ABSTRACT

This study investigates the autoignition of Primary Reference Fuels (PRFs) using a detailed kinetic model. The chemical kinetics software CHEMKIN is used to facilitate solutions in a constant volume reactor and a variable volume reactor, with the latter representing an IC engine. Experimental shock tube and HCCI engine data from literature is compared with the present predictions in these two reactors. The model is then used to conduct a parametric study in the constant volume reactor of the effect of inlet pressure, inlet temperature, octane number, fuel/air equivalence ratio, and exhaust gas recirculation (EGR) on the autoignition of PRF/air mixtures. A number of interesting characteristics are demonstrated in the parametric study. In particular, it is observed that PRFs can exhibit single or two stage ignition depending on the inlet temperature. The total ignition delay, whether single or two stage, is correlated with \( n-C_7H_{16}/O_2 \) ratio. Thermodynamic and chemical effects are identified for the EGR constituents CO\(_2\), H\(_2\)O, and N\(_2\). The former effect is due to the difference in specific heats and is well known. Introduction of each diluent reduces the mole fraction of O\(_2\) which has the chemical effect of delaying ignition. In addition, H\(_2\)O as a diluent is shown to directly affect key species and reactions involved in high temperature kinetics, resulting in the enhancement of the ignition process relative to N\(_2\).

1. INTRODUCTION

As a simple Otto-cycle analysis would illustrate, the fuel conversion efficiency of a 4-stroke SI engine increases with the compression ratio \( r_c \). However, limits are imposed on \( r_c \) by knocking combustion, which is essentially the uncontrolled spontaneous ignition, or autoignition, of a portion of the charge within an engine cylinder where energy is released at a faster than normal rate. This rapid energy release can cause substantial damage to the engine structure. As \( r_c \) increases, the gas pressure and temperature increase, which generates conditions more favorable to knock. Consequently, knock is arguably one of the largest barriers to efficiency improvements in SI engines. Knock at its most fundamental level is a chemical kinetics phenomenon. In fact, the study of any combustion system requires knowledge of the kinetic interaction among a large number of species and reactions. A significant effort in the combustion field involves the development of models to represent the chemical kinetics of fuel oxidation. Applied to automotive combustion, an accurate model can be useful for predicting the onset of knock as well as other important concerns such as pollutant formation. Methods for suppressing knock are currently the subject of much investigation relying heavily on not only experimental but also computational studies via kinetic models.

Homogeneous charge compression ignition (HCCI) is a promising technology for IC engines that is in many ways kinetically similar to knock. HCCI relies on controlled autoignition via compression of a homogeneously mixed fuel and oxidizer. It is attractive because it possesses the positive qualities of both CI and SI engines, namely high efficiency similar to CI engines and low emissions of particulates and NO\(_x\) that can be achieved with aftertreatment in SI engines.
Despite nearly 30 years of research, HCCI engines are yet to reach the mass production level primarily due to difficulties in controlling the ignition event over a wide range of speeds and load conditions. However, advancements in control methods such as electronic sensors and EGR may allow HCCI engines to become a practical technology. EGR involves the recirculation of inert exhaust gas into the engine intake which acts as an energy absorber during compression, inhibiting the temperature rise. It has also been demonstrated to suppress knock in SI engines.

Several efforts have investigated the phenomenon of autoignition in an environment similar to that of an engine. Hu and Keck [1] developed a branched chain kinetic model consisting of 18 reactions to correlate experimental data of explosion limits of saturated hydrocarbons in a constant volume bomb and homogeneous autoignition in a rapid compression machine (RCM). The mechanism reproduced much of the low and intermediate temperature chemistry and predicted the well known two stage ignition. Key branching agents and reactions as well as terminating reactions governing the first and second stage ignition were identified. Tanaka et al. [2] expanded the Hu and Keck mechanism to 55 reactions by including those important to the high temperature regime responsible for the majority of energy release. They also included an interaction between PRFs n-heptane (n-C7H16) and iso-octane (i-C8H18) to facilitate the use of fuels with varying octane number (ON). Comparisons with RCM experiments using fuels representing a wide range of ON [3] have shown excellent agreement.

Curran et al. [4] developed a complex reaction mechanism of 4238 reactions to describe the oxidation of PRF mixtures over a broad range of conditions. The mechanism represents a compilation of their previous work on n-heptane and iso-octane oxidation. Using experimental results of ignition behind a reflected shock wave, they were able to describe low, intermediate, and high temperature chemistry and predict much of the intermediate product formation that is characteristic of smaller mechanisms. Model comparisons with experiment were favorable for various flow reactors, a jet-stirred reactor, and a shock tube. Modeling of a motored engine revealed some agreement with experimentally determined critical compression ratios.

Methods to suppress knock have been the subject of research for some time, including retardation of spark timing and/or fuel enrichment to limit the charge temperature. However, fuel enrichment is detrimental to fuel consumption and also to emissions as a result of the departure from stoichiometric operation needed for efficient three-way catalytic conversion. Several studies have investigated the potential of using EGR as a knock suppressant. To avoid the power loss associated with replacing a portion of the intake air with diluent gases, EGR is often used in turbocharged engines. Brüstle and Hemmerlein [5] studied EGR in a turbocharged SI engine and found that it could be used to raise the mean effective pressure or increase the compression ratio. Grandin et al. [6] investigated the use of cooled EGR in a turbocharged SI engine and observed a decreased combustion rate leading to lower peak cylinder pressure and temperature which were favorable to knock suppression. Diana et al. [7] used EGR in a naturally aspirated engine and discovered that an increase in \( r_c \) from 10 to 13 could be achieved using 11% EGR with spark timing set for maximum brake torque. A recent investigation by Sjöberg et al. [8] attempted to quantify the thermodynamic and chemical effects of EGR and its major constituents on HCCI autoignition. The primary mechanisms identified as being responsible for retarding the start of combustion were a thermodynamic cooling effect due to the high specific heat capacities of CO\(_2\) and H\(_2\)O, and an O\(_2\) reduction effect resulting from a portion of the intake air being displaced by the EGR gases. It was also discovered that H\(_2\)O had a chemical effect of enhancing autoignition which negated its thermodynamic cooling effects for PRF 80 but had less of an impact on iso-octane and gasoline. The effect of trace species such as CO, NO, and unburned hydrocarbons were also found to possess both enhancement and suppression tendencies depending of the type of fuel used.

