Lawrence Livermore National Laboratory

Chemical Kinetic Modeling of Fuels

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Lawrence Livermore National Laboratory
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Project ID # FT010

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

Washington, DC

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LLNL-PRES- 427942

Overview

Timeline

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

Budget

Project funded by DOE/VT:

- FY09: 325K
- FY10: 500K

Partners

- Project Lead: LLNL – W. J. Pitz (PI), C. K. Westbrook, M. Mehl, M. Sarathy
- FACE Working group (Industry, National Labs)
- 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

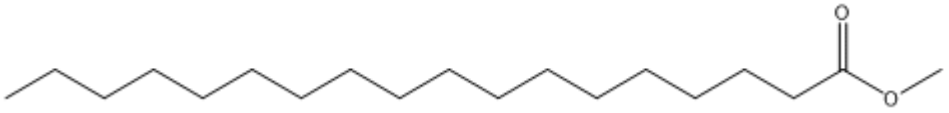
Barriers/Targets

- Technical Barrier: Chemical kinetic models for fuel components and their mixtures are a critical need to enable optimization of fuel formulations for high engine efficiency and very low emissions
- Targets: Meeting the targets below relies heavily on predictive engine models for optimization of fuel formulations and engine design:
  - Potential for replacement of petroleum, greater than 5% by 2018
  - 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

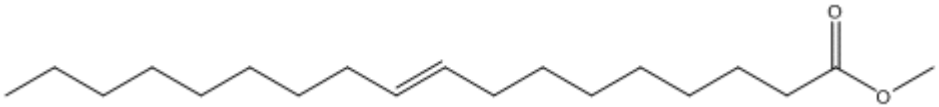
Objectives and relevance to DOE objectives

- Objectives:
  - Develop predictive chemical kinetic models for components and surrogate mixtures to represent advanced petroleum-based and non-petroleum based fuels. These models can be used to optimize fuel formulations in advanced combustion engines for maximum engine efficiency and very low pollutant emissions, thereby allowing the utmost petroleum displacement

- FY10 Objectives:
  - Develop a chemical kinetic model for actual biodiesel components:
    - Methyl stearate

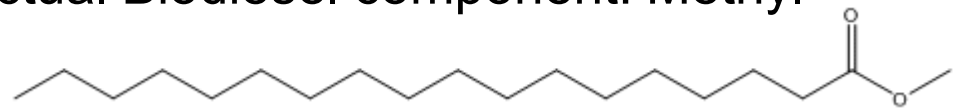


    - Methyl oleate

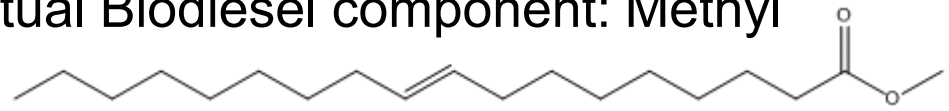


Milestones

- ✓ March, 2010
  Develop chemistry model for actual Biodiesel component: Methyl stearate



- September, 2010
  Develop chemistry model for actual Biodiesel component: Methyl oleate



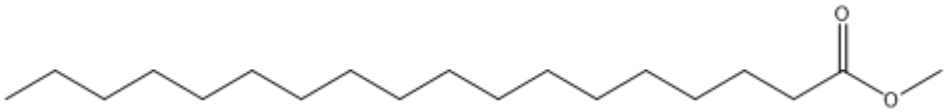
- September, 2010 Provide technical support for the Fuels for Advanced Combustion Engines (FACE) working group

Approach

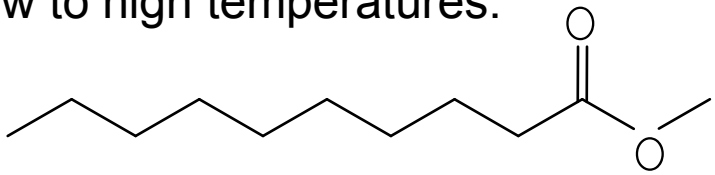
- Develop chemical kinetic reaction models for each individual fuel component of importance for advanced petroleum based and non-petroleum based fuels
- Combine mechanisms for representative fuel components to provide surrogate models for
  - Advanced petroleum based fuels
  - Non-petroleum based fuels:
    - Biodiesel and new generation biofuels
    - Fischer-Tropsch (F-T) fuels
    - Oil sand derived 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 advanced combustion engines, as needed
- Iteratively improve models as needed for applications

Technical Accomplishment Summary

- Developed chemical kinetic model for actual biodiesel component: methyl stearate:



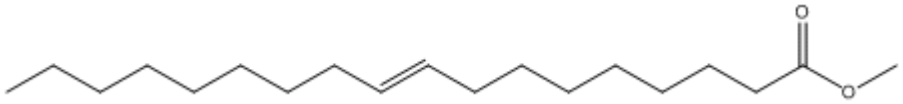
- Developed a reduced model for methyl decanoate (a biodiesel surrogate compound), valid from low to high temperatures:



