Lawrence Livermore National Laboratory

Chemical Kinetic Modeling of Non-Petroleum Based 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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Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

LLNL-PRES-543382

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:

- FY11: 438K
- FY12: 265K

Partners

- Project Lead: LLNL – W. J. Pitz (PI), C. K. Westbrook, S. M. Sarathy, M. Mehl, A. Polo
- 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

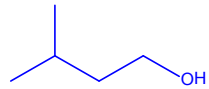
- Technical Barrier: Chemical kinetic models for fuel components and their mixtures are a critical need to enable optimization of fuel formulations for high engine efficiency and very low emissions
- Targets: Meeting the targets below relies heavily on predictive engine models for optimization of fuel 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 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

- FY12 Objectives:
  - Further validations and improvements for chemical kinetic models for saturated and unsaturated large methyl esters

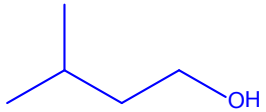
  - Develop a chemical kinetic mechanism for isomers of pentanol
  - Develop a chemical kinetic model for larger cyclohexanes
  - Further validation and improvements of iso-pentanol mechanism



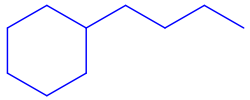
  - Develop reduced mechanisms for alternative fuel surrogates for multi-dimensional CFD simulations of diesel combustion
  - Provide technical support for the Fuels for Advanced Combustion Engines (FACE) working group

Milestones

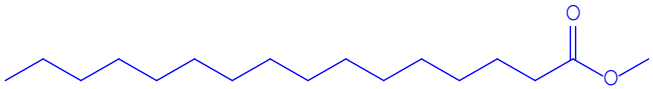
- June, 2012
  Further validation and improvements of iso-pentanol mechanism



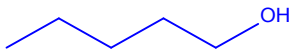
- June, 2012
  Develop a chemical kinetic model for larger cyclohexanes



- ✓ September, 2012
  Further validations and improvements for chemical kinetic models for saturated and unsaturated large methyl esters



- September, 2012
  Develop reduced mechanisms for alternative fuel surrogates for multi-dimensional CFD simulations of diesel combustion
- September, 2012
  Develop a chemical kinetic mechanism for isomers of pentanol



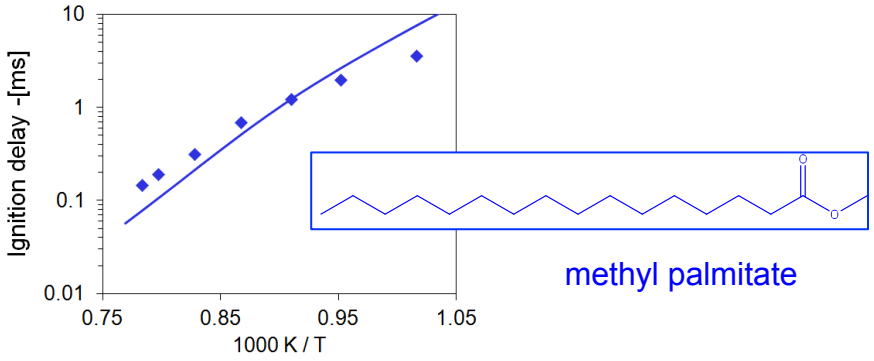
- September, 2012
  Provide technical support for the Fuels for Advanced Combustion Engines (FACE) working group

