Autoignition Studies of Alternative Fuels

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Accomplishments – Year 2

• **Alcohol Fuels**
  – Autoignition of Methanol
  – Autoignition of Butanol Isomers
  – Autoignition of 2-Butenol
  – Autoignition of *iso*-Pentanol
  – Autoignition of *n*-Butanol/*n*-Heptane Blends

• **Foundation Fuels**
  – Autoignition of Moist Hydrogen and Syngas

• **In Situ IR Absorption Spectroscopy in Rapid Compression Machine** *(presented by Jay Uddi)*

* Bryan Weber, Kamal Kumar, Yu Zhang
Autoignition of Methanol (1)

(a) Methanol/O₂/Ar, φ=0.25, Pₘₐₓ=15 bar

(b) Methanol/O₂/Ar, φ=1.0, Pₘₐₓ=15 bar

Comparative Ignition Delay Trend

- Current RCM (7-30 bar)
- Bowman (1975)
- Cooke et al. (1971)
- Natarajan & Bhaskaran (1981)
- Shocktube (P<5 bar, T>1300 K)

\[ \text{Ignition Delay} \times [O_2] \text{ (ms mol/cm}^3\text{)} \]

\[ \frac{1000}{T} \text{ (K}^{-1}\text{)} \]

φ=0.25-2.0

P=0.33-30 bar
**Autoignition of Methanol (2)**

**Effect of Pressure on Ignition Delay**

- \( \phi=1.0 \)
- \( O_2 : Ar = 1 : 3.76 \)

**Effect of Equivalence Ratio on Ignition Delay**

- \( P_C = 15 \text{ bar} \)
- \( O_2 : Ar = 1 : 3.76 \)

**Effect of Oxygen on Ignition Delay**

- \( P_C = 15 \text{ bar} \)
- \( X_{\text{fuel}} = 12.3\% \)

- \( \phi=0.67 \) (\( X_{O_2}=27.6\% \))
- \( \phi=1.00 \) (\( X_{O_2}=18.4\% \))
• In the Li et al. (2007) mechanism, the methanol chemistry has been validated against flow reactor, laminar flame, and shock-tube experimental data available in the literature.

• The pressure, temperature, and equivalence ratio range of the data used for validation of methanol were $T=750–2180$ K, $P=1–20$ bar, and $\phi=0.05–6.0$.

• Ignition delay validations were based on the shock-tube study by Bowman (1975) in the range of $1545–2180$ K, $1.2–4.8$ bar, and $\phi=0.375–6.0$. 

(a) Methanol/O$_2$/Ar, $\phi=1.0$, $P_C=30$ bar

(b) Comparative Experimental and Simulated Data

Filled Symbols : Experiment
Empty Symbols : Simulation (Li et al. 2007)

$O_2 : Ar = 1 : 3.76$

$T_C=905$ K
$P_C=30$ bar

\begin{align*}
\text{Ignition Delay (ms)} \\
\text{1000/}T_C
\end{align*}

\begin{align*}
\phi = 1.0 \\
O_2 : Ar = 1 : 3.76
\end{align*}
Autoignition of Methanol (4)

- Morris analysis:
  - 10 random orientation matrices \((r=10)\) and 4-level grid \((p=4)\)
  - Elementary effect \((d_i)\) is defined as
    \[
    d_i = \left[ Y(A_i, A_{i+1}, \ldots, A_k) - Y(A) \right] / \Delta
    \]
    \[
    \Delta = p/[2 \times (p - 1)]
    \]
  - The mean and the standard deviation of the distribution of the elementary effect \((d_i)\) for the \(r\) orientations is a measure of the sensitivity of the parameter \(A_i\).
  - The perturbed pre-exponential factor range is limited to
    \[
    10^{-0.2} < \frac{A_{\text{perturbed}}}{A_i} < 10^{+0.2}
    \]

\[
\text{Morris Analysis for the Mechanism of Li et al. (2007)}
\]