3012 => 648 species

(almost a factor of 5 reduction)

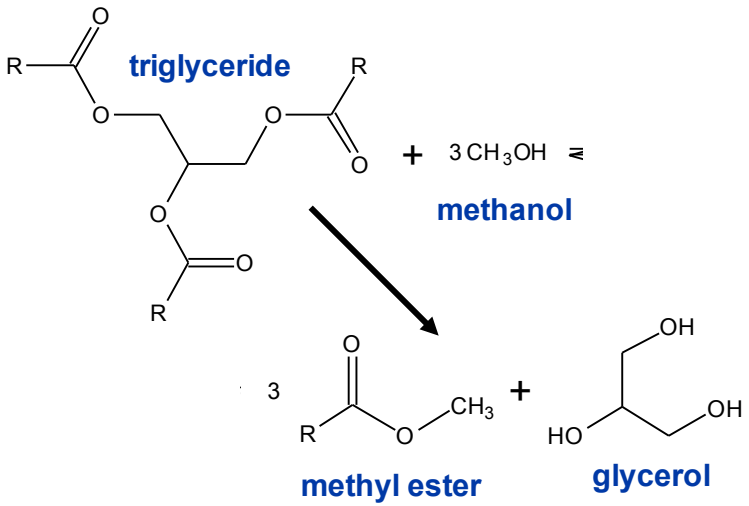
- Developed preliminary chemical kinetic model for actual biodiesel component: methyl oleate:

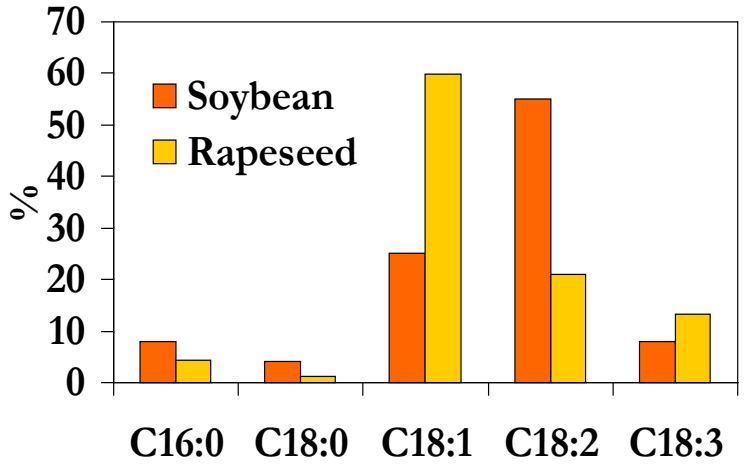


- Submitted review paper on Diesel surrogate fuels for the FACE working group:

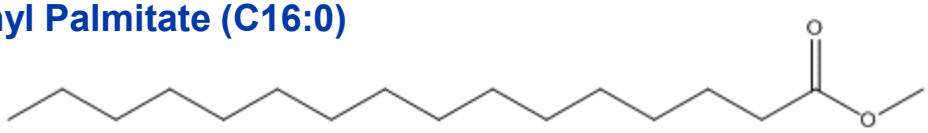
W. J. Pitz and C. J. Mueller, "Recent Progress in the Development of Diesel Surrogate Fuels," Progress in Energy and Combustion Science (2010), submitted.

Soybean and rapeseed derived biodiesel has only 5 principal components

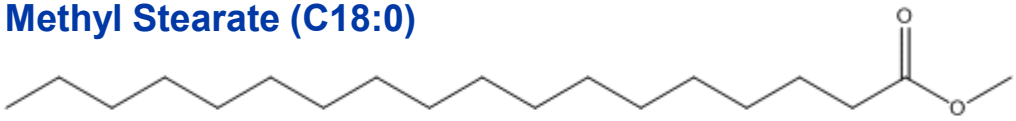




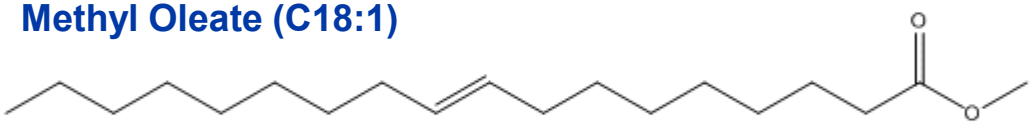
Methyl Palmitate (C16:0)



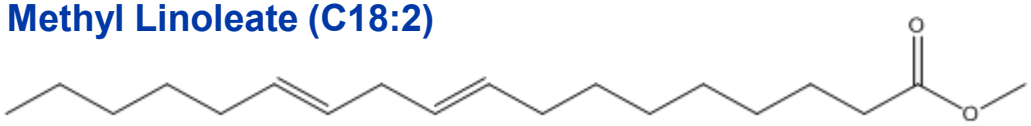
Methyl Stearate (C18:0)



