Summary of Simplified Two Time Step Method for Calculating Combustion Rates and Nitrogen Oxide Emissions for Hydrogen/Air and Hydrogen/Oxygen

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Abstract

A simplified single rate expression for hydrogen combustion and nitrogen oxide production was developed. Detailed kinetics are predicted for the chemical kinetic times using the complete chemical mechanism over the entire operating space. These times are then correlated to the reactor conditions using an exponential fit. Simple first order reaction expressions are then used to find the conversion in the reactor. The method uses a two time step kinetic scheme. The first time averaged step is used at the initial times with smaller water concentrations. This gives the average chemical kinetic time as a function of initial overall fuel air ratio, temperature, and pressure. The second instantaneous step is used at higher water concentrations (>1x10^30 moles/cc) in the mixture which gives the chemical kinetic time as a function of the instantaneous fuel and water mole concentrations, pressure and temperature (T_4). The simple correlations are then compared to the turbulent mixing times to determine the limiting properties of the reaction.

The NASA Glenn GLSENS kinetics code calculates the reaction rates and rate constants for each species in a kinetic scheme for finite kinetic rates. These reaction rates are used to calculate the necessary chemical kinetic times. This time is regressed over the complete initial conditions using the Excel regression routine. Chemical kinetic time equations for H_2 and NO_2 are obtained for H_2/Air fuel and for H_2/O_2.

A similar correlation is also developed using data from NASA's Chemical Equilibrium Applications (CEA) code to determine the equilibrium temperature (T_4) as a function of overall fuel/air ratio, pressure and initial temperature (T_3). High values of the regression coefficient R^2 are obtained.

Introduction

Hydrogen is the fuel of the future. Iceland is converting their economy to hydrogen and several countries (United States, Germany, Australia, Mexico, China, Canada, Japan, and Russia) are strongly interested in the technology because of global warming concerns from CO_2 and the unlimited supply of hydrogen from water conversion. It is important to have a simple, quick method of computing the chemical rates for prediction of times of conversion and for the design of combustors. Accurate chemical kinetic mechanisms exist for hydrogen reaction, but they involve as many as 21 chemical steps with the production of intermediate species like OH, HO_2, H and O atoms with H_2O_2 as an intermediary. We have used the H_2 mechanism of S.L. Hwang, et al. (ref. 1) as the basis of this report. No changes in the hydrogen mechanism were made in switching from H_2/Air to H_2/O_2. We have taken a fourty-two step mechanism for the production of nitrogen oxides from GRI-Mech 2.1 without the carbon reactions, used in reference 2, and correlated the formation rate of nitrogen oxides in the presence of hydrogen by a similar two time step method. Any detailed mechanism could have been used to compute the chemical kinetic time constants.

The hydrogen reactions are about seven times as fast as hydrocarbon fuels and the reactions require small time steps to integrate accurately. We have used the NASA Glenn GLSENS kinetics code (ref. 3) to integrate the progress of the reaction accurately. The classical methods were used to compute over two thousand cases at constant T and P. Then the results were correlated with a simple two time step approach to predict the chemical kinetic time constants. The derived method involves only the principal species H_2, and H_2O and NO_2 for nitrogen oxides, species which are predicted routinely by computer codes. We do not require tracking the intermediate free radicals, as the kinetic times in step one before the radicals become large are practically constant and in step two are related to the instantaneous H_2, O_2, and H_2O concentrations.

This report is a summary of a more detailed summary report (ref. 4). The two time step approach was used successfully by Molnar and Marek in reference 2 for Jet-A and methane. The two time step approach is used because the free radicals OH, etc., catalyze the reactions and act as important intermediates. The principle reaction for water production is OH through the reaction:

$$H_2 + OH = H_2O + H$$

We think that the more water that is present in the reactor then the more OH would be present accelerating all of the reactions. So H_2O can be used as an indicator of the OH present.

In order to obtain the chemical source term, a comparison can be made of the turbulent mixing time $\tau_\text{mix}$ or $k/\epsilon \tau_\text{kin}$ with $k$ being the turbulent kinetic energy, $\epsilon$ is the dissipation rate and the chemical kinetic time $\tau_\text{kin}$ and the longest time is used as the overall time (ref. 5). This may also be represented by the following relationship:
\[ \tau = \max (\tau_m, \tau_z) \]

With the approach derived here, a simple direct comparison can be made between the mixing and chemical kinetic times and the minimum rate used for all points and at each iteration of a CFD code.