The objective of this work is to further study the spontaneous ignition and combustion of a homogeneous mixture of PRF and air in connection with both engine knock and HCCI combustion. The detailed chemical kinetic model by Curran et al. [4] describing the oxidation of PRFs capable of representing a wide range of fuel octane numbers is used in conjunction with CHEMKIN [9] to simulate the combustion. Experimental data of ignition delay times in a shock tube reactor are first compared to constant volume homogeneous reactor calculations to assess accuracy of the kinetic model in predicting the ignition event in an easily controlled environment. The kinetic model is then extrapolated to the more complex environment of an engine. Experimental data representing a range of engine geometry and operating conditions is taken from literature. Upon validation of the kinetic model, the effect of operating parameters, such as inlet pressure and temperature, ON, equivalence ratio, and EGR, on the autoignition and combustion are investigated. Since, in addition to reducing emissions, EGR can be used for controlling the timing of the autoignition event, its constituents CO\(_2\), H\(_2\)O, and N\(_2\) are investigated separately, with a specific focus on the chemical effects of H\(_2\)O.

Following the introduction, Section 2 briefly discusses the two stage ignition phenomenon, and Section 3 describes the modeling procedure adopted in the present work. Section 4 compares the predictions of the detailed kinetic model with experimental data available in literature. Results of the parametric study are presented in Section 5, followed by concluding remarks in Section 6.
2. IGNITION FUNDAMENTALS

The explosion limits for a specific fuel/oxidizer mixture are formed by pressure and temperature boundaries as illustrated in Fig. 1 taken from Glassman [10]. Much of the understanding of pure hydrogen oxidation developed through the study of explosion limits [11]. For hydrocarbons, as either pressure or temperature is increased the general tendency of the mixture to become explosive increases. Of the saturated hydrocarbons C_nH_{2n+2}, methane (CH_4) exhibits the highest resistance to explosion due to the comparatively large energy required to break the C-H bond. For higher order hydrocarbons, the chain reaction initiation is dominated by the breaking of a C-C bond, which is substantially weaker than the C-H bonds in the molecule. Inflections exist in the explosion limit curves for saturated hydrocarbons with n > 2. These inflections are a result of the negative temperature coefficient (NTC) of reaction rate in which chain branching and terminating steps are in competition as temperature increases [10]. This phenomenon manifests itself in the form of a two stage ignition. The first stage ignition termination is a result of the inhibited branching, termed degenerate branching. This mechanism is commonly referred to as the low temperature kinetic scheme because of the modest temperature rise associated with it. The chain terminating step becomes dominant and prevents the mixture from completely reacting to reach its adiabatic flame temperature. The system then returns to the non-explosive regime, and an induction time follows until branching again becomes dominant, leading to the second-stage or hot ignition where the majority of heat is released. These fundamentals are critical to the material presented in this work.

3. MODELING PROCEDURE

CHEMKIN [9] features a large variety of flame simulators and reactor models, including the closed homogeneous reactor and closed internal combustion engine simulator used in the present work.

3.1 CONSTANT VOLUME REACTOR MODEL - A constant volume closed homogeneous reactor is used for calculation of ignition delay times. Kinetic model rate parameters are often optimized according to ignition delay comparisons with experimental shock tube results. One advantage of using shock tubes to study autoignition of fuel/air mixtures is that the compression time (~ 1 ns) is sufficiently short to reduce any effects of the compression process such as increased heat transfer [12,13]. The ignition delay times measured are typically on the scale of 10^{-4} to 10^{-3} seconds, however, extension to lower initial temperatures lengthens this time and an adiabatic assumption may come into question at sufficiently low temperatures. Nonetheless, it is a common practice to neglect heat loss when calculating ignition delays for comparison to shock tube results, as will be followed in the present work. Ignition time is defined in the model as the time of maximum heat release as indicated by the inflection point in the temperature profile.

3.2 INTERNAL COMBUSTION ENGINE MODEL - The IC engine model simulates combustion of a single-zone, homogeneous mixture under autoignition conditions in a closed reactor, hence it is relevant to the studies of fuel autoignition, engine knock, and HCCI engines. Since the model is valid only for closed systems, the appropriate time for simulation is the interval in which both the intake and exhaust valves are closed. The time-varying cylinder volume is readily determined following Heywood [14]. Heat transfer is based on the Woschni correlation [15] where the convective heat transfer coefficient is

$$ h = a d^{c-1} \frac{k}{\mu^b} w^p \rho^s \quad (1) $$

with

$$ w = \left( C_{11} + C_{12} \frac{V}{S_p} \right) \frac{1}{S_p} + C_{15} \frac{VT_i}{P_i} \left( \rho - \rho_m \right). \quad (2) $$

Modeling parameters used in Eqs. (1) and (2) are provided in Table 1. Note that C_2 is reduced to 1/6 of the value proposed by Woschni [15] following the work by Chang et al. [16], who modified the Woschni correlation for HCCI modeling. For the purposes of heat transfer, a constant wall temperature of 400 K is assumed.

<table>
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<th>Value</th>
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<td>b</td>
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<tr>
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</tr>
<tr>
<td>C_{12}</td>
<td>0.054</td>
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</table>

3.3 FUEL AND KINETIC MODEL - The tendency of a fuel to autoignite is measured by its ON. ONs are defined by the tendency of the PRFs n-heptane (n-C_7H_{16}) and iso-octane (i-C_8H_{18}) to ignite; which have assigned values of 0 and 100, respectively, where the larger ON represents a greater resistance to
autoignition. When the investigation of ignition timing is important, a fuel with any ON in the range 0-100 is easily modeled by the appropriate combination of PRFs. With this realization, several studies have aimed to develop chemical kinetic models describing the oxidation of PRFs. These mechanisms vary in complexity from fewer than ten to thousands of reactions. The most complex ones attempt to include all the important reactions and species, including intermediates, which contribute to the overall oxidation process. Reduced models are driven by the desire to minimize the computational demand required of the detailed mechanisms, particularly when coupled with computational fluid dynamics (CFD) calculations. Since the present work examines only single-zone models, the use of a detailed kinetic mechanism is feasible.