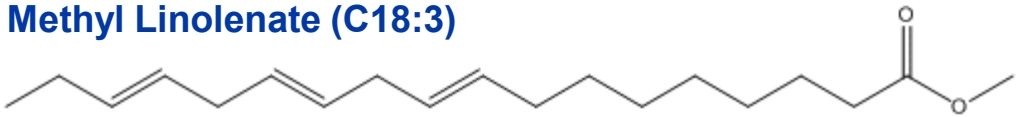
Methyl Oleate (C18:1)



Methyl Linoleate (C18:2)

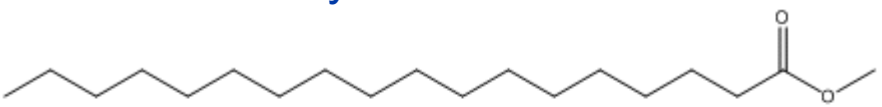


Methyl Linolenate (C18:3)

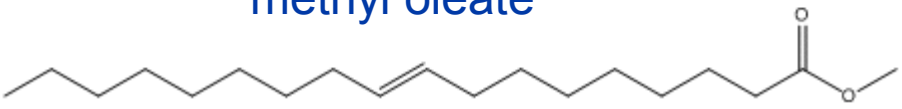


Assembled chemical kinetic model for two of the five main components in biodiesel derived from soybeans or rapeseed oil

methyl stearate



methyl oleate



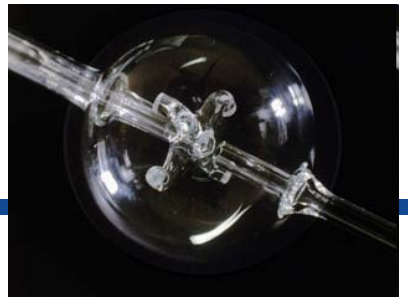
Built with the same reaction rate rules as our successful methyl decanoate mechanism

Approximately

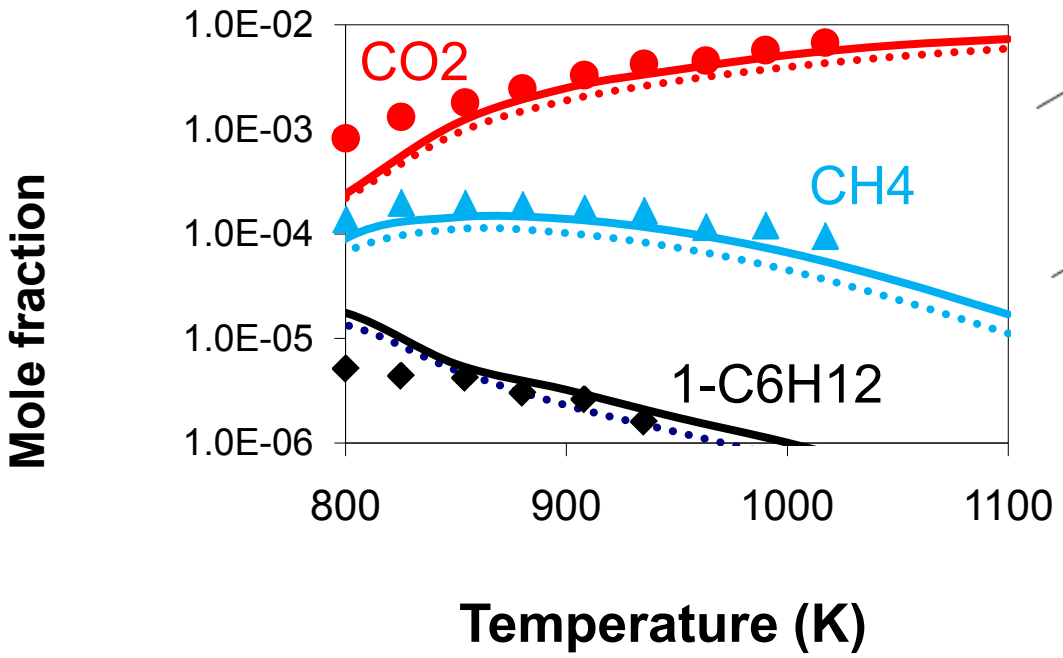
3,500 species

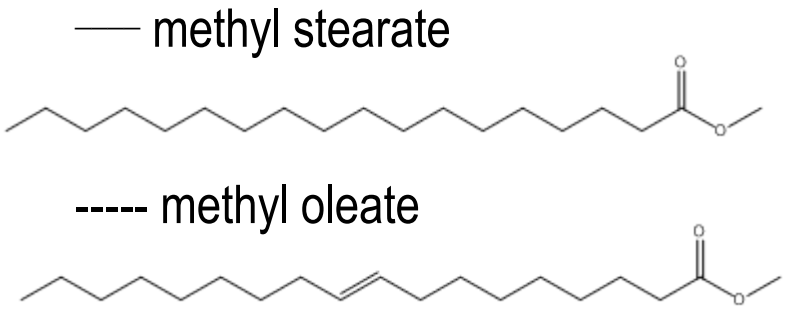
17,000 reactions

Methyl stearate or methyl oleate mechanisms simulate well the oxidation of rapeseed-derived methyl esters



