ABSTRACT
Applications of natural gas and hydrogen co-firing have received increased attention in the gas turbine market, which aims at higher flexibility due to concerns over the availability of fuels. While much work has been done in the development of a fuels database and corresponding chemical kinetics mechanism for natural gas mixtures, there are nonetheless few if any data for mixtures with high levels of hydrogen at conditions of interest to gas turbines. The focus of the present paper is on gas turbine engines with primary and secondary reaction zones as represented in the Alstom and Rolls Royce product portfolio.

The present effort includes a parametric study, a gas turbine model study, and turbulent flame speed predictions. Using a highly optimized chemical kinetics mechanism, ignition delay times and laminar burning velocities were calculated for fuels from pure methane to pure hydrogen and with natural gas/hydrogen mixtures. A wide range of engine-relevant conditions were studied: pressures from 1 to 30 atm, flame temperatures from 1600 to 2200 K, primary combustor inlet temperature from 300 to 900 K, and secondary combustor inlet temperatures from 900 to 1400 K. Hydrogen addition was found to increase the reactivity of hydrocarbon fuels at all conditions by increasing the laminar flame speed and decreasing the ignition delay time. Predictions of turbulent flame speeds from the laminar flame speeds show that hydrogen addition affects the reactivity more when turbulence is considered. This combined effort of industrial and university partners brings together the know-how of applied, as well as experimental and theoretical disciplines.

INTRODUCTION
As variations in fuel compositions are expected to increase, applications of natural gas and hydrogen co-firing are receiving increased attention in the gas turbine market. Higher fuel flexibility of gas turbines is important as fuel availability changes. Additionally, with hydrogen co-firing, reduced CO₂ emissions can be achieved due to the lower carbon content of the fuel. Natural gases that are hydrogen-rich can be derived from the gasification of coal or biomass and are characterized by increased reactivity when compared to natural gas without hydrogen [1,2].

The reheat concept, described in [3], which is used in Alstom’s GT24/GT26 gas turbines, offers a pathway to ultralow emissions, high efficiency, and high flexibility. In this system, two combustors, separated by a high-pressure turbine stage, are arranged in series: a primary annular combustor with premix burners (environmental (EV) burner), is followed by an annular reheat combustor equipped with sequential environmental (SEV) burners in the secondary combustion stage which is shown in Fig. 1 [1].
The high efficiency and flexibility provided by serial combustion is also used in the Rolls-Royce RB211 DLE engine (Fig. 2). The RB211 DLE is a lean premix aero-derivative gas turbine equipped with nine can annular combustors positioned around the engine centerline (Fig. 2). Similar to the reheat concept, the design philosophy is to arrange combustion processes in series. The function of the upstream or primary stage is to create combustion stability with a zone temperature held constant at a minimum margin above weak extinction and stability. The downstream or secondary stage benefits from the hot exhaust of the primary stage, thus enabling the use of much leaner premixed air-fuel mixtures without stability issues or excessive CO production. Moreover, combustion processes occur away from the cool walls preventing quenching phenomena despite the use of conventional, low-cost film cooling.

The study of fuel reactivity is used to find operation conditions that allow the inherently high flexibility of the GT24/GT26 and RB211 DLE engines to extend the acceptable fuel range even further. For this approach, the stability limits of the two burners have to be tested. In general, the operation range of a premixed burner is determined by flame loss following blow out on the low reactivity side and by flashback on the high reactivity side, when the flame approaches the burner parts and increases the heat load. For the primary burners, in which reactivities are determined by the conditions of the flame propagation mechanism, the lowest reactivities occur for lean conditions and highest reactivities for rich conditions. The secondary stage burners of both engines are based on autoignition of the fuel and are therefore more sensitive to the inlet conditions than to the equivalence ratio or the product range of the combustion process [3]. Autoignition is the spontaneous, homogeneous ignition of the fuel-air mixture. The time for a mixture to reach autoignition is referred to as the ignition delay time ($t_{\text{ign}}$), which is heavily dependent on the reactivity of the mixture.

Both processes are naturally also dependent on the fuel composition, which affects the chemical kinetics and the required fuel flow rate in the fuel injection systems to achieve a target heat rate. The laminar reactivities, and to some degree the turbulent reactivities, of a specific fuel composition can be predicted and used to propose operating conditions for GT engines.

The lower end of the reactivity scale for both primary combustors is determined by a minimum reactivity, which can be estimated by the laminar flame speed or burning velocity ($S_{\text{L}}$). As a fuel decreases in reactivity, $S_{\text{L}}$ decreases and blowout can destabilize the flame. On the high reactivity end, increased reactivity, induced by either the fuel/air ratio of the inlet conditions or the fuel composition, brings the heat release zone too close to the burner and fuel injectors. Additionally, the reactivity of the fuel in the primary burners is controlled by transport of species across the flame front and kinetic rates at high temperatures. Due to this sensitivity to temperature, the flame temperature of the primary burners is more important than the inlet temperature when the reactivity of the fuel is changed.

