Ignition delay time experiments and mechanism validation for natural gas/hydrogen blends at elevated pressures

Nicola Donohoe\textsuperscript{a,\*}, Alexander Heufer\textsuperscript{a}, Wayne K. Metcalfe\textsuperscript{a}, Henry J. Curran\textsuperscript{a}, Marissa L. Brower\textsuperscript{b}, Olivier Mathieu\textsuperscript{b}, Eric L. Petersen\textsuperscript{b}, Gilles Bourque\textsuperscript{c}, Felix G"{u}the\textsuperscript{d}

\textsuperscript{a}National University of Ireland, Galway, Ireland
\textsuperscript{b}Texas A\&M University, College Station, TX, USA
\textsuperscript{c}Rolls-Royce Canada, Montreal, Canada
\textsuperscript{d}Alstom, Baden, Switzerland

Abstract

New experimental ignition data measured in both a shock tube and in a rapid compression machine were taken to determine the increase in reactivity due to the addition of hydrogen to mixtures of methane and natural gas. Test conditions were determined using a statistical Design of Experiments approach which allows the experimenter to probe a wide range of variable factors with a comparatively low number of experimental trials. Experiments were performed at 1, 10 and 30 atm in the temperature range 850 – 1800 K, at equivalence ratios of 0.3, 0.5, and 1.0 and with dilutions ranging from 72 – 90%. Pure methane and hydrogen mixtures were prepared in addition to two synthetic ‘natural gas’ mixtures comprising methane, ethane, propane, \textit{n}-butane and

\*Corresponding author at: National University of Ireland, Galway, Ireland
Email address: n.donohoe1@nuigalway.ie (Nicola Donohoe)
\( n \)-pentane, one comprising 81.25/10/5/2.5/1.25\% while the other consisted of 62.5/20/10/5/2.5\% \( \text{C}_1/\text{C}_2/\text{C}_3/\text{C}_4/\text{C}_5 \) components in order to encompass a wide range of possible natural gas compositions. These experiments have been simulated using a detailed chemical kinetic model. Overall good agreement is observed between the simulations and the experimental results. A discussion of the important reactions promoting and inhibiting reactivity is included.

Keywords:
hydrogen, natural gas, rapid compression machine, shock tube, flame speed
1. Introduction

Fuel flexibility, increasing efficiency and reduction in harmful emissions pose ever increasing challenges to the power generation industry. Due to increasing energy costs, dwindling traditional feedstocks and the simultaneous demand for cleaner energy in a power generation market competitive for efficiency and flexibility the importance of alternative fuels sources is increasing. Energy sources such as coal gas, gases from industrial processes like coke manufacturing, biomass gasification and energy storage via hydrogen electrolysis have become potential alternative energy sources for the gas turbine industry. These gases are typically comprised of hydrogen, syngas and short chain hydrocarbons generally classified as natural gas. Interest in hydrogen as a renewable energy source for use in gas turbines, fuel cells and as a transportation fuel has increased in recent years, as it is considered energy dense, and environmentally friendly. New routes to hydrogen formation have also led to increased attention; these include steam reformation of hydrocarbons, water electrolysis and coal/biomass gasification. With the objective of reducing emissions and increasing fuel flexibility, a growing number of technologies are now harnessing the power of hydrogen to achieve this goal such as integrated gasification combined cycle power plants with carbon capture and storage and I.C. engines. All this has made hydrogen fuel of particular interest to the gas turbine industry. While operating gas turbines with pure hydrogen fuels poses some difficulties and requires significantly changed combustion systems and turbomachinery, the addition of hydrogen
to natural gas mixtures is expected to alter the combustion properties only slightly leading to a reduction in the carbon monoxide, carbon dioxide and NO\textsubscript{x} emissions from power generation gas turbine plants.

Even though natural gas is being widely used in the gas turbine industry, it does have some un-favorable combustion characteristics. These can be improved by the addition of hydrogen which can significantly lower the flammability limit of natural gas mixtures and extend the operability of natural gas turbines to leaner burning regimes [1]. Hydrogen can be mixed with natural gas and/or methane in concentrations of up to around 70% hydrogen fuel percentage, in order to assist the complete combustion of mixtures, and reduce emissions. Previous studies have shown that up to approximately 50% hydrogen content the effect on fuel behavior is slight [2].