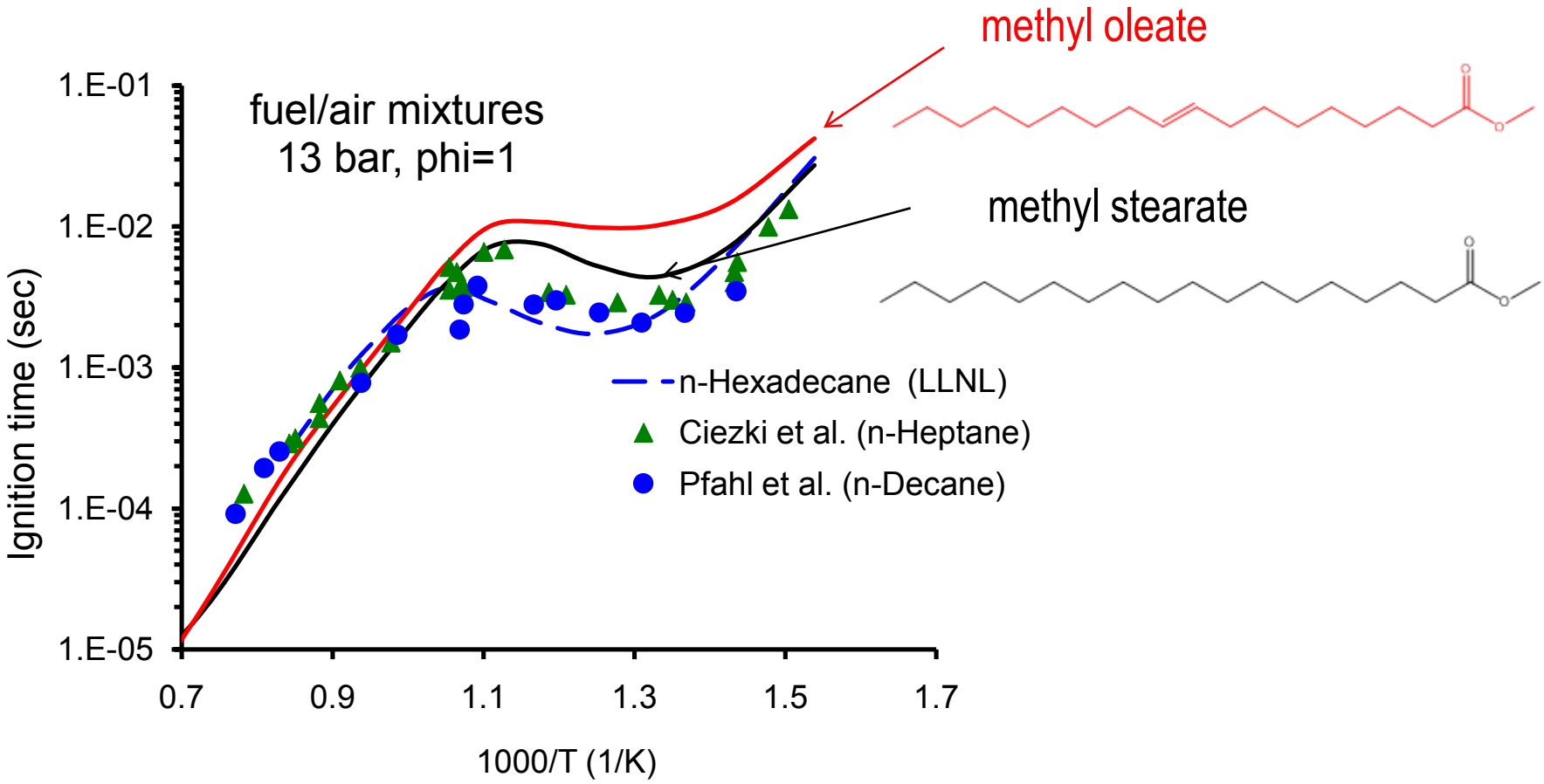
Jet-stirred reactor at 10 bar, ϕ=0.5





Symbols: Experimental data of Dagaut et al. 2007 on rapeseed methyl esters

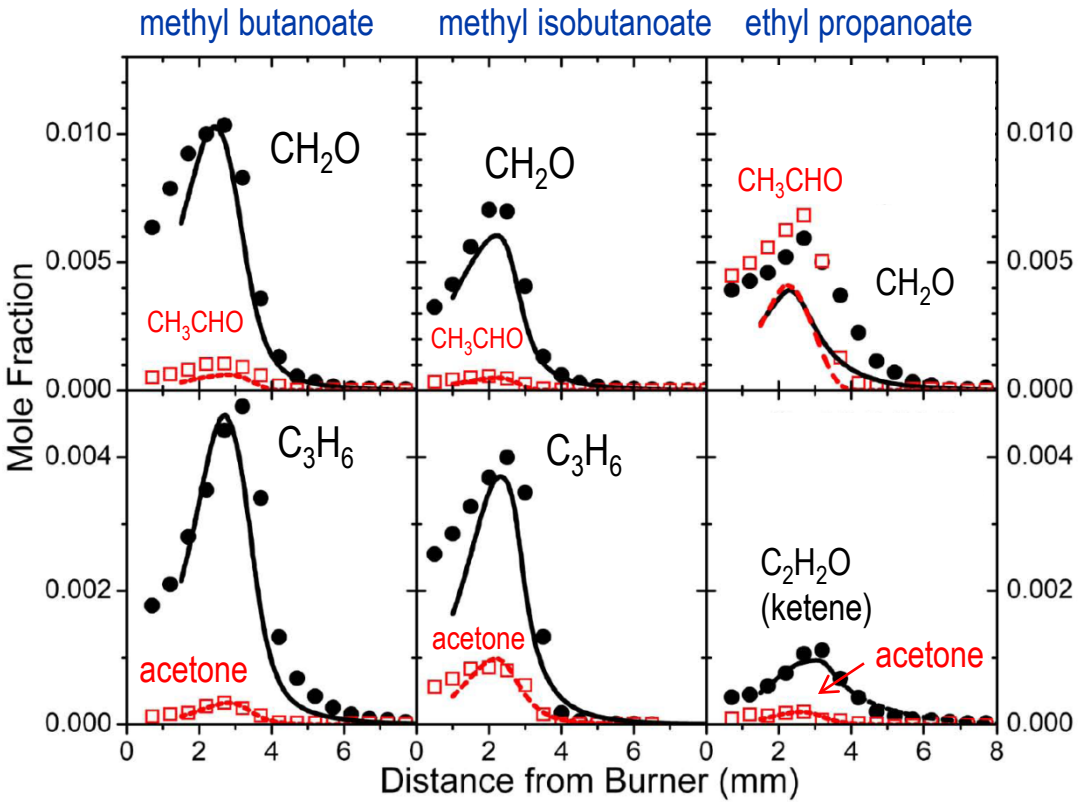
Methyl stearate is more reactive than methyl oleate in low T region



Double bond inhibits low temperature chemistry

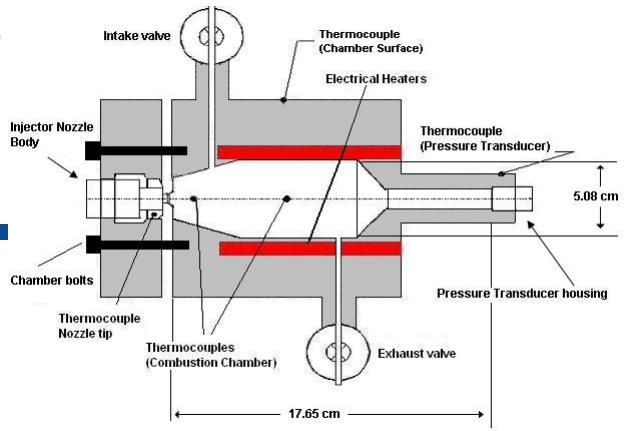
Validating fundamental reaction paths in the biodiesel mechanisms: C5 methyl esters