**Simple Model Equations**

Only the following equations can be used to model the chemical system.

\[
\begin{align*}
\text{H}_2 + \frac{1}{2} \text{O}_2 & \xrightarrow{\tau_{\text{Fuel}}} \text{H}_2\text{O} \\
\frac{1}{2} \text{N}_2 + \frac{1}{2} \text{O}_2 & \xrightarrow{\tau_{\text{NO}}} \text{NO}
\end{align*}
\]

The following first order reaction is used to represent the rate of fuel burning. We compute the net reaction time so we do not worry about the forward and reverse processes, only the net process. We assume that the fuel goes to zero at the end of the reaction and that the NO\textsubscript{x} increases linearly and it is far from equilibrium. (In this report, \(t\) and \(\tau\) are given in milliseconds, while concentrations are given in gmoles/cc):

\[
\frac{d\text{H}_2}{dt} = \frac{c\text{H}_2}{\tau_{\text{H}_2}}; \quad \tau_{\text{H}_2} = -\frac{c\text{H}_2}{\sum \left( \frac{d\text{H}_2}{dt} \right)}; \quad \text{OR if } \tau_{\text{H}_2} \text{ is constant: } \text{H}_2 = \text{H}_{2,0} e^{\left( \frac{-t}{\tau_{\text{H}_2}} \right)}
\]

The chemical time \(\tau_{\text{H}_2}\) can be computed from the concentration of \(\text{H}_2\) and its net rate of production.

The nitrogen oxide formation rate, a species important for combustor emissions, was modeled as a simple zero order expression.

\[ \frac{d\text{NO}_x}{dt} = \frac{t}{\tau_{\text{NO}_x}}; \quad \text{OR } \tau_{\text{NO}_x} \text{ is constant } \frac{d\text{NO}_x}{dt} = \frac{1}{\tau_{\text{NO}_x}} \]

where \(\tau_{\text{NO}_x}\) has units of \(\frac{\text{ms}\cdot\text{cc}}{\text{gmoles}}\)

**H\textsubscript{2}/Air Initial conditions for chemical kinetic**

- Temperature = 1000, 1500, 2000, 2500 K
- Pressure = 1, 10, 20, 30, 40 atm
- Lean equivalence ratios = 0.3 to 1.0 increments of 0.1
- Rich equivalence ratios = 1.05, 1.1 to 2.0 increments of 0.1

**H\textsubscript{2}/O\textsubscript{2} Initial conditions for chemical kinetic times for advanced rocket combustors (ref. 6)**

- Temperature = 1000, to 4000, increments of 500, then 5000 K
- Pressure = 0.5, 1.0, 10, 50, 100, 200, 300, 400 atm
- Lean equivalence ratio = 0.1 to 1.0 increments of 0.1
- Rich equivalence ratio = 1.05, 1.1, 1.2 to 3.0 increments of 0.2
- Time steps for Step 2 were the same as Step 1 with integration to 3 milliseconds. The output tabulated at least 20 points per case. For the approximately 2000 cases, the total number of points correlated could exceed 40,000 per regression. Excel can handle up to 65,000 points.

The kinetic mechanism of Hwang, S.M., et al. (ref. 1), next page, was used for the full range of conditions without modification.

Even though the mechanism was tested to a temperature of 3000 K and 4 atmospheres, we felt that the mechanism would extrapolate and give reasonable results for design because nothing else was available at the high temperature and high pressure conditions. The differences between the H\textsubscript{2}/Air and the H\textsubscript{2}/O\textsubscript{2} is the absence of nitrogen in the H\textsubscript{2}/O\textsubscript{2} set, and in H\textsubscript{2}/O\textsubscript{2} the maximum temperatures were twice that of H\textsubscript{2}/Air and the maximum pressures were an order of magnitude higher. We computed and correlated the chemical kinetic times over the full range of conditions.
H₂ Kinetic Scheme for Step 1(Average) and Step 2 (Instantaneous) Methods

CC S.M. Hwang, et al. (ref. 1) H₂ Combustion Over a Range of Conditions

&RTYPE GLOBAL=.TRUE.,GRONYL=.FALSE. &END
H   O₂ = OH  O  6.73E+15  -0.499  16671.6
O   H₂ = OH  H  5.06E+04  2.67  6289.2
OH  H₂ = H₂O  H  2.16E+08  1.510  3430.0
O   H₂O = 2.OOH  4.51E+04  2.7  14551.4
O   O = O₂  M  1.00E+17  -1.  0.0