In order to implement mixtures of these fuels in gas turbines, detailed chemical kinetic mechanisms describing their combustion properties must be developed and validated against a wide range of experimental data. In this study, a rapid compression machine (RCM), shock tube and bomb calorimeter have been employed to study the oxidation of natural gas/hydrogen blends over gas turbine relevant conditions. Two natural gas mixtures have been studied to better reflect the varying composition of natural gas blends containing greater amounts of higher hydrocarbons derived from sources such as coal used in the power generation industry. The study of quaternary natural gas mixtures reflects better the real natural gas blends used in the gas turbine industry as opposed to their single and binary component counterparts,
which have traditionally been utilized as natural gas surrogates.

Natural gas blends of interest to the gas turbine industry have been characterized previously. Healy et al. [3–8] studied quaternary natural gas mixtures in the temperature range 630 – 1550 K, in the pressure range 10 – 30 bar and developed a detailed chemical kinetic mechanism for natural gas mixtures. Natural gas/hydrogen blends have also come under investigation recently. Park et al. [9] observed a reduction in reactivity when hydrocarbons such as propane or n-butane replaced methane in hydrogen/methane and syngas/methane flame mixtures. This was determined to be as a result of the depletion of hydrogen radicals through their consumption in reactions with ethylene (C₂H₄) and ethyl (C₂H₅) radicals. Reactivity also decreased due to the increased concentrations of methyl (CH₃) radical, which consumed further hydrogen atoms through the reactions CH₄ + H = CH₃ + H₂ and CH₃ + H (+M) = CH₄ (+M), lowering the overall rate of the main chain branching reaction H + O₂ = O + OH [9]. Gersen et al. [10] reported ignition delay times of methane/hydrogen mixtures recorded in a rapid compression machine (RCM) at high pressure (10 – 70 bar) and intermediate temperature (950-1060 K). They observed that for hydrogen mole fractions above 50% there is a significant decrease in the ignition delay compared to hydrogen concentrations below 20%, where the effect was slight.

Gersen et al. [10] also observed an increase in global activation energy with higher hydrogen content in the mixture, by reason of the differences in activation energy (Ea) between the two pure fuels. Therefore, at high
temperatures, the ignition delay time is more greatly reduced when compared to low temperatures. Gersen et al. [10] attributed this effect to the increasing importance of the $\dot{H} + O_2 = \dot{\text{O}} + \dot{\text{OH}}$ and $H_2 + \dot{\text{OH}} = H_2O + \dot{\text{H}}$ reactions at higher temperatures. Recently, Gersen et al. [11] expanded their study to the effect of carbon monoxide on methane, hydrogen and binary mixtures of the two fuels at high pressures (20 to 80 bar) and a lean equivalence ratio ($\phi = 0.5$). They found that for CH$_4$/H$_2$/CO mixtures there was no inhibiting effect of CO addition compared to binary methane/hydrogen mixtures [11].

Crossley et al. [12] observed the effect of adding ethane, propane, $n$-butane, and $n$-pentane fractions to methane fuel. They determined that the addition of larger hydrocarbons led to a significant reduction in ignition delay time, and this effect was determined to be due to the faster kinetics of the higher hydrocarbon fuels. De Vries and Petersen [13] measured undiluted natural-gas-based mixtures combining methane with ethane, propane, $n$-butane, $n$-pentane, and hydrogen at gas turbine relevant conditions in a shock tube. The results obtained showed a definite decrease in activation energy at lower temperatures and higher pressures as seen in the work of Gersen et al. [10]. Yu et al. [14] and Huang et al. [15] studied methane/hydrogen and propane/hydrogen and methane/ethane/propane/hydrogen laminar burning velocities respectively, they determined that an increase in hydrogen mole fraction in any case leads to increase in laminar burning velocities. Little data has been published on hydrogen/hydrocarbon blends ignition delay times and to the authors knowledge no hydrogen/ quaternary natural gas
mixture blend ignition delay times at gas turbine relevant conditions have been published previously.

2. Experimental setup

2.1. NUIG Rapid Compression Machine

Experiments were performed in the Rapid Compression Machine (RCM) facility at the National University of Ireland Galway (NUIG). The NUIG RCM has a horizontally-opposed twin-piston design that has been described in previous studies [16, 17]. Compression times below 16 ms are achieved using this set up. The diameter of the reaction chamber is 38.2 mm. The chamber and sleeves are pre-heated to ensure a homogeneous temperature, and this can be done up to 160°C. With the addition of creviced pistons, boundary layer effects are negligible and the reacting core is temperature homogeneous and adiabatic. By varying the initial temperature, initial pressure, the diluent gas composition, and the volumetric compression ratio a wide temperature range can be investigated.

