Lawrence Livermore National Laboratory

Chemical Kinetic Research on HCCI & Diesel Fuels

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DOE National Laboratory Advanced Combustion Engine R&D Merit Review and Peer Evaluation

Washington, DC

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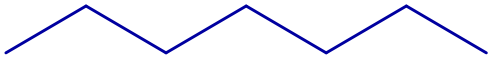
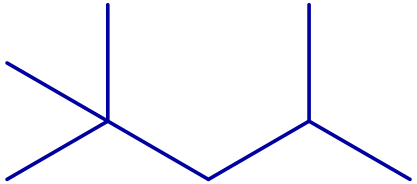
Purpose of work

- Improving models for diesel engines
  - n-hexadecane: important fuel component for diesels

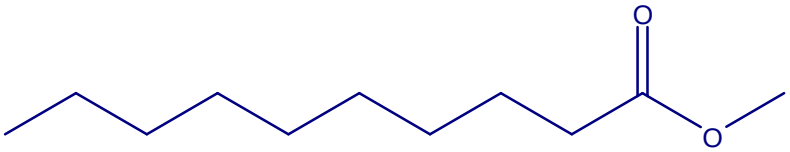
- Improved base chemistry up though n-heptane and iso-octane





- Improving models for HCCI engines
  - Understanding the effect of boost pressure

- Improving models for bio-derived, renewable fuel
  - methyl decanoate, bio-diesel surrogate



FY2007 Reviewer's Comment and Response

- Reviewer comment: "Even if some accuracy is sacrificed, production of models with a substantially reduced reaction count would be an added contribution."
- Response: We have developed a reduced model for a biodiesel surrogate (methyl decanoate) during the last year.

- Reviewer comment: "It will be very important to evaluate the mechanisms that are developed for engine conditions. The time rate of change of pressure and temperature in an engine are important aspects of the mechanism evaluation."

- Response: During the last year, we have done extensive modeling of the Sandia HCCI engine under boosted conditions with several fuel types.

Barriers

- 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
  - Our project is improving the ability to simulate these processes by developing better and more complete detailed chemical kinetic models of gasoline, diesel and alternative fuels

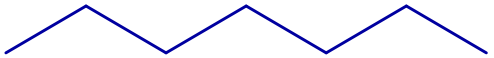
Approach

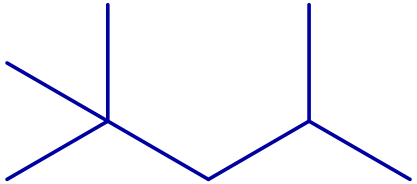
- Develop chemical kinetic reaction models for each individual fuel component of importance for fuel surrogates of gasoline, diesel, and alternative fuels.
- Combine mechanisms for representative fuel components to provide surrogate models for practical fuels
  - diesel fuel
  - gasoline (HCCI and/or SI engines)
  - Oil-sand derived fuels
  - Biodiesel and oxygenated fuels
- 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

Technical Accomplishment Summary

- Improving models for diesel engines
  - Completed of high and low temperature, C8-C16 mechanism

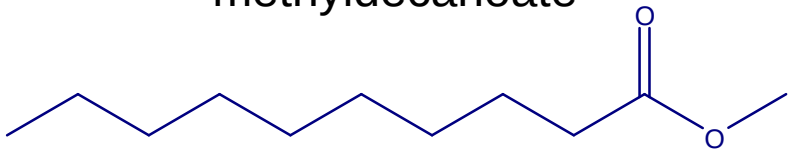
- Completed validation of base chemistry up to n-heptane and iso-octane





- Improving models for HCCI engines
  - Simulated HCCI engine experiments at Sandia using new chemical kinetic mechanisms for gasoline surrogate, cyclohexane and PRF fuels.

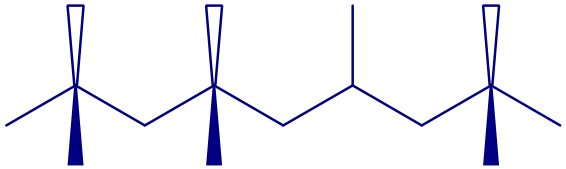
- Improving models for bio-derived, renewable fuel
  - Validated both low and high temperature mechanism for biodiesel surrogate
    - methyldecanoate



We have developed a model for n-hexadecane, a primary reference fuel for diesel

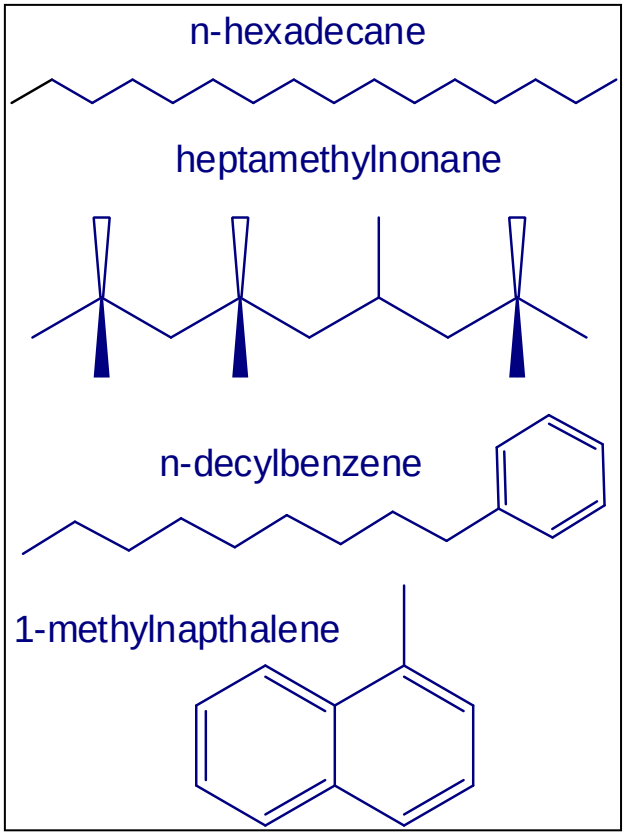
- One of the two primary reference fuels for diesel ignition properties (cetane number)
  - n-hexadecane

