IGNITION DELAY TIME EXPERIMENTS FOR NATURAL GAS/HYDROGEN BLENDS
AT ELEVATED Pressures

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ABSTRACT

Applications of natural gases that contain high levels of hydrogen have become a primary interest in the gas turbine market. While the ignition delay times of hydrogen and of the individual hydrocarbons in natural gases can be considered well known, there have been few previous experimental studies into the effects of different levels of hydrogen on the ignition delay times of natural gases at gas turbine conditions. To examine the effects of hydrogen content at gas turbine conditions, shock-tube experiments were performed on nine mixtures of an L9 matrix. The L9 matrix was developed by varying four factors: natural gas higher-order hydrocarbon content of 0, 18.75, or 37.5%; hydrogen content of the total fuel mixture of 30, 60, or 80%; equivalence ratios of 0.3, 0.5, or 1; and pressures of 1, 10, or 30 atm. Temperatures ranged from 1092 K to 1722 K, and all mixtures were diluted in 90% Ar. Correlations for each mixture were developed from the ignition delay times and, using these correlations, a factor sensitivity analysis was performed. It was found that hydrogen played the most significant role in the ignition delay times of a mixture. Pressure was almost as important as hydrogen content, especially as temperature increased. Equivalence ratio was slightly more important than hydrocarbon content of the natural gas, but both were less important than pressure or hydrogen content. Comparison with a modern chemical kinetic model demonstrated that the model captures well the relative impacts of H₂ content, temperature, and pressure, but some improvements are still needed in terms of absolute ignition delay times.

INTRODUCTION

As fuel availability changes, the need for gas turbines with greater fuel flexibility increases. Gas turbine manufacturers would like to determine if current engines are flexible enough to be operated with different, sometimes lower quality, fuels while maintaining safety and mandated pollutant levels. Specifically, natural gases with high levels of hydrogen have recently become of great interest. Gaseous fuels with high levels of hydrogen can come from gasification processes like gasification of coal or biomass. However, introducing a fuel with the possibility of significantly different reactivity from traditional natural gas can lead to issues within the combustor including flashback, blowout, and changes in autoignition of the fuel. Ignition delay times of these mixtures are of primary importance because using a fuel with a significantly different ignition delay time than what is normally used in the engine could lead to ignition of the fuel in the mixer before the primary combustor, or loss of flame stability in the secondary combustor [1, 2].

There is an extensive database of knowledge for the ignition delay time of methane, the primary component of natural gas (NG), at different conditions, as well as for the primary higher-order hydrocarbons found in NG including ethane, propane, butane, and pentane (albeit the quantity of data varies somewhat inversely with the size of the hydrocarbon) [3–14]. Research has also fully characterized the ignition delay time chemistry of hydrogen due to the important role of the H₂–O₂ system in hydrocarbon combustion and due to the importance of hydrogen as a fuel in its own right. A sampling of H₂-related ignition and kinetic studies can be found in Refs. [15–
results is provided next, including correlations developed from the experimental data and a factor sensitivity analysis.

**EXPERIMENT DETAILS**

All experiments were performed behind reflected shock waves in a shock-tube facility. Provided below are details of the facility, followed by an overview of the test matrix that was employed to efficiently cover a wide range of mixtures and conditions with a relatively few number of experiments.

**Shock-Tube Experiment**

Experiments were performed in the high-pressure shock-tube facility described in detail by Aul [23]. The shock tube is made entirely of 304 stainless steel. The driven section is 4.72-m long with an internal diameter of 15.24 cm, and the driver section is 2.46-m long with an internal diameter of 7.62 cm. The large diameter of the driven section allows for experiments to be performed with minimal boundary layer effects. The length of the shock tube allows the observation of ignition delay times of up to 2 ms before any significant pressure drop due to test-ending expansion waves is observed. The inner diameter of the driver section is expanded to the driven section inner diameter through a diverging section located directly after the diaphragm location.