Low pressure flame
Advanced light source
LBL



Experimental data: Yang, Cool, Hansen, 2010

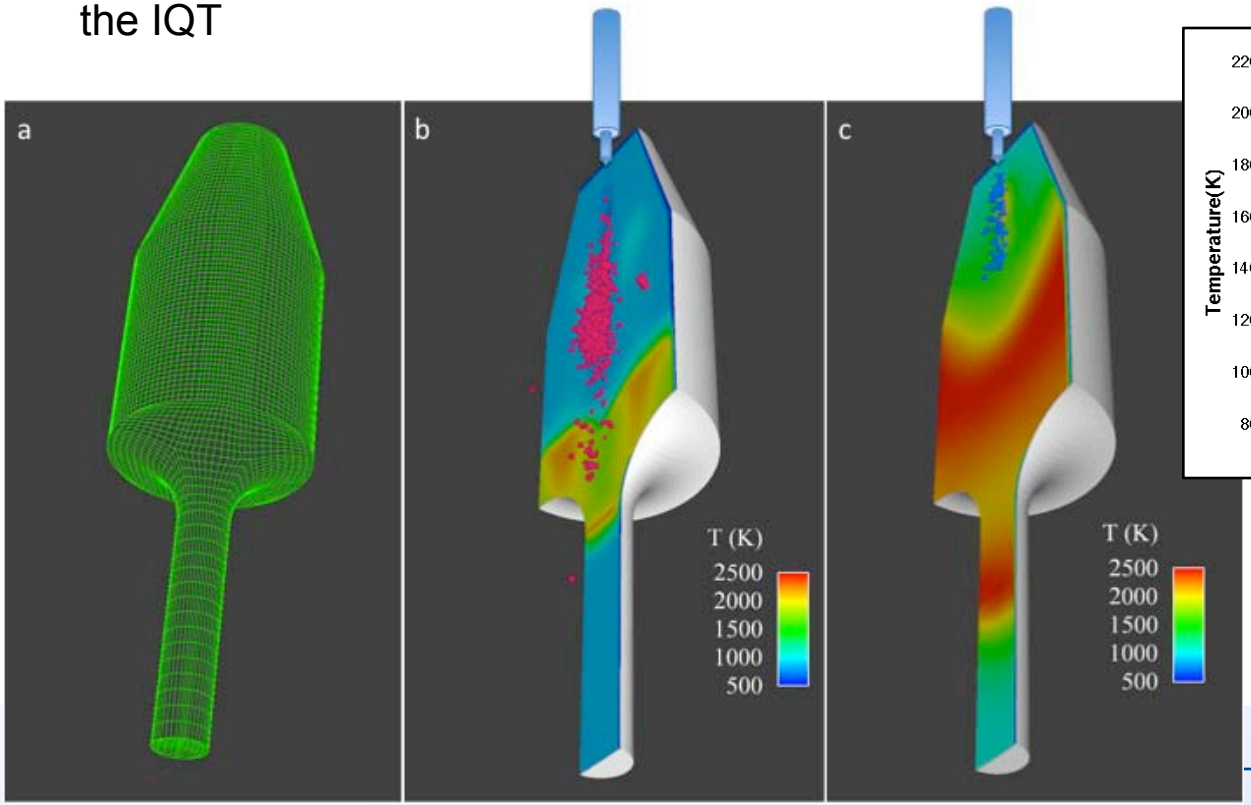
We are developing the capability to simulate the IQT which predicts derived Cetane number (Flowers, Aceves, Chen)

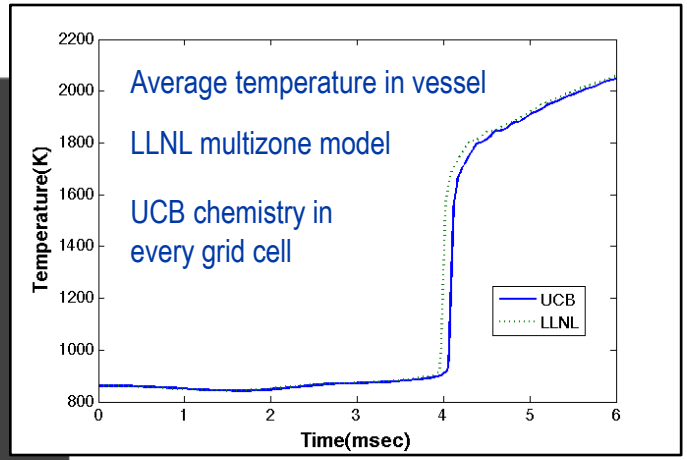


Ignition Quality Tester (IQT)

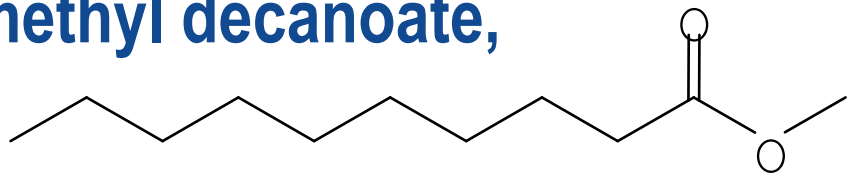
Objectives:

- Extend multi-zone model to stratified DI cases in collaboration with NREL and UC Berkeley
- Ensure chemical kinetic models can predict derived Cetane number measured in IQT
- Characterize fuel chemistry under diesel-like conditions in the IQT