- Standard Deviation for Elementary Effect, \(\sigma\)
- Mean Elementary Effect, \(\mu\) (ms)
- Ignition promoted
- Ignition retarded

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{HO}_2 &\rightarrow \text{H}_2\text{O}_2 + \text{CH}_2\text{OH} \quad (1) \\
\text{H}_2\text{O}_2(+)M &\rightarrow 2\text{OH}(+)M \\
\text{CH}_3\text{OH} + \text{O}_2 &\rightarrow \text{CH}_2\text{OH} + \text{HO}_2 \\
\text{CH}_2\text{O} + \text{HO}_2 &\rightarrow \text{HCO} + \text{H}_2\text{O}_2 \\
\text{H} + \text{O}_2 &\rightarrow \text{O} + \text{OH} \\
\text{CH}_3\text{OH} + \text{H} &\rightarrow \text{CH}_2\text{OH} + \text{H}_2 \\
\text{H}_2\text{O}_2 + \text{OH} &\rightarrow \text{HO}_2 + \text{H}_2\text{O} \\
2\text{HO}_2 &\rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (\text{dup}) \\
2\text{HO}_2 &\rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\end{align*}
\]

\(\phi = 1.0\)

\(P_{C} = 30\text{ bar}\)

\(T_{C} = 905\text{ K}\)

\(O_2 : \text{Ar} = 1 : 3.76\)
Autoignition of Methanol (5)

Integrated Consumption Pathways until the Onset of Ignition

Li et al. (2007)

\[ \phi = 1.0 \]
\[ P_C = 30 \text{ bar} \]
\[ T_C = 905 \text{ K} \]
\[ O_2 : Ar = 1 : 3.76 \]

Rate Constant for \( \text{CH}_3\text{OH} + \text{HO}_2 \rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O}_2 \)

\[ k(T) (\text{cm}^3/\text{mol}/\text{s}) \]

\[ \frac{1000}{T} \text{ (K}^{-1}) \]

- Tsuboi & Hashimoto (1981)
- Tsang (1987)
- Li et al. (2007)
Autoignition of Methanol (6)

Sample Trace Outputs from Simulations

Pressure (bar)

Time (ms)

Probability Density

Ignition Delay (ms)

Experimental Ignition Delay

Scatter Plot of Ignition Delay and Pre-Exponential Factor

CH₃OH+HO₂ ⇒ CH₂OH+H₂O₂

Base (A, τ)

Experiment (τ)

Line: Linear Least Square Fit

Rate Constant Comparison for CH₃OH+HO₂ ⇒ H₂O₂+CH₂OH

Tsuboi and Hashimoto (1981)

Tsang (1987)

Li et al. (2007)

Klippenstien et al./Skodje et al. (2010)

k(T) (cm³/mol/s)

1000/T (K⁻¹)
Autoignition of Methanol (7)

(a) Comparison of Experimental and Simulated Results

Shock Tube (Bowman, 1975)
RCM (Current)
Simulation (Mechanism of Li et al., 2007)
Simulations (Modified Mechanism of Li et al. (2007) using rate expression from Tsang (1987) for 
$CH_3OH+HO_2 \rightarrow H_2O_2+CH_2OH$)

(b) Effect of Updated Rate Constant for $CH_3OH+HO_2 \rightarrow H_2O_2+CH_2OH$ on RCM Results

- However, $CH_3OH+HO_2$ reaction is very sensitive at flow reactor conditions.
- Lowering the rate as suggested deteriorates agreement against flow reactor species data.
Autoignition of $n$-Butanol (1)

$n$-Butanol/$O_2/N_2$, $\phi=0.5$, $P_C=15$ bar

$n$-Butanol/$O_2/N_2$, $\phi=1.0$, $P_C=15$ bar

Ignition Delay (s) vs. $1000/T_C$ (1/K)

Current Data
- Black et al. (2010)
- Moss et al. (2008)
- Grana et al. (2010)
- Harper et al. (2010)

$O_2 : N_2 = 1 : 3.76$
from Ravi Fernandes & Stijn Vranckx

Autoignition of \( n \)-Butanol (2)