For the experiments, either polycarbonate or aluminum diaphragms were used, depending on the desired experimental pressure. Helium was used as the driver gas, and the driver section was filled slowly until the diaphragm burst to ensure repeatability between experiments. Ultra-high purity (UHP, 99.9995%) gases were used to make the test mixtures containing Ar, O₂, CH₄, C₂H₆, C₃H₈, n-C₄H₁₀, n-C₅H₁₂, and H₂. The two natural gases used in the study were each prepared separately from the main fuel-O₂-Ar mixtures to ensure repeatability with the natural gases used. The natural gases were prepared using the partial pressure method in tanks that were vacuumed below 1×10⁻⁷ Torr. The partial pressure of pentane was kept well below the vapor pressure of pentane to ensure that it was always in the gaseous phase and well mixed in the natural gas mixtures. After the natural gas mixtures were prepared, the mixtures from the test matrix were made. All mixtures from the L9 test matrix (described later) were diluted in 90% argon. Each mixture was made in a mixing tank connected to the shock tube using the partial pressure method.

The conditions at which the combustion event occurs are dictated by the conditions behind the shock wave after it is reflected off the endwall of the driven section of the shock tube. For the shock tube used herein, incident-shock velocity in the test region was found using five, PCB 113 pressure transducers connected to four, Fluke PM 6666 time-interval counters. From these counters, the velocity of the incident shock wave was found. Using this velocity and the standard one-dimensional shock relations, conditions behind the reflected shock wave for each experiment was calculated. Petersen et al. [24] showed that this method is highly reliable and determines reflected-
shock temperatures that are within ±10 K of the actual temperature.

In shock-tube experiments with significant energy release, it is ideal to measure the ignition event from the endwall using the endwall pressure signal [25], as depicted in Fig. 1. In the present experiments, the combustion event was exothermic enough in certain mixtures to produce a significant and measurable rise in pressure, such as shown in Fig. 1. Because of the relatively large inner diameter of the shock-tube driven section (15.24 cm), boundary-layer effects on the test conditions were minimal over the range of the experimental results. Typical pressure increases due to the boundary layer, or \( dP/dt \), were on the order of 1.5% per ms (2% worst case). The pressure signal shown in Fig. 1 is indicative of the typical experiment with minimal \( dP/dt \). This level of pressure increase produces a corresponding temperature increase of about 7 K after 1 ms.

Fig. 1 Ignition delay time measurement from endwall pressure signal. Experiment shown was performed with a mixture of NG3 (Table 2) and 30% H\(_2\) with an equivalence ratio of 1 at conditions of 9.6 atm and 1199 K. The pressure spike at time zero is due to the vibration of the endwall at arrival of the shock wave.

All mixtures herein were diluted in 90% argon and, due to this moderate dilution level, some of the mixtures used were not exothermic enough at all conditions to produce a strong pressure rise at the endwall. In these few cases, the sidewall OH (A→X) (hereafter referred to as OH*) emission was used to determine the ignition delay time per Petersen [25], as shown in Fig. 2. The beginning of the ignition delay time was defined by the sidewall pressure signal, and ignition was indicated by the rise in OH* emission.

Test Matrix

The effect of hydrogen addition to methane and natural gas has been shown to vary with the amount of higher-order hydrocarbons in the natural gas, the equivalence ratio (\( \phi \)), and the pressure. However, putting together a test program that covers the desired range of pressures, %H\(_2\), stoichiometry, and fuel blend could prove daunting due to the large number of conceivable combinations. As aforementioned, the preferred approach was to design an experiment that covered the desired range of conditions. A test matrix was therefore developed to test these different aspects in an organized yet efficient manner. Three levels of each variable were assembled into the L9 Taguchi array [26], shown in Table 1. The specific mole fractions for the NG2 and NG3 blends are provided in Table 2.

