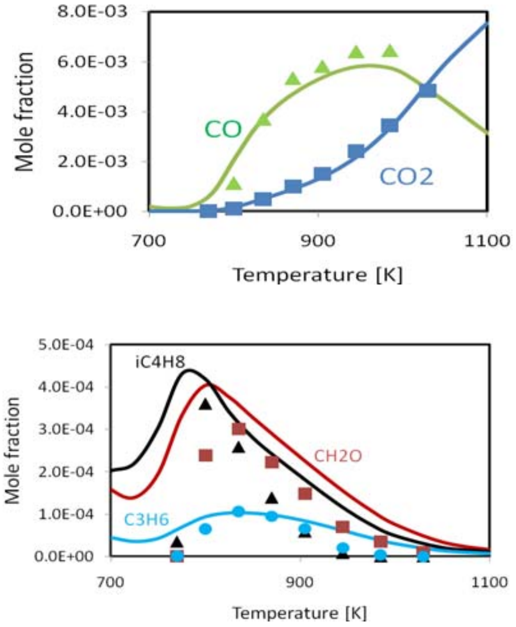

Ignition delay time - s
1.0000
0.1000
0.0100
0.0010
0.0001
0.8
1.3
1.8
1000 / T
ic8
ic16
nc7
nc16

Figure 4



8.0E-03
6.0E-03
4.0E-03
2.0E-03
0.0E+00
Mole fraction
CO
CO2
700
900
1100
Temperature [K]
5.0E-04
4.0E-04
3.0E-04
2.0E-04
1.0E-04
0.0E+00
Mole fraction
iC4H8
CH2O
C3H6
700
900
1100
Temperature [K]

Figure 5

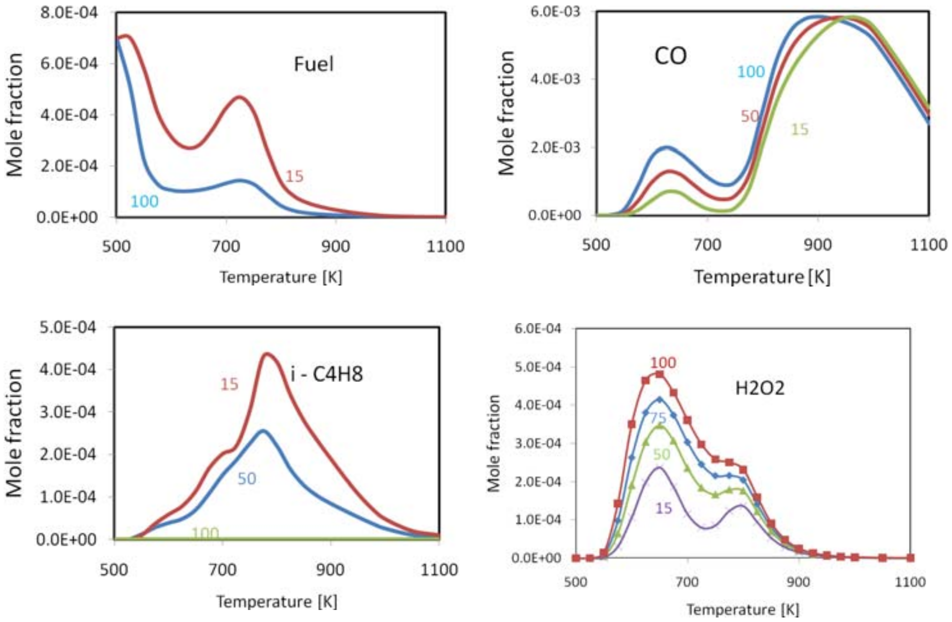

Fuel
Mole fraction
8.0E-04
6.0E-04
4.0E-04
2.0E-04
0.0E+00
500
700
900
1100
Temperature [K]
15
100
CO
6.0E-03
4.0E-03
2.0E-03
0.0E+00
100
50
15
i - C4H8
5.0E-04
4.0E-04
3.0E-04
2.0E-04
1.0E-04
0.0E+00
15
50
100
H2O2
6.0E-04
5.0E-04
4.0E-04
3.0E-04
2.0E-04
1.0E-04
0.0E+00
100
75
50
15

Figure 6

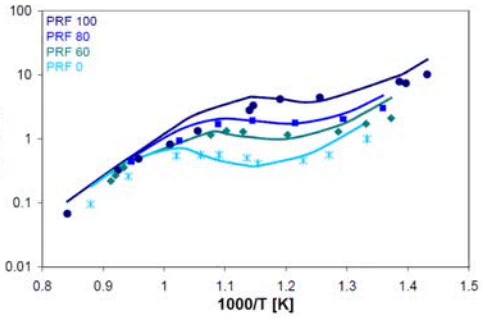
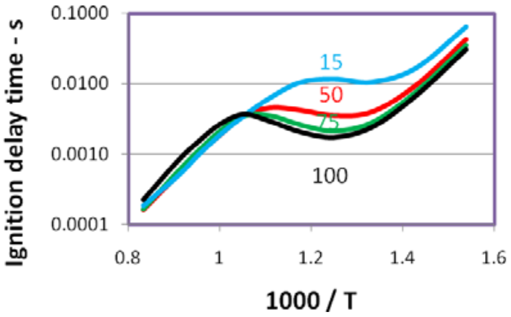

PRF 100
PRF 80
PRF 60
PRF 0
100
10
1
0.1
0.01
tau [ms]
0.8
0.9
1
1.1
1.2
1.3
1.4
1.5
1000/T [K]

Figure 7


Ignition delay time - s
0.1000
0.0100
0.0010
0.0001
0.8
1
1.2
1.4
1.6
1000 / T
15
50
75
100

SUPPLEMENTAL MATERIAL

Table S1. Chemistry input file in Chemkin format for PRF mechanism

Table S2. Thermochemistry input file in JANAF format for PRF mechanism