  - 2,2,4,4,6,8,8 heptamethylnonane

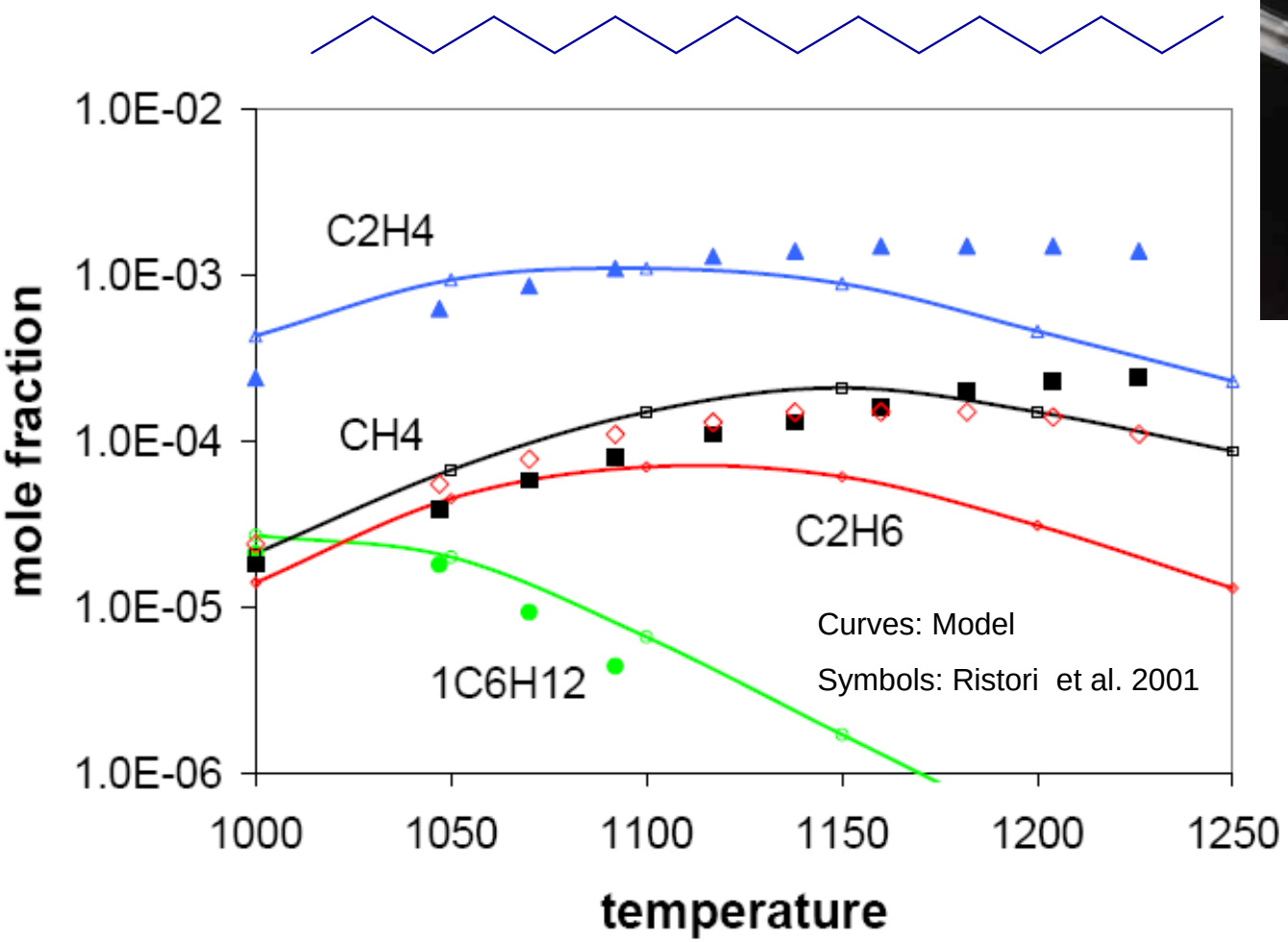


- **High and low temperature portion of the n-hexadecane mechanism complete**
  - Low temperature kinetics most important for diesel and HCCI engines: Low temperature mechanism developed next.
  - First-ever complete set of high and low temperature kinetic mechanisms for all C_8 - C_{16} n-alkanes

Recommended surrogate for diesel fuel (Farrell et al., 2007):

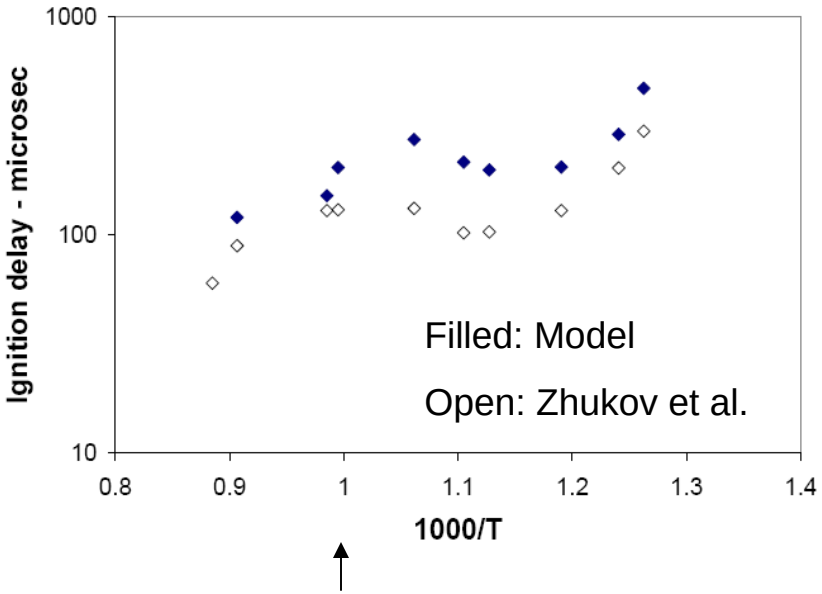


n-Hexadecane model behavior agree well with experiments



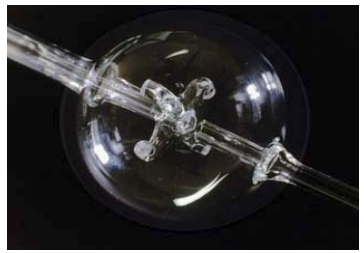
In stirred reactor at 1 atm, 1000-1250K, ϕ=1.5