As seen in Table 1, the four independent variables, or factor, selected were fuel (CH\(_4\), NG2, NG3); percent H\(_2\) in the fuel (30, 60, 80 by volume); the equivalence ratio (0.3, 0.5, 1.0); and the target pressure (1, 10, 30 atm). Note that the NG2 and NG3 fuel blends are based on the blends used by the authors in previous work [2, 3]. Of course, temperature is perhaps the most important variable with regard to its effect on the ignition delay time, so this variable was not included in the matrix but rather was changed over its practical, possible range for each mixture, within the limits of the shock-tube test time. Experiments were performed for each combination at the designated pressure and at 9–20 different temperatures. The temperature ranges were varied to obtain ignition delay times from around 100 μs to 2 ms for each combination. As mentioned above, each of the Table 1 mixtures was diluted in 90% Ar, by volume.
Table 1 L9 test matrix developed using the Taguchi method for balanced, orthogonal arrays [26]. Three levels of each factor were used. NG2 and NG3 are defined in Table 2.

<table>
<thead>
<tr>
<th>Combo</th>
<th>Fuel</th>
<th>%H₂</th>
<th>φ</th>
<th>P (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₄</td>
<td>30</td>
<td>0.3</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>CH₄</td>
<td>60</td>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>CH₄</td>
<td>80</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>NG2</td>
<td>30</td>
<td>0.5</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>NG2</td>
<td>60</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>NG2</td>
<td>80</td>
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<tr>
<td>7</td>
<td>NG3</td>
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<td>10</td>
</tr>
<tr>
<td>8</td>
<td>NG3</td>
<td>60</td>
<td>0.3</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>NG3</td>
<td>80</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2 Fuel mixture compositions in percent volume.

<table>
<thead>
<tr>
<th>Species</th>
<th>CH₄</th>
<th>NG2</th>
<th>NG3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>100</td>
<td>81.25</td>
<td>62.5</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0</td>
<td>10.00</td>
<td>20.0</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>0</td>
<td>5.00</td>
<td>10.0</td>
</tr>
<tr>
<td>nC₄H₁₀</td>
<td>0</td>
<td>2.50</td>
<td>5.0</td>
</tr>
<tr>
<td>nC₅H₁₂</td>
<td>0</td>
<td>1.25</td>
<td>2.5</td>
</tr>
</tbody>
</table>

KINETIC MODEL

A single chemical kinetics mechanism was utilized for the calculations in this work. It is based on the hierarchical nature of combustion mechanisms. The H₂/CO/O₂ sub-mechanism is based on the work of O Conaire et al. [15] with several significant updates based on recent experimental and kinetic data. The changes are partially described in Kéromnès et al. [27] and are fully detailed in an upcoming separate publication [18]. The C₁–C₃ sub-mechanisms are based on previous work by the authors [28] with the most recent refinements described in Metcalfe et al. [29]. As for the updated H₂/CO sub-mechanism, the final mechanism is described in detail in a manuscript published elsewhere [30]. The butane and pentane sub-mechanisms are unchanged from the authors’ previous work [4].

RESULTS

Experiments were performed for each of the 9 combinations at the designated pressure and at least nine different temperatures for each combination. The temperature ranges were varied to obtain ignition delay times from around 100 µs to 2 ms for each combination. The experimental data and conditions are listed for each combination of the L9 matrix in the appendix. The experimental ignition delay times are compared in each figure to ignition delay times predicted by the Galway mechanism. This comparison between the model and the experimental results shows areas where the model performs well and where improvement of the model could be implemented. The datasets are presented in the order of the test matrix. After each of the three combinations from the same base natural gas (i.e. methane, NG2, or NG3), the three combinations are plotted together to draw further conclusions. All ignition delay times are plotted on a base 10-logarithmic scale as a function of the inverse of the temperature.

