Rate Constant Estimation for Large Chemical Kinetic Models and Application to Biofuels

ICCK 2001, MIT

July 28, 2011

William J. Pitz, Henry J. Curran, Charles Westbrook, Marco Mehl, S. M. Sarathy and Taku Tsujimura

Lawrence Livermore National Laboratory

Lawrence Livermore National Laboratory, P. O. Box 808, Livermore, CA 94551

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344
Development of chemical kinetic models for fuels

Ab initio calculations

Fundamental experimental measurements

Thermodynamic database

Detailed chemical kinetic model for practical fuels

Reaction rate rules

Reaction rate constants

C1C2 base chemistry

High temperature mechanism

Reaction class 1: Unimolecular fuel decomposition
Reaction class 2: H atom abstractions from fuel
Reaction class 3: Alkyl radical decomposition
Reaction class 4: Alkyl radical + $\text{O}_2 = \text{olefin} + \text{HO}_2$
Reaction class 5: Alkyl radical isomerization
Reaction class 6: H atom abstraction from olefins
Reaction class 7: Addition of radical species to olefins
Reaction class 8: Alkenyl radical decomposition
Reaction class 9: Olefin decomposition
Need reaction rate rules for many chemical classes of fuels

- Alkanes
- Alkenes
- Cycloalkanes
- Aromatics
- Alcohols
- Methyl esters (biodiesel compounds)
- Carbenes (aldehydes, ketenes)
- Special structures in intermediate species:
  - Alkylhydroperoxides
  - Alkylperoxy
Need reaction rate rules for many types of reaction steps

- RH

+ O₂

OOH

- OH

HOO

Fast High Temperature Combustion

Long Chain Alkanes

Low T Mechanism

Hi T Mechanism

NTC

Reactor Temperature

Reactivity

Degenerate Branching Path

Lawrence Livermore National Laboratory

LLNL-PRES-490531
Assign reaction rate rules by reaction classes

*High temperature mechanism*

Reaction class 1: Unimolecular fuel decomposition
Reaction class 2: H atom abstractions from fuel
Reaction class 3: Alkyl radical decomposition
Reaction class 4: Alkyl radical + O₂ = olefin + HO₂
Reaction class 5: Alkyl radical isomerization
Reaction class 6: H atom abstraction from olefins
Reaction class 7: Addition of radical species to olefins
Reaction class 8: Alkenyl radical decomposition
Reaction class 9: Olefin decomposition
Reaction classes for low temperature reactions

**Low temperature mechanism**

Reaction class 10: Alkyl radical addition to O$_2$ (R + O$_2$)

Reaction class 11: R + R’O$_2$ = RO + R’O

Reaction class 12: Alkylperoxy radical isomerization

Reaction class 13: RO$_2$ + HO$_2$ = ROOH + O$_2$

Reaction class 14: RO$_2$ + H$_2$O$_2$ = ROOH + HO$_2$

Reaction class 15: RO$_2$ + CH$_3$O$_2$ = RO + CH$_3$O + O$_2$

Reaction class 16: RO$_2$ + R’O$_2$ = RO + R’O + O$_2$

Reaction class 17: ROOH = RO + OH

Reaction class 18: RO Decomposition

Reaction class 19: QOOH = Cyclic Ether + OH

Reaction class 20: QOOH = Olefin + HO$_2$

Reaction class 21: QOOH = Olefin + Aldehyde or Carbonyl + OH

Reaction class 22: Addition of QOOH to molecular oxygen O$_2$

Reaction class 23: O$_2$QOOH isomerization to carbonylhydroperoxide + OH

Reaction class 24: Carbonylhydroperoxide decomposition

Reaction class 25: Reactions of cyclic ethers with OH and HO$_2$
Reaction rate rules make the assignment of reaction rate constants manageable

Fuel + (H, OH, CH₃, HO₂) => fuel radical + (H₂, H₂O, CH₄, H₂O₂)