THIRD BODY
H₂O  18.5 H₂  2.9 O₂  1.2 END
H   H = H₂  M  6.4E+17  -1.  0.0

THIRD BODY
H₂O  12.0 H₂  4.0 H  26. END
H   O = OH  M  6.2E+16  -0.6  0.0

THIRD BODY
H₂O  5.0 END
H   OH = H₂O  M  8.4E+21  -2.  0.0

THIRD BODY
H₂O  16.25 H₂  2.5 END
H   O₂ = H₂O  M  5.55E+18  -1.15  0.0

THIRD BODY
H₂O  21.3 H₂  3.33 O₂  1.33 END
HO₂ H = OH  OH  8.4E+13  0.0  635.0
HO₂ H = H₂O  O₂  2.5E+13  0.0  693.1
HO₂ H = H₂O  O  5.0E+12  0.0  1410.1
HO₂ O = O₂  OH  2.0E+13  0.0  0.0
HO₂ OH = H₂O  O₂  2.0E+13  0.0  0.0
HO₂ HO₂ = H₂O₂  O₂  1.3E+11  0.0  -1630.0
HO₂ HO₂ = H₂O₂  O  4.2E+14  0.0  1999.5
M  H₂O₂ = 2.OOH  M  1.2E+17  0.0  45506.7

THIRD BODY
H₂O  6.0 O₂  0.78 END
H₂O₂ H = HO₂  H₂  1.7E+12  0.0  3776.3
H₂O₂ H = H₂O  OH  1.0E+13  0.0  3585.1
H₂O₂ O = HO₂  OH  2.8E+13  0.0  6405.4
H₂O₂ OH = H₂O  HO₂  1.0E+12  0.0  0.0
H₂O₂ OH = H₂O  HO₂  5.75E+12  0.0  9559.8
N  NO = N₂  O  3.500E+13  .000  330.00
N  O₂ = NO  O  2.650E+12  .000  6400.00
N  OH = NO  H  7.333E+13  .000  1120.00
HO₂ NO = NO₂  OH  2.110E+12  .000  -480.00
NO O = NO₂  M  1.060E+20  -1.410  .00

THIRD BODY
H₂  2.0O H₂O  6.0O N₂  0.625 END
NO₂ O = NO  O₂  3.900E+12  .000  -240.00
NO₂ O = NO  OH  1.320E+14  .000  360.00
PLUS 33 REACTIONS FOR N₂O, NH, NH₂, N₂H, HNO, and NH₃
H   O₂ = H₂O  H₂O  9.380E+18  -760  .00
H   O₂ = N₂  H₂O  3.750E+20  -1.720  .00

Some reactions are bimolecular and some are trimolecular expressions so the kinetics code GLSENS was used.

Correlation Results

Equilibrium Lean and Rich H₂/Air Correlations

The H₂ equilibrium correlation for T₄ was correlated for both the lean and rich cases (ref. 7). The exponential function did not correlate the complete data over the total equivalence ratio from 0.2 to 2.0, because of the peak in the values at the stoichiometric conditions. We chose to correlate the values from lean (ϕ = 0.2 to 1.) and then rich from (ϕ >1.05 to 2.0). A similar approach was used for the chemical kinetic times. The T₄ equations were correlated over the complete temperature, pressure and equivalence ratio ϕ. The stoichiometric ϕ was included on the lean side.
Although these equations seem complex, they are simple to program and use. Calculations can even be done on a hand calculator.

\[ T_4 = A(P)^a (T_3)^b (\Phi)^c \]

R-square values have been included to demonstrate the strength of the correlation. R-squared is a measure of the error in the model; an R-squared value of one is ideal. The good R^2 values obtained are typical of all the variables.