\( n \)-Butanol/O\(_2\)/N\(_2\), \( \phi = 1.0 \)

\( O_2 : N_2 = 1 : 3.76 \)

\[ \frac{1000}{T} (1/K) \]

Current Data, \( P_C = 30 \) bar

Heufer et al. (2010), 10-11 bar

Heufer et al. (2010), 18-22 bar

Heufer et al. (2010), 36-42 bar

Ignition Delay (s)

\[ \frac{1000}{T} (1/K) \]

\( n \)-Butanol ignition delays 30 bar

Aachen shock Tube 30 bar

Sung RCM 30 bar

model Aachen

model Galway

model MIT

model MIT

model Sarathy et al.

model LLNL

model Nancy
Autoignition of $n$-Butanol (3)

- The Aachen mechanism under-predicts the experimental data for $n$-butanol.
- Modification of the mechanism by Black et al. to include peroxy chemistry of the primary radicals, which lead to possible reaction sequence $R + O_2 \rightarrow RO_2 \rightarrow QOOH$, $QOOH + O_2 \rightarrow 2OH + \text{product}$.
- Treated all the primary radicals equal and estimated the rate coefficients based on the similar reactions of other fuels combustion (ethanol etc.).
- Pressure dependence of the rate coefficients for the QOOH reactions is not included.
- The overestimation of the low-T branching pathways gives rise to the incorrect two-stage ignition observed in the simulations.
• There does not appear to be a negative temperature coefficient region.
• The order of reactivity of the isomers changes with pressure.
  – $P_C=15 \text{ bar}$: $n$-butanol $> sec$-butanol $\approx iso$-butanol $> tert$-butanol
  – $P_C=30 \text{ bar}$: $n$-butanol $> tert$-butanol $> sec$-butanol $> iso$-butanol
• The pressure traces of tert-butanol show pre-ignition heat release may be contributing to the increase in reactivity of tert-butanol.
In general, the performance of the latest (July) mechanism we had available from MIT is worse compared to the mechanism from the National Combustion Meeting in March. The reasons for this are unclear at the moment, and the situation may have improved (cf. Bill Green’s presentation).
Pathway Analysis for \( n \)-Butanol (1)

- \( n \)-Butanol is chosen as a representative fuel to perform pathway analysis to reveal the differences in chemistry between the mechanisms.

- The destruction rate of each species (mol/cm\(^3\)-sec) by each reaction is computed for constant volume, adiabatic simulations at four conditions: 800 K and 1600 K, and 15 bar and 30 bar.

- The destruction rate is integrated up to the time of 20% fuel consumption.

- The results for each reaction are expressed as a percentage of the total destruction up to the time of 20% fuel consumption.

- Changing the pressure produces very small variations in creation and destruction (<5%); therefore, only 30 bar cases are shown.
Pathway Analysis for \(n\)-Butanol (2)

- Better agreement with experiments.
• Production of $\alpha$-hydroxybutyl dominates.
• Most QOOH and RO$_2$ produce 1-buten-1-ol.
• MIT CEFRC Publication Mechanism produced July 23, 2011.

• Worse agreement with experiments.
• α-hydroxybutyl production dominates, especially at low temperature.
• RO₂ produces butanal exclusively (chain-terminating).
• QOOH primarily produces RO₂.
• Aachen Mechanism published in 2011.
• Modification of the mechanism by Black et al. to include per oxy chemistry.
• All primary fuel radicals are assumed to have the same per oxy chemistry.
Due to the appearance of two-stage ignition in the pressure traces and the path analysis, the simplistic implementation of per oxy chemistry used here is insufficient.
Why Interested in \( n \)-Butanol/\( n \)-Heptane Blends

- \( n \)-Butanol is going to be used primarily as a blending component in petroleum-derived transportation fuels in the near future.

- \( n \)-Heptane not only is a component in the primary reference fuels for rating gasoline octane number, but also has a cetane number within the cetane rating range of petroleum-derived diesel fuels.