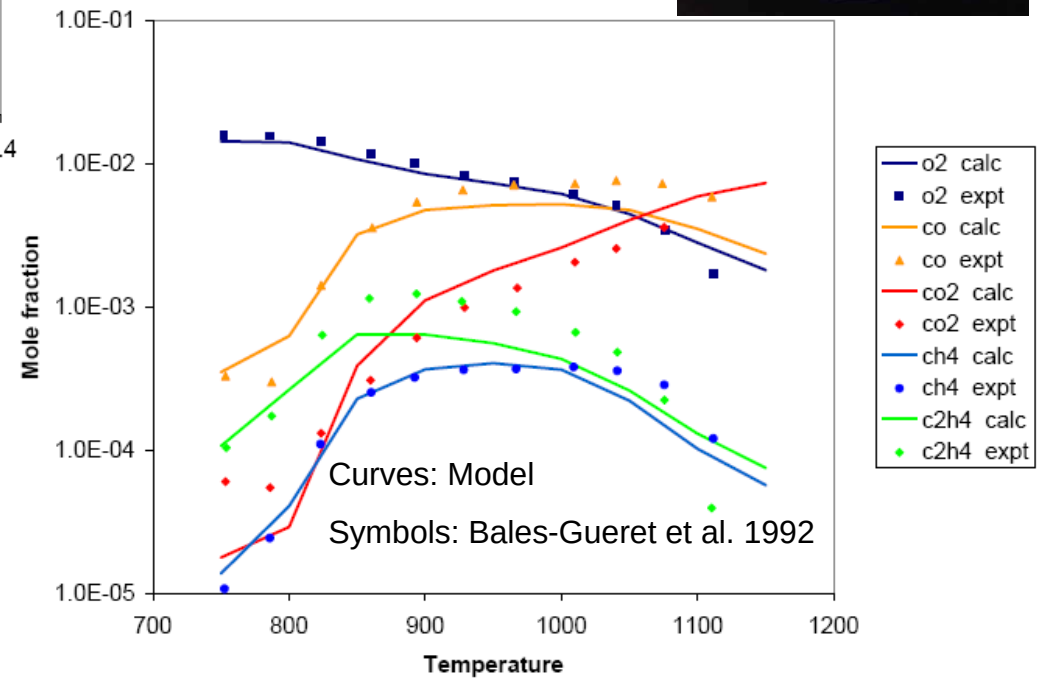
n-Decane model agrees well with experiments under engine-type conditions



In shock tube at
80 atm
800-1100K
ϕ=1

In stirred reactor at
10 atm
750-1150K
ϕ=1

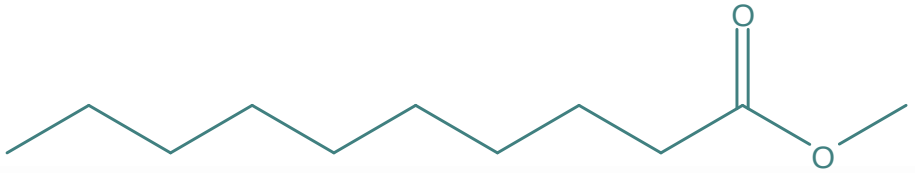




We have developed a low and high temperature mechanism for methyldecanoate, a surrogate for biodiesel:

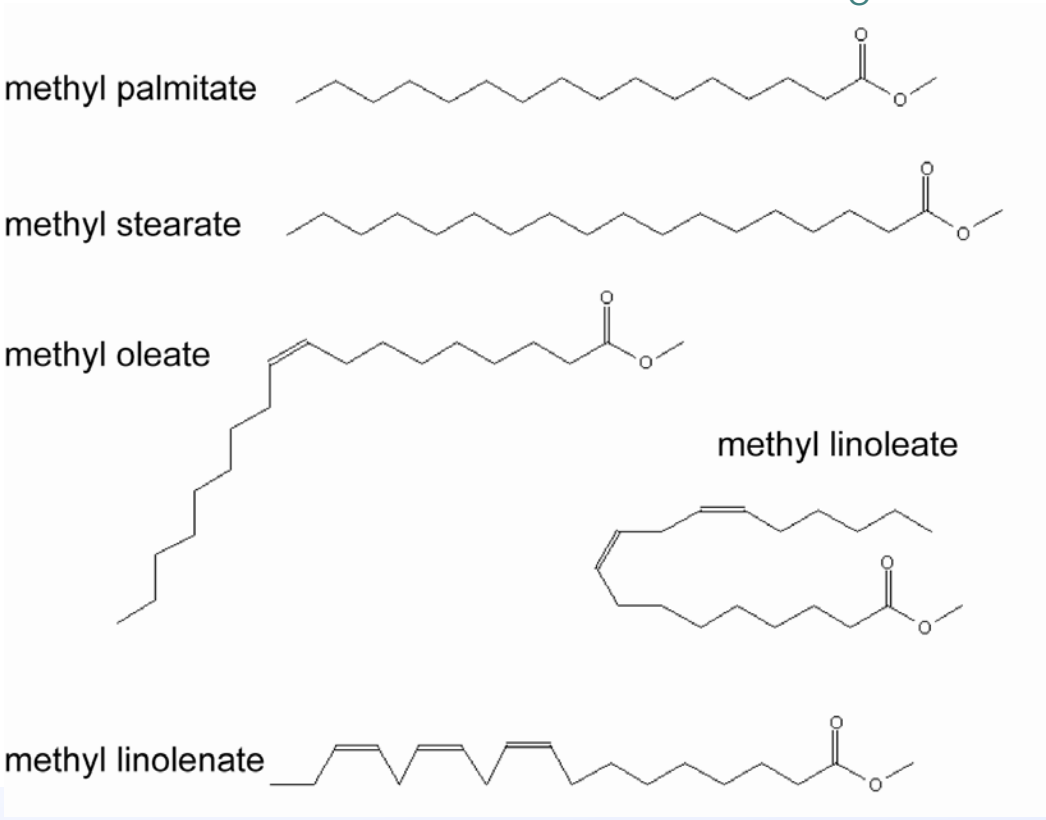
Methyldecanoate represents key features of biodiesel components:

methyldecanoate

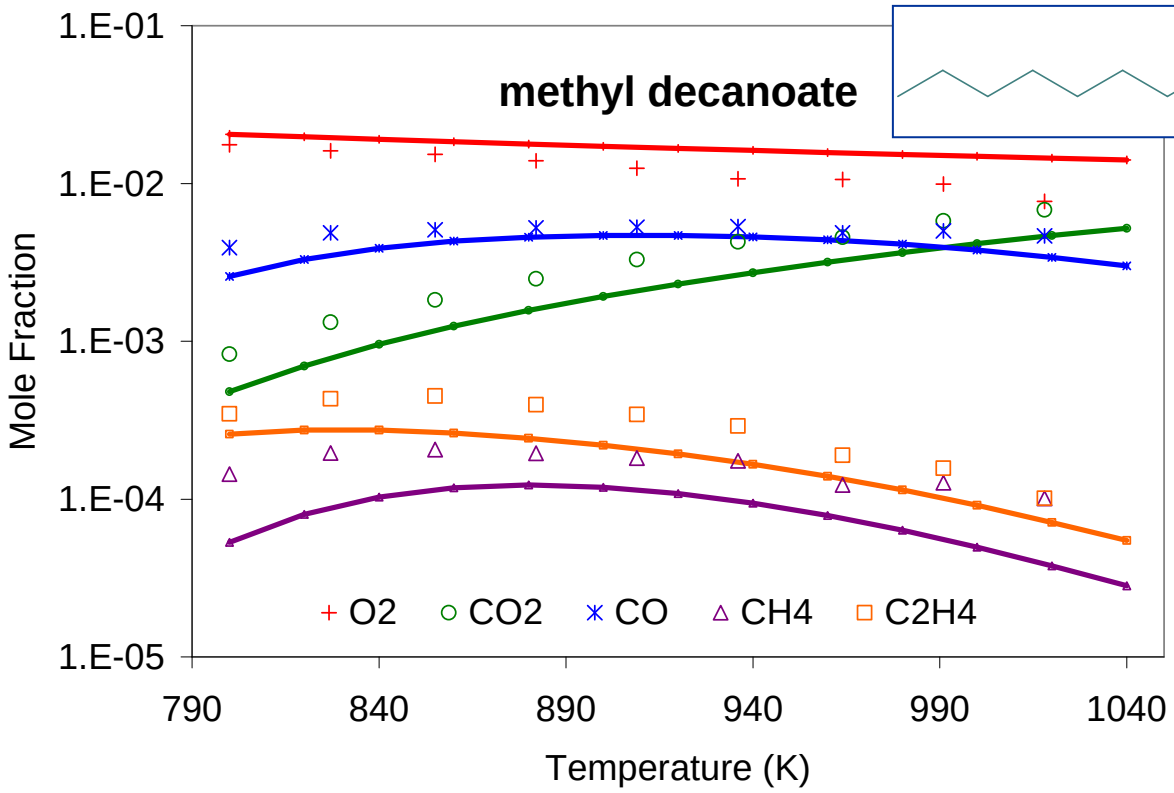


3000 species
8000 reactions

Soy and rapeseed oil components:

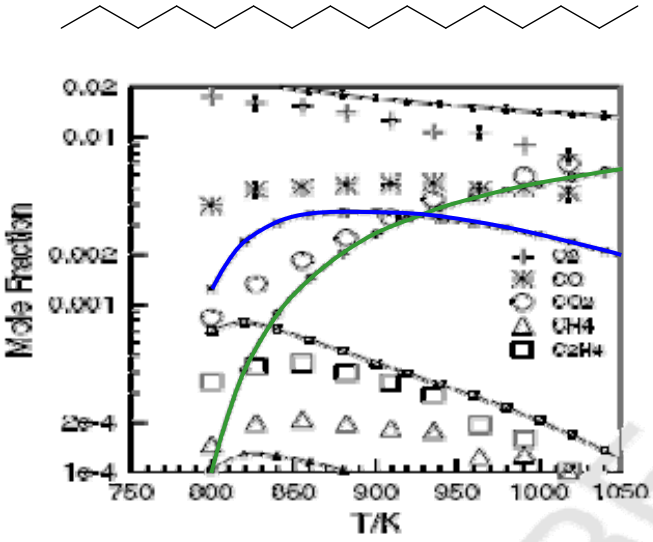


Biodiesel surrogate model of methyl decanoate results compare well with experiments at engine type conditions (10 atm and 790-1040K)



Experiment:
Rapeseed methyl esters

n-hexadecane (Dagaut et al.)

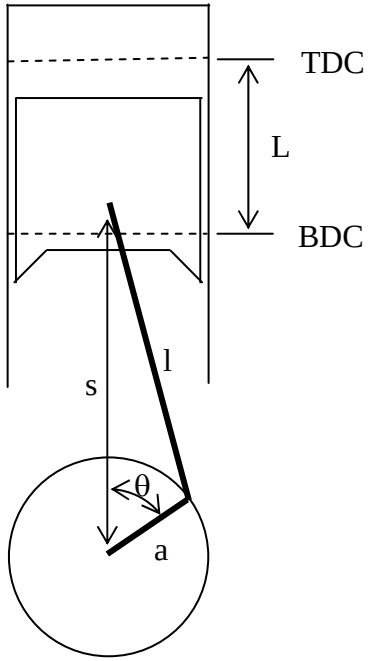


The early formation of CO_2 is better reproduced by the MD mechanism

Early CO_2 formation reduces effectiveness of oxygenated fuels for reducing soot formation

Partial burn, HCCI experiments on Methyl decanoate (Szybist et al.)

- Motored engine with adjustable compression ratio (no spark)
- Increase compression ratio until autoignition occurs
- Measure species in exhaust of engine
- Assumptions required for simulations:
  - temperature at bottom dead center adjusted
  - In-cylinder gases are homogeneous
  - No heat losses
- Chemkin 4.1 code
- Residual gases taken in account by computing several cycles