Approach

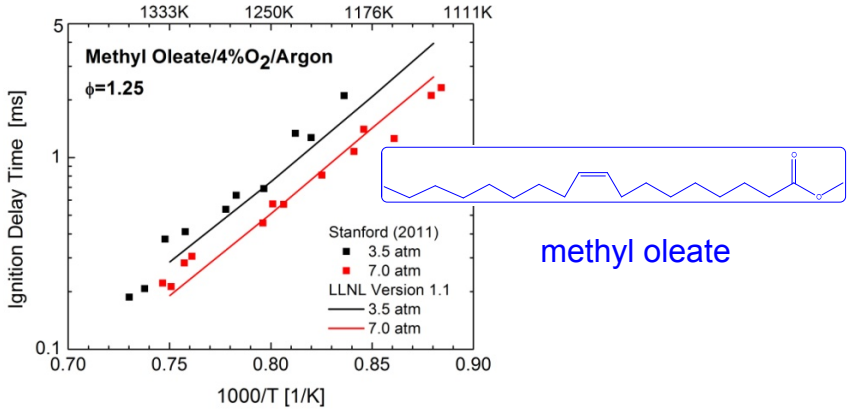
- Develop chemical kinetic reaction models for each individual fuel component of importance for advanced non-petroleum based fuels
- Combine mechanisms for representative fuel components to provide surrogate models for non-petroleum based fuels:
  - Biodiesel
  - Gasoline fuels with alcohol
  - New generation biofuels
  - Fuels from biomass
  - Fischer-Tropsch (F-T) fuels
  - Oil-sand derived fuels
  - Mixtures of alternative fuels with conventional 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

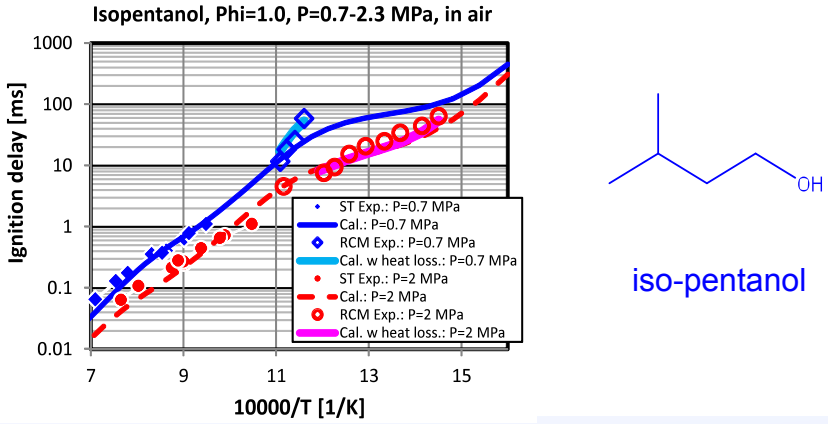
- Validated chemical kinetic model for real biodiesel component methyl palmitate:



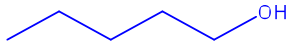
- Validated chemical kinetic model for real biodiesel component methyl oleate:

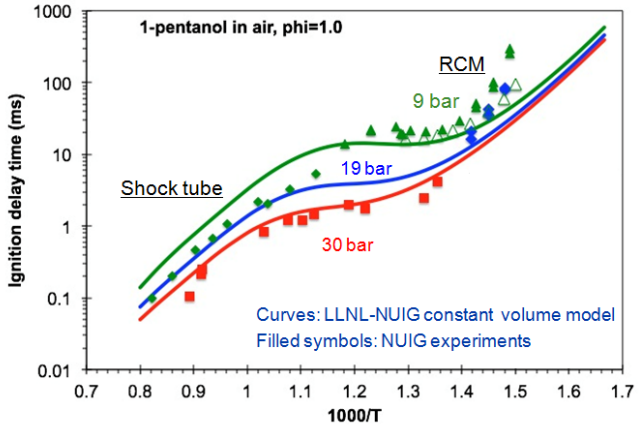


- Further validation of chemical kinetic model for advanced biofuel iso-pentanol

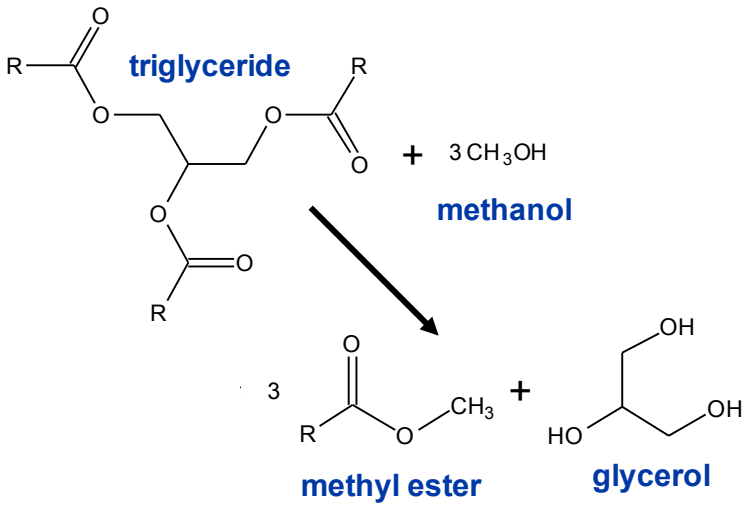


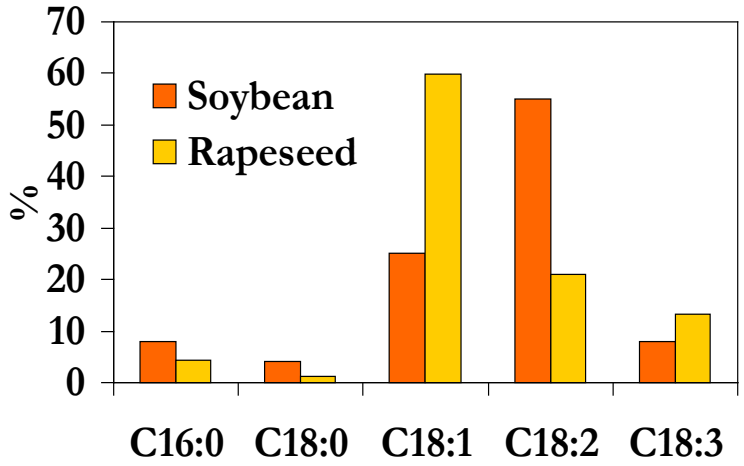
- Development and validation of a chemical kinetic model for 1-pentanol





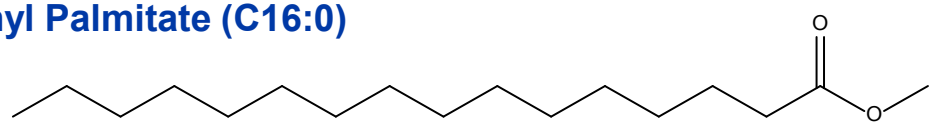
Soybean and rapeseed derived biodiesels have only 5 principal components



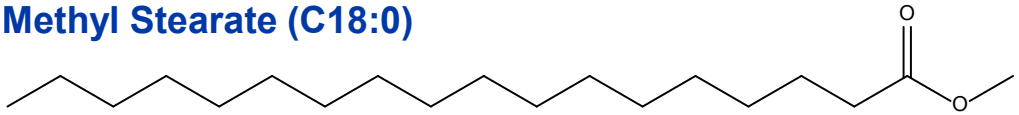


Fatty acid methyl esters (FAMEs):

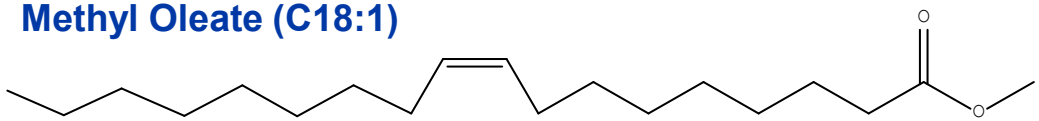
Methyl Palmitate (C16:0)