In the mixing zone of the GT24/GT26 SEV burner, fuel is injected into the exhaust gases from the primary burners, which are at temperatures greater than 1000 K [1]. This high inlet temperature places the fuel injected into the secondary burners into the autoignition regime because chemical rates are high enough for combustion to occur without additional diffusion of radicals and heat. This mechanism also applies for the RB211 secondary stage. However, the temperature of the combustion gases into which fresh fuel and air are introduced is a few hundred degrees higher and therefore autoignition will occur significantly faster in the RB211 secondary stage than in the GT24/GT26 SEV burner.

Additionally, the $t_{\text{ign}}$ of the fuel changes with reactivity. At the low reactivity end, the SEV burner and, to a lesser extent, the RB211 secondary stage exhibit increased CO emissions due to increased ignition delay times and insufficient time for CO-burnout within the combustor residence time. Nevertheless, even at low reactivity both secondary burners do not completely lose their flame in a single event as is common for premix flames like those in the primary burners. It rather gradually switches into a regime of partial oxidation where
most of the heat release still takes place within the combustor. The ignition delay time of the fuel also changes with inlet temperature. One benefit of serially staged combustion systems is that the inlet temperature of the secondary stage can be tailored to the reactivity of the fuel at similar hot gas temperature.

The reactivity of methane has been studied extensively at gas turbine conditions, and the flame speed and ignition delay time of this fuel can be considered well known [4, 5]. Additionally, several studies have been performed to determine the flame speeds [6, 7] and ignition delay times [7, 8, 9] of different methane-based fuels that simulate natural gas. The reactivity of hydrogen has also been extensively studied [1, 10]. Several studies have been performed on the reactivity of methane/hydrogen mixtures [11, 12] as well as natural gas/hydrogen mixtures [13, 14]. However, most studies have covered conditions only up to 20% hydrogen addition. It has been found that adding hydrogen increases the reactivity of the mixture (for a constant flame temperature) by either increasing $S_L$ or decreasing $\tau_{\text{ign}}$. Calculations of laminar burning velocities for methane mixtures with higher contents of hydrogen were conducted by Sarli et al. [15]. Chemical kinetic calculations predicted a drastic increase in laminar burning velocity for a hydrogen content of larger than 50%. However, calculations were only performed at 300 K and 1 atm.

To add to the existing fuels database with a corresponding chemical kinetics mechanism for natural gas mixtures, this paper addresses the topic of ignition delay times and laminar burning velocities of fuels from pure methane to pure hydrogen and natural gas/hydrogen mixtures of varying concentrations of higher hydrocarbons. Using a robust chemical kinetic mechanism [16], calculations have been performed over a wide range of pressure, inlet temperature, flame temperature, and equivalence ratio, at levels relevant to gas turbine applications. Two sets of calculations were performed: a parametric study and a study utilizing a gas turbine model developed by the authors. Both studies examined methane and NG2, detailed in Table 1, to which 0 – 100% hydrogen was added. For this range of fuels, calculations of laminar flame speeds and ignition delay times were performed at pressures between 1 and 30 atm, with varying inlet temperature, flame temperature, and equivalence ratio. Further explanation of the chemical kinetics model used for the calculations is presented followed by detailed explanations of the parametric study and the gas turbine model study. The results from these calculations are presented followed by a brief analysis of the effects of hydrogen addition on turbulent flame speed. The most relevant experiments to perform for validation purposes are then discussed. No study found in the literature has performed calculations on such a wide range of gas turbine relevant conditions with fuels containing such a large concentration of hydrogen.

### CHEMICAL KINETICS MODEL

The detailed chemical kinetic mechanism utilized in this work is under constant development and optimization at the Combustion Chemistry Centre [16]. It is based on the hierarchical nature of combustion mechanisms. The H$_2$/CO/O$_2$ sub-mechanism is based on the work of P Conaïre et al. [17] with several significant updates based on recent experimental and kinetic data. The changes are partially described in Kéromnès et al. [18] and are fully detailed in an upcoming separate publication [19]. The C1–C3 sub-mechanisms are based on our previous work [20, 21] with the most recent refinements described in Metcalfe et al. [22]. The chemistry of some important unsaturated species including 1,3-butadiene, propene and allene are taken from Laskin et al. [23], primarily based on the earlier work of Davis and law [24]. The butane and pentane sub-mechanisms are unchanged from the authors’ previous work [21].

### PART 1: PARAMETRIC CALCULATIONS

A parametric study was performed on the effect of H$_2$ addition to pure methane and NG2 to investigate the effect on laminar flame speed and ignition delay time. A brief overview of the simulations is provided first followed by a summary of results obtained for the laminar flame speed simulations and for the ignition delay time simulations. The composition of NG2, detailed in Table 1, is predominantly methane with smaller concentrations of higher hydrocarbons.