The ignition delay time \( \tau \) was defined as the time from the end of compression, taken as the time of peak compressed pressure, to the onset of ignition, Fig. 1. In order to account for the heat losses inherent in RCM experiments, non-reactive experiments were performed in which the oxygen content of the mixture is replaced by nitrogen and then simulated to produce a volume/time history which was used as the input in the Chemkin-Pro [18] simulation. Nitrogen is used because it has similar thermodynamic properties
to those of oxygen. The recorded pressure profile presents the same pressure drop as a reactive trace as a result of very similar heat loss properties.

Recent experiments in shock tubes and in RCMs have shown that the pressure transducer (Kistler 603B) used in the NUIG facilities is sensitive to heat loads during the experiments. Heat flux from the hot gas into the sensor reduces the output signal so that a lower pressure is measured compared to reality. We have modified our experimental procedure to overcome this problem. The pressure transducer is covered by a thin silicone layer. This layer acts to shield the sensor against the heat load during the experiment. From these experiments the true experimental compression ratio and pressure profile is determined. Since we deduce the temperature profile from the pressure profile via the isentropic relationship, the apparent measured temperature would also be lower compared to reality using the profiles from
the non-shielded sensor. This would result in longer ignition delay times in the simulation compared to simulation using the profile measured with the shielded sensor. Furthermore, the temperature at the end of compression would be lower using the end of compression pressure of the non-shielded sensor. Thus, this method reduces uncertainties in the temperature of the experiment and simulation.

2.2. TAMU Shock Tube

Experiments were performed in the high-pressure shock-tube facility described in detail by Aul [19, 20]. The shock tube is made entirely of 304 stainless steel. The driven section is 4.72 m long with 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 aluminium 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.

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. [21] 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 [22], as depicted in Fig. 2. 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. 2. 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. 2 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.

2.3. 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 list covering a wide range of pressures, % hydrogen, stoichiometry, and fuel blend could prove a huge task due to the large number of possible combinations. A test matrix was therefore developed to test these different properties in an organized yet efficient manner. Three levels of each variable were assembled into the L9 Taguchi array [23], shown in Table 1. The specific mole fractions for the NG2 and NG3 blends are provided in Table 2. The four independent variables, selected were fuel (\( \text{CH}_4, \text{NG2}, \text{NG3} \)); % 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). The temperature was changed in order
to cover the entire possible range for each mixture, the temperature ranges varied to obtain ignition delay times from around 100 µs to 200 ms for each combination. Therefore temperature was not included in the test matrix. Tables of data recorded in both the RCM and in the shock tube are provided in the Supplementary material.

<table>
<thead>
<tr>
<th>Mix</th>
<th>CH₄</th>
<th>H₂</th>
<th>O₂</th>
<th>Diluent</th>
<th>φ</th>
<th>% H₂</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01135</td>
<td>0.00486</td>
<td>0.08378</td>
<td>0.9</td>
<td>0.3</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.0125</td>
<td>0.01875</td>
<td>0.06875</td>
<td>0.9</td>
<td>0.5</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>2b</td>
<td>0.0125</td>
<td>0.01875</td>
<td>0.06875</td>
<td>0.2586</td>
<td>0.5</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>0.01111</td>
<td>0.04444</td>
<td>0.04445</td>
<td>0.9</td>
<td>1.0</td>
<td>80</td>
<td>30</td>
</tr>
<tr>
<td>3b</td>
<td>0.01111</td>
<td>0.04444</td>
<td>0.04445</td>
<td>0.1672</td>
<td>1.0</td>
<td>80</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>NG2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.0146</td>
<td>0.0063</td>
<td>0.0791</td>
<td>0.9</td>
<td>0.5</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>4b</td>
<td>0.0146</td>
<td>0.0063</td>
<td>0.0791</td>
<td>0.2975</td>
<td>0.5</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>0.0174</td>
<td>0.0261</td>
<td>0.0564</td>
<td>0.9</td>
<td>1.0</td>
<td>60</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>0.005</td>
<td>0.02</td>
<td>0.0749</td>
<td>0.9</td>
<td>0.3</td>
<td>80</td>
<td>10</td>
</tr>
<tr>
<td>6b</td>
<td>0.005</td>
<td>0.02</td>
<td>0.0749</td>
<td>0.2819</td>
<td>0.3</td>
<td>80</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>NG3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.0217</td>
<td>0.0093</td>
<td>0.0691</td>
<td>0.9</td>
<td>1.0</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>0.0067</td>
<td>0.0101</td>
<td>0.0832</td>
<td>0.9</td>
<td>0.3</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>0.0067</td>
<td>0.0268</td>
<td>0.0666</td>
<td>0.9</td>
<td>0.5</td>
<td>80</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 1: Mixtures studied chosen using the Taguchi method for balanced, orthogonal arrays [20]. Three levels of each factor were used. Mixtures 2b, 3b, 4b, and 6b are fuel mixtures diluent in ‘air’.