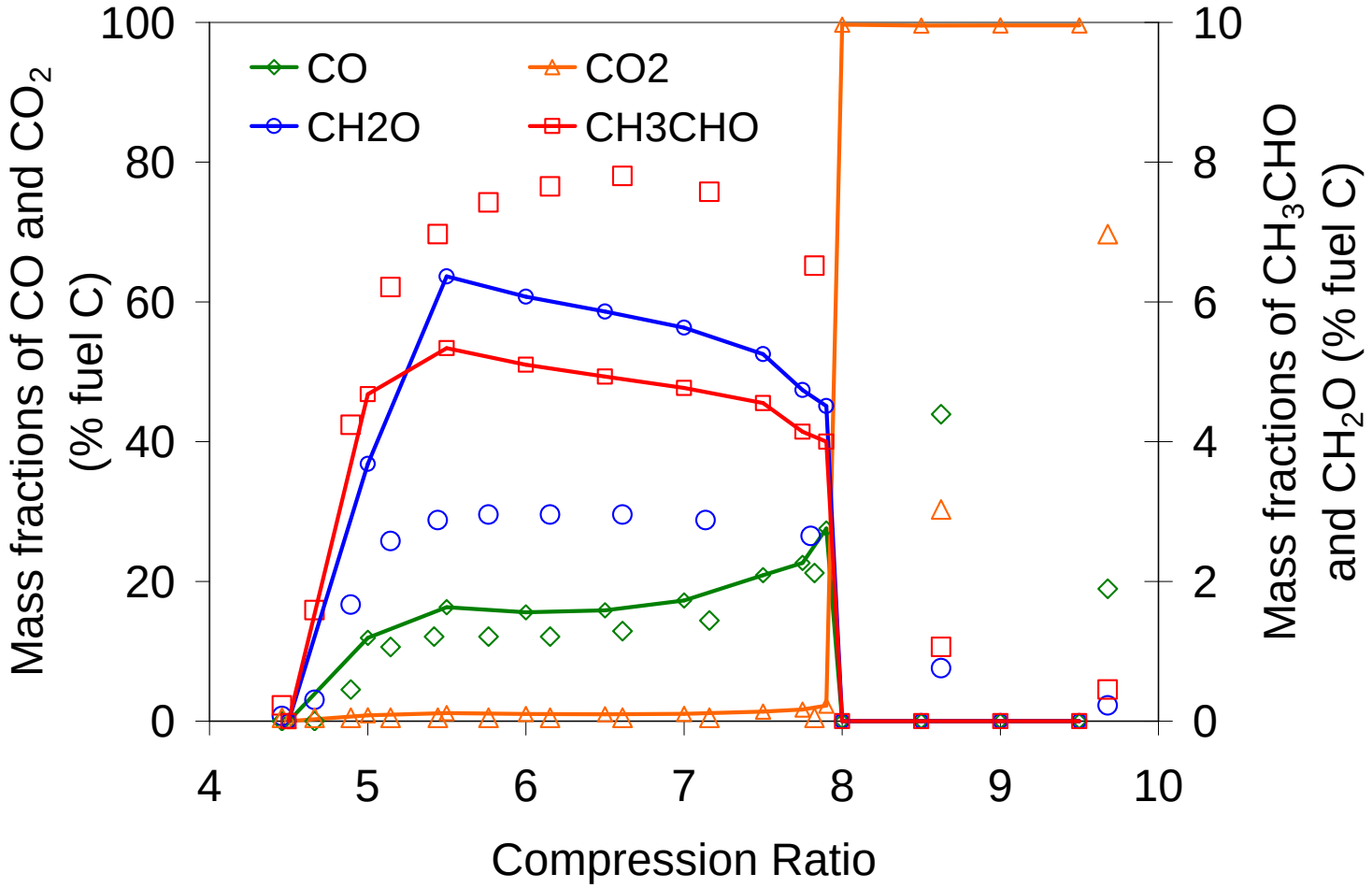


Validate approach with partial burn, HCCI of n-heptane

Test with n-heptane

Mechanism developed in 1998

Mature and well validated

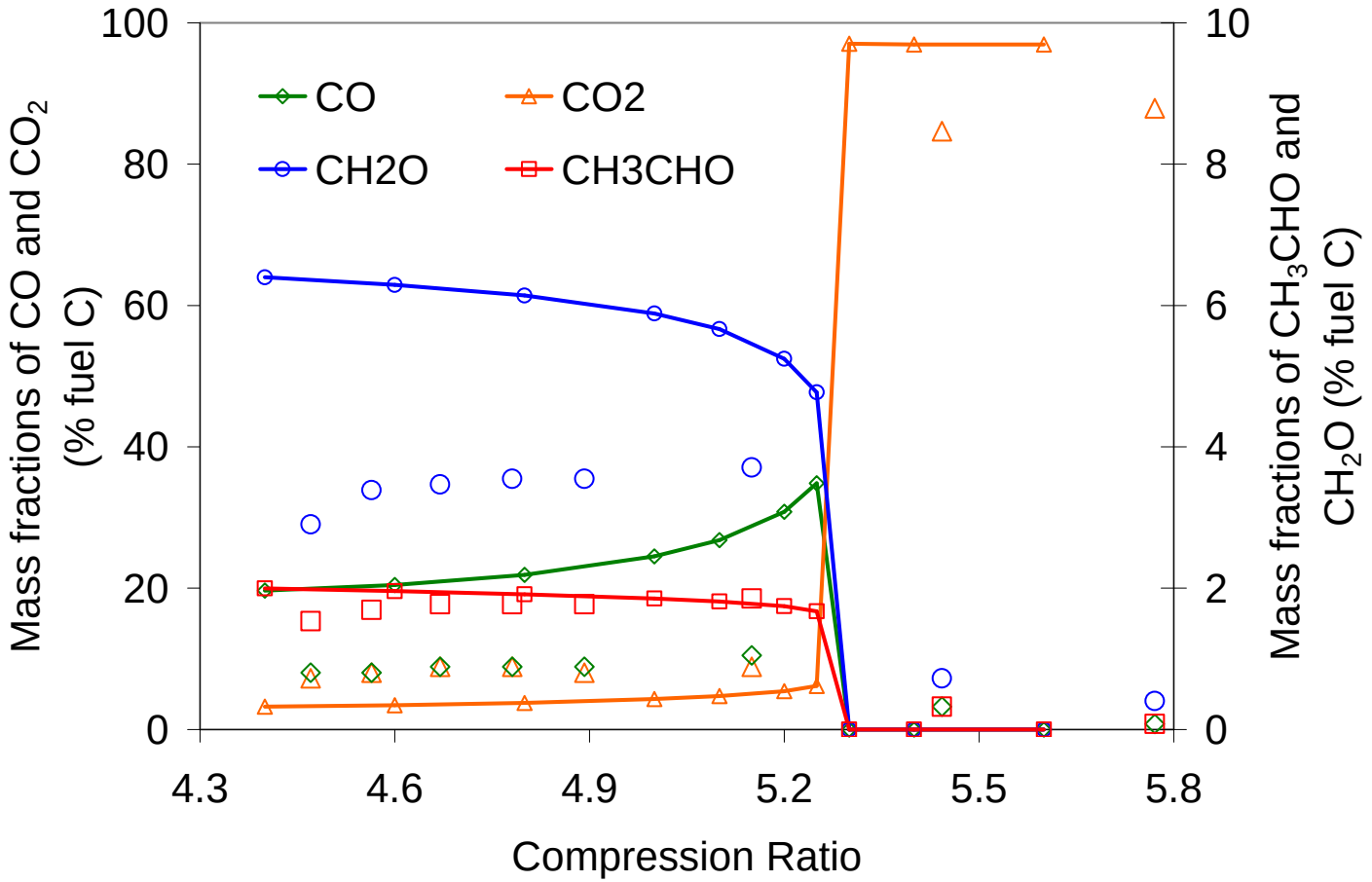


Partial burn, HCCI of Methyl decanoate

Agreement satisfactory

Concentration profiles very similar

Early formation of CO_2



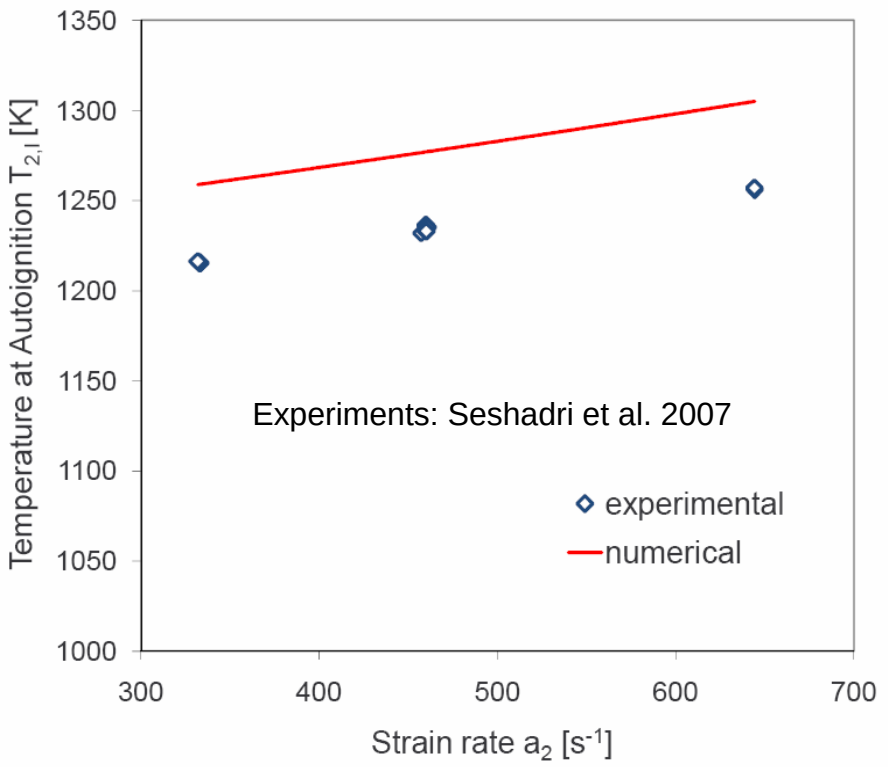
Developed reduced methyl decanoate mechanism for use in reacting flow codes