H⁺ atom abstraction rate rules for alkanes

<table>
<thead>
<tr>
<th>C-H type</th>
<th>A (cm³ mol⁻¹ s⁻¹)</th>
<th>n</th>
<th>Eₐ (cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1° H</td>
<td>2.22E+05</td>
<td>2.54</td>
<td>6,756</td>
</tr>
<tr>
<td>2° H</td>
<td>6.50E+05</td>
<td>2.40</td>
<td>4,471</td>
</tr>
<tr>
<td>3° H</td>
<td>6.02E+05</td>
<td>2.40</td>
<td>2,583</td>
</tr>
<tr>
<td>1° OH</td>
<td>1.76E+09</td>
<td>0.97</td>
<td>1,586</td>
</tr>
<tr>
<td>2° OH</td>
<td>2.34E+07</td>
<td>1.61</td>
<td>-35</td>
</tr>
<tr>
<td>3° OH</td>
<td>5.73E+10</td>
<td>0.51</td>
<td>63</td>
</tr>
<tr>
<td>1° CH₃</td>
<td>1.51E-01</td>
<td>3.65</td>
<td>7,154</td>
</tr>
<tr>
<td>2° CH₃</td>
<td>7.55E-01</td>
<td>3.46</td>
<td>5,481</td>
</tr>
<tr>
<td>3° CH₃</td>
<td>6.01E-10</td>
<td>6.36</td>
<td>893</td>
</tr>
<tr>
<td>1° HO₂</td>
<td>6.80E+00</td>
<td>3.59</td>
<td>17,160</td>
</tr>
<tr>
<td>2° HO₂</td>
<td>3.16E+01</td>
<td>3.37</td>
<td>13,720</td>
</tr>
<tr>
<td>3° HO₂</td>
<td>6.50E+02</td>
<td>3.01</td>
<td>12,090</td>
</tr>
</tbody>
</table>
Alkanes

- Set by reverse reaction
  - Exothermic direction
  - C-C bond breaking most important
  - Some variations in forward rate constants, even though you think they should be all the same

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fwd</th>
<th>n fwd</th>
<th>AT°</th>
<th>EA fwd</th>
<th>Rev</th>
<th>n rev</th>
<th>EA rev</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3H8=C2H5+CH3</td>
<td>1.77E+23</td>
<td>-1.889</td>
<td>2.32E+17</td>
<td>9.04E+04</td>
<td>145</td>
<td>1.00E+13</td>
<td>0</td>
</tr>
<tr>
<td>C4H10=CH3+NC3H7</td>
<td>1.59E+23</td>
<td>-1.848</td>
<td>2.80E+17</td>
<td>9.03E+04</td>
<td>184</td>
<td>1.00E+13</td>
<td>0</td>
</tr>
<tr>
<td>C4H10=c2h5+c2h5</td>
<td>6.73E+24</td>
<td>-2.297</td>
<td>4.73E+17</td>
<td>8.93E+04</td>
<td>456</td>
<td>8.00E+12</td>
<td>0</td>
</tr>
<tr>
<td>NC10H22=C7H15-1+NC3H7</td>
<td>4.78E+24</td>
<td>-2.206</td>
<td>6.47E+17</td>
<td>8.89E+04</td>
<td>745</td>
<td>8.00E+12</td>
<td>0</td>
</tr>
<tr>
<td>NC10H22=C6H13-1+PC4H9</td>
<td>7.54E+24</td>
<td>-2.3</td>
<td>5.18E+17</td>
<td>8.88E+04</td>
<td>613</td>
<td>8.00E+12</td>
<td>0</td>
</tr>
<tr>
<td>NC10H22=C5H11-1+C5H11-1</td>
<td>9.81E+23</td>
<td>-2.023</td>
<td>4.92E+17</td>
<td>8.86E+04</td>
<td>622</td>
<td>8.00E+12</td>
<td>0</td>
</tr>
</tbody>
</table>
Reaction rate rules for H-atom abstraction from alkanes

\[ \text{Fuel} + (H, OH, CH_3, HO_2) \rightarrow \text{fuel radical} + (H_2, H_2O, CH_4, H_2O_2) \]