Ultra-high purity (UHP, 99.9995%) gases were used to make the test mixtures. The two natural gases used in the study were each prepared separately from the main fuel-O₂-diluent mixtures to ensure repeatability with the natural gases used. The natural gases were prepared using the partial pressure method in tanks that were vacuumed. The partial pressure of pentane was
kept well below the vapor pressure of the fuel to ensure that it remained in
the gaseous phase and was well incorporated in the natural gas mixtures.
After the natural gas mixtures were prepared, the mixtures from the test
matrix were made. All mixtures from were diluted in 90% diluent. For the
shock tube measurements the diluent used was argon, while a 50/50 mixture
of argon and nitrogen was used the RCM experiments. Fuel in ‘air’ experi-
ments were also performed in the RCM to determine the effect of dilution
on the mixtures as detailed in Table 1.

<table>
<thead>
<tr>
<th>Species</th>
<th>CH₄</th>
<th>CH₂</th>
<th>CH₃</th>
<th>n-C₄H₁₀</th>
<th>n-C₅H₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>100</td>
<td>81.25</td>
<td>62.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.0</td>
<td>10.0</td>
<td>20.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.0</td>
<td>5.0</td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>0.0</td>
<td>2.50</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C₅H₁₂</td>
<td>0.0</td>
<td>1.25</td>
<td>2.50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Fuel mixture compositions in percentage volume.

3. Chemical kinetic mechanism

The chemical kinetic mechanism used in this study has previously been
published by Healy et al. [3–8] and was built on the hierarchical nature of
hydrocarbon mechanisms with the inclusion of our recently updated hydro-
gen/carbon monoxide sub-mechanism [24]. In addition, considerable changes
have been made to the C₁–C₂ portion of the mechanism [25]. The chemistry
of some important unsaturated species including 1,3-butadiene, propene and
allene has been taken from Laskin et al. [26], primarily based on the earlier
work of Davis and law [27]. The C$_4$ and C$_5$ sub-mechanisms are taken from
the previously mentioned Healy et al. [3–8]. Originally the NUIG Aramco-
Mech 1.3 under predicted the flame speeds for high hydrogen content lam-
nar flames. In order to achieve better agreement three reactions were altered.
The rate constant for reaction $\dot{\text{H}} + \dot{\text{OH}} (+\text{M}) = \text{H}_2\text{O} (+\text{M})$ from Li et al. [28]
was revised and the water efficiency from the GRI 3.0 mechanism [29] was
adopted. The $\text{H}_2 + \dot{\text{OH}} = \text{H}_2\text{O} + \dot{\text{H}}$ reaction rate from Stanford [30] was
adopted. The reaction rate for $\dot{\text{O}} + \text{H}_2\text{O} = \dot{\text{OH}} + \dot{\text{OH}}$ was also changed
to the rate from Sutherland et al. [31]. All experiments were compared to
the current NUIG Aramco-Mech 1.3 chemical kinetic mechanism. For com-
parison simulations were also performed with GRI Mech 3.0 [29]. For the
natural gas mixtures the C$_4$ and C$_5$ NUIG sub-mechanisms were added as
GRI-Mech 3.0 is only validated up to C$_3$ which will hereby be referred to as
the modified GRI-Mech 3.0.

For the ignition calculations in a rapid compression machine, a volume
profile is generated from the non-reactive pressure trace. The volume history
used for the simulation includes the heat loss during the compression stroke
and the heat loss after the end of compression was accounted by adiabatic
core expansion approach [32]. The volume history is then used as an input
in the Chemkin input file.

The shock tube data of TAMU [33] have been simulated using constant
volume adiabatic simulation with the reflected shock pressure and tempera-
ture as initial conditions. In the case of the shock tube data from Zhang et
al. [34] our simulations take 4%/ms pressure rise due to the facility-dependent boundary layer into account as stated by the authors.

4. Results

Figures 3–5 detail the experimental results obtained in the TAMU shock tube and the NUIG RCM. In all figures closed symbols represent RCM data, while open symbols represent shock tube data. The lines are model simulations (AramcoMech 1.3); solid lines correspond with closed symbols, dashed lines with open symbols. In addition, the dotted lines represent mechanism predictions obtained with GRI-Mech 3.0 [29]. For all conditions the agreement between the NUIG AramcoMech 1.3 simulation and experiment is quite good.