Ignition delay times for combinations 1, 2, and 3 are plotted in Fig. 3. The reactivity appears to increase from combination 1 to combination 2 and then from combination 2 to combination 3. Additionally, combination 1 is much less reactive than both combinations 2 and 3, which are similar in reactivity to each other. The trends all appear to be linear with inverse temperature on the log plot, both for the data and the model. Combination 3 appears to be the most-significantly under predicted combination, while only combination 1 is over predicted by the model. Due to the nature of the experimental matrix, conclusions on which single factor influences the reactivity of the methane fuels cannot be made from just looking at the first three combinations since more than one parameter was changed between each combination. However, such details can be inferred after analyzing the results of the entire L9 matrix. As seen in Fig. 3, the model tends to overpredict the ignition delay time for Combination 1 (30% H₂, φ = 0.3, 1 atm) by about 20-30%.

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Measured and calculated ignition delay times for combinations 4, 5, and 6 are plotted together in Fig. 4. Combination 5 appears to be the least-reactive combination, while combination 6 is the most reactive. The trends of combinations 4 and 5 appear to be purely linear, while the slope of the linear trend of combination 6 changes around 1150 K. The order of reactivity of the combinations follows decreasing order of equivalence ratio, indicating that equivalence ratio could play a significant role for these combinations. However, since this variable is not the only factor changing between combinations 4, 5, and 6, a factor sensitivity analysis was performed to find the factor that is playing the most significant role, as shown later. The Galway model does fairly well at predicting the data for these three combinations, although it does under-predict the ignition delay time at the higher temperature seen in combination 6.

![Fig. 4 Ignition delay times from NG2-based combinations 4 (30% H₂, Φ = 0.5, 30 atm), 5 (60% H₂, Φ = 1.0, 1 atm), and 6 (80% H₂, Φ = 0.3, 10 atm) are plotted as a function of the inverse of temperature. Model predictions for each combination are plotted as lines.](image)

The ignition delay times for all three combinations containing NG3 (combinations 7 through 9) are shown in Fig. 5. One noticeable feature seen in this figure is that two of the combinations, 8 and 9, have overlapping ignition delay times. Combination 9 is seen to cross over combination 8. Additionally, combination 7 is seen to be significantly less reactive than the other two combinations. Although the kinetic model under predicts all of the data for the NG3 combinations, the relative trends are nonetheless accurately predicted. For example, in the model predictions, combination 9 is seen to cross combination 8, and combination 7 is significantly less reactive than the other two combinations.

**DISCUSSION AND ANALYSIS**

Using the chemical kinetics model that has been demonstrated above to perform rather well over the range of conditions, a sensitivity analysis was conducted to identify the important reactions for promoting and inhibiting the ignition process. Further analysis of the results was performed in an attempt to determine which factor (natural gas composition, H₂ content of the fuel mixture, equivalence ratio, or pressure) played the largest role in the ignition delay times of the combinations studied. In subsections below, experimental correlations are developed for each individual combination and for each set of three combinations (based on the natural gas of the combination). Then, a factor sensitivity analysis on the L9 matrix using the correlations developed for each combination is discussed.

![Fig. 5 Ignition delay times from NG3-based combinations 7 (30% H₂, Φ = 1.0, 10 atm), 8 (60% H₂, Φ = 0.3, 30 atm), and 9 (80% H₂, Φ = 0.5, 1 atm) are plotted as a function of the inverse of temperature. Model predictions for each combination are plotted as lines.](image)

**Sensitivity Analysis**

A sensitivity analysis was performed for mixtures 2, 4, and 9, all at a fuel/air ratio of 0.5, and at a temperature of 1250 K. Each reaction was tested by multiplying \((k^+)^n\) and dividing \((k^-)^m\) both the forward and reverse rate constant by a factor of two, without affecting the equilibrium, and recording the resulting ignition delay time \((τ^+\text{ and } τ^-)\). The logarithmic sensitivity coefficient, \(S\), is then defined as:

\[
\ln S = \frac{\ln(τ^+/τ^-)}{\ln(k^+/k^-)} = \frac{\ln(τ^+) - \ln(τ^-)}{\ln(4)}
\]

A positive sensitivity coefficient is one in which the ignition delay time increases and thus corresponds to a decrease in ignition delay time, Fig. 6, while a negative sensitivity coefficient corresponds to a decrease in ignition time and thus an increase in reactivity, Fig. 7.