<table>
<thead>
<tr>
<th>C-H type</th>
<th>( A ) (cm(^3) mol(^{-1}) s(^{-1}))</th>
<th>( n )</th>
<th>( E_A ) (cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1^\circ )</td>
<td>2.22E+05</td>
<td>2.54</td>
<td>6,756</td>
</tr>
<tr>
<td>H</td>
<td>2.50E+05</td>
<td>2.40</td>
<td>4,471</td>
</tr>
<tr>
<td>( 3^\circ )</td>
<td>6.02E+05</td>
<td>2.40</td>
<td>2,583</td>
</tr>
<tr>
<td>( 1^\circ )</td>
<td>1.76E+09</td>
<td>0.97</td>
<td>1,586</td>
</tr>
<tr>
<td>OH</td>
<td>2.34E+07</td>
<td>1.61</td>
<td>-35</td>
</tr>
<tr>
<td>( 3^\circ )</td>
<td>5.73E+10</td>
<td>0.51</td>
<td>63</td>
</tr>
<tr>
<td>( 1^\circ )</td>
<td>1.51E-01</td>
<td>3.65</td>
<td>7,154</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>7.55E-01</td>
<td>3.46</td>
<td>5,481</td>
</tr>
<tr>
<td>( 3^\circ )</td>
<td>6.01E-10</td>
<td>6.36</td>
<td>893</td>
</tr>
<tr>
<td>( 1^\circ )</td>
<td>6.80E+00</td>
<td>3.59</td>
<td>17,160</td>
</tr>
<tr>
<td>HO(_2)</td>
<td>3.16E+01</td>
<td>3.37</td>
<td>13,720</td>
</tr>
<tr>
<td>( 3^\circ )</td>
<td>6.50E+02</td>
<td>3.01</td>
<td>12,090</td>
</tr>
</tbody>
</table>
New Argonne data for OH + alkanes

Sirvaramakrishnan et al. 2009 (Argonne)

\[ n\text{-butane} + \text{OH} = \text{butyl} + \text{H}_2\text{O} \]

Droege and Tully 1986 (Sandia)

LLNL-NUIG Reaction rate rules
New measured and calculated rate constants for OH + alkanes are higher at T > 900K

propane + OH = propyl + H2O
Ab initio calculations show higher rates due to higher primary rate.

propane + OH = propyl + H2O

Argonne's calculated cross-over

LLNL primary
LLNL secondary
Argonne primary (ab initio)
Argonne secondary (ab initio)
Tully primary (Experimental)
Tully secondary (Experimental)

propane + OH = propyl + H2O

1E+13
1E+12

Lawrence Livermore National Laboratory

Experimental crossover
H-atom abstraction from the fuel: HO2 + alkanes
Uncertainty in rate of a factor of 3 - 6

Ignition very sensitive to this rate constant under RCM conditions

Figure 6. \( k(\text{C}_3\text{H}_8 + \text{HO}_2 \rightarrow i\text{C}_3\text{H}_7 + \text{H}_2\text{O}_2) \). This work (■), Carstensen\(^{18}\) (○), Scott\(^{8}\) (–Δ–), Orme\(^{14}\) (---∇---), Baldwin\(^{11}\) (◆).
Fuel + HO2 shows high sensitivity when the fuel is hydrogen

Sensitivity results under conditions in rapid compression machine:

H2O2+H ⇌ H2+HO2

New rate constant fit:

Important branching sequence at high pressure:

H2+HO2=>H+H2O2
H2O2=>OH+OH

Retarding reaction:

HO2+HO2=>H2O2+O2

Lawrence Livermore National Laboratory

LLNL-PRES-490531
Class 3: alkyl radical decomposition.

