Overview

Timeline

- Project provides fundamental research to support DOE/industry advanced engine projects
- Project directions and continuation are evaluated annually

Budget

Project funded by DOE/VT:
- FY09: 400K
- FY10: 400K

Partners

- Project Lead: LLNL – W. J. Pitz (PI), C. K. Westbrook, M. Mehl, M. Sarathy
- Part of Advanced Engine Combustion (AEC) working group:
  - 15 Industrial partners: auto, engine & energy
  - 5 National Labs & 2 Univ. Consortiums
  - Sandia: Provides HCCI Engine data for validation of detailed chemical kinetic mechanisms
  - FACE Working group

Barriers/Targets

- Technical Barrier: Increases in engine efficiency and decreases in engine emissions are being inhibited by an inadequate ability to simulate in-cylinder combustion and emission formation processes
  - Chemical kinetic models for fuels are a critical part of engine models

- Targets: Meeting the targets below relies heavily on predictive engine models for optimization of engine design:
  - Fuel economy improvement of 25 and 40% for gasoline/diesel by 2015
  - Increase heavy duty engine thermal efficiency to 55% by 2018.
  - Attain 0.2 g/bhp-h NOx and 0.01 g/bhp-h PM for heavy duty trucks by 2018
Objectives and relevance to DOE objectives

- **Objectives:**
  - Develop predictive chemical kinetic models for gasoline, diesel and next generation fuels so that simulations can be used to overcome technical barriers to low temperature combustion in engines and needed gains in engine efficiency and reductions in pollutant emissions

- **FY10 Objectives:**
  - Development of high and low temperature mechanisms for selected higher molecular weight iso-alkanes
  - Development of improved toluene and benzene mechanisms
  - Development of a high and low temperature mechanism for a high molecular weight alkyl-benzene
  - Development of efficient software to create reduced mechanisms for use in multidimensional engine simulation codes
Chemical kinetic milestones

✓ December, 2009
Development of improved toluene and benzene mechanisms
✓ May, 2010
Development of a high and low temperature mechanisms for selected higher molecular weight iso-alkanes
  ▪ September, 2010
Development of a high and low temperature mechanism for a high molecular weight alkyl-benzene
  ▪ September, 2010
Development of efficient software to create reduced mechanisms for use in multidimensional engine simulation codes
Approach

- Develop chemical kinetic reaction models for each individual fuel component of importance for fuel surrogates of gasoline, diesel, and alternative fuels.

- Combine mechanisms for representative fuel components to provide surrogate models for practical fuels:
  - diesel fuel
  - gasoline (HCCI and/or SI engines)
  - Fischer-Tropsch derived fuels
  - Biodiesel, ethanol and other biofuels

- Reduce mechanisms for use in CFD and multizone HCCI codes to improve the capability to simulate in-cylinder combustion and emission formation/destruction processes in engines.

- Use the resulting models to simulate practical applications in engines, including diesel, HCCI and spark-ignition, as needed.

- Iteratively improve models as needed for applications.
Assembled high and low temperature model for a series of iso-alkanes, an important chemical class in gasoline and diesel fuels

Improved chemical kinetic models for toluene and benzene, important fuel component and intermediate species, respectively

Successfully simulated intermediate heat release in Sandia HCCI engine, obtaining new understanding

Developed a functional-group kinetics modeling approach for n-alkanes that greatly reduces the size of the mechanism

n-cetane: 2100 species => 216 species
Assembled chemical kinetic model for a whole series of iso-alkanes to represent this chemical class in gasoline and diesel fuels

Includes all 2-methyl alkanes up to C20 which covers the entire distillation range for gasoline and diesel fuels

Built with the same reaction rate rules as our successful iso-octane and iso-cetane mechanisms.

7,900 species
27,000 reactions
Have assembled primary reference fuel mechanism for diesel fuel

- Diesel PRF:
  - n-cetane
  - iso-cetane

- PRF for Diesel mechanism:
  - 2,837 species
  - 10,719 reactions
PFR Ignition results at 13 bar:

-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

log $\tau$ [ms]

1000/T [K]

fuel/air stoichiometric 13 bar

Iso-octane

n-alkanes

HMN

nc7h16 expt
nc7h16 calc
nc10h22 calc
nc10h22 expt
iso-c8h18 calc
ic8h18 expt
hmn calc
PFR Ignition results at 40 bar:

- Fuel/air mixtures
- Stoichiometric
- 40 bar

- Iso-octane
- HMN

- n-hexadecane
- 2,2,4,4,6,8,8-heptamethylnonane

- n-alkanes
- CN 50
Diesel PRFs: Cetane number has a big effect at low temperatures

High cetane PRFs lead to more H2O2 which decomposes to reactive OH radicals

Perfectly stirred reactor stoichiometric mixtures 10 atm
Recent improvements to fuel surrogate models: Gasoline

Improved component models

- n-alkane
- branched alkane
- olefins
- cycloalkanes
- aromatics
- oxygenates

Components:
- Ethanol
- Toluene
- Xylene
- Methylcyclohexane
- Cyclohexane
- Iso-pentanes
- Iso-hexanes
- Iso-octane
- Pentenes
- Hexenes
- n-Butane
- n-Pentane
- n-Hexane
- n-Heptane
- n-alkane
- branched alkane
- olefins
- cycloalkanes
- aromatics
- oxygenates
Improved toluene model well predicts ignition at high pressure

Experimental data: Shen, Vanderover and Oehlschlaeger (2009)
Improving building blocks for toluene: benzene