Combination 2 comprises 40% CH₄ with 60% H₂ as the fuel at a pressure of 10 atm, mix 4 comprises 30% H₂ and 70% NG2 at 30 atm, and mix 9 comprises 80% H₂ and 20% NG3 at 1 atm. Each of these three matrix combinations for the analysis were with Φ = 0.5. Under these conditions, similar reactions dominate the reaction kinetics controlling ignition delay time predictions, but these reactions have different relative...
sensitivities depending on the mixture. In general, mixtures 2 and 9 contain more hydrogen fuel relative to methane and thus hydrogen-atom kinetics dominate, whereas methane is high in concentration compared to hydrogen in mix 4, and thus methyl radical chemistry is relatively more important compared to combos 2 and 9.

The most important reaction promoting reactivity for all mixtures is the main, high-temperature chain branching reaction $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$, Fig. 7, and it can be stated that any reaction that competes for or reduces the concentration of hydrogen atoms will lead to a reduction in reactivity and a positive sensitivity coefficient. The next most important reaction promoting reactivity for mix 2 is the reaction of hydrogen with hydroxyl radicals $\text{H}_2 + \text{OH} \rightleftharpoons \text{H} + \text{H}_2\text{O}$. Under these conditions of temperature and pressure, 1250 K and 10 atm, hydroperoxyl radical chemistry is important, due to the reaction $\text{H} + \text{O}_2 (+\text{M}) \rightleftharpoons \text{HO}_2 (+\text{M})$. The HO$_2$ so formed abstracts a hydrogen atom for another molecule to generate hydrogen peroxide (H$_2$O$_2$) which decomposes to two hydroxyl (OH) radicals.

The reaction which most inhibits reactivity for all mixtures is the reaction of methane with a hydroxyl radical, $\text{CH}_4 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O}$, Fig. 6, as this step competes with the reaction of hydroxyl radicals with hydrogen fuel, producing less-reactive methyl radicals compared to reactive hydrogen atoms.

Similarly, the reaction of oxygen atoms with molecular hydrogen ($\text{H}_2 + \text{O} \rightleftharpoons \text{H} + \text{OH}$) promotes reactivity as it produces a hydrogen atom and a hydroxyl radical, but the reaction of an oxygen atom with methane ($\text{CH}_4 + \text{O} \rightleftharpoons \text{CH}_3 + \text{OH}$) inhibits reactivity as its rate is increased relative to reaction with hydrogen, reducing the concentration of hydrogen atoms in the system.

The second most-inhibiting reaction for combination 2 is the recombination of a methyl radical with a hydrogen atom, $\text{CH}_3 + \text{H} (+\text{M}) \rightleftharpoons \text{CH}_4 (+\text{M})$, which consumes two radicals and reproduces stable methane and also consumes hydrogen atoms in the process. Similarly, the recombination of two methyl radicals ($\text{CH}_3 + \text{CH}_3 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_6 (+\text{M})$) reduces reactivity as it consumes two radicals producing a stable molecule. This reaction shows a higher sensitivity to mix 4 compared to mix 2 and 9, since mix 2 contains the highest concentration of methane.

The reaction of methyl radicals with hydroperoxyl radicals can either promote ($\text{CH}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{OH}$) or reduce ($\text{CH}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_4 + \text{O}_2$) reactivity depending on whether radicals, produced in the former reaction, or stable molecules, produced in the latter reaction, are generated. For mix 4 with a relatively high concentration of methane, these reactions are more prominent than for combos 2 and 9, where hydrogen comprises a large part of the fuel component.