The trend and effect of hydrogen concentration at all equivalence ratios and pressures is captured by the AramcoMech 1.3 chemical kinetic mechanism. This mechanism has previously been validated against RCM ignition delay measurements for pure hydrogen and syngas mixtures [24] and natural gas [3–8] mixtures taken in the NUIG facility. Over the temperature range in this study, increasing pressure results in higher reactivity of the mixture and shorter ignition delay times. For the high hydrogen content fuels, hydrogen chemistry is dominant. In the temperature regime studied, hydrogen reactivity is mainly controlled by the competition between the chain-branching reaction \( \hat{H} + O_2 = \hat{O} + \cdot OH \) and the pressure-dependent chain-propagating reaction \( \hat{H} + O_2 (+M) = H\hat{O}_2 (+M) \) leading to a cross over in reactivity
Figure 3: Ignition delay times of CH$_4$/H$_2$ mixtures, □ Mix 1 ST, ○ Mix 2 ST, ● Mix 2 RCM, △ Mix 3 ST, ▲ Mix 3 RCM. Solid and dashed lines are AramcoMech 1.3 predictions, dotted lines are GRI-Mech 3.0 predictions.
at higher temperature as can be seen in Fig. 4. In hydrocarbon fuels, low-temperature alkane chemistry and alkyl radical reactions with hydroperoxyl radicals particularly the reaction \( \text{RH} + \text{HO}_2 = \dot{\text{R}} + \text{H}_2\text{O}_2 \) followed by hydrogen peroxide decomposition, \( \text{H}_2\text{O}_2 (+\text{M}) = \dot{\text{OH}} + \dot{\text{OH}} (+\text{M}) \), control the reactivity as described previously by Healy et al. [7]. This is accurately captured by the mechanism.

The shock tube ignition delay experiments, whose chemistry is governed by the reaction \( \dot{\text{H}} + \text{O}_2 = \ddot{\text{O}} + \dot{\text{OH}} \) and the concentration of oxygen in the system, agree well with those taken in the RCM and the effect of adding higher hydrocarbons and the effect of increasing higher hydrocarbon content is demonstrated precisely. The agreement between shock tube and RCM is quite good and it captures the facility effects exhibited by both machines.
accurately. In Fig. 3, mixture 3 shows the highest reactivity, with mixture 1 exhibiting the slowest reactivity. The reason for the observed increase in reactivity of mixture 3 is due to the high hydrogen mole fraction and pressure of the mixture (80% H₂, φ = 1.0, 30 atm) compared to mixture 1 (30% H₂, φ = 0.3, 1 atm). The same is true of Figs. 4 and 5 with the NG2 and NG3 mixture containing the largest hydrogen mole fraction exhibiting the highest reactivity over all conditions studied.

For methane/hydrogen mixtures, GRI-Mech 3.0 does not accurately reproduce the NUIG RCM or the TAMU shock tube results except for mixtures 1 and 3 for the shock tube conditions and does not capture the crossover point between RCM and shock tube. For the NG2/hydrogen and NG3/hydrogen mixtures, the NUIG AramcoMech 1.3 mechanism performs better for both
Figure 6: Effect of dilution on ignition delay times of NG2/H2 mixtures in NUIG RCM, □ Mix 4 diluted ■ Mix 4 fuel-in-air, ○ Mix 6 diluted, ● Mix 6 fuel-in-air. Solid lines are AramcoMech 1.3 predictions, dashed lines are GRI-Mech 3.0 predictions.

the RCM and Shock tube experiments than the modified GRI-Mech 3.0 except for the shock tube data of mixture 8. AramcoMech 1.3 slightly overpredicts the ignition delay time for mixture 1 in Fig. 3. There is a discrepancy between the mechanism predictions of GRI 3.0 and the experimental data. This can possibly explained by the fact that GRI 3.0 has a tendency to over predict ignition delay times for hydrogen and under predict hydrocarbon ignition delay times compared to AramcoMech 1.3. Overall AramcoMech 1.3 performs well compared to the experimental data presented here.

Figure 6 illustrates the effect of dilution on experiments taken in the NUIG RCM. Closed symbols represent fuel/air experiments and open symbols diluted data and lines are model simulations, solid lines correspond to closed symbols and dashed lines to open symbols using AramcoMech 1.3
while the dotted line represents the GRI-Mech 3.0 simulations [29]. For all mixtures, dilution leads to lower reactivity and longer ignition delay times, as there is less charge in the mixture. The trends for both the non-diluted and diluted experiments are captured well by AramcoMech 1.3. GRI-Mech 3.0 does not describe the trend of the data for both the diluted and the fuel-in-air mixtures or the effect of dilution on the mixtures. Further comparisons of model predictions versus our experimental data are provided in Fig. 1 of the Supplementary material.