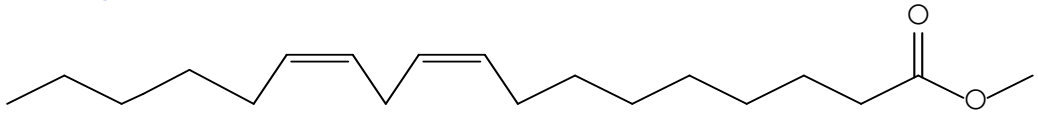
Methyl Stearate (C18:0)



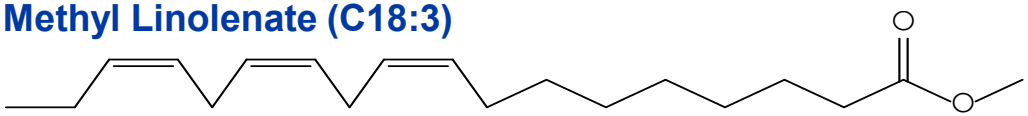
Methyl Oleate (C18:1)



Methyl Linoleate (C18:2)



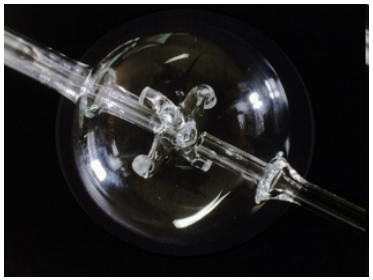
Methyl Linolenate (C18:3)



Experimental validation of biofuel mechanisms

- Idealized chemical reactors with/without simplified transport phenomenon

Jet Stirred Reactors



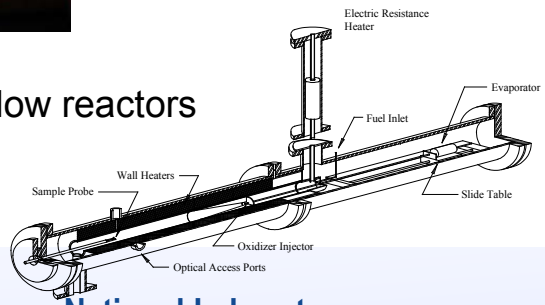
Premixed Laminar Flames

Shock tube

Non Premixed Flames

Rapid Compression Machine

High pressure flow reactors



Engine Combustion

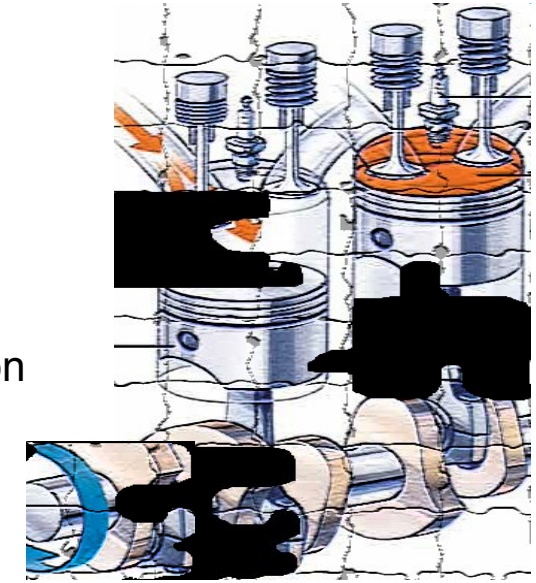
<u>Combustion Parameters</u>

Temperature

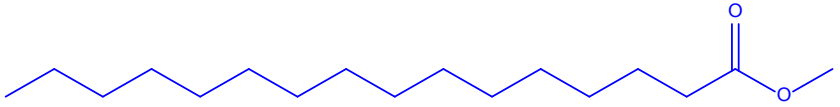
Pressure

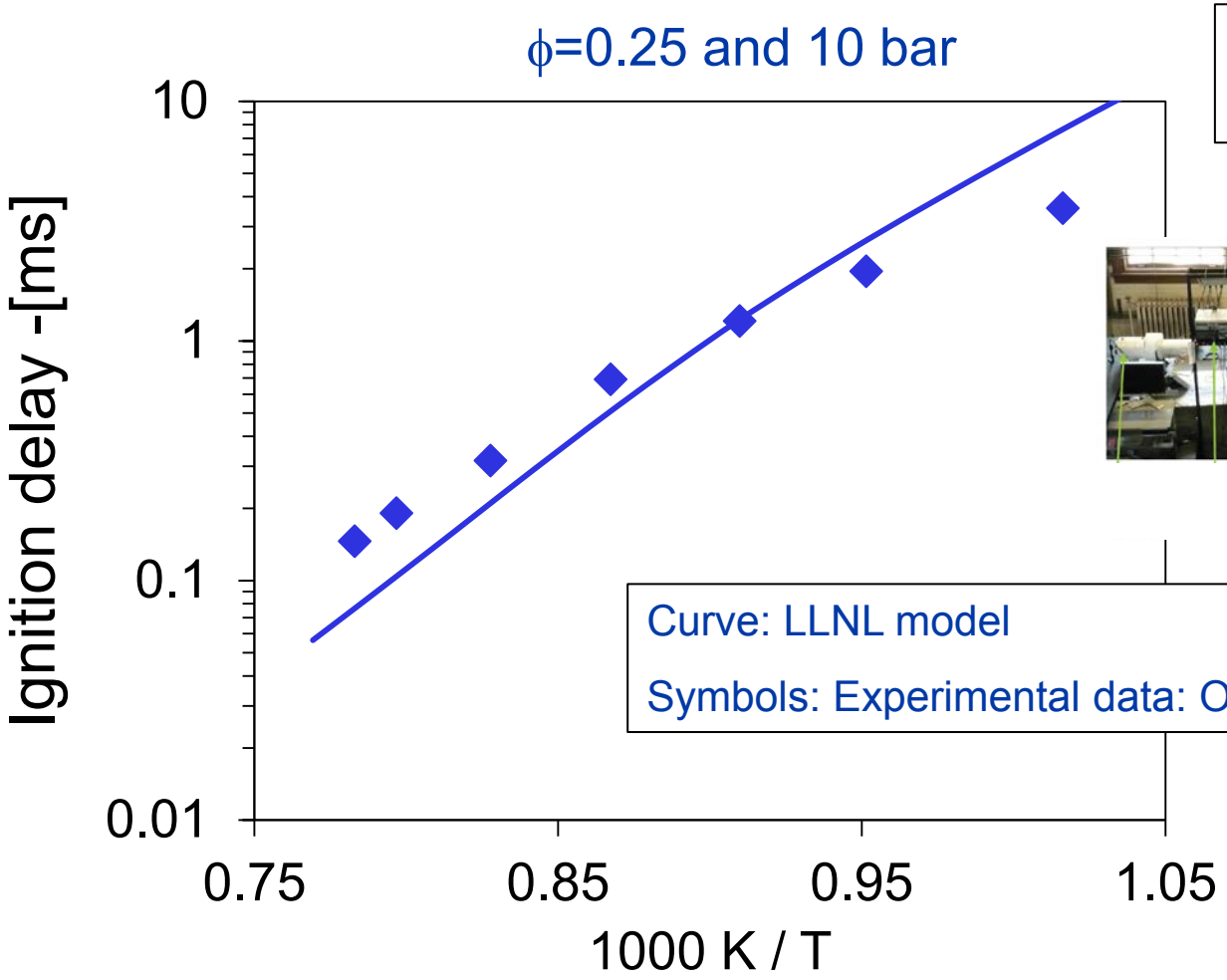
Mixture fraction (air-fuel ratio)

Mixing of fuel and air



Methyl palmitate model simulates shock-tube ignition delay times at 10 bar





Methyl palmitate:

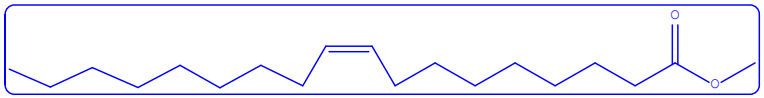
Real biodiesel methyl ester

Shock tube

Curve: LLNL model

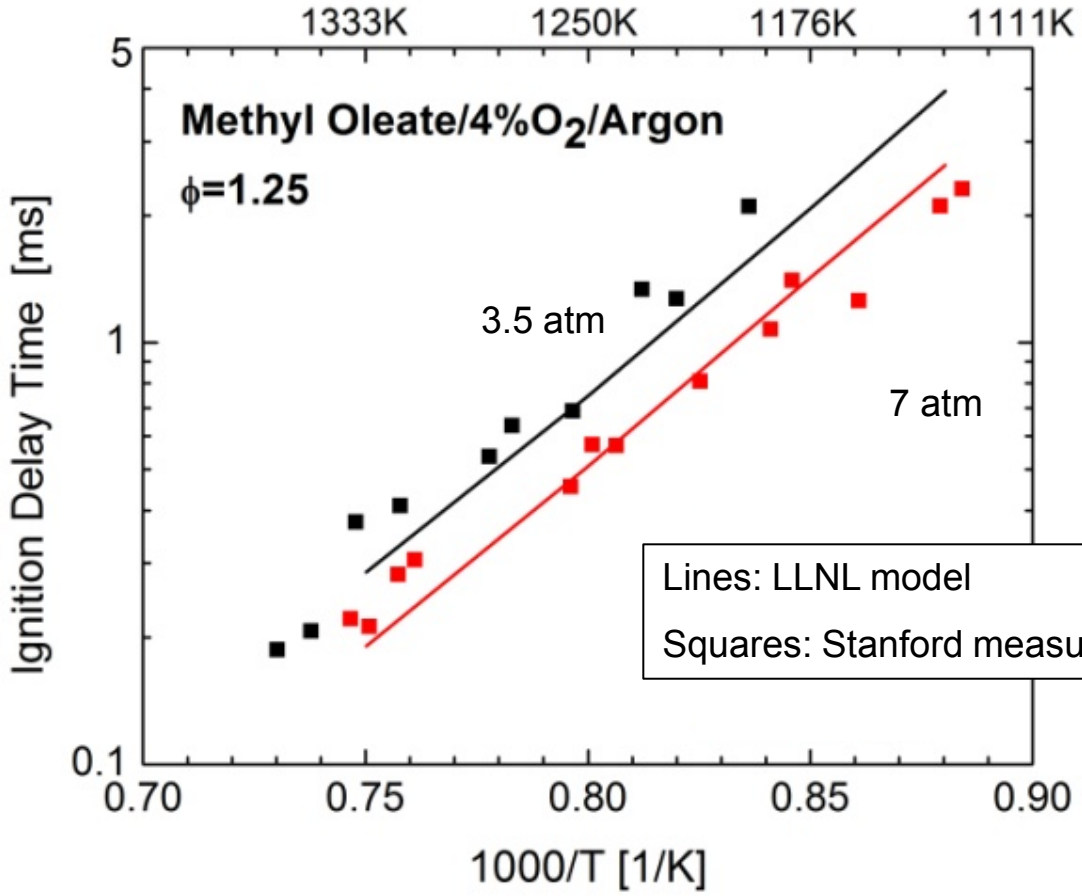
Symbols: Experimental data: Oehlschlaeger et al., RPI

Methyl oleate model compares well to shock tube ignition experiments at elevated pressures



methyl oleate:

Real biodiesel methyl ester



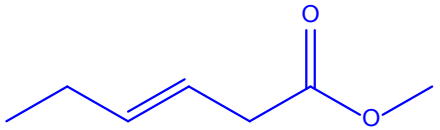
Shock tube

Lines: LLNL model