Perhaps the most widely used kinetic model for PRF oxidation is the Lawrence Livermore National Laboratory (LLNL) mechanism by Curran et al. [4], comprised of 1034 species and 4238 reactions. This includes all reactions known to be relevant to both high and low temperature kinetics. The mechanism has been validated with experimental data from flow reactors, jet-stirred reactors, and shock tubes, and compared favorably to autoignition experiments in a cooperative fuels research (CFR) engine though the extent of investigation reported has been limited. It has also been used successfully for kinetic modeling of combustion in HCCI engines [17,18].

4. COMPARISON WITH EXPERIMENTS

4.1 SHOCK TUBE IGNITION DELAY DATA - Fieweger and co-workers [12] have measured ignition delay times of PRF mixtures in a shock tube using the reflected shock technique. Their maximum measuring time of 12 ms represents a time scale comparable to that available for autoignition in an engine. The shock tube was constructed to support pressures up to 700 bar resulting from the ignited fuel/air mixture. Pressure data was obtained via acceleration-compensated piezoelectric transducers. Temperature behind the reflected shock was calculated from the velocity of the incident shock taking into account real gas properties. Ignition delay was defined as the time interval from the reflected shock passing the pressure transducer until explosion of the gas, which was determined from the pressure records.

4.2 IGNITION DELAY IN THE CONSTANT VOLUME REACTOR - Figure 2 shows experimental data from Fieweger et al. [12] for the dependence of total ignition delay on temperature and the predictions from the present study using the constant volume homogeneous reactor in CHEMKIN of the dependence of ignition delay on temperature for three different PRF mixtures at 40 bar and \( \phi = 1.0 \). A similar figure has been generated by Andrae et al. [19]. In general, the kinetic model calculations are similar to experimental data and capture the overall trend of temperature influence for each fuel. However, the predictions are observed to consistently predict a longer ignition delay, particularly in view of the logarithmic scale used, even though heat loss is neglected. As discussed earlier, an adiabatic assumption is generally considered valid provided that time scales are sufficiently small. The largest disagreement between experiment and model occurs at lower temperatures or longer ignition delay times. At approximately 700 K, the model predicts an ignition delay of more than 1.5 times greater than that measured for iso-octane (PRF 100). Since neglecting heat loss in model calculations would tend to decrease ignition delay compared to experiment, the over-predictions at low temperatures are particularly alarming. This suggests that the low temperature kinetics of the model may be less accurate than those at higher temperatures.

4.3 HCCI ENGINE DATA - HCCI engine combustion of PRF 20 (20% \( i-C_8H_{18} \), 80% \( n-C_7H_{16} \)) representing ON = 20 has been studied by Zheng et al. [20]. A single cylinder, four-stroke, air cooled research engine with specifications given in Table 2 was used to collect the data. For brevity, this engine will be referred to as the “PRF 20 engine”. The engine was operated at \( N = 750 \) rpm with inlet manifold pressure of 1 atm at fuel/air equivalence ratio \( \phi = 0.4 \). The inlet temperature was varied from 393-453 K. Complete vaporization and mixing were assured by injecting the fuel into the air stream of the heated inlet manifold sufficiently far upstream of the intake valve. Cylinder pressure data were collected via a wall mounted piezoelectric transducer. Temperature was then calculated from this data using a thermodynamic model.

PRF 84 (84% \( i-C_8H_{18} \), 16% \( n-C_7H_{16} \)) representing ON = 84 was studied by Kalghatgi et al. [21] in a single cylinder, four-stroke, water cooled HCCI engine with port fuel injection. Specs for this engine, denoted as the “PRF 84 engine”, are also provided in Table 2. The data that follows represents operation at \( N = 900 \) rpm, intake air temperature and pressure of 393 K and 1 bar, respectively, and \( \lambda = 1/\phi = 3.5 \). The fuel was injected at bottom dead center (180° BTDC) and cylinder pressure was measured with a piezoelectric transducer.

![Figure 2. Ignition Delay vs. 1000/T, Experiments [12] vs. Predictions for 4 Fuels, \( P = 40 \) bar, \( \phi = 1.0 \).](image-url)
4.4 HCCI ENGINE COMBUSTION – Pressure profiles vs. crank angle degree (CAD) from experiments for both engines are shown in Fig. 3 with the corresponding predictions from the present study superimposed. Top dead center (TDC) is represented by 0 CAD. Many trends are captured by the model, such as the two stage ignition of the PRF 20 engine (the first stage occurring at approximately 33° and 23° BTDC for the experiment and model, respectively), the total pressure rise due to combustion, and the pressure rise rate due to combustion. However, the model clearly predicts late ignition for both engines. Three potential sources for this error are proposed. First, Fig. 2 demonstrates that there are likely inaccuracies associated with the kinetic model, which are in agreement with the discrepancies observed in the HCCI engine model. Second, a level of uncertainty remains associated with the heat transfer correlation. There are a number of engine heat transfer correlations in existence \([15,16,22,23]\) which can produce significantly different results \([16]\). Furthermore, the values of the parameters used in a particular correlation may be suited well for one engine, and not for another exhibiting different geometric or operating conditions.