Benzene ignition delay times in a shock tube

![Graph showing benzene ignition delay times](image)

- **Ignition delay [μs]**
- **1000/T[K]**
- **Experimental data: Burcat et al. 1986**
Improved the predictive behavior of hexenes and pentenes mechanisms over the entire temperature range


RCM experiments: Vanhove et al. 2007
Shock tube experiments: Yasunaga and Curran, 2010
Successful simulation of intermediate heat release in HCCI engine using gasoline surrogate blends

Dec and Yang, 2010: Intermediate heat release allows highly retarded combustion phasing and high load operation with gasoline

Gasoline: Sandia Experiments

Gasoline Surrogate: Calculations

(Curves are aligned by time of peak heat release and normalized by total heat release)
**4-component gasoline surrogate:**
Matched gasoline composition targets and reactivity

**Gasoline surrogate:**

<table>
<thead>
<tr>
<th>Component</th>
<th>Surrogate (%Vol)</th>
<th>Gasoline (%Vol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-alkanes</td>
<td>0.16</td>
<td>0.731</td>
</tr>
<tr>
<td>iso-alkanes</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>olefins</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>aromatics</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>A/F Ratio</td>
<td>14.60</td>
<td>14.79</td>
</tr>
<tr>
<td>H/C</td>
<td>1.92</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Matched the reactivity of a mixture having the same RON and MON as the gasoline.
Reaction contributions to intermediate heat release rate

- HRR $\text{[Erg/CAD]}$
  - $1.00 \times 10^9$
  - $5.00 \times 10^8$
  - $0.00 \times 10^0$
  - $5.00 \times 10^8$
  - $1.00 \times 10^9$
  - $1.50 \times 10^9$
  - $2.00 \times 10^9$
  - $2.50 \times 10^9$
  - $3.00 \times 10^9$

HRR 200kPa 377K

- Formaldehyde oxidation to CO
- $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$
- Methyl radical oxidation to formaldehyde
- $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$

CAD ATDC
With the newly available mechanism reduction tools, LLNL mechanisms are being reduced for use in reacting flow codes:

![Graph showing ignition delay times for n-decane/air mixtures at different pressures.](image)

<table>
<thead>
<tr>
<th>LLNL mechanism</th>
<th>Researchers</th>
<th>Reduction method</th>
<th>Total number species before reduction</th>
<th>Species reduction factor</th>
<th>CPU Speed-up factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-cetane</td>
<td>Mehl et al., 2010</td>
<td>Functional group</td>
<td>2116</td>
<td>10</td>
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<td>n-decane</td>
<td>Niemeyer et al., 2010</td>
<td>Directed relational graph</td>
<td>940</td>
<td>5</td>
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<tr>
<td>PRF for gasoline (n-heptane &amp; iso-octane)</td>
<td>He et al., 2010</td>
<td>On-the-fly</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>n-heptane</td>
<td>Lu and Law, 2009</td>
<td>Directed relational graph, lumping, QSSA</td>
<td>561</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Methyl decanoate (biodiesel surrogate)</td>
<td>Sarathy et al., 2010</td>
<td>Directed relational graph</td>
<td>3034</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Experimental data from Shen et al., 2009 and Pfahl et al., 1996.
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 halogen 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.
Collaborations

- Our major current industry collaboration is via the DOE working groups on HCCI and diesel engines
  - All results presented at Advanced Engine Combustion Working group meetings (Industry, National labs, Univ. of Wisc., U. of Mich.)
  - Collaboration with John Dec and Magnus Sjöberg at Sandia on HCCI engine experiments
- Second interaction is participation with universities
  - Collaboration with Curran at National Univ. of Ireland on many fuels
  - Collaboration with Prof. Oehlschaeger at RPI on large alkanes
  - Collaboration with Prof. Ranzi’s group, Milan, Italy on toluene
  - Collaboration with Prof. Lu, U. of Conn. on mechanism reduction
- Participation in other working groups with industrial representation
  - Fuels for Advanced Combustion Engines (FACE) Working group
Special recognitions and awards during FY10

Charles Westbrook:
- Wilhelm Jost Memorial Lectureship from the Deutsche Bunsengesellschaft fur Physikalische Chemie
- President of the Combustion Institute

William J. Pitz:
- Best paper of the year award 2009: Combustion Society Japan

S. M. Sarathy:
- Postdoctoral fellowship from Natural Sciences and Engineering Research Council of Canada
Activities for Next Fiscal Year

- Develop detailed chemical kinetic models for another series iso-alkanes: 3-methyl alkanes
- Validation of 2-methyl alkanes mechanism with new data from shock tubes, jet-stirred reactors, and counterflow flames
- Develop detailed chemical kinetic models for alkyl aromatics:
- More accurate surrogates for gasoline and diesel
- Further develop mechanism reduction using functional group method

**n-decylbenzene - Diesel Fuels**
Summary

- **Approach to research**
  - Continue development of surrogate fuel mechanisms to improve engine models for HCCI and diesel engines

- **Technical accomplishments:**
  - Assembled reaction mechanism for the high and low temperature oxidation of a series of 2-methyl alkanes that covers the entire distillation range of gasoline and diesel

- **Collaborations/Interactions**
  - Collaboration through AEC working group and FACE working group with industry. Many collaborators from national labs and universities

- **Plans for Next Fiscal Year:**
  - Whole series of 3-methyl alkanes
  - Alkyl aromatics class of fuels