3036 species

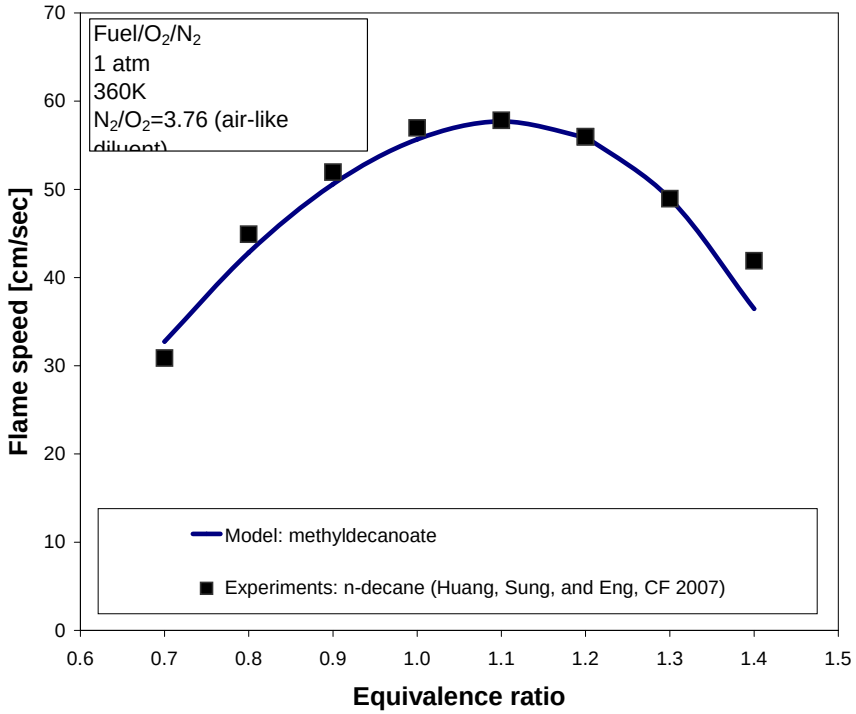
8555 reactions

125 species

712 reactions

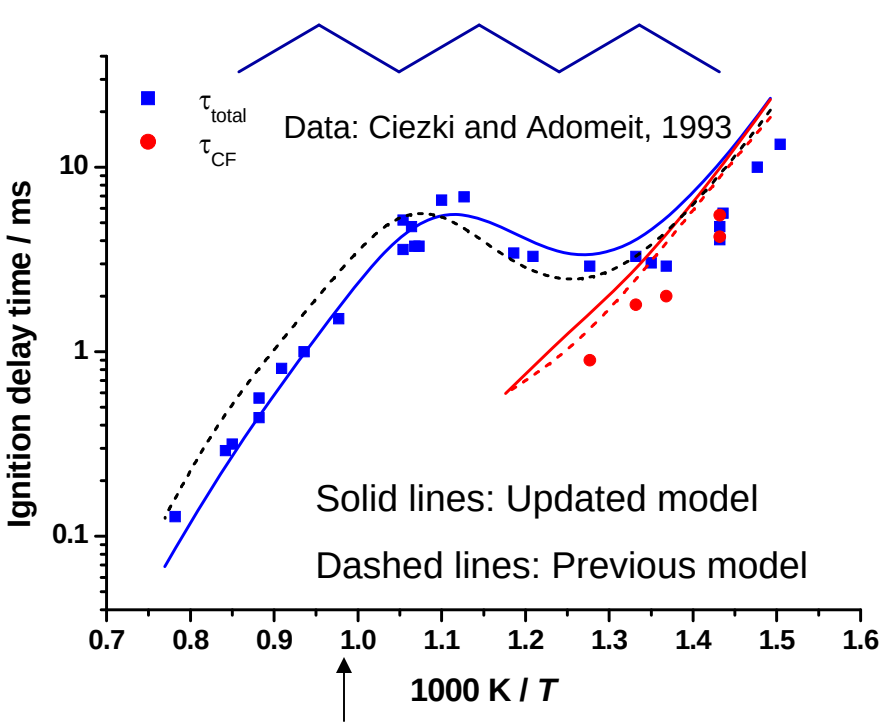


Ignition in counter-flow flame



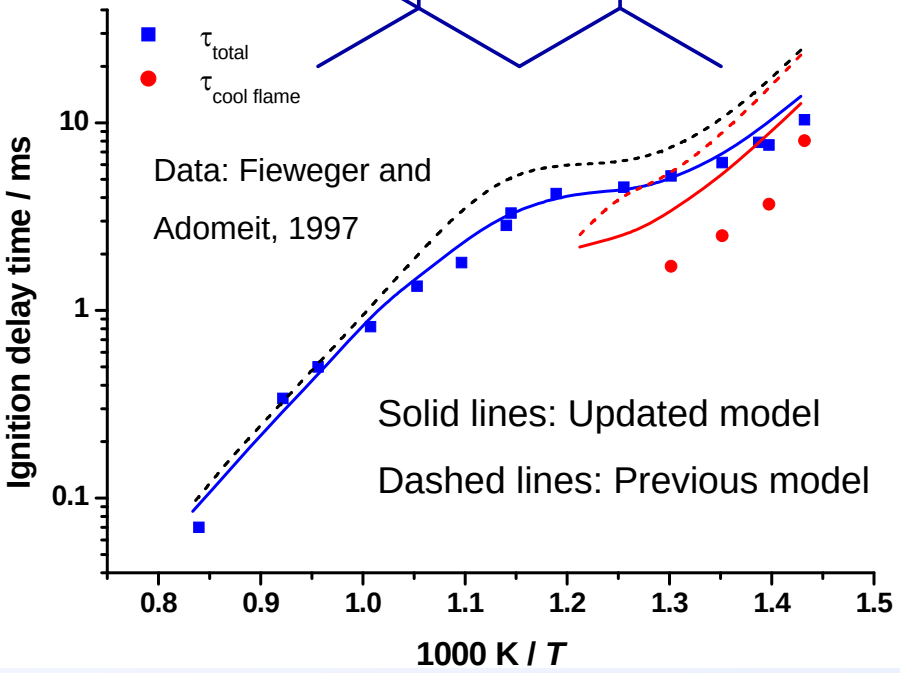
Laminar flame speeds compare well with n-decane

Improved base chemistry give better model predictions at engine conditions:



n-heptane in shock tube
13 atm
650-1250K
stoichiometric

Iso-octane in shock tube
13 atm
1000-1300K
stoichiometric



Mechanisms are available on LLNL website and by email

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

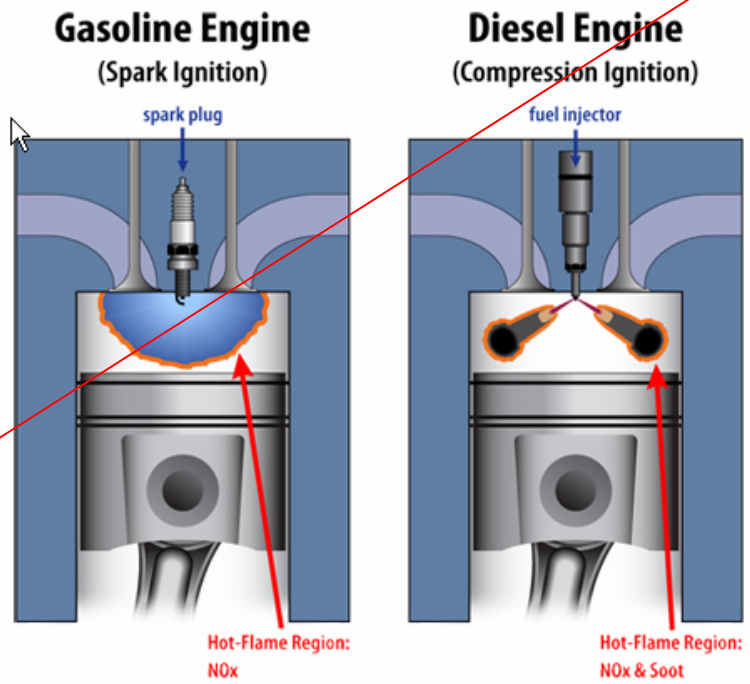
- Hydrogen
- Ethanol
- Dimethyl Ether
- Dimethyl Carbonate
- CH4, C2H4, C2H6, C3H8, and nC4H10
- NOx and CH4, C2H4, C2H6, C3H6, and C3H8
- Methyl Butanoate and Methyl Formate
- Heptane, Detailed Mechanism
- n-Heptane, Reduced Mechanism
- iso-Octane
- Primary Reference Fuels: iso-Octane / n-Heptane Mixtures
- Organophosphorus Compounds under Incineration Conditions
- Organophosphorus Compounds in Propane Flames