![Figure 3. Pressure vs. CAD for Experiment and Model.](image)

The third potential source of discrepancy between model and experimental data is the non-ideal conditions of a real engine. The HCCI engine model assumes perfect mixing and uniform temperature distribution. In reality, hot spots will form in the charge due to either residual gases or hot surfaces within the cylinder. Ignition will start at these hot spots where temperature is higher than the bulk gas temperature \([24]\), and therefore ignition will advance from that of a truly isothermal mixture. To address this discrepancy, Andrae et al. \([19]\) have suggested adding the difference in temperature \(\Delta T\) between the hot spots and the bulk gas to the inlet temperature in modeling studies. Since such a temperature difference is difficult to measure, the approach taken here for the PRF 20 engine was to guess a value until the calculated temperature profile approximates, to within 5 K, that measured late in the compression stroke but before the ignition. By trial and error, it was discovered that \(\Delta T = 40\ K\ (T_{in} = 463\ K)\) approximated the temperature well at 40° BTDC, the point where experimental data is made available. In working with the same experimental data for the PRF 84 engine used here, Andrae et al. \([19]\) have chosen 25 K to represent the hot spot temperature difference at these conditions. However, the modeling in that work was adiabatic and thus \(\Delta T\) should consider not only residual gas hot spots but also the temperature decrease due to heat loss in the experimental engine. Therefore, when modeling with heat transfer, \(\Delta T\) would presumably need to be larger. However, since temperatures are over-predicted for the compression process even for \(\Delta T = 25\ K\), \(\Delta T\) is not determined by matching temperature profiles as before. Rather, the value of \(\Delta T = 35\ K\ (T_{in} = 428\ K)\) is calculated from

\[
\left(\frac{\Delta T}{T_{peak} - T_{in}}\right)_{PRF84} = \left(\frac{\Delta T}{T_{peak} - T_{in}}\right)_{PRF20},
\]

where \(T_{in}\) and \(T_{peak}\) are the experimental inlet and peak cylinder temperatures, respectively, and \(\Delta T = 40\ K\) for PRF 20 as previously designated. Peak temperatures are approximately 1880 K and 1600 K for the PRF 20 and PRF 84 engines, respectively. This is a somewhat crude estimation technique, but it at least recognizes the effect of peak temperature on residual gas hot spot temperature and inlet temperature on \(\Delta T\). To summarize, the parameters used in CHEMKIN to model each engine are presented in Table 3 along with the specs in Table 2 and the heat transfer correlation parameters of Table 1.

![Table 3. IC Engine Modeling Parameters](image)

5. PARAMETRIC STUDY

Despite the difficulties associated with reproducing the exact experimental data, the agreement of trends observed in the constant volume and IC engine model reactors with the experimental data allows a valuable parametric study to be conducted. This is most easily done in the constant volume reactor because complexities associated with the IC engine model are reduced. Specifically, the effects of inlet pressure, temperature, ON, equivalence ratio, and EGR rate on fuel autoignition and combustion are investigated.
5.1 EFFECT OF INLET PRESSURE – The transient temperature profiles for PRF 20 at $T_{in} = 850 \text{ K}$, $\phi = 0.4$, and three different inlet pressures are shown in Fig. 4. The inlet temperature and pressures are similar to those that would be generated in an engine near the point of autoignition. Figure 4 clearly illustrates that ignition is two stage for each case. A higher inlet pressure causes earlier ignition of both the first and second stages, with the most dramatic effect being on the timing of the hot second stage. Since temperature is the most important parameter governing the rate of branching reactions responsible for ignition, Tanaka et al. [3] suggested that the induction time between the first and second stages is simply the time required for the energy released by the second stage reactions to raise the temperature from the value generated by the first stage reactions to the second stage ignition (explosion) temperature. Since the ignition temperature is approximately constant for each $P_{in}$, the shorter second stage induction time (that is the time interval between the conclusion of the first stage reactions and the beginning of the hot second stage ignition) at higher $P_{in}$ is due to a larger energy release during the first stage which results in a higher temperature, though only slight, at the beginning of the second stage.

5.2 EFFECT OF INLET TEMPERATURE – Figure 5 shows transient temperature profiles in the constant volume reactor for PRF 20 at $P_{in} = 40 \text{ atm}$, $\phi = 0.4$, and varying $T_{in}$. A number of interesting observations can be made. First, in agreement with the constant $T_{in}$ calculations of Fig. 4, the induction time between the end of the first stage ignition and the second stage explosion decreases with increasing first stage energy release. Figure 5 also reveals that the temperature at the conclusion of the first stage reactions is independent of $T_{in}$ with a value of approximately 926 K and thus the first stage energy release increases (as indicated by the temperature increase) as $T_{in}$ decreases. This seems to indicate that at this critical temperature of 926 K, the reactions responsible for degenerate branching begin to dominate. Note also that for $T_{in} = 1000 \text{ K}$, ignition is single stage, and it can be inferred that such is the case for $T_{in} > 926 \text{ K}$. For further illustration, consider again Fig. 1. Traversing the constant pressure line from point 1 to point 4, the system passes through the first stage explosion in region 2 until a critical temperature is reached separating regions 2 and 3. This corresponds to the end of the first stage ignition. In region 3, steady reaction again dominates until a second critical temperature is reached sending the system into the second stage explosion. Thus, a saturated hydrocarbon $C_nH_{2n+2}$ for which $n > 2$ may exhibit a single or two stage ignition depending on the initial conditions. In terms of the process described above, a system initially at point 1 of Fig. 1 will exhibit two stage ignition, whereas one initially at point 3 will be single stage.