For mixture 9, which contains the highest concentrations of larger hydrocarbons, ethyl radical chemistry shows some importance. Ethane, propane, and butane all react with a hydrogen atom, reactions which compete with hydrogen atoms with molecular oxygen in the main chain-branching reaction ($\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$), and these reactions all show positive sensitivity coefficients, reducing reactivity. Hydrogen atom abstraction by a hydrogen atom from ethane produces an ethyl radical, and also the decomposition of the radicals produced by hydrogen atom abstraction for propane and butane also produce ethyl radicals. Ethyl radical decomposition to ethylene and a hydrogen atom promote reactivity, as it produces a hydrogen atom but also generates ethylene which undergoes hydrogen atom abstraction generating vinyl radicals which react with molecular oxygen forming two radicals in a chain-branching process ($\text{C}_2\text{H}_5 + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_4\text{CHO} + \text{O}$), Fig. 7.

The reaction of an ethyl radical with a hydrogen atom generating two ethyl radicals, $\text{C}_2\text{H}_5 + \text{H} = \text{C}_2\text{H}_3 + \text{CH}_3$, shows a high positive sensitivity coefficient for combination 9, Fig. 6.
This reaction consumes one hydrogen atom and prevents the generation of another \((\text{C}_2\text{H}_3 (+\text{M}) = \text{C}_2\text{H}_4 + \text{H (M)})\).

Other reactions either promoting or reducing reactivity can be easily explained by the consumption of radical species generating stable molecules or by a competition between the formation of a hydrogen atom, which is promoting, or another radical such as methyl, which inhibits reactivity due to the overshooting sensitivity of ignition delay times to the main chain branching reaction \(\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}\) under these conditions.

**Correlations**

To further understand the trends within the data and to provide a means of predicting ignition delay times outside of the data set without the use of the detailed mechanism, correlations were developed. These correlations for each individual combination were derived using Eqn. 1. In this equation, \(\tau_{\text{ign}}\) is the ignition delay time, \(A\) is the correlation constant, \(E\) is an ignition activation energy of the combination in kcal/mol, \(R\) is the universal gas constant in units of kcal/mol-K, and \(T\) is the temperature in K.

\[
\tau_{\text{ign}} = A \exp \left( \frac{E}{RT} \right)
\]

Three separate correlations were developed for each set of 3 combinations that contained each natural gas (CH\(_2\), NG2, or NG3). These correlations are described in further detail in each subsection for that natural gas below and are generally of the form of Eqn. 2.

\[
\tau_{\text{ign}} = A[\text{NG}]^x[\text{H}_2]^y[\text{O}_2]^z \exp \left( \frac{E}{RT} \right)
\]

In Eqn. 2, \(\text{NG}\) indicates the natural gas common to the set of three combinations, \([\ ]\) indicates the concentration of the species inside the brackets in mol/cm\(^3\), and \(x\), \(y\), and \(z\) are empirically derived correlation exponents.

Using Eqn. 1, individual correlations were found for combinations 1 through 3. The values for \(A\) and \(E\) for each combination are listed in Table 3. The activation energies of the combinations are seen to increase from combinations 1 to 3. This trend implies increasing reactivity in the combinations, which was seen in the experimental results. Each correlation is provided in Fig. 8 for the first 3 L9 matrix combinations, in comparison with their respective experimental data points.

After the correlations for the individual combinations were found, a correlation for the natural gas set was obtained, using the form shown in Eqn. 2. This multiple-combination correlation is described in Table 4 for the first 3 combinations.
Although this correlation has a coefficient of multiple determination, $R^2$, value above 0.9, the exponents $x$, $y$, and $z$ are quite large. Generally, the absolute value of exponents of a correlation of this form should be on the order of 1 or less. Since the exponents in this case are so large, it is possible that some factor, like pressure or $\phi$, is over specified. Due to this potentially misleading result, other forms of the correlation were explored using different variables to describe the combinations. The correlation that ultimately gave the most physically realistic exponents was of the form of Eqn. 3.

$$\tau_{ign} = A[CH_4]^x[H_2]^y[Ar]^z\phi^w \exp\left(\frac{E}{RT}\right)$$  \hspace{1cm} (3)

In this equation, $x$, $y$, $z$, and $w$ are the empirically derived correlation exponents that describe the contribution of each aspect on the ignition delay time, and $\phi$ is the equivalence ratio of the combination. The new values for the coefficients are listed in Table 5, and Fig. 8 shows how Eqn. 3 compares with the ignition delay time data for the first 3 combinations. Note how the combination correlation agrees very well with the individual correlations for each Combo, as well as with the data.