- Organophosphorus Compounds Effect on Flame Speeds
- Cyclohexane
- Methyl Decanoate

Combustion Chemistry

Go Directly to Mechanisms...

The central feature of the Combustion Chemistry project at LLNL is our development, validation, and application of det mechanisms for the combustion of hydrocarbon and other types of chemical fuels. For the past 30 years, our group ha for fuels from hydrogen and methane through much larger fuels including heptanes and octanes. Other classes of fuels developed include flame suppressants such as halons and organophosphates, and air pollutants such as soot and oxide

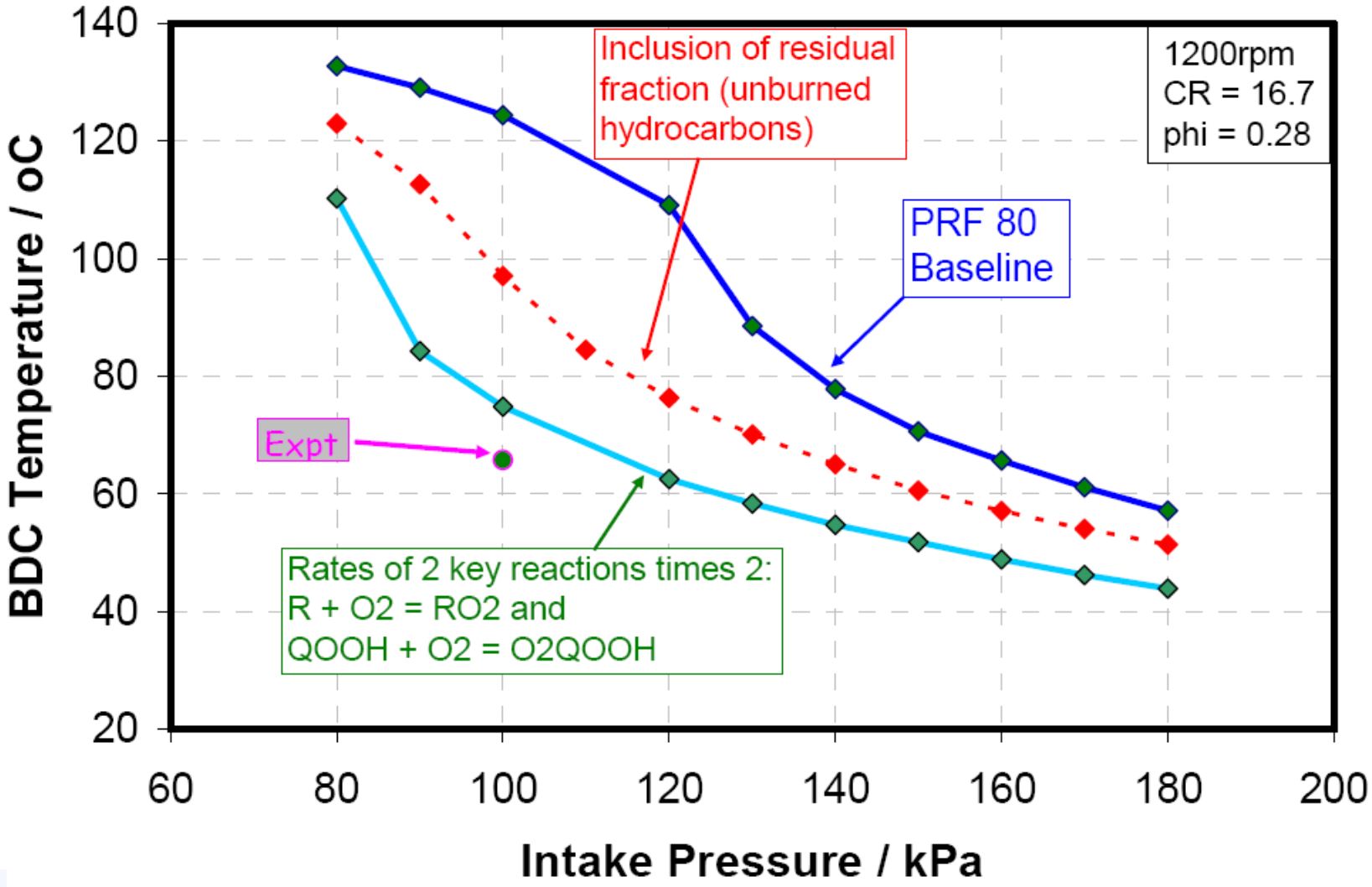
Reaction mechanisms have been tested and validated extensively through comparisons between computed results and experiments (e.g., shock tubes, laminar flames, rapid compression machines, flow reactors, stirred reactors) and from engines, spark-ignition engines, homogeneous charge, compression ignition (HCCI) engines). We have used these kin range of combustion systems.