5.3 EFFECT OF OCTANE NUMBER – To illustrate the effect of ON, consider the temperature profiles in Fig. 6 for the constant volume reactor with varying ON. In these calculations, inlet pressure and temperature have been held constant at 40 atm and 800 K with $\phi = 0.4$, leading to a two stage ignition for each fuel mixture. Note that the fuels with lower ON have a larger first stage energy release resulting in shorter second stage induction times. Comparing the first stage ignition of the ON = 0 (100% $n$-C$_7$H$_{16}$) and ON = 100 (100% $i$-C$_8$H$_{18}$) of Fig. 6 reveals that the first stage reactions of $n$-C$_7$H$_{16}$ occur at a much faster rate and are more exothermic than those of $i$-C$_8$H$_{18}$. This behavior can be explained on the basis of the isomerization of the alkylperoxy (RO$_2$) radical to yield an alkylhydroperoxide (ROOH) radical, which is a key step in the low temperature kinetic scheme of the hydrocarbon oxidation mechanism. In a typical hydrocarbon fuel molecule, the different C-H bonds can be described as primary, secondary, or tertiary, depending on the number of other carbon atoms (one, two, or three) the C atom is connected to, with the primary bond being the most difficult to break and the tertiary the easiest [25]. Unlike the $C_7H_{15}O_2$ radical, $C_8H_{17}O_2$ has the secondary C-H bonds only at the C atom closest to the O$_2$ site, making it a poor candidate for H abstraction due to the high ring strain energy, with
all the remaining H atoms occupying primary sites. Consequently, the isomerization step occurs more rapidly for \( n\text{-C}_7\text{H}_{16} \) than \( i\text{-C}_8\text{H}_{18} \). Hence the first stage ignition commences earlier and releases more energy for lower ON due to a higher percentage of \( n\text{-C}_7\text{H}_{16} \) in the fuel composition. The temperature at the conclusion of the first stage reactions for each ON in Fig. 6 are used to generate Fig. 7, which shows the approximate critical temperature separating single and two stage ignition processes for each ON at \( P_\text{in} = 40 \text{ atm} \) and \( \phi = 0.4 \). 

Additionally, the burn rate, along with the ignition timing, is a critical parameter for control in HCCI combustion over a wide range of speed and load conditions.

In their experimental work with a rapid compression machine, Tanaka et al. [3] found that ignition delay times for the second stage were much more strongly correlated with the \( n\text{-C}_7\text{H}_{16}/O_2 \) molar ratio than \( i\text{-C}_8\text{H}_{18}/O_2 \) and were independent of the ON and \( \phi \). To assess this finding here with the kinetic model, the second stage ignition delay times \( \tau_\text{ig} \) (that is the time interval from the beginning of simulation to the second stage explosion) in the constant volume homogeneous reactor were calculated for multiple \( n\text{-C}_7\text{H}_{16}/O_2 \) and \( i\text{-C}_8\text{H}_{18}/O_2 \) ratios at \( P_\text{in} = 40 \text{ atm} \) and \( T_\text{in} = 820 \text{ K} \) to generate two stage ignition for all fuel mixtures. The ignition delay is determined by CHEMKIN and corresponds to the time of the maximum temperature gradient. The test matrix for the present work is outlined in Table 4 along with the results under the column “\( \tau_\text{ig} \) 2-Stage”. As can be seen from Fig. 9, a good correlation indeed exists for \( n\text{-C}_7\text{H}_{16}/O_2 \). This is not the case for \( \tau_\text{ig} \) vs. \( i\text{-C}_8\text{H}_{18}/O_2 \) of Fig. 10, which shows no correlation.

Table 4. Ignition Delay Test Matrix and Results for Varying Fuel/O_2 Ratios.

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<th>ON</th>
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<th>( i\text{-C}<em>8\text{H}</em>{18}/O_2 )</th>
<th>( \tau_\text{ig} ) 2-Stage (ms)</th>
<th>( \tau_\text{ig} ) 1-Stage (ms)</th>
<th>( \tau_\text{ig} ) Intermediate (ms)</th>
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</tbody>
</table>
It is interesting to examine whether a correlation exists between $r_{ig}$ and $n$-C$_7$H$_{16}$/O$_2$ when ignition is single stage. As suggested by Fig. 7, $T_{in}$ was increased (from 820 K of Fig. 9) to 940 K to achieve single stage ignition. Results are provided in Table 4 under column “$r_{ig}$ 1-Stage”. Figure 11 reveals a correlation similar to that for two stage ignition shown in Fig. 9. Note that despite an increase of 120 K in $T_{in}$, $r_{ig}$ is approximately the same between both types of ignition for a given $n$-C$_7$H$_{16}$/O$_2$ except near $n$-C$_7$H$_{16}$/O$_2 = 0$. The constant ignition delay in this temperature range is reflected in Fig. 2 for each fuel mixture. This implies that, since the transition between single and two stage ignition for each ON is approximately in the constant $r_{ig}$ temperature range of 800 – 950 K (see Figs. 2 and 7), the type of ignition does not affect the delay time. To see this explicitly, calculations were made at an intermediate $T_{in} = 900$ K generating single and two stage ignition depending on ON (see again Fig. 7). The ignition delay corresponding to the hot ignition (that is from time = 0 to the time of the final gas explosion), whether single or two stage, is reported in the column heading “$r_{ig}$ Intermediate” of Table 4. Figure 12 demonstrates for $T_{in} = 900$ K that the correlation between $r_{ig}$ and $n$-C$_7$H$_{16}$/O$_2$ is preserved.

5.5 EFFECT OF EXHAUST GAS RECIRCULATION – EGR can have both thermodynamic and chemical effects on autoignition. The thermodynamic effects are well known and have been demonstrated previously [8]. Typically, EGR is composed of N$_2$ and the combustion products CO$_2$ and H$_2$O. Introduction of these species usually results in a retarded ignition due primarily to the thermodynamic effects, which are caused by differences in specific heat $c_p$ of the species. Figure 13 demonstrates the effect of each constituent on the adiabatic compressed gas temperature of the motored PRF 20 engine. Motored operation indicates no heat release due to chemical reaction and therefore temperature differences are due only to differences in $c_p$. A baseline condition of 100% O$_2$ is contrasted with mixtures of 20% O$_2$ and 80% diluent. The highest temperatures are achieved for 80% N$_2$, which is close to
the composition of air (21% O₂ and 79% N₂). CO₂ as the diluent generates the most modest temperature rise. This ordering follows the order of \( c_p \) for each constituent.