5. Mechanism Validation

The chemical kinetic mechanism (AramcoMech 1.3) was also validated against recently available experimental data for methane/hydrogen blends by Zhang et al. [34]. In this study ignition delay measurements were taken behind reflected shock waves for methane/hydrogen mixtures at 5, 10 and 20 atm and an equivalence ratio of 0.5. In Fig. 7 the symbols represent the experimental data while the lines are model simulations. The solid lines correspond with AramcoMech 1.3, and the dotted lines represent GRI-Mech 3.0 [29]. Further comparisons of model predictions versus Zhang et al.’s experimental data are provided as Figs. 2 and 3 in the Supplementary material.

The agreement between the AramcoMech 1.3 and the experimental results is very good. The effect of hydrogen on methane ignition delay times is captured showing that the addition of even small amounts of hydrogen to methane leads to an increase in reactivity and shorter ignition delay times
Figure 7: Effect of hydrogen concentration on ignition delay times for CH$_4$/H$_2$ mixtures in a shock tube at 20 atm [34], ■ 100% CH$_4$, ◆ 80% CH$_4$/20% H$_2$, ▲ 60% CH$_4$/40% H$_2$, ▼ 40% CH$_4$/60% H$_2$, ● 20% CH$_4$/80% H$_2$, ★ 100% H$_2$. Solid lines are AramcoMech 1.3 predictions, dashed lines are GRI-Mech 3.0 predictions.

illustrating the promoting effect of hydrogen on the methane chemistry. Increasing the temperature also leads to shorter ignition times regardless of whether hydrogen or methane is controlling the reactivity. While modeling these experiments a 4%/ms pressure rise due to the facility-dependent boundary layer was taken into account as described by the authors [34]. For all pressures and all conditions, AramcoMech 1.3 performs better than GRI-Mech 3.0, which does not accurately capture the effect of hydrogen addition. As mentioned previously, GRI-Mech 3.0 has a tendency to under-predict the reactivity of high hydrogen containing fuels while over-predicting the reactivity of hydrocarbon fuels for ignition delays. This is reflected in data presented below.

Figures 8–10 show laminar flame speed measurement for different hydro-
Figure 8: Laminar flame speeds of 90% \( \text{H}_2 \) + 10% \( \text{NG}_2 \) at 5 atm and 300 K in \( \text{O}_2 : 6 \) \( \text{He} \), • Experimental data, lines are model predictions.

Figure 9: Laminar flame speeds of 50% \( \text{CH}_4 \) + 50% \( \text{H}_2 \) at 1 atm and 300 K in "air", • Experimental data, lines are model predictions.
Figure 10: Laminar flame speeds of 50% CH$_4$ + 50% H$_2$ at 1 atm and 300 K in "air", • Experimental data, lines are model predictions.

gas/natural gas mixtures in comparison to simulations. For AramcoMech 1.3 the overall agreement between experiment and mechanism is quite good. AramcoMech 1.3 accurately predicts the flame speeds for 90% H$_2$ + 10% NG2 at 5 atm and 300 K in 1 O$_2$: 6 He and 50% CH$_4$ + 50% H$_2$ at 1 atm and 300 K in ‘air’. There is still a slight under prediction of flame speed at 10% CH$_4$ + 90% H$_2$ at 1 atm and 450 K in ‘air’. At low pressures (1 atm) and low temperatures reactivity is mainly controlled by the competition between the chain-branching reaction $\ddot{H} + O_2 = \ddot{O} + \ddot{OH}$ and the pressure-dependent chain-propagating reaction $\ddot{H} + O_2 (+M) = H\ddot{O}_2 (+M)$. This reaction has been found to inhibit the reactivity of flame speeds under very lean conditions and promotes the reactivity under stoichiometric to rich conditions. The simulations with GRI-Mech 3.0 predict the flame speed data well for the methane/hydrogen mixtures but under predicts the flame speeds
of the natural gas/hydrogen mixture. This could be explained by the fact that the GRI-Mech 3.0 hydrogen mechanism has slower reactivity and the hydrocarbon mechanism has a faster reactivity than AramcoMech 1.3.

AramcoMech 1.3 is also shown to perform well compared with GRI-Mech 3.0 for pure methane (Fig. 11) and pure hydrogen (Fig. 12). This is due to the previously discussed differences in reactivity of the two mechanisms. However, Fig. 13 shows the large uncertainty in 80% methane/20% hydrogen laminar flame speeds at 1 atm and 298 K reported in the literature [14, 50–52]. AramcoMech 1.3 and GRI-Mech 3.0 both fall within this uncertainty and perform equally well. Overall, the mechanism has been revised to reflect the new data presented here and performs well against these experiments and for both pure fuels and mixtures available in the literature [14, 35–52].
Figure 12: Laminar flame speeds for 100% $\text{H}_2$ at 1 atm and 298 K in ‘air’, ■ Wu et al. [42], □ Dowdy et al. [43], • Tse et al. [44], ○ Law et al. [45], ▲ Egolfopoulos et al. [46], △ Vagelopoulos et al. [47], ♦ Aung et al. [48], ★ Kwon et al. [49], lines are model predictions.