- Few studies have been focused on the autoignition of \( n \)-butanol fuel blends under the conditions relative to those in homogeneous charge compression ignition (HCCI) engines.

- Lack of fundamental study on the autoignition of \( n \)-butanol-blended fuel mixtures at low to intermediate temperatures.
Test Conditions

\[ P_C=20 \text{ bar}, \ T_C=700–907 \text{ K}, \ \phi=0.4, \ X_{\text{N}_2} : X_{\text{O}_2} = 3.76 : 1 \]

**Mixture Composition**

<table>
<thead>
<tr>
<th>Mixture</th>
<th>( n )-Butanol</th>
<th>( n )-Heptane</th>
<th>( \text{N}_2 )</th>
<th>( \text{O}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>But100</td>
<td>1.38</td>
<td>0</td>
<td>77.90</td>
<td>20.72</td>
</tr>
<tr>
<td>But80</td>
<td>0.95</td>
<td>0.24</td>
<td>78.05</td>
<td>20.76</td>
</tr>
<tr>
<td>But60</td>
<td>0.62</td>
<td>0.42</td>
<td>78.17</td>
<td>20.79</td>
</tr>
<tr>
<td>But40</td>
<td>0.37</td>
<td>0.56</td>
<td>78.26</td>
<td>20.81</td>
</tr>
<tr>
<td>But20</td>
<td>0.17</td>
<td>0.67</td>
<td>78.33</td>
<td>20.83</td>
</tr>
</tbody>
</table>
Among the low temperature reaction channels, key steps are those involving internal H-atom transfer reactions by forming transition state (T.S.) rings.

Among the T.S. rings, six-membered ring is generally considered to have the most rapid reaction rate, which requires the carbon chain structure like -C-C-C- or C-C-C-. 
The presence of hydroxyl group in \( n \)-butanol may help to promote certain chain propagation channels (e.g., concerted elimination of \( \text{HO}_2 \) from the \( \alpha \)-peroxyhydroxybutyl radical (I)), competing with intramolecular H-atom abstraction reaction channels (II) important in the low temperature chain-branching path, and thereby causing the lack of low temperature reactivity for \( n \)-butanol.
Binary blends of \( n \)-butanol and \( n \)-heptane can exhibit pronounced two-stage ignition at low temperatures due to the presence of \( n \)-heptane in the fuel blends.

Two-stage ignition response for the fuel blends gradually diminishes with the increase of compressed temperature.

For the \( n \)-butanol/\( n \)-heptane blends, ignition delay does not vary monotonically with compressed temperature. NTC behavior is observed.
- Total Ignition delay decreases as the concentration of \( n \)-heptane in the fuel blend increases.
- The difference in total ignition delay between neat \( n \)-butanol and a \( n \)-butanol/\( n \)-heptane blend is temperature-dependent.
- The temperature-dependent nature of the difference in total ignition delay between neat \( n \)-butanol and a \( n \)-butanol/\( n \)-heptane blend can be attributed mainly to the progressive diminishing of cool flame response for the \( n \)-butanol/\( n \)-heptane blend when the compressed temperature migrates from the low temperature range to the intermediate temperature range.
With the presence of \( n \)-heptane in the fuel blends, total ignition delay is significantly shortened as compared to that for neat \( n \)-butanol. Neat \( n \)-butanol shows only single-stage ignition while all of the four binary fuel blends exhibit two-stage ignition. Two-stage ignition response becomes increasingly stronger as the concentration of \( n \)-heptane in the fuel blend increases. Ignition delay varies nonlinearly with the blending ratio between \( n \)-butanol and \( n \)-heptane at low temperatures.
Future Work

• Alcohol Fuels – Autoignition of Butanol Isomers and \( n \)-Butanol/\( iso \)-Octane Blends

• Biodiesel – Autoignition of Methyl Butanoate

• Foundation Fuels – Autoignition of Syngas/Oxidizer Mixtures under Elevated Pressures (>40 bar)

• *In Situ* IR Absorption Spectroscopy in Rapid Compression Machine