Although the constant volume reactor eliminates temperature increases due to compression, the thermodynamic effect of inhibiting the gas temperature rise resulting from exothermic reactions remains. The first stage ignition delay, however, is nearly independent of the type of diluent as depicted in Fig. 15 due to limited exothermic reactions that increase the temperature preceding the first stage ignition. This is not the case for the second stage ignition, though, as the temperature will be affected by the energy released from the first stage.

Sjöberg et al. [8] have shown that the reduction of mole fraction of O₂, \( y_{O2} \), in the reactant mixture with introduction of EGR has the chemical effect of retarding ignition in an HCCI engine. The influence of \( y_{O2} \), or volume percentage O₂, in the constant volume reactor can be observed in Fig. 14. In these calculations, PRF 20 with a fuel/O₂ equivalence ratio of 0.4, providing \( y_{O2} = 0.975 \), was used as the base reactant mixture at \( P_n = 40 \) atm and \( T_n = 900 \) K. To generate a volume percentage of O₂ similar to air, each diluent was added in increments of 1% from 78% to 85% of the total reactant mixture. The test matrix and ignition delay \( t_{ig} \) corresponding to the maximum temperature gradient for each diluent is given in Table 5. Note that all cases exhibit two stage ignition and \( t_{ig} \) in Table 5 corresponds to the hot second stage ignition. Figure 14 clearly shows an increase in ignition delay as \( y_{O2} \) decreases. It is expected that the delay is largest for CO₂ as the diluent based on its high thermodynamic cooling as seen in Fig. 13.

Although the constant volume reactor eliminates temperature increases due to compression, the thermodynamic effect of inhibiting the gas temperature rise resulting from exothermic reactions remains. The first stage ignition delay, however, is nearly independent of the type of diluent as depicted in Fig. 15 due to limited exothermic reactions that increase the temperature preceding the first stage ignition. This is not the case for the second stage ignition, though, as the temperature will be affected by the energy released from the first stage.

Table 5. Test Matrix and Results for PRF 20 Second Stage \( t_{ig} \) with Varying \( y_{O2} \).

<table>
<thead>
<tr>
<th>Mole Fraction Diluent</th>
<th>Mole Fraction O₂</th>
<th>( t_{ig} ) (ms) with CO₂</th>
<th>( t_{ig} ) (ms) with H₂O</th>
<th>( t_{ig} ) (ms) with N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.78</td>
<td>0.213</td>
<td>2.404</td>
<td>1.636</td>
<td>2.010</td>
</tr>
<tr>
<td>0.79</td>
<td>0.203</td>
<td>2.650</td>
<td>1.813</td>
<td>2.232</td>
</tr>
<tr>
<td>0.80</td>
<td>0.194</td>
<td>2.932</td>
<td>2.021</td>
<td>2.491</td>
</tr>
<tr>
<td>0.81</td>
<td>0.184</td>
<td>3.259</td>
<td>2.267</td>
<td>2.796</td>
</tr>
<tr>
<td>0.82</td>
<td>0.174</td>
<td>3.637</td>
<td>2.561</td>
<td>3.158</td>
</tr>
<tr>
<td>0.83</td>
<td>0.165</td>
<td>4.080</td>
<td>2.916</td>
<td>3.592</td>
</tr>
<tr>
<td>0.84</td>
<td>0.155</td>
<td>4.600</td>
<td>3.352</td>
<td>4.120</td>
</tr>
<tr>
<td>0.85</td>
<td>0.145</td>
<td>5.218</td>
<td>3.890</td>
<td>4.693</td>
</tr>
</tbody>
</table>

It is observed from Fig. 13 that thermodynamic cooling is greater for H₂O as the diluent than N₂, yet as Fig. 14 shows, the total ignition delay is shorter with H₂O than N₂. Since the kinetic model by Curran and co-workers [4] considers N₂ to be an inert species (that is not involved in any chemical reaction in the model), only thermodynamic effects of N₂ exist. This suggests a chemical effect of H₂O that enhances ignition relative to the addition of inert N₂. Sjöberg et al. [8] discovered

![Figure 13. Compressed Gas Temperature vs. CAD in the Modeled PRF 20 Engine, \( P_n = 1 \) atm, \( T_n = 463 \) K.](image1)

![Figure 14. \( t_{ig} \) vs. \( y_{O2} \), Constant Volume Reactor, PRF 20, \( P_n = 40 \) atm, \( T_n = 900 \) K, Fuel/O₂ Equivalence Ratio = 0.4.](image2)

![Figure 15. First Stage Ignition Delay vs. \( y_{O2} \), PRF 20, \( P_n = 40 \) atm, \( T_n = 900 \) K, Fuel/O₂ Equivalence Ratio = 0.4.](image3)
similar ignition enhancement with H2O in their experiments with an HCCI engine. To further illustrate this effect, consider Figs. 16 – 20 which show the variation of the species H, O, OH, HO2, and H2O2, respectively, for each diluent at 79% of the total mixture corresponding to yO2 = 0.203 in the constant volume reactor for PRF 20 at Pn = 40 atm, Tin = 900 K, and fuel/O2 equivalence ratio = 0.4. Appendix A provides the reactions governing autoignition according to the Hu and Keck mechanism [1]. Though not explicitly shown in those ten reactions, the radicals H and O are involved in the chain reaction mechanisms that characterize explosive gas mixtures. The first stage ignition, occurring at approximately the same instant for each diluent, is readily seen in the profiles of yH and yO in Figs. 16 and 17. It is interesting that the peak for both radicals during the first stage ignition is smallest for H2O as the diluent. Following the first stage, however, the mole fractions of H, O, OH, and HO2 increase faster for mixtures diluted with H2O than with CO2 or N2. Note the relationship between OH, HO2, and H2O2 (HOOH) in reactions R8 – R10 of Appendix A. R8, producing HO2, is responsible for degenerate branching, and as Fig. 19 shows, a peak in HO2 occurs just after the first stage ignition. The mole fraction of HO2 then decreases as a sharp increase in H2O2 is observed following ignition in Fig. 20 as R9 predicts. HO2 begins to accumulate again as degenerate branching (R8) continues, faster now for H2O as the diluent, and H2O2 continues to increase though at a slower rate. It is also during this time that OH begins to accumulate (see Fig. 18) as predicted by the branching reaction R10. Soon HO2 and H2O2 peak and then rapidly decrease while OH increases exponentially. The second stage ignition, as indicated by the occurrence of the maximum temperature gradient, follows.