Cyclohexane

Methyl Decanoate

Modeling of HCCI engine to understand behavior at high boost pressure



Technical Publications during FY08

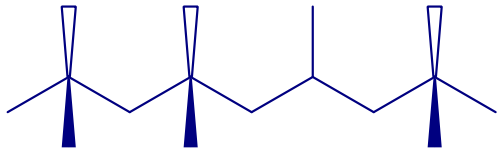
- C. K. Westbrook, W. J. Pitz, O. Herbinet, H. J. Curran and E. J. Silke, "A Detailed Chemical Kinetic Reaction Mechanism For n-Alkane Hydrocarbons From n-Octane to n-Hexadecane," *Combust. Flame* (2008) Submitted.
- E. J. Silke, W. J. Pitz, C. K. Westbrook, M. Sjöberg and J. E. Dec, "Understanding the Chemical Effects of Increased Boost Pressure under HCCI Conditions", 2008 SAE World Congress, Detroit, MI, SAE 2008-01-0019, 2008.
- R. P. Hessel, D. E. Foster, S. M. Aceves, M. L. Davisson, F. Espinosa-Loza, D. L. Flowers, W. J. Pitz, J. E. Dec, M. Sjöberg and A. Babajimopoulos, Modeling Iso-octane HCCI using CFD with Multi-Zone Detailed Chemistry; Comparison to Detailed Speciation Data over a Range of Lean Equivalence Ratios, *2008 SAE World Congress*, SAE 2008-01-0047, Detroit, MI, 2008.
- Sakai, Y., Ozawa, H., Ogura, T., Miyoshi, A., Koshi, M. and Pitz, W. J., "Effects of Toluene Addition to the Primary Reference Fuel at High Temperature," SAE Commercial Vehicle Engineering Congress & Exhibition, Chicago, IL, 2007.
- Y. Sakai, A. Miyoshi, M. Koshi and W. J. Pitz, "A Kinetic Modeling Study on the Oxidation of Primary Reference Fuel–Toluene Mixtures Including Cross Reactions between Aromatics and Aliphatics", *Proc. Combust. Inst.,* Montreal, Canada, submitted, 2008.
- O. Herbinet, W. J. Pitz and C. K. Westbrook, "Detailed chemical kinetic oxidation mechanism for a biodiesel surrogate," Combust. Flame (2008) submitted.
- K. Seshadri, T. Lu, O. Herbinet, S. Humer, U. Niemann, W. J. Pitz and C. K. Law, "Ignition of Methyl Decanoate in Laminar Nonpremixed Flows," *Proceedings of The Combustion Institute* (2008) Submitted.
- C. K. Westbrook, W. J. Pitz, P. R. Westmoreland, F. L. Dryer, M. Chaos, P. Osswald, K. Kohse-Hoinghaus, T. A. Cool, J. Wang, B. Yang, N. Hansen and T. Kasper, "A Detailed Chemical Kinetic Reaction Mechanism for Oxidation of Four Small Alkyl Esters in Laminar Premixed Flames", *Proc. Combust. Inst.,* Montreal, Canada, submitted, 2008.

Industry Collaboration

- 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.)
  - Collaboration with Magnus Sjöberg and John Dec at Sandia on HCCI engine experiments
  - Collaboration with Randy Hessel at Univ. of Wisconsin on CFD simulations.
  - Collaboration with Jim Szybist (ORNL) and Andre Boehman (Penn State).
- Second interaction is participation with universities
  - Collaboration with C. K. Law's group, Princeton University on mechanism reduction
  - Collaboration with Curran at National Univ. of Ireland
  - Collaboration with Prof. Koshi at University of Tokyo on toluene.
- Participation in other working groups with industrial representation
  - Fuels for Advanced Combustion Engines (FACE) Working group
  - Surrogate fuel working group with representatives from industry (Exxon, Caterpillar, Chevron, United Technologies)

Activities for Next Fiscal Year

- Kinetic model for large iso-alkanes present in Diesel fuel: 2,2,4,4,6,8,8 hepta-methyl-nonane



- Further modeling of enhanced surrogate fuels with comparisons to engine experiments
  - Improved n-heptane, iso-octane, toluene surrogate model for gasoline
- Longer term:
  - Large aromatic for diesel fuel

  - Assess the effect of molecular structure by examining a biodiesel surrogate component with a double bond

Summary

- Approach to research
  - Continue development of surrogate fuel mechanisms to improve engine models for HCCI and diesel engines
- Technical accomplishments:
  - Completed reaction mechanism for the high and low temperature oxidation of n-hexadecane

- Collaborations/Interactions
  - Collaboration through AEC working group with industry. Many collaborators from National Labs and Universities.
- Plans for Next Fiscal Year
  - Complete low/high temperature mechanism to represent large iso-alkanes in a diesel surrogate fuel: 2,2,4,4,6,8,8 hepta-methyl nonane, diesel reference fuel