Figure 13: Laminar flame speeds for 80% $\text{CH}_4$/20% $\text{H}_2$ at 1 atm and 298 K, ▼ Yu et al. [14], ● Hermanns et al. [50], • Dirrenberger et al. [51], ▲ Halter et al. [52], lines are model predictions.
Comparisons of model predictions compared to experimental data taken by Hermanns et al. [50] are provided in Fig. 4 of the Supplementary material.

6. Sensitivity Analysis

A sensitivity analysis was performed for mixtures 2, 4, and 9, all at an equivalence ratio of 0.5, and at a temperature of 1250 K. The Sensitivity analysis were carried out using a brute force analysis which increases and decreases both the forward and reverse rate constants by a factor of two using an automated code developed in-house, with sensitivities expressed using the formula:

\[
\ln S = \frac{\ln(\tau + /\tau-)/\ln(k + /k-)}{\ln(k + /k-)} = \frac{\ln(\tau + /\tau-)}{\ln(2/0.5)}
\]

A negative sensitivity coefficient is one in which the ignition delay time decreases and thus corresponds to an increase in reactivity, Fig. 14, contrarily a positive sensitivity coefficient corresponds to an increase in ignition delay time and thus a decrease in reactivity, Fig. 15.

These three mixtures were chosen due to their excellent agreement to the mechanism, mix 2 comprising 40% CH\(_4\) + 60% H\(_2\) at 10 atm, mix 4 containing 30% H\(_2\) + 70% NG2 at 30 atm, and mix 9 composed of 80% H\(_2\) + 20% NG3 at 1 atm. As all the sensitivities are performed at the same equivalence ratio and temperature, similar reactions dominate the reaction kinetics controlling ignition delay time predictions, but these reactions have different relative sensitivities depending on the mixture composition. In general, mixtures 2
Figure 14: Important reactions promoting reactivity to ignition delay times for mixtures 2 (60% H\textsubscript{2}, 40% CH\textsubscript{4}, φ = 0.5, 10 atm), 4 (30% H\textsubscript{2}, 70% NG\textsubscript{2}, φ = 0.5, 30 atm), and 9 (80% H\textsubscript{2}, 20% NG\textsubscript{3}, φ = 0.5, 1 atm) at 1250 K.

and 9 contain a higher hydrogen mole fraction relative to methane and thus hydrogen kinetics will tend to dominate, whereas in mix 4 there is a high concentration of hydrocarbons, and thus methyl radical chemistry will be of more importance than in mixtures 2 and 9. This is reflected in the individual sensitivity analyses detailed below.

For all mixtures, the reaction most promoting reactivity is the high temperature chain branching reaction \( \dot{H} + O_2 = \ddot{O} + \dot{OH} \). This reaction is most important for high hydrogen content mixtures 2 and 9 and lower pressures. Any reaction that depletes (\( \dot{H} + O_2 (+M) = H\ddot{O}_2 (+M) \)) or increases (\( \dot{OH} + H_2 = \dot{H} + H_2O \)) the hydrogen atom concentration will have a positive or
Figure 15: Important reactions inhibiting reactivity to ignition delay times for mixtures 2 (60% H$_2$, φ = 0.5, 10 atm), 4 (30% H$_2$, φ = 0.5, 30 atm), and 9 (80% H$_2$, φ = 0.5, 1 atm) at 1250 K.
negative sensitivity coefficient respectively. At the conditions investigated hydroperoxyl radical chemistry is important (\( \cdot \text{CH}_3 + \text{HO}_2 = \text{CH}_3\cdot \text{O} + \cdot \text{OH} \)) due to the reaction \( \cdot \text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M}) \). The \( \text{HO}_2 \) radical formed abstracts a hydrogen atom from another molecule to generate hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) which decomposes to two hydroxyl (\( \cdot \text{OH} \)) radicals. The reaction \( \text{H}_2 + \text{O} = \cdot \text{H} + \cdot \text{OH} \) promotes reactivity as it produces two radicals including a \( \cdot \text{H} \) atom while consuming just one, but \( \text{CH}_4 + \text{O} = \cdot \text{CH}_3 + \cdot \text{OH} \) inhibits reactivity even though it also produces two radicals while consuming one, but this reaction competes for oxygen atoms and reduces the concentration of hydrogen atoms in the system.