Figure 16: Mole Fraction H vs. Time, PRF 20, yO2 = 0.203, Pn = 40 atm, Tin = 900 K, Fuel/O2 Equivalence Ratio = 0.4.

Figure 17: Mole Fraction O vs. Time, PRF 20, yO2 = 0.203, Pn = 40 atm, Tin = 900 K, Fuel/O2 Equivalence Ratio = 0.4.

Figure 18: Mole Fraction OH vs. Time, PRF 20, yO2 = 0.203, Pn = 40 atm, Tin = 900 K, Fuel/O2 Equivalence Ratio = 0.4.

Figure 19: Mole Fraction HO2 vs. Time, PRF 20, yO2 = 0.203, Pn = 40 atm, Tin = 900 K, Fuel/O2 Equivalence Ratio = 0.4.
High temperature kinetics involves $\text{H}_2\text{O}_2$ producing OH through reaction R10, which then reacts with formaldehyde $\text{CH}_2\text{O}$, though not shown in the Hu and Keck mechanism [1] presented in Appendix A, to produce HCO and $\text{H}_2\text{O}$. HCO in turn reacts with $\text{O}_2$ to give CO and $\text{HO}_2$, which then gives back $\text{H}_2\text{O}_2$ through reaction R9. To examine the effect of adding $\text{H}_2\text{O}$ as a diluent on high temperature kinetics, rate of production (ROP) analyses were performed in CHEMKIN for the species shown in Figs. 16-20. ROP predictions were used to identify the most prominent reactions contributing to the production/consumption of particular species, for example, $\text{H}_2\text{O}_2$ as depicted in Fig. 21 (negative reaction rates indicate consumption of $\text{H}_2\text{O}_2$ and positive rates its production). Comparison of the three most prominent reactions for $\text{H}_2\text{O}_2$ production in oxidation of mixtures with 79% $\text{H}_2\text{O}$ and 79% $\text{N}_2$ shows that while reactions R9 and R10 exhibit similar behavior, the reaction

$$\text{H}_2\text{O}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{HO}_2$$

changes direction. The presence of excess $\text{H}_2\text{O}$ in the charge causes the reaction to proceed in the reverse direction, producing $\text{H}_2\text{O}_2$ and OH instead of consuming them. The $\text{H}_2\text{O}_2$ produced in turn contributes to further OH generation through reaction R10. As OH is a highly reactive radical, the presence of additional OH is expected to accelerate the overall oxidation mechanism.

Also, note that in Fig. 21, with respect to the second stage ignition, the reaction rates start increasing earlier when $\text{H}_2\text{O}$ is the diluent, suggesting that the radical concentrations build up more rapidly in the presence of excess water. This behavior becomes more clear in Fig. 22, which compares the concentrations of $\text{H}_2\text{O}_2$, $\text{HO}_2$, OH, $\text{CH}_2\text{O}$, HCO, $\text{i-C}_8\text{H}_{18}$, and $\text{n-C}_7\text{H}_{16}$ for the diluents $\text{H}_2\text{O}$ and $\text{N}_2$, respectively. The excess $\text{H}_2\text{O}$ in the charge causes a rapid rise in the OH concentration, which is accompanied by an increase in the concentrations of HCO and $\text{HO}_2$, resulting in a faster overall reaction. A comparison of the heat release from the three highest contributing reactions in the mechanism as well as the overall reaction, as depicted in Fig. 23, illustrates the resulting advance in timing of the second stage ignition. These observations suggest that $\text{H}_2\text{O}$ added as a diluent actively influences the oxidation process by affecting the production of key species like OH, HO$_2$, and H$_2$O$_2$, and consequently accelerates the ignition process.
Sjöberg et al. [8] also found that the chemical effect of \( \text{H}_2\text{O} \) ignition enhancement is stronger for two stage ignition fuels than single stage ignition fuels. Since it has been shown previously in Fig. 7 that a PRF can exhibit single or two stage ignition, calculations were made for PRF 20 at fuel/O\( \text{O}_2 \) equivalence ratio = 0.4, \( P_{in} = 40 \) atm, and \( T_{in} = 960 \) K in the constant volume reactor to generate single stage ignition. The test matrix is the same as that given in Table 5. Figure 24 provides the percent difference between the ignition delay using \( \text{N}_2 \) and \( \text{H}_2\text{O} \) as the diluents, calculated as

\[
\% \text{ Difference} = \left[ \frac{(r_{ig})_{N_2} - (r_{ig})_{H_2O}}{(r_{ig})_{N_2}} \right] \times 100
\]  

(5)
for both single and two stage ignition. The delay times for single stage ignition differ somewhat more than those for two stage. For PRF 20, the kinetic model therefore predicts that the chemical effect of H_2O ignition enhancement relative to N_2 addition is somewhat stronger for single stage than two stage ignition. While this trend may appear to be contrary to the findings of Sjöberg et al. [8], there is a subtle difference between the two. The predictions of Fig. 24 are for single and two stage ignition behavior of the same fuel (PRF 20) under different initial (temperature) conditions. Comparisons made by Sjöberg et al. [8], instead, are for different fuels that exhibit only single stage or two stage ignition, under identical initial conditions.