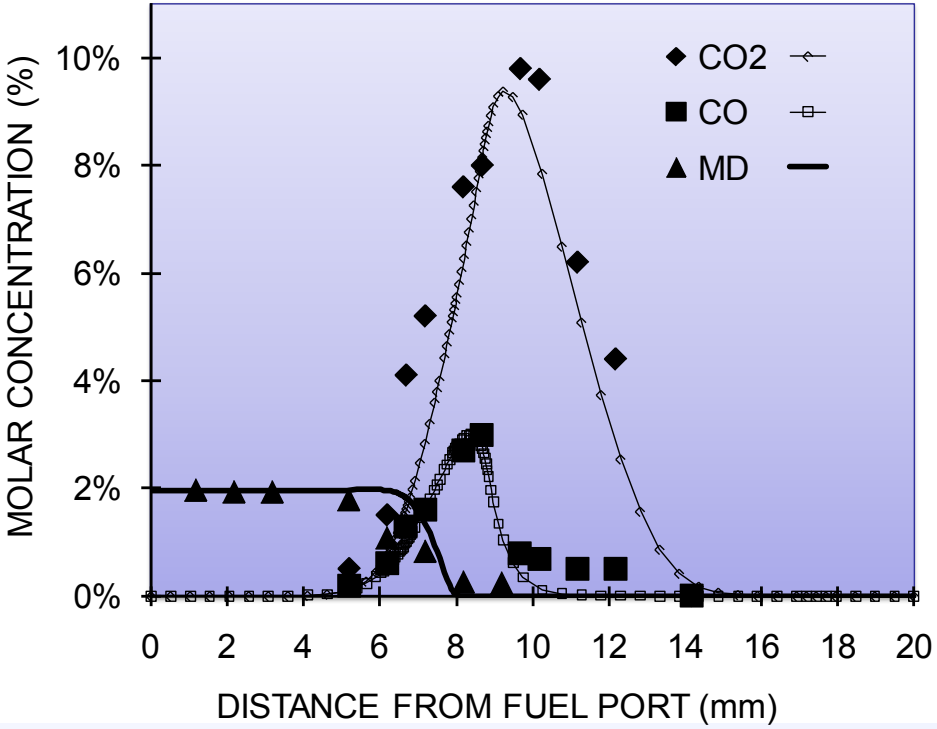
Developed a reduced model for methyl decanoate, a biodiesel surrogate compound



Mechanism reduced:

3012 => 648 species

8820 => 2998 reactions



Fuel port

Oxidizer port

Counterflow diffusion flame

Sarathy, Thomson, Pitz and Lu, "An Experimental and Kinetic Modeling Study of Methyl Decanoate Combustion," The 33rd International Symposium on Combustion, 2010.

Mechanisms are available on LLNL website and by email

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

- Ethanol
- Dimethyl Ether
- CH4, C2H4, C2H6, C3H8, and nC4H10
- CH4, C2H4, C2H6, C3H6, C3H8, and NOx
- C8-C16 n-Alkanes
- Cyclohexane
- Methylcyclohexane
- Methyl Butanoate and Methyl Formate
- Methyl Decanoate
- Methyl Decenoates
- Biodiesel Surrogates
- Dimethyl Carbonate
- Heptane, Detailed Mechanism
- Heptane, Reduced Mechanism
- iso-Octane
- Primary Reference Fuels: iso-Octane / n-Heptane Mixtures
- 2,2,4,4,6,8,8-Heptamethylnonane
- Organophosphorus Compounds under Incineration Conditions
- Organophosphorus Compounds in Propane Flames
- Organophosphorus