Table 5 Correlation for combinations 1-3, utilizing Eqn. 3.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>w</th>
<th>E</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$6.37 \times 10^{-9}$</td>
<td>0.0</td>
<td>-2.32</td>
<td>1.9</td>
<td>3.1</td>
<td>34.2</td>
<td>0.962</td>
</tr>
</tbody>
</table>

This correlation describes a few features of combinations 1 through 3. First, since the exponent $x$ is zero, the effect of the concentration of methane on the reactivity is negligible. This result is likely because changes in the methane concentration are a function of the concentrations of the other species. The negative sign for the exponent that corresponds to the concentration of hydrogen, $y$, indicates that increasing the hydrogen concentration decreases the ignition delay time. This effect of the $H_2$ was expected as the reactivity of hydrogen is much higher than that of methane. Since the argon dilution was the same for each combination, the effect of the argon concentration can be used as an indication of the effect of the ratio of pressure and temperature. The positive exponent for argon concentration, $z$, implies that as the ratio between pressure and temperature decreases, ignition delay time decreases. Similarly, the positive exponent for the equivalence ratio, $w$, indicates that the ignition delay time decreases as equivalence ratio decreases.

Next, correlations were developed for the NG2 combinations. Individual correlations were developed for combinations 4 through 6 using Eqn. 1. The correlation constants ($A$) and activation energies ($E$) for each of these correlations are listed in Table 3. Unlike combinations 1 through 3, the activation energy of the combinations 4-6 is not seen to increase with the increase of any specific factor (hydrogen, pressure, or equivalence ratio). This shifting activation energy indicates that these combinations are exhibiting a more complex relationship between the three different factors than the methane combinations. This result shows the benefit of using an L9 matrix to capture complex effects of combination variation since more than one value is changing between each experiment. Figure 9 plots each of the individual correlations against the experimental data; the goodness of fit for each correlation is evident from the graph.

In addition, a correlation using Eqn. 2 was developed for these three combinations. This multiple-combination correlation is described in Table 4. The coefficients derived for the correlation of combinations 4 through 6 are significantly closer to unity than the coefficients derived for the initial correlation of combinations 1 through 3. Due to this favorable result, no other correlation attempts were performed. Figure 9 provides the predictions from the master correlation for the combinations 4–6, in comparison with the data and with the individual correlations. Again, the goodness of fit for the overall correlation for the NG2 results is evident in Fig. 9.

From the correlation for NG2 (Combos 4–6) described in Table 4, a few trends in these combinations can be observed. First, the two negative coefficients, $x$ and $y$, indicate that the ignition delay time decreases as the concentrations of both NG2 and hydrogen increase. The larger exponent for the hydrogen concentration indicates that small changes in the concentration of hydrogen will affect the ignition delay time more than small changes in the concentration of NG2. The positive exponent for the oxygen concentration, $z$, indicates that as the concentration...
of oxygen increases the ignition delay time will also increase. The $R^2$ value for this correlation is higher than for the previous combination set, which shows that it will likely do a better job of predicting ignition delay times for these combinations, even outside of the experimental conditions tested, although extrapolation of the correlations beyond their stated range of applicability is discouraged.

Finally, correlations were developed for the NG3 correlations. Individual correlations were developed first for combinations 7 through 9. The correlation coefficients ($A$) and activation energies ($E$) for these correlations are listed in Table 3. The activation energies in this case increase with pressure. This trend with pressure indicates that, for these combinations, pressure likely plays a significant role on the reactivity of the combination. Calculations using the three individual correlations for Combos 7–9 are presented in Fig. 10, in comparison with the experimental data.