The mechanism utilized in this work is denoted C5_54.1 and contains 316 species and 1799 reactions. This mechanism is thoroughly validated against ignition delay time, laminar flame speed, and speciation measurements at gas turbine conditions, as mentioned above. The mechanism is of considerable size as it contains the full, low-temperature chemistry. To increase computational efficiency, all flame speed calculations were performed with a high-temperature version of the mechanism, from which all the low-temperature species (peroxy radicals, alkyl hydroperoxides, ketohydroperoxides etc.) and their reactions were removed. The high-temperature version of the mechanism contains 188 species and 1267 reactions.

#### Table 1 NG2 composition used in the parametric study in percent volume.

<table>
<thead>
<tr>
<th>NG2 Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>81.25%</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>10.00%</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>5.00%</td>
</tr>
<tr>
<td>nC$<em>4$H$</em>{10}$</td>
<td>2.5%</td>
</tr>
<tr>
<td>nC$<em>5$H$</em>{10}$</td>
<td>1.25%</td>
</tr>
</tbody>
</table>

**Laminar Flame Speed Simulation** Flame speed simulations were performed for pure methane and NG2 in synthetic air (oxygen-to-nitrogen ratio of 1:3.76) with 5, 50, 70, 80, and 90% H$_2$ addition. Simulations of pure hydrogen were also performed. The equivalence ratios ($\phi$) of the mixtures were 0.5 $\leq \phi \leq$ 3.0, with primary stage initial temperatures ($T_{\text{in, p1}}$) between 300 and 900 K and initial pressures ($P_i$) from 1.0 to 35 atm. All simulations were performed with the Premix module of Chemkin Pro [25] with solutions converged to approximately...
800 grid points, essentially providing a grid-independent solution. Mixture-averaged transport equations were utilized instead of the multi-component description to reduce computational cost. Mixture-averaged transport simulations took an average of 82% less time than multi-component simulations with an average difference in laminar flame speed of only 1.7%.

Ignition Delay Time Simulations Ignition delay time simulations were also performed for CH₄/NG2 in air. Hydrogen concentrations included 0, 5, 50, 70, 90, and 100% by volume. The same pressure and equivalence ratio variations as the flame speed simulations were performed, with secondary stage initial temperatures (T_in_2nd) between 900 and 1400 K. Ignition delay time was defined as the time when the change of pressure with time reached a maximum (dP/dt=maximum). Simulations were performed with the Aurora module of Chemkin Pro.

Laminar Flame Speed Results
A selection of results from the flame speed analysis is plotted in Fig. 3 –Fig. 6. Fig. 3 depicts experimental measurements [7] of pure methane and NG2 and is included to show the excellent performance of the model under atmospheric conditions and to highlight the similarities between the flame speeds of pure methane and NG2. In Fig. 4 and Fig. 5, the results are shown for several different mixtures containing CH₄ and NG2, respectively. From these figures, it can be seen that, for both CH₄ mixtures and NG2 mixtures, the S_l increases with H₂ content, decreasing pressure, and increasing inlet temperature. Additionally, it can be seen that most mixtures have peak reactivity at equivalence ratios that are slightly richer than stoichiometric, as expected. However, for the pure-H₂ mixtures, this peak is seen to be more of a plateau for all rich mixtures. Fig. 6 shows the effect of H₂ addition on the normalized S_l of both CH₄ and NG2 mixtures with different equivalence ratios at constant T_in_1st and P_i. It can be seen that H₂ addition has a greater effect on increasing the reactivity of CH₄ compared to NG2, and that rich mixtures have higher reactivity than lean mixtures, especially with a large H₂ mole fraction.

![Fig. 3 Laminar flame speed of CH₄/Air [20] and NG2/Air [7] at atmospheric conditions. Symbols are experimental data, lines are simulations.](image)

![Fig. 4 Sample of results of parametric flame speed study of CH₄ with varying H₂ additions. Color dictates % H₂ (black: 0%, red: 5%, green: 50%, tan: 70%, blue: 100%). Line type dictates pressure and inlet temperature (Solid: 15 atm, 300 K; Dashed: 15 atm, 600 K; Dotted: 35 atm, 600 K; Dot Dash: 15 atm, 900 K).](image)

![Fig. 5 Sample of results of parametric flame speed study of NG2 with varying H₂ additions. Color dictates % H₂ (black: 0%, red: 5%, green: 50%, tan: 70%, blue: 100%). Line type dictates pressure and inlet temperature.](image)
temperature (Solid: 15 atm, 300 K; Dashed: 15 atm, 600 K; Dotted: 35 atm, 600 K; Dot Dash: 15 atm, 900 K).

Fig. 6 Effect of H₂ addition to the normalized laminar flame speed of CH₄ and NG2. Tₐₘ₃; P₁ = constant. Color indicates CH₄ (black) or NG2 (red). Line dictates equivalence ratio (Solid: ϕ = 0.5; Dashed: ϕ = 0.7; Dotted: ϕ = 1.1; Dot Dash: ϕ = 1.5).

Ignition Delay Time Results
A selection of results from the ignition delay time analysis is displayed in Fig. 7 – Fig. 10. These figures show the data plotted as a function of pressure for pure H₂ and for several mixtures of NG2 and CH₄ with different amounts of H₂. These calculations were performed for secondary combustor inlet temperatures (Tₐₘ₂ₙ) of 1100 K and 1300 K at ϕ = 0.7 and for 1100 K at ϕ = 1.1.

Fig. 7 shows the counter intuitive effect on pressure hydrogen chemistry. This pressure effect is due to the well-known competition between branching and termination for the H + O₂ reaction. At lower pressures (and higher temperatures), the branching path H + O₂ ⇄ OH + O dominates, while at higher pressures (and lower temperatures) the less reactive termolecular path forming HO₂ dominates, H + O₂ + M ⇄ HO₂ + M [17]. The transition between these two competing reactions occurs for the present conditions (Fig. 7) between about 1250 and 1400 K for the higher pressures, evident by the dramatic change in slope in this temperature range. Note also in Fig. 7 that at temperatures less than about 1150 K, the ignition delay times for the 15- and 30-atm cases are actually longer than the ignition delay times at 1 atm.

To determine how much H₂ addition would cause the same pressure effects on CH₄/H₂ and NG2/H₂ mixtures, different levels of H₂ were added to CH₄ and NG2 over a wide range of pressures. In Fig. 8 and Fig. 9 it can be seen that this hydrogen reactivity trend only affects the exponential reactivity of mixtures of NG2 and CH₄ containing 70% H₂ and above. This relative insensitivity to hydrogen below about 70% of the fuel blend indicates that the ignition delay time is dominated by the hydrocarbon content rather than the H₂ content.

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Gas Turbine Model
To provide a more detailed analysis of the combustion process in the reheat gas turbine cycle, two models using several Chemkin modules were developed. Schematics for the primary and secondary (i.e. EV and SEV) burner models are shown in Fig. 11 and Fig. 12, respectively. The primary burner model calculated laminar burning velocities, while the secondary burner model calculated ignition delay times. This approach is equally relevant for the Alstom and the RB211 DLE combustion system. However, as already mentioned, the inlet temperature for the secondary stage of the RB211 DLE is higher than for the SEV burner, which will result in shorter autoignition times.

Primary Burner A schematic of the primary combustor model is shown in Fig. 11. The inputs to the primary burner model included the flame temperature (T_{flame}), air inlet temperature (T_{in, 1st}), and fuel temperature (T_{fuel}), specified fuel composition, and pressure. The air composition used for every calculation of S_L is given in Table 1. It represents air with 60 percent humidity.

Table 3 Air Composition into EV burner used in all calculations in percent volume.

<table>
<thead>
<tr>
<th>Air Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>O_2</td>
<td>20.7%</td>
</tr>
<tr>
<td>H_2O</td>
<td>1.01%</td>
</tr>
<tr>
<td>N_2</td>
<td>77.3%</td>
</tr>
<tr>
<td>Ar</td>
<td>0.91%</td>
</tr>
<tr>
<td>CO_2</td>
<td>0.04%</td>
</tr>
</tbody>
</table>

Instead of defining the equivalence ratio for each mixture, T_{flame} was held constant, and a premixer tool was used to determine the reactor input conditions. This tool started from given fuel and air compositions at different temperatures at user-defined inlet conditions. Thereafter, the fuel mass fraction was iterated until the correct T_{flame} was found to determine the mixing temperature and the composition of the unreacted mixture. For this flame temperature calculation, the Chemkin equilibrium module was called for each iteration. The inlet composition was then used as a starting value for the Chemkin Premix reactor module to obtain laminar flame speeds and species concentrations.

Secondary Burner A schematic of the secondary burner model is shown in Fig. 12. The development of this model was
slightly more complex as effects from the primary burner needed to be included. Specifically, the primary outlet composition was desired for this model, as this product mixture becomes the air composition into the secondary zone or the real secondary burner. This composition was especially important in the present study since the oxidizer mixture entering the secondary burner will contain differing amounts of CO₂ and H₂O depending on the amount of H₂ in the fuel blend. The inputs to the secondary burner model included T_{\text{flame}}, T_{\text{in,1st}}, secondary combustor inlet Temperature (T_{\text{in,2nd}}), fuel composition, and pressure. First, fuel at T_{\text{fuel}} and air at T_{\text{in,1st}} were mixed in the premixer tool to determine the composition of the exhaust gases of the primary burner for the desired T_{\text{in,2nd}}. The effect of the HP turbine in the GT24/GT26 reheat engine is accounted for by reducing the primary burner outlet temperature by a fixed temperature difference.

After the primary burner exhaust gas composition was defined, T_{\text{flame}} was held constant, and the mass flow rates of the fuel and exhaust gas were determined using a second premixer tool. Similar to the primary burner model, this tool started from the fuel and exhaust gas compositions, and the fuel mass fraction was iterated until the correct T_{\text{flame}} was found. Using the Chemkin equilibrium module for each iteration, the mixing temperature and composition of the unreacted mixture were found. The mixing temperature of the fuel and air was then used as the input temperature for the \( \tau_{\text{ign}} \) calculation in the Chemkin plug flow reactor (PFR) module. Finally, the PFR module determined the \( \tau_{\text{ign}} \) for the given T_{\text{flame}}, reactant compositions, and pressure.

**Laminar Flame Speed Results**

An extensive list of laminar flame speed calculations was performed using the primary burner model for the conditions listed in Table 4. Calculations were performed for mixtures of CH₂/H₂ and mixtures of NG2/H₂ ranging from pure CH₂ or pure NG2 all the way to pure H₂.

**Table 4 Laminar flame speed calculation parameters.**

<table>
<thead>
<tr>
<th></th>
<th>-</th>
<th>Reference</th>
<th>+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (atm)</td>
<td>1</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>T_{\text{in,1st}} (°C)</td>
<td>420</td>
<td>480</td>
<td>540</td>
</tr>
<tr>
<td>T_{\text{flame}} (K)</td>
<td>1600</td>
<td>1750</td>
<td>2150</td>
</tr>
<tr>
<td>Fuel/air Ratio</td>
<td>( \phi &lt; 1 )</td>
<td>( \phi = 1 )</td>
<td>( \phi &gt; 1 )</td>
</tr>
</tbody>
</table>

Fig. 13 shows the laminar flame speed calculations at 25 atm plotted as a function of H₂ addition to CH₂ and NG2. For most cases at this pressure, mixtures containing NG2 have a larger flame speed than mixtures containing CH₂. The effect of equivalence ratio used to obtain the desired flame temperature can also been seen in Fig. 13. The rich mixtures at a higher flame temperature have smaller flame speeds than the same lean mixtures at the same T_{\text{flame}}, except for the case of pure hydrogen. A rich mixture of pure hydrogen has a flame speed about two times larger than the lean mixture of pure hydrogen. Additionally, it can be seen (somewhat unsurprisingly) that stoichiometric mixtures are the most reactive of all the mixtures.

For all three pressures, there are a few apparent trends within the data, and these are displayed in Fig. 14 –Fig. 17. In Fig. 14, normalized flame speeds are plotted for all mixtures at all pressures at the base condition of a flame temperature of 1750 K, inlet temperature of 420°C, and \( \phi < 1 \). It can be seen in this figure that the effect of hydrogen addition is greater for CH₂ mixtures than for NG2 mixtures. At 25 atm, the pure hydrogen mixture flame speed is 6.5 times larger than the pure CH₂ mixture while it is only 5.5 times larger than the pure NG2 mixture. In general, hydrogen addition at lower pressures has an even greater effect on the reactivity of the fuel. For example, the flame speed of pure hydrogen is 5.5 times larger than NG2 at 25 atm and 7.5 times larger than NG2 at 1 atm. This nonlinear pressure effect due to the hydrogen content is related to the two H₂+O₂ competitive branches mentioned above.

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In Fig. 15, the same data are plotted as a function of power of the percent of power that comes from H2. To calculate this value, the lower heating value (LHV) of each mixture was used, and the hydrogen power percent was found from Equation 1.

\[
P_{H_2} = \frac{LHV_{H_2}}{LHV_{Fuel}} \times x_{H_2} \quad (1)
\]

In Equation 1, \(P_{H_2}\) is the power percent from hydrogen, and \(x_{H_2}\) is the mole fraction of hydrogen in the fuel blend. The increase in laminar flame speed, which increases sharply towards very high H2 content in Fig. 14, rises less sharply (almost linearly) when plotted versus H2 power fraction as shown in Fig. 15. This result indicates that laminar flame speed is mainly dominated by the heat input of the specific fuel component and is not so much dependent on the specific fuel triggering the chemistry as in the case of ignition delay time.

Flame temperature also plays a significant role in the laminar flame speed of a mixture, as can be seen in Fig. 16. The normalized flame speeds of mixtures that contain 50% HC (either CH4 or NG2) and 50% H2 at an inlet temperature of 420°C are shown as a function of flame temperature. For a mixture of 50% CH4 at 25 atm, an increase of 150 K in flame temperature increases the flame speed by a factor of three, while an increase of 550 K in flame temperature increases the flame speed by a factor of over ten. Similarly, for a mixture of 50% NG2 at 25 atm, an increase of 150 K in flame temperature increases the flame speed by a factor of three while an increase of 550 K in flame temperature increases the flame speed by a factor of nine. This effect of flame temperature decreases slightly with pressure, but the effect is always somewhat greater for mixtures containing CH4 than for mixtures containing NG2.

The effect of the inlet temperature is relatively small compared to the effect that the flame temperature has on laminar flame speed (Fig. 17). The normalized flame speeds of mixtures that contain 50% HC and 50% H2 at a flame temperature of 1750 K are shown compared to the inlet temperature. For an increase in inlet temperature of 120°C, all mixtures are shown to have a \(S_L\) increase of less than 50%.

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Ignition Delay Time Results

An extensive list of ignition delay time calculations was performed using the secondary burner model for the conditions given in Table 5. Calculations were performed for mixtures of CH₄/H₂ and mixtures of NG2/H₂ ranging from pure CH₄ or pure NG2 all the way to pure H₂. For all calculations, the composition of inlet gases was determined as previously described.

Table 5 Ignition delay time calculation parameters.

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Median</th>
<th>+</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>T_{in,2nd} (K)</td>
<td>1100</td>
<td>1300</td>
</tr>
<tr>
<td>T_{flame} (K)</td>
<td>1600</td>
<td>1750</td>
</tr>
<tr>
<td>T^{r}_{ign} (s)</td>
<td>1E+0</td>
<td>1E-1</td>
</tr>
<tr>
<td>T^{i}_{ign} (s)</td>
<td>1E-3</td>
<td>1E-2</td>
</tr>
</tbody>
</table>

Several trends are seen within the ignition delay time calculations. Fig. 18 shows the normalized ignition delay times of all mixtures as a function of hydrogen addition at all three pressures with a T_{flame} of 1750 K and a T_{in,2nd} of 1300 K. This figure shows that hydrogen addition significantly decreases the ignition delay time, and therefore increases the reactivity, from either pure CH₄ or pure NG2. At 15 atm, the \( \tau_{ign} \) of the pure CH₄ mixture is 57 times larger than the \( \tau_{ign} \) of the pure hydrogen mixture, and the \( \tau_{ign} \) of the pure NG2 mixture is 11 times larger than the \( \tau_{ign} \) of the pure hydrogen mixture. This effect decreases with pressure, and the CH₄ mixtures are more affected by the addition of hydrogen than the NG2 mixtures. In Fig. 19, the same data are plotted as a function of the percent of power that comes from H₂, which was found using Equation 1 as described previously. It can be seen that, especially for pure CH₄ mixtures at 1 atm, ignition delay time decreases by a large magnitude with H₂ power percent. At higher pressures, the ignition delay time plateaus around 50% H₂ power percent.

Flame temperature does not have as large an influence on \( \tau_{ign} \) as it does on \( S_L \). This trend is due to the fact that the chemical reactivity varies only slightly with equivalence ratio in regard to ignition delay time, unlike that for laminar flame speed. However, the mixing of cold fuel and exhaust gas results in lower mixing temperature for fuel-rich flames and therefore leads to a reduction in reactivity. As a result, both effects seem to compensate for each other, and the T_{flame} effect is therefore small.

However, inlet temperature plays a significant role on reactivity and secondary combustor operation as shown in Fig. 20. Normalized \( \tau_{ign} \) are shown as a function of inlet temperature for 50% HC and 50% hydrogen mixtures at a flame temperature of 1750 K for all pressures. At 15 atm, an increase in inlet temperature of 250 K is seen to decrease the \( \tau_{ign} \) of both the 50% CH₄ and the 50% NG2 mixtures by almost a factor of 30. Additionally, this effect is seen to be higher with lower pressures (per the effect of pressure on the hydrogen kinetics, as discussed above). This effect is important for the secondary burner since the inlet temperature is easier to control using the primary combustor. The secondary burner flame temperature is determined by the power demand of the engine and, within the secondary burner, the flame behavior is dominated by \( \tau_{ign} \) rather than laminar flame speed. Therefore, since \( \tau_{ign} \) has been shown to be more dependent on the inlet temperature than on the flame temperature, this reduced dependence on flame temperature gives the secondary burner a large flexibility in the limits of the reactivity of fuels used. Additionally, adjusting the SEV inlet temperature by changing the EV burner equivalence ratio can easily compensate for changes in fuel reactivity. Similarly but to a lesser extent, the split of heating rate between the primary and the secondary stages of the RB211 DLE system can be adjusted to cope with varying fuel reactivities.

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the turbulent flame speed correlations or models shall be substantiated with the Lewis number effects.

In the present case, the laminar flame speeds for CH₄ (or NG2)-H₂ are calculated for planar flames, and Equation 2 shall be used as it is with effective Lewis number to determine the turbulent flame speed. Various relations are available in the literature for estimating the effective Lewis number. In the current study, the effective Lewis number was estimated based on the mole fractions of different species in the fuel and their individual Lewis numbers, see Equation 3.

\[
\frac{S_T}{S_{L0}} = 1 + \frac{0.46}{e^{(Le-1)}} Re_i^{0.25} \left( \frac{u'}{S_{L0}} \right)^{0.3}
\]  

(2)

\[
\frac{1}{Le} = \frac{D'}{\alpha} = \frac{x_{CH_4} D_{CH_4}}{\alpha} + \frac{x_{H_2} D_{H_2}}{\alpha} = \frac{x_{CH_4}}{Le_{CH_4}} + \frac{x_{H_2}}{Le_{H_2}}
\]  

(3)

By employing Equations 2 and 3 and the calculated laminar flame speeds for different mixtures, the turbulent flame speeds are calculated with the preferential diffusion (Le). The calculated normalized flame speeds are shown in Fig. 21. The turbulent flame speed estimated with molecular effects is higher than the laminar flame speed calculated from Chemkin, as expected. All values are normalized to the value for the pure hydrocarbon fuel blend (i.e. CH₄ or NG2 with no H₂).

The increase of reactivity due to H₂ addition appears to occur at lower H₂ contents for turbulent flame speeds. For CH₄ mixtures, Sₜ doubles when 70% H₂ is added, while Sₜ doubles when only 50% H₂ is added. Similarly, for NG2 mixtures, Sₜ doubles when 85% H₂ is added, while Sₜ doubles when only 55% H₂ is added. The largest increase in reactivity is observed at high volumetric H₂ contents when the energy contributed from the H₂ system becomes significant, as indicated in Fig. 21.

\[
\begin{align*}
\text{Fig. 20} & \quad \text{Effect of inlet temperature on ignition delay time of CH₄ (black) and NG2-based (red) mixtures. 50% H₂, } \phi < 1. \text{ Solid lines: 30 atm; Dashed lines: 15 atm; Dotted lines: 1 atm.} \\
\text{PART 3: INFLUENCE OF MOLECULAR TRANSPORT EFFECTS ON TURBULENT FLAME SPEED} \\
\text{Combustion in the real gas turbine combustor is more complex than what can be predicted by chemical kinetics alone. This is especially true when the aerodynamics of the flow fields, turbulent chemistry interaction, stretch and curvature effects are neglected. While for the secondary combustor ignition delay time appears to dominate, the reactivity changes in the primary zones are induced by the flame speed or burning velocity. Since turbulent chemistry interactions are highly fuel dependent, they should be considered when investigating the effects of fuel composition on flame speed calculations in the primary zone.}
\end{align*}
\]

While a satisfying turbulent flame speed description would include a very elaborate study, the kinetic values were evaluated with care by using a simplified method to weigh the results according to a Lewis number scaling, as described in this section. This approach does not attempt to match or predict real engine behavior but is rather a first step towards an improved evaluation of the pure chemical results. A comparison to full scale burner combustion tests will eventually give more foundation to an improved evaluation procedure.

The physics of lean H₂ combustion differ significantly with those of typical light hydrocarbon fuels. In H₂ combustion under lean or very lean conditions, interactions between thermo-diffusive effects attributed to the combined Lewis number (ratio of thermal and mass diffusivity) and preferential diffusion and stretch of laminar-premixed flames strongly affect the properties of premixed turbulent flames [26, 27, 28]. In planar premixed flames, the combined reaction rate and transport processes are included in the laminar burning velocity. The use of these planar laminar burning velocities in estimating the turbulent flame speeds in the case of Le < 1 leads to an under-prediction of turbulent flame speeds and an over-prediction for Le > 1 [29]. For the correct prediction of turbulent flame speeds, it is appropriate to use the laminar flame speeds including stretch and curvature effects. Otherwise the turbulent flame speed correlations or models shall be substantiated with the Lewis number effects.

The parametric study herein revealed several important characteristics of H₂ addition to hydrocarbon fuels. Hydrogen
addition was found to always increase the reactivity of CH₄ and NG2 mixtures by increasing S_l and decreasing τ_ign. Also, the effect of H₂ addition has a greater impact on CH₄ mixtures than on NG2 mixtures. For laminar flame speeds, the reactivity is mainly determined by the relative heat input that a certain fuel component contributes. In this case, CH₄ has less impact on the heat balance of the total fuel composition than NG2 and therefore is more affected by H₂ addition. For the ignition delay times, the effect of H₂ addition has a greater impact on CH₄ mixtures due to the fact that the chemistry is strongly dominated by the most reactive species triggering the heat release reactions. This effect is actually strongest when small amounts are added. Compared to CH₄, which is the least-reactive fuel in this study, the NG2 mixture already contains higher hydrocarbons that accelerate the combustion of the CH₄ flame, so further acceleration from H₂ addition is less effective.

The parametric study also found that for laminar flame speeds, the effect of H₂ addition increased with increased H₂ content, lower pressure, and higher inlet temperature. Most mixtures were found to have peak reactivity with equivalence ratios slightly richer than stoichiometric. Additionally, for ignition delay times, reactivity increased with both higher initial temperature and initial pressure. However, equivalence ratio was not seen to greatly affect the τ_ign of each mixture.

The study performed under gas turbine conditions revealed several aspects of importance to the gas turbine application of these high-hydrogen fuels. Stoichiometric mixtures gave the highest S_l at the same condition, indicating that equivalence ratio in the primary burner plays a significant role on the reactivity of the mixture. It was also found that H₂ addition at a constant T_flame_1st, T_in_1st, and pressure can significantly increase the S_l of CH₄ or natural gas, but the S_l does not increase by a factor of two until about 60% H₂ addition. This is important for the GT24/GT26 EV burner and the RB211 DLE primary stage applications because it shows that the addition of H₂ to a fuel will not affect the S_l dramatically until the fuel is more than 60% H₂. In the secondary burner, T_flame_1st at constant inlet temperature has a larger influence on the S_l of a fuel mixture than has the T_in_1st at constant flame temperature. This effect allows increased reactivity to be compensated for in the EV burner and the RB211 primary stage by a slight reduction in T_flame_1st.

The ignition delay time calculations at gas turbine conditions revealed the effect of adding H₂ to fuels in the GT24/GT26 SEV burner and the RB211 DLE secondary stage. At 15 atm, pure H₂ was shown to decrease the τ_ign of CH₄ by a factor of 1/100 and the τ_ign of NG2 by a factor of 1/10. Therefore, hydrogen greatly increased the reactivity of the each fuel mixture. Additionally, T_flame_2nd had a smaller effect compared to T_in_2nd on the τ_ign, calculated for each mixture. This result is important for the secondary burner because a change in fuel reactivity can be compensated for by changing T_in_2nd without a reduction of T_flame_2nd, which would be accompanied by a power loss.

Finally, to include the effect of molecular transport and turbulence on flame speed, an effective Lewis number approach was used to estimate turbulent flame speeds from laminar flame speeds found from the gas turbine model. It was found that the addition of H₂ to the fuel at constant T_flame, T_in_1st, and pressure affects the magnitude of the flame speed at much lower concentrations of H₂ than with laminar flame speeds. This higher sensitivity to H₂ addition is important to predict the engine behavior of the gas turbine burners since their behavior is not determined by the kinetics alone but also by the aerodynamics, mixing and turbulence levels.

Although engine operation concepts will ultimately be derived by high-pressure tests and engine validations, the approach presented here gives a reasonable tool to predict engine behavior and fuel operation ranges. To further refine these predictions, the derived results will be used to design laboratory-scale experiments required to validate and improve the kinetic schemes that have been used.

CONCLUSIONS

Calculations were performed to determine the effect of large amounts of H₂ addition to hydrocarbon fuels under gas turbine conditions. Both a parametric study and a study using a gas turbine model were performed to calculate laminar flame speeds and ignition delay times. The data found from both studies provide several implications for the use of fuels containing different amounts of H₂ in gas turbines. When flame speeds are the main concern for the burner, as in the GT24/GT26 EV and RB211 DLE primary stage burners, hydrogen addition of up to 30 or 40% will not affect the reactivity of the fuel to a great extent. When ignition delay time is the main concern for the burner, as in the GT24/GT26 SEV and RB211 DLE secondary stage burners, the inlet temperature can be changed to adapt to changes in the reactivity of the fuel. Additionally, compared to the primary burners, reactivity changes in the secondary burners are relatively small with H₂ addition and can be compensated for by a slight reduction in T_flame_1st. This result also benefits the operability of the secondary burner as the reactivity can be compensated for by operation at a lower T_in_2nd without reduction of T_flame_2nd, which would be accompanied by power loss. Furthermore, turbulence was shown to increase the effect of H₂ addition on flame speed.

Using the data obtained in this study, a test matrix is in development to validate the calculations and the chemical kinetics mechanism. Laminar flame speeds will be measured using cylindrical bomb experiments, and ignition delay times will be measured using both a shock tube and a rapid compression machine. Results from these experiments will allow greater insight into the reactivity of these mixtures and hopefully validate the findings of the current study regarding hydrocarbons with high percentages of hydrogen.

NOMENCLATURE

- EV: Environmental~1st
- SEV: Sequential Environmental ~2nd
- τ_ign: Ignition Delay Time
- S_l: Laminar Flame Speed

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NG2: Base Natural Gas defined in [7]

φ : fuel-to-oxygen Equivalence Ratio

T_{\text{flame}}: Flame Temperature

T_{\text{fuel}}: Fuel Temperature

T_{\text{in,1st}}: Primary (EV) Burner Inlet Temperature

T_{\text{in,2nd}}: Secondary (SEV) Burner Inlet Temperature

T_{\text{flame,1st}}: Primary (EV) Burner Flame Temperature

T_{\text{flame,2nd}}: Secondary (SEV) Burner Flame Temperature

P_{\text{i}}: Inlet Pressure

HC: Hydrocarbon

PFR: Plug Flow Reactor

LHV: Lower Heating Value

P: Power

x: Mole Fraction

S_{T}: Turbulent Flame Speed

REFERENCES