### Chemical Kinetic Times for H\(_2\)/Air

#### Step One Equations for H\(_2\)/Air Chemical Kinetic Time Correlations

The following form of equation was used for the H\(_2\) and NO\(_x\) step one correlations:

\[ \tau = A(P)^a (\Phi)^b \exp \left[ \frac{E}{T} \right] \]

where \( \tau \) is the chemical kinetic time in milliseconds, \( P \) is pressure in atm, \( \alpha \) is the initial or overall mass fuel air ratio as in reference 2, and \( T \) is the temperature in Kelvin. The correlation is switched to Step Two when the water molar concentration is greater than \( 1 \times 10^{-20} \) moles/cc. This value was chosen arbitrarily as a simple switch. Step two can not be used with small concentrations of water because if the value of the water concentration were zero, the entire correlation time would go to zero or predict an infinite rate.

### Step One H\(_2\)/Air

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>R-squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)/Air Lean</td>
<td>1.82E-7</td>
<td>0.673</td>
<td>20580</td>
<td>-0.128</td>
<td>0.794</td>
</tr>
<tr>
<td>H(_2)/Air Rich</td>
<td>2.48E-7</td>
<td>-0.455</td>
<td>20044</td>
<td>0.661</td>
<td>0.900</td>
</tr>
<tr>
<td>NO(_x) Lean</td>
<td>8.547</td>
<td>-1.45</td>
<td>30928</td>
<td>0.169</td>
<td>0.895</td>
</tr>
<tr>
<td>NO(_x) Rich</td>
<td>2115.6</td>
<td>-1.60</td>
<td>25986</td>
<td>1.377</td>
<td>0.922</td>
</tr>
</tbody>
</table>

#### Step Two Equations for H\(_2\)/Air

The following form of equation was used for both the \( \tau_{12} \) step two fuel and NO\(_x\) correlations except for different constants. This form of the equation produced the best fit:

\[ \tau = A(P)^a (c_{H_2})^b (c_{H_2O})^c \exp \left[ \frac{E}{T} \right] \]

where \( P \) is pressure in atm, \( c_{H_2} \) is the instantaneous molar concentration of H\(_2\) and \( c_{H_2O} \) is the instantaneous water concentration, moles/cc, and \( T \) is the mixture temperature in Kelvin. We have correlated to only the major species hoping that \( c_{H_2O} \) will track the minor species (OH, H, O, etc.) to allow good overall correlation and easy to use equations.

### Step Two H\(_2\)/Air Chemical Kinetic Time Correlations

<table>
<thead>
<tr>
<th></th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>R-squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)/Air Lean</td>
<td>3.06E-17</td>
<td>0.797</td>
<td>-0.855</td>
<td>-0.870</td>
</tr>
<tr>
<td>H(_2)/Air Rich</td>
<td>1.99E-18</td>
<td>1.09</td>
<td>17980</td>
<td>-0.923</td>
</tr>
<tr>
<td>NO(_x) Lean</td>
<td>0.126</td>
<td>-1.19</td>
<td>21201</td>
<td>0.348</td>
</tr>
<tr>
<td>NO(_x) Rich</td>
<td>9.302E-4</td>
<td>-2.15</td>
<td>22305</td>
<td>0.978</td>
</tr>
</tbody>
</table>

### H\(_2\)/O\(_2\) Equilibrium Correlations

The H\(_2\)/O\(_2\) presentation closely follows the H\(_2\)/Air presentation.
\[ T_4 = A(P)^a (\Phi)^b (T_3H_2)^c (T_3O_2)^d \]

**Equilibrium Lean and Rich H\(_2/O_2\) Correlations**

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(R)-squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean (T_4)</td>
<td>1.46E-109</td>
<td>0.0248</td>
<td>0.393</td>
<td>8.96</td>
<td>58.4</td>
</tr>
<tr>
<td>Rich (T_4)</td>
<td>0.96</td>
<td>0.021</td>
<td>-0.427</td>
<td>0.395</td>
<td>1.752</td>
</tr>
</tbody>
</table>

Again a good correlation is obtained.

**Chemical Kinetic Times for H\(_2/O_2\)**

**Step One Equations for H\(_2/O_2\)**

The lean and rich step one H\(_2/O_2\) chemical kinetic time correlations are of the following form:

\[ \tau = A(P)^a (\Phi)^b \exp \left[ \frac{D}{T} \right] \]

where \(P\) is pressure in atm, \(\Phi\) is the initial or overall equivalence ratio and \(T\) is the temperature in Kelvin.