The most inhibiting reaction for all mixtures is \( \text{CH}_4 + \cdot \text{OH} = \cdot \text{CH}_3 + \text{H}_2\text{O} \), as this reaction competes with the promoting reaction \( \text{H}_2 + \cdot \text{OH} = \cdot \text{H} + \text{H}_2\text{O} \) for hydroxyl radicals, producing less reactive methyl radicals compared to more reactive hydrogen atoms. For mix 2 the recombinaction of a methyl radical with a hydrogen atom, \( \cdot \text{CH}_3 + \cdot \text{H} (+\text{M}) = \text{CH}_4 (+\text{M}) \) is the second most inhibiting reaction, as it consumes two radicals and produces stable methane. As is the case with the reaction \( \cdot \text{CH}_3 + \cdot \text{CH}_3 (+\text{M}) = \text{C}_2\text{H}_6 (+\text{M}) \). This reaction shows a higher sensitivity to mix 4 compared to mix 2 and 9, since mix 4 contains the highest concentration of methane. For mix 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 \( \cdot \text{H} + \text{O}_2 = \cdot \text{O} \)
+ ·OH, and these reactions all show positive sensitivity coefficients, reducing reactivity. \( \text{C}_2\text{H}_6 + \cdot\text{H} = \cdot\text{C}_2\text{H}_5 + \text{H}_2 \), 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 promotes 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 \( \cdot\text{C}_2\text{H}_3 + \text{O}_2 = \cdot\text{CH}_2\text{CHO} + \cdot\text{O} \), Fig. 14.

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 overarching sensitivity of ignition delay times to the main chain branching reaction \( \cdot\text{H} + \text{O}_2 = \cdot\text{O} + \cdot\text{OH} \) under these conditions. \( \text{CH}_4 + \cdot\text{O} = \cdot\text{CH}_3 + \cdot\text{OH} \) has an inhibiting effect as it reduces the concentration of hydrogen atoms in the system and produces a less reactive methyl radical. The reaction of an ethyl radical with a hydrogen atom, \( \cdot\text{CH}_3 + \cdot\text{CH}_3 (+\text{M}) = \cdot\text{C}_2\text{H}_5 + \cdot\text{H} (+\text{M}) \), shows a high positive sensitivity coefficient for mix 9, Fig. 15.

7. Conclusions

New experimental data has been taken for natural gas/hydrogen blends over a wide range of conditions. These new results were compared to the current AramcoMech 1.3 chemical kinetic mechanism developed at the NUIG
research facility and excellent agreement was observed. The experimental data shows that ignition delay time decreases with increasing temperature, pressure, hydrogen fuel fraction and increase in long chain hydrocarbons. The current AramcoMech 1.3 mechanism was also validated against shock tube ignition delay times and new flame speed data from TAMU and laminar flame speed and ignition delay time data available in the literature. The agreement between the TAMU shock tube and NUIG RCM ignition delay time data is very good and is accurately captured by the NUIG AramcoMech 1.3 mechanism. The effect of hydrogen on hydrocarbon mixture ignition delay times is captured at all pressures showing that the addition of hydrogen to hydrocarbon fuels leads to higher reactivity and shorter ignition delay times demonstrating the promoting effect of hydrogen on the hydrocarbon chemistry. Equivalence ratio was seen to have the smallest effect on ignition delay time but was not negligible. The mechanism accurately predicts the Zhang et al. [34] shock tube ignition delay times except at the highest pressures for pure hydrogen. The TAMU laminar flame speeds also provide good agreement with AramcoMech 1.3. Overall the agreement between the experimental data and the AramcoMech 1.3 mechanism is quite good. For comparison, simulations with GRI-Mech 3.0 and modified GRI-Mech 3.0 including the C_4 and C_5 NUIG sub-mechanisms have been performed. GRI-Mech 3.0 does not accurately describe the new ignition delay time experimental data, the TAMU natural gas flame speeds and Zhang et al. [34] shock tube ignition delays. However; it agrees well for the TAMU methane/hydrogen flame speeds.
This is possibly due to the tendency of GRI 3.0 to under-predict hydrogen reactivity and over-predict hydrocarbon reactivity compared to AramcoMech 1.3. Nevertheless, there is a large uncertainty in the literature for laminar flame speeds taken at the same conditions and both mechanisms fall within this uncertainty. We believe, that this work offers a great contribution to the gas turbine industry. The NUIG AramcoMech 1.3 chemical kinetic mechanism has been shown to predict accurate results for natural gas/hydrogen mixtures and might be used to precisely validate other natural gas experimental data at gas turbine relevant conditions.

References