Improvements for iso-octane

Stoichiometric mixtures

Dashed Previous mechanism on website
Solid: Updated version

1000K/T

1000

100

10

1

0.1

1.0

1.1

1.2

1.3

1.4

1.5

1.6

10 atm

55 atm
More accurate estimate for iso-octyl radical decomposition rate constant:

\[
\text{cC8H17} \rightarrow \text{tC4H9} + \text{iC4H8}
\]

- LLNL original
- Colorado School of Mines \textit{ab initio}
- Klippenstein \textit{ab initio}
- Milano generic for alkyl radicals
Low temperature reactions:
Effect of R-O2 bond strength varies with bond type and controls amount of low temperature chemistry

Class 10
R+O2 ⇌ RO2

Values used in LLNL models

Bond dissociation energy ($\Delta H_{298}^\circ$): R-OO ⇒ R + O2

Diagram showing bond dissociation energy values for different compounds.
Low temperature chemistry: $\text{ROO} \rightarrow \text{QOOH}$ isomerizations

6 Member ring isomerization

\[ K_6 = 2.5 \times 10^{10} \cdot \exp(-20450/RT) \]

5 Member ring isomerization

\[ K_5 = 2.0 \times 10^{11} \cdot \exp(-26450/RT) \]
Activation energy depends on ring size and overall thermochemistry
Amenable to rule generation
Significant differences in CSM vs. LLNL rate constants: RO2 isomerization

- CBS-QB3 results generally lower than LLNL values for 5-member TS
- CBS-QB3 results much higher than LLNL values for 6-member TS
  - Mainly due to higher A-factors (much higher than alkyl isomerizations)
- Differences lead to significantly different reaction pathways
Mechanisms for fuels are built in a hierarchical manner and increase rapidly in size with fuel size.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Species</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>8 Species</td>
<td>20 Reactions</td>
</tr>
<tr>
<td>Methane</td>
<td>30 Species</td>
<td>200 Reactions</td>
</tr>
<tr>
<td>Propane</td>
<td>100 Species</td>
<td>400 Reactions</td>
</tr>
</tbody>
</table>

[Diagram showing molecular structures and chemical reactions]
Fuels Size and Mechanism Size

n-Alkane

C\textsubscript{8}H\textsubscript{18} (700 Species, 3150 Reactions)

C\textsubscript{10}H\textsubscript{22} (950 Species, 4050 Reactions)

C\textsubscript{12}H\textsubscript{26} (1250 Species, 5150 Reactions)

C\textsubscript{14}H\textsubscript{30} (1650 Species, 5150 Reactions)

C\textsubscript{16}H\textsubscript{34} (2100 Species, 8150 Reactions)
Application of rules to biofuels

- **Biodiesel**
  - Large methyl esters

- **Alcohols**
  - Iso-pentanol
  - Butanol

- **Aromatics**

- **Olefins**
Biofuels

• Biodiesel
• New types of biofuels
  – Biomass
  – derived from algae and other single cell organisms

Algal oil-derived fuels contain additional esters

Approximate weight percent of fatty acids in various vegetable and algal oil feedstocks [15,19, present work]. The nomenclature Cx:y denotes the length of the hydrocarbon chain (x) and the number of double bonds in the hydrocarbon chain (y) of the fatty acid.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>C8:0</th>
<th>C10:0</th>
<th>C12:0</th>
<th>C14:0</th>
<th>C16:0</th>
<th>C16:1</th>
<th>C18:0</th>
<th>C18:1</th>
<th>C18:2</th>
<th>C18:3</th>
<th>C20:0</th>
<th>C20:4</th>
<th>C20:5</th>
<th>C22:6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>4</td>
<td>24</td>
<td>54</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Canola</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>2</td>
<td>64</td>
<td>20</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coconut</td>
<td>9</td>
<td>6</td>
<td>49</td>
<td>17</td>
<td>8</td>
<td>2</td>
<td>5</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palm</td>
<td>1</td>
<td>42</td>
<td></td>
<td></td>
<td>5</td>
<td>41</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jatropha</td>
<td>11</td>
<td>17</td>
<td>13</td>
<td>47</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nannochloropsis Oculata</td>
<td>4</td>
<td>29</td>
<td>24</td>
<td>9</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iso. Galbana</td>
<td>13</td>
<td>36</td>
<td>32</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 1 also includes the fatty acid composition for two algal oils: *Nannochloropsis Oculata* and *Isochrysis Galbana*. The former algae species is currently under consideration for wide scale production and its fatty acid composition was measured from algal oil samples provided by Solix Biofuels [18].