![Figure 24. Percent Difference of N_2 and H_2O Ignition Delay vs. \( y_{O_2} \). PRF 20, \( P_{in} = 40 \) atm, Fuel/O_2 Equivalence Ratio = 0.4.](image)

6. SUMMARY AND CONCLUSIONS

An investigation of the autoignition characteristics of PRFs using a detailed kinetics mechanism has been conducted. CHEMKIN was used for computations in constant volume and variable volume (IC engine) reactors in combination with the kinetic model developed by Curran et al. [4]. The predictions were then compared with experimental data of shock tube ignition delay times first followed by HCCI engine parameters. Trends with varying temperature were captured over a wide range of ON; however, the model was observed to consistently predict longer ignition delay than the shock tube data. Many of the experimental trends of HCCI engine combustion were captured by the model though there were some difficulties attributed primarily to non-ideal conditions of the real engine combustion, such as temperature inhomogeneities. Regardless, the agreement of trends facilitated a parametric study. The constant volume adiabatic reactor was used to isolate effects of the parameter being studied. The effects of inlet pressure \( P_{in} \), inlet temperature \( T_{in} \), ON, equivalence ratio \( \phi \), and EGR were studied. The following represents significant observations:

- The induction time between the first and second stages of two stage ignition is dependent upon the energy released during the first stage ignition. A larger first stage energy release results in a shorter induction time.
- For two stage ignition, a higher \( P_{in} \) or lower \( T_{in} \) results in a larger first stage energy release.
- The temperature at the end of first stage in two stage ignition (that is the temperature where degenerate branching overcomes the first stage reactions) is independent of \( T_{in} \).
- Fuels with lower ON exhibit larger first stage energy release for two stage ignition, primarily due to a higher percentage of \( n-C_7H_{16} \) in the fuel composition.
- Fuels with a range of \( ON = 0 - 100 \) can exhibit single or two stage ignition for given \( P_{in} \) and \( \phi \). The critical \( T_{in} \) separating single and two stage ignition decreases approximately linearly with increasing ON.
- The total energy release increases with \( \phi \) for the range studied here (\( \phi = 0.2 - 0.6 \)). For two stage ignition, the first stage energy release also increases with \( \phi \), and the burn rate decreases significantly with decreasing \( \phi \), particularly below \( \phi = 0.4 \).
- The total ignition delay, single or two stage, is correlated with \( n-C_7H_{16}/O_2 \) ratio and not with \( i-C_9H_{18}/O_2 \).
- EGR can have both thermodynamic and chemical effects on ignition.
- The thermodynamic effect of EGR is due to changes in the mixture specific heat \( c_p \). Addition of a diluent with higher \( c_p \) than air will inhibit temperature increases and delay ignition.
- The reduction of \( O_2 \) mole fraction as a result of EGR introduction is a chemical effect that increases ignition delay and occurs regardless of diluent.
- Addition of H_2O as a diluent causes a rapid rise in the concentrations of key species such as OH, HO_2, H_2O_2, and HCO involved in high temperature reactions (that is the temperature where degenerate branching overcomes the first stage reactions) is independent of \( T_{in} \).

This study has identified a number of characteristics of the autoignition of PRF mixtures with varying reactor types and inlet conditions as predicted by the kinetic model. Reproducing experimental HCCI combustion data with CHEMKIN’s IC Engine model is not without difficulty and at this point fails to accurately reproduce the complete measured pressure and temperature profiles. Nonetheless, the material presented here using the model can be useful for identifying mechanisms that affect PRF autoignition.

REFERENCES

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**NOMENCLATURE**

- \( a, b \) Constants in the Woschni correlation
- ATDC After top dead center
- BTDC Before top dead center
- \( C_{11}, C_{12}, C_2 \) Constants in the Woschni correlation
- \( c_p \) Specific heat at constant pressure
- CAD Crank angle degree
- CFR Cooperative fuels research
- \( D \) Cylinder bore
- EGR Exhaust gas recirculation
- EVO Exhaust valve opening
- \( h \) Convective heat transfer coefficient
- IVC Inlet valve closing
- \( k \) Gas thermal conductivity
- \( \lambda \) Air-fuel equivalence ratio
- \( \mu \) Gas viscosity
The construction of kinetic mechanisms to model the autoignition of saturated hydrocarbon fuels closely follows the work of Hu and Keck [1] who have described the general sequence of reactions responsible for two stage ignition as follows.

Reaction is initiated by the abstraction of a hydrogen atom \( H \) from the saturated hydrocarbon molecule \( RH \) forming the alkyl radical \( R \) (C\(_n\)H\(_{2n+1}\)) and HO\(_2\):

\[
RH + O_2 \rightarrow R + HO_2 . \tag{R1}
\]

The main chain cycle is begun with subsequent oxidation of the alkyl radical forming the alkylperoxy radical RO\(_2\):

\[
R + O_2 \leftrightharpoons RO_2 \tag{R2}
\]
which then undergoes internal hydrogen abstraction to produce ROOH:

\[
RO_2 \leftrightharpoons ROOH . \tag{R3}
\]

Oxidation of ROOH ensues by the addition of oxygen to form O\(_2\)ROOH:

\[
ROOH + O_2 \leftrightharpoons O_2ROOH \tag{R4}
\]
which subsequently decomposes irreversibly into OROOH and the hydroxyl radical OH:

\[
O_2ROOH \rightarrow OH + OROOH . \tag{R5}
\]

The cycle is completed when the hydroxyl radical reacts with a fuel molecule producing an alkyl radical and H\(_2\)O:

\[
OH + RH \rightarrow R + H_2O . \tag{R6}
\]

The associated branching reaction is

\[
OROOH \rightarrow ORO + OH . \tag{R7}
\]

Reactions (R1-R7) describe the low temperature kinetic scheme in which the temperature rises rapidly until the competing reaction

\[
R + O_2 \rightarrow \text{olefin} + HO_2 \tag{R8}
\]
becomes faster than (R2) thus terminating the first stage of ignition. (R8) is the mechanism responsible for degenerate branching, which is followed by the reactions

\[
HO_2 + HO_2 \rightarrow HOOH + O_2 \tag{R9}
\]
and

\[
HOOH + M \rightarrow 2OH + M \tag{R10}
\]
where M represents any third body in the system. The branching of hydrogen peroxide HOOH (or H\(_2\)O\(_2\)) to produce 2OH accelerates the reaction into the explosive regime leading to the hot second stage ignition.