![Fig. 10 Data from combinations 7 through 9 (Table 1) are compared to the individual correlations (Eqn. 1, Table 3) for each combination, and the correlation for combinations 7 through 9 (Eqn. 2, Table 4).](image)

Additionally, a master correlation using the data from all three combinations 7–9 was developed using Eqn. 2. The coefficients for this correlation are shown in Table 4, and the results of the correlation are compared with the experimental data and the individual correlations in Fig. 10. The coefficients that were found for the correlation of combinations 7 through 9 were close to or less than unity, so no further correlations were attempted. The correlation described in Table 4 for NG3 (Combs 7–9) indicates a few trends in combinations 7 through 9. First, unlike the previous correlation for combinations 4 through 6, the coefficient for the natural gas (NG3), $x$, is positive. This outcome could indicate that the ignition delay times decrease with decreasing NG3 concentration (and increasing H$_2$ concentration). Similar to the previous multiple-

combination correlations, the coefficient for hydrogen concentration, $y$, is negative, while the coefficient for oxygen concentration, $z$, is positive. Therefore, the ignition delay time will decrease with increasing hydrogen concentration, and the ignition delay time will increase as the oxygen concentration increases. Additionally, the hydrogen concentration has the largest coefficient, so it is likely that hydrogen concentration will play the largest role in determining the ignition delay time of the combinations.

**Factor Sensitivity**

A factor sensitivity analysis was performed on the results from the L9 matrix to determine which aspect of the combinations plays the largest role in reactivity. By utilizing the L9 Matrix in this manner, fewer experiments can be performed to gain the same information. The four factors considered for the sensitivity analysis were $C_{2s}$ (hydrocarbons higher than methane) content of the natural gas, hydrogen percentage of the fuel, equivalence ratio, and pressure.

The correlations for each individual combination (described above) were used to predict ignition delay times for each combination at four different temperatures: 1100 K, 1150 K, 1200 K, and 1250 K. These correlations were used because it was found that for every combination, the single combination correlations very accurately described the data, usually without the risk of over or under prediction of the ignition delay time outside of the experimental temperature range.

Figure 11 shows a factor sensitivity analysis for predicted ignition delay times of the full L9 matrix. This analysis indicates that the hydrogen content of the fuel mixture is the most important factor. It was not unexpected that hydrogen would play a significant role in determining the reactivity of these combinations because hydrogen reactivity is known to be significantly higher than for hydrocarbons at the same conditions. The second most important factor in the matrix studied was pressure. The effect of pressure is seen to increase as temperature increases and is nearly as important as hydrogen content at the highest temperature. This level of importance was expected since, for all of the base components of the combinations, variations in pressure have been shown to greatly affect the ignition delay time.

Equivalence ratio was a moderately significant factor in the matrix studied. Although the effect was not negligible, equivalence ratio did not affect the reactivity of the combinations as strongly as hydrogen content or pressure. The effect of equivalence ratio at lean conditions is due to the increased importance of oxygen for chain branching kinetics. However, this effect is also closely linked to the effects of pressure and composition of the fuel mixture.

Finally, the $C_{2s}$ fraction of natural gas was seen to have the smallest effect on the ignition delay times. However, the effect was not negligible. This smaller effect was expected since the reactivities of the different natural gases used in this matrix were relatively similar when compared to the reactivity of hydrogen. However, the effect of $C_{2s}$ content of the natural gas
increased relative to the effects of the other factors with temperature. This result is likely due to the fact that ignition delay times of methane decrease as temperature increases at a much slower rate than NG2 or NG3 ignition delay times [3].

found that hydrogen played the most significant role, and pressure played an important role that was only slightly smaller than the role of hydrogen, especially as temperature increased. The effect of higher-order hydrocarbon content on ignition delay times was moderate and always less than the effects of pressure or hydrogen content. Equivalence ratio was seen to have the smallest effect on ignition delay time but was not negligible.

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