Soybean and rapeseed derived biodiesels have only 5 principal components

Fatty acid methyl esters (FAMEs):

- Methyl Palmitate (C16:0)
- Methyl Stearate (C18:0)
- Methyl Oleate (C18:1)
- Methyl Linoleate (C18:2)
- Methyl Linolenate (C18:3)
Assembled chemical kinetic model for all of the five main components in biodiesel derived from soybeans or rapeseed oil

- methyl palmitate
- methyl stearate
- methyl oleate
- methyl linoleate
- methyl linolenate

Built with the same reaction rate rules as our successful methyl decanoate and methyl dodecanoate mechanism

Model with all 5 components now published and available:

Experimental validation: New biodiesel model reproduces oxidation of n-decane/methyl palmitate mixture in jet stirred reactor

Stoichiometric fuel/O\textsubscript{2}/He mixtures
1 atm
1.5 s residence time

Jet stirred reactor data: Hakka et al. Comb Flame 2009
Many of the predicted species profiles compare well with experiments: e.g. 1-heptene

Jet stirred reactor data:
Hakka et al. Comb Flame 2009
Biodiesel components ignite in order of number of double bonds

Engine-like conditions:
13.5 bar Stoichiometric fuel/air mixtures
Increased number of double bonds reduces low T reactivity of individual components in stirred reactor at diesel conditions

Diesel engine conditions of high pressure and fuel-rich mixtures: 50 bar, $\Phi=2$ (Fuel: 200 ppm, residence time = 0.05 s)

Simulated conversions of biodiesel components

Jet stirred reactor

Derived cetane numbers from Knothe (2010)
C = C double bonds reduce low T reactivity

- Inserting one C=C double bonds changes the reactivity of 4 carbons atoms in the C chain
- Allylic C – H bond sites are weaker than most others
- Therefore they are preferentially abstracted by radicals
- O₂ is also very weakly bound at allylic sites and falls off rapidly, inhibiting low T reactivity
We have seen the same effect in hydrocarbon fuels: hexenes

\[
\begin{align*}
C &= C - C - C - C - C & \text{1-hexene} \\
C - C &= C - C - C - C & \text{2-hexene} \\
C - C - C &= C - C - C & \text{3-hexene}
\end{align*}
\]

RO2 isomerization initiates low temperature reactivity

Moving the double bond towards the center of the molecule “blocks” more RO2 kinetics

Ignition delay times in a rapid compression machine of hexene isomers (0.86-1.09 MPa, \(\Phi=1\)):

Experimental data: Vanhove et al. PCI2005
Simulations: Mehl, Vanhove, Pitz, Ranzi Combustion and Flame 2008
Plant and animal fat oils have different fatty acid profiles that affect reactivity in a diesel engine

<table>
<thead>
<tr>
<th></th>
<th>Sunflower</th>
<th>Safflower</th>
<th>Linseed</th>
<th>Jatropha</th>
<th>Cottonseed</th>
<th>Corn</th>
<th>Olive</th>
<th>Beef tallow</th>
<th>Palm</th>
<th>Peanut</th>
<th>Soy</th>
<th>Rapeseed</th>
</tr>
</thead>
<tbody>
<tr>
<td>palmitate</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>4</td>
<td>23</td>
<td>10</td>
<td>13</td>
<td>28</td>
<td>46</td>
<td>11</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>stearate</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>8</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>21</td>
<td>4</td>
<td>8</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>oleate</td>
<td>19</td>
<td>13</td>
<td>19</td>
<td>49</td>
<td>20</td>
<td>38</td>
<td>72</td>
<td>47</td>
<td>40</td>
<td>49</td>
<td>25</td>
<td>60</td>
</tr>
<tr>
<td>linoleate</td>
<td>68</td>
<td>78</td>
<td>19</td>
<td>38</td>
<td>53</td>
<td>48</td>
<td>10</td>
<td>3</td>
<td>10</td>
<td>32</td>
<td>55</td>
<td>21</td>
</tr>
<tr>
<td>linolenate</td>
<td>1</td>
<td>0</td>
<td>54</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>14</td>
</tr>
<tr>
<td>CN</td>
<td>49</td>
<td>50</td>
<td>39</td>
<td>58</td>
<td>51</td>
<td>49</td>
<td>55</td>
<td>58</td>
<td>62</td>
<td>54</td>
<td>47</td>
<td>54</td>
</tr>
</tbody>
</table>