**Step One H\(_2/O_2\) Chemical Kinetic Time Correlations**

<table>
<thead>
<tr>
<th></th>
<th>(A)</th>
<th>(a)</th>
<th>(b)</th>
<th>(D)</th>
<th>(c)</th>
<th>(d)</th>
<th>(R)-squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean</td>
<td>8.07E-07</td>
<td>-0.648</td>
<td>19469</td>
<td>0.491</td>
<td>0.928</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rich</td>
<td>1.50E-06</td>
<td>-0.713</td>
<td>18718</td>
<td>0.918</td>
<td>0.946</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Step Two Equations for H\(_2/O_2\)**

The following form of equation was used for all lean and rich H\(_2/O_2\) step two correlations:

\[ \tau = A(P)^a (c_{fuel})^b (c_{H_2, 0})^c \exp \left[ \frac{E}{T} \right] \]

**Step Two H\(_2/O_2\) Chemical Kinetic Time Correlations**

<table>
<thead>
<tr>
<th></th>
<th>(A)</th>
<th>(a)</th>
<th>(E)</th>
<th>(b)</th>
<th>(c)</th>
<th>(R)-squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean</td>
<td>9.832E-09</td>
<td>-0.471</td>
<td>16964</td>
<td>0.325</td>
<td>-0.596</td>
<td>0.930</td>
</tr>
<tr>
<td>Rich</td>
<td>1.621E-17</td>
<td>1.069</td>
<td>19794</td>
<td>-1.255</td>
<td>-0.590</td>
<td>0.941</td>
</tr>
</tbody>
</table>

**Comparison of the Model With the Full Mechanism Kinetics**

The predictions of the full mechanism (H\(_2\), H, O, OH and H\(_2\)O) are plotted in figure1, and then our model predictions are superimposed on the calculations. The model predictions are close to the full mechanism predictions. The model used a very simple mass balance for the water concentration. We have not included the intermediate species in our predictions, but we correlate the chemical kinetic times to the overall species concentrations. The H\(_2\)O model concentration is higher than the full mechanism, because no intermediate H species exist in the model. The ignition delay time (3E-4 milliseconds) is closely predicted. As expected, OH, H and O increase at almost the same rate as H\(_2\)O, so H\(_2\)O is a good indicator of the reaction rate.

Since we use the model predictions of concentration to predict the chemical kinetic times, we have correlated the full mechanism chemical kinetic times against the model concentrations of H\(_2\) and H\(_2\)O. The chemical kinetic time for this condition is about one microsecond so the integration requires only about 3000 steps.

**Reduced Model used**

These simple equations in an Excel spreadsheet.

\[ \text{INEFF} = \frac{c_{H_{2n}}}{c_{H_{2n-1}}} = \exp \left( -\frac{ln - In - 1}{\tau F} \right) \]

\[ c_{H_{2n}} = c_{H_{2n-1}} \times \text{INEFF} \]
\[ c_{\text{H}_2\text{O}} = (c_{\text{H}_2}^0 - c_{\text{H}_2}) \]

\[ c_{\text{NO}x} = c_{\text{NO}x_{n-1}} + \frac{\ln_{\tau_{\text{NO}x}}}{\tau_{\text{NO}x}} \]

Used backward differencing \( \Delta t = 1.0 \times 10^{-6} \) for this comparison.

**Figure 1. H2/Air Concentration (Full Mechanism) Compared to Reduced Model vs Time ms**

**Conclusions**

A simplified kinetic scheme for H\(_2\)/Air and H\(_2\)/O\(_2\) fuels resulted in a two time step correlation that calculates chemical kinetic times for fuel and NO\(_x\). These models are simple enough to use in spreadsheet calculations and they are very accurate. These chemical kinetic time equations can then be used in a numerical combustor code to compare the chemical kinetic time with the turbulent mixing time at every grid point and for every iteration step. Strong step one and step two H\(_2\) correlations were developed (\( R^2 > 0.9 \)) for all relations, both the H\(_2\)/Air and H\(_2\)/O\(_2\) correlations. However, because we are trying to correlate so many values over a wide range of conditions, error exists. These model equations are believed to be extremely useful in the comparison of kinetic reaction and turbulent mixing times and in the computation of kinetic rate results. In our model we have only two equations and four major species, therefore the step size can be large and the rates are no longer coupled.

**References**

1. S.M. Hwang; Si-Ok Ryu; K.J. De Witt; and M.J. Rabinowitz: Rate Coefficient Measurements of H + O\(_2\) = Products Manuscript in Publication. August 2004