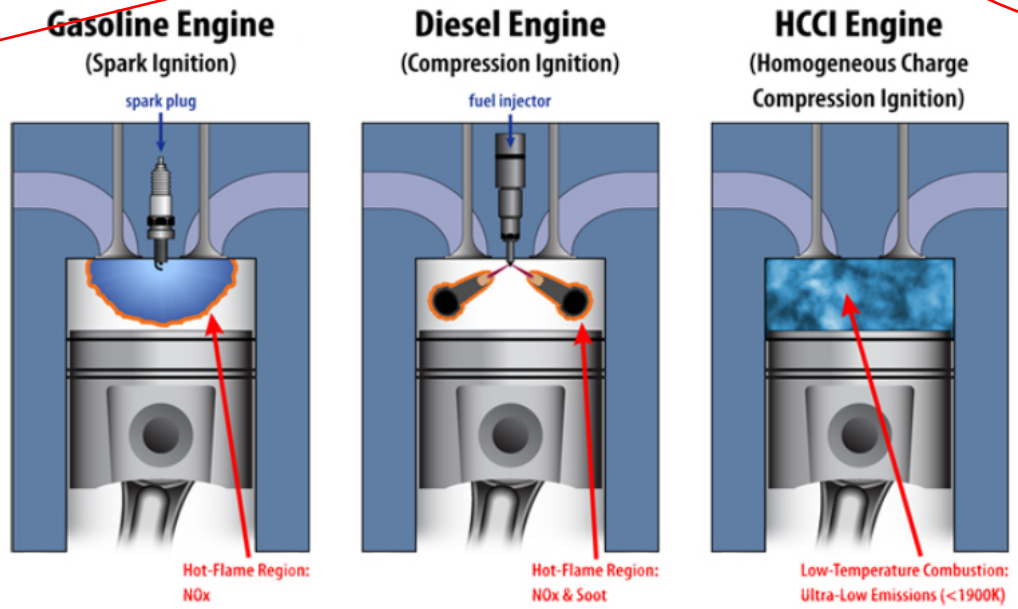
Combustion Chemistry

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 fuels from hydrogen and methane through much larger fuels including heptanes and octanes. Othe classes of fuels for which models have been developed include flame suppressants such as halons 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.

Biodiesel Surrogates



Collaborations

- Our major industrial 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 Magnus Sjöberg and John Dec at Sandia on HCCI engine experiments on many fuels
- Second interaction is participation with many universities
  - Collaboration with Univ. of Toronto on methyl decanoate
  - Collaboration with Curran at National Univ. of Ireland on many fuels
  - Collaboration with Prof. Lu, U. of Conn. on mechanism reduction
  - Collaboration with Prof. Oehlschaeger at RPI on large alkanes
- Participate in Fuels for Advanced Combustion Engines (FACE) Working group (Industry, National Labs)

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:

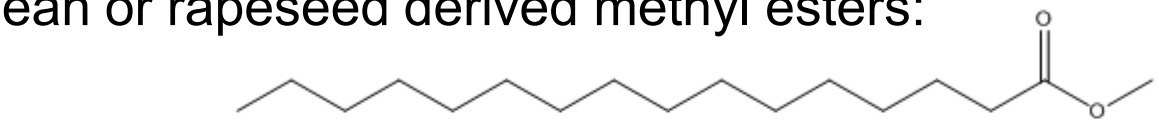
- Best paper of the year award 2009: Combustion Society Japan

S. M. Sarathy:

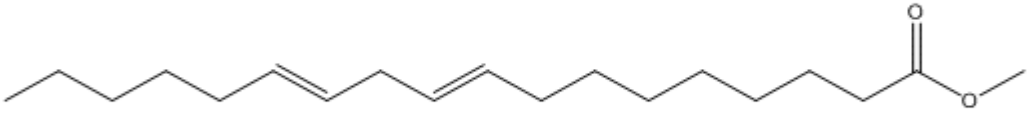
- Postdoctoral Fellowship from Natural Sciences and Engineering Research Council of Canada

Activities for Next Fiscal Year

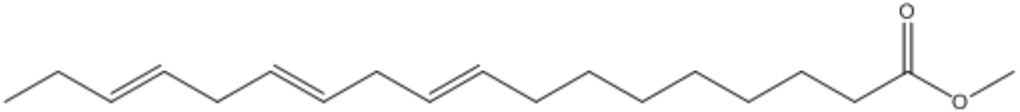
- Develop detailed chemical kinetic models the other remaining soybean or rapeseed derived methyl esters:



methyl palmitate

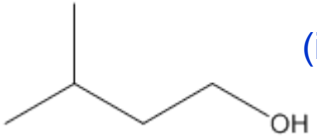


methyl linoleate



methyl linolenate

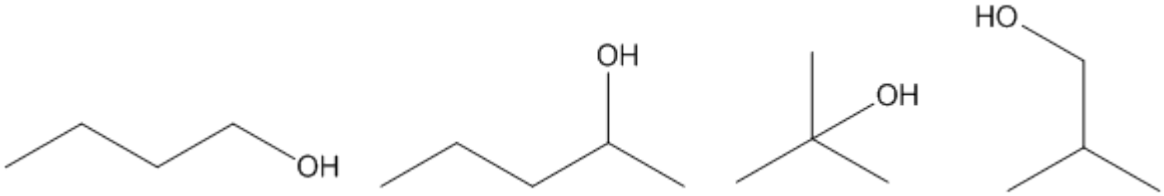
- Develop detailed chemical kinetic model for a new biofuel fermented from sugar:



(iso-pentanol)

Biofuel targeted by JBEI (U.S. Department of Energy Bioenergy Research Center)

- Develop mechanisms for butanols (4 isomers)



Summary

- Approach to research
  - Continue development of surrogate fuel mechanisms for non-petroleum based fuels and advanced petroleum based to obtain predictive models that can optimize fuel formulations
- Technical accomplishments:
  - Developed chemical kinetic model for methyl stearate, actual biodiesel component
- Collaborations/Interactions
  - Collaboration through AEC working group and FACE working group with industry. Many collaborations with national labs and universities
- Plans for Next Fiscal Year:
  - Develop chemical kinetic models for 3 remaining biodiesel components and new biofuel, iso-pentanol