With models for all 5 major components, we can now model all these types of biodiesel:

- Not a surrogate model, but a real biodiesel (B100) model!
Use Diesel PRF as a scale to compare reactivity of biodiesel compounds

As CN increases, reaction in PSR starts at lower temperatures and has a greater extent of low T combustion
Diesel PRF scale allows assessment of the reactivity of biodiesel from different sources

Simulated reactivity profiles for biodiesel fuels

- linseed
- beef tallow
- peanut
- olive
- soy
- rapeseed
- CN20 (PRF)
- CN60 (PRF)

Jet stirred reactor

50 bar
\( \Phi=2 \)
fuel: 200 ppm
\( \tau=0.05s \)
Observations on reactivity of biodiesel fuels from different oils

- Methyl ester fuels from different plant and animal fats and oils have different reactivity.

- Detailed composition of these biodiesel fuels determine their reactivity.

- Biggest factor for reactivity variability of biodiesel, large methyl ester fuels is the number of C=C double bonds.

- We can model kinetics of most of these biodiesel fuels using the new biodiesel kinetic mechanism.

- The mechanisms still need refinements and testing, and careful laboratory experiments would be very valuable.
What & Why Isopentanol?

A Next Generation BioFuel:

- Isopentanol (3-Methyl-1-Butanol or 3 Methylbutane-1-ol) is one of biomass derived alcoholic fuel, like Ethanol.

- The challenge of JBEI: To convert all monomer sugars (hexoses and pentoses) released from depolymerization of lignocellulosic biomass into transportation fuels and other chemicals. And the initial targets of JBEI is ethanol, butanol, isopentanol, hexadecane, and geranyl decanoate ester.

- Higher alcohols such as isopentanol has higher energy density and lower hygroscopicity compared to ethanol.

- Volatility is moderate like gasoline, “Not” too high.
Approach

- Development of Isopentanol reaction mechanism
- Single-zone Simulations → Validation
- Study of the kinetics involved in the auto-ignition process
- Simulate an HCCI Engine Combustion
- Compare with representative experimental results
Development of Reaction Mechanism

High temperature chemistry:
- Unimolecular decomposition and H atom abstraction from fuel by activated radicals mainly occur
- Alcohols have weak C-H bonds at $\alpha$ site

Low temperature chemistry:
- Based on low temp. chemistry of isoctane because isoctane has some similar structures to isopentanol
- Results showed “Too Short Ignition Delay & Too Strong NTC”

Concerted elimination of $\text{HO}_2$:
- Concerted elimination forming aldehyde and $\text{HO}_2$ from $\text{RO}_2$ is so fast that low temperature reactions would be slowed down
Schematic Energy Diagram for the Concerted Elimination of HO₂

H abstraction by radicals

I

II

OH
Isopentanol model developed in this study can reproduce the experimental data which were acquired under various $\Phi$, $T$, and $P$ conditions with a shock tube and an RCM.

Shock tube experiments: Kenji Yasunaga, Fiona Gillespie, and Henry Curran (NUI Galway - Ireland)
Rapid compression machine (RCM) experiments: Bryan Weber, Yu Zhang and Chih-Jen Sung (UConn.)
Developed chemical kinetic model for new biofuel iso-pentanol and compared it to experiments in Sandia HCCI engine.

Iso-pentanol mechanism

HCCI engine experiments: Yang and Dec, Sandia, SAE 2010

New generation biofuel proposed by DOE Joint BioEnergy Institute (JBEI)

Reaction rate rules on successful iso-octane because it has some similar structures

Model development and application: LLNL visiting scientist Dr. Taku Tsujimura National Institute of Advanced Industrial Science and Technology, Japan
Iso-pentanol model predicts correct combustion phasing as load is increased in Sandia HCCI engine.

Experiments and Calculations:
Required $T_{BDC}$ for constant combustion phasing

- **Iso-pentanol**
- **with EGR**

$\Phi_m: 0.38$
Iso-pentanol model predicts intermediate heat release that allows high load operation for HCCI

**Iso-pentanol**

**Experiments**

- CA10: 368.6 deg.CA
- $\Phi_m$: 0.38
- no EGR

**Calculations**

- CA50: 368.6 deg.CA
- $\Phi_m$: 0.38
- no EGR

HCCI engine experiments:
Yang and Dec, Sandia, SAE 2010

---

Lawrence Livermore National Laboratory
LLNL-PRES-490631
Developed model for 4 isomers of butanol and compared model predictions to flame experiments at USC

Flame speed measurements: Egolfopoulos et al. USC

Twin premixed counterflow flames

butanol mechanism: 4 isomers

Iso-butanol is a new type of biofuel that can be made directly from cellulose using bacteria
Butanol mechanism accurately simulates flame speeds important for predicting spark ignition engine combustion.

Experimental data: Veloo, Egolfopoulos et al. 2010, 2011

Fuel/air mixtures 1 atm
Butanol model well predicts ignition delay times at pressures and temperatures found in IC engines.

Symbols:
- experimental data Sung et al., Rapid compression machine, AIAA paper, 2011

Rapid compression machine

1.05  1.15  1.25  1.35  1.45
1000/T (1/K)

0.001  0.01  0.1  1
Ignition Delay time (s)

2-butanol
iso-butanol
tert-butanol
n-butanol
butanol isomers
15 atm, phi=1, in air

Rapid compression machine
University of Connecticut
The kinetic mechanism of the aromatics has an intrinsic hierarchical structure.

A new module specific to C8 alkyl aromatics is now under development.
p-Xylene mechanism well reproduces species profiles in jet stirred reactor

Jet stirred reactor

P = 1 atm, Φ = 1, τ = 0.1s

Experiments: Gail and Dagaut
Combustion and Flame 2005
Ortho-, para- and ethyl-benzene models compare well to ignition delay times measured at pressure and temperatures relevant to engines.

Ignition delay times in a shock tube for aromatics

Shock tube experimental data: Shen and Oehlschlaeger, Combustion and Flame 2009
Mechanisms are available on LLNL website and by email

http://www-pls.llnl.gov/?url=science_and_technology-chemistry-combustion

**Combustion Chemistry**

**Go Directly to Mechanisms...**

The central feature of the Combustion Chemistry project at LLNL is our development, validation, and application of detailed chemical kinetic reaction mechanisms for the combustion of hydrocarbon and other types of chemical fuels. For the past 30 years, our group has built hydrocarbon mechanisms for fuels from hydrogen and methane through much larger fuels including heptanes and octanes. Other classes of fuels for which models have been developed include flame suppressants such as halogenated organophosphates, and air pollutants such as soot and oxides of nitrogen and sulfur.

Reaction mechanisms have been tested and validated extensively through comparisons between computed results and measured data from laboratory experiments (e.g., shock tubes, laminar flames, rapid compression machines, flow reactors, stirred reactors) and from practical systems (e.g., diesel engines, spark-ignition engines, homogeneous charge compression ignition (HCCI) engines). We have used these kinetic models to examine a wide range of combustion systems.
Summary

- Reaction classes and reaction rate rules greatly simplify the task of developing chemical kinetic models and assigning rate constants.
- Continually updating reaction rate rules and adding new rules for new moieties such as those from new biofuels.
- Made a lot of progress in chemical kinetic modeling new classes of compounds like esters and alcohols and difficult compounds to model like aromatics.
Acknowledgements

- Fokion Egolfopoulos, butanol
- Jackie Sung, iso-pentanol
- John Dec and Yi Yang, iso-pentanol
Acknowledge support from:

- DOE Office of Vehicle Technologies
  - Gurpreet Singh
  - Kevin Stork

- DOE Office of Basic Energy Sciences
  - Wade Sisk

- DOD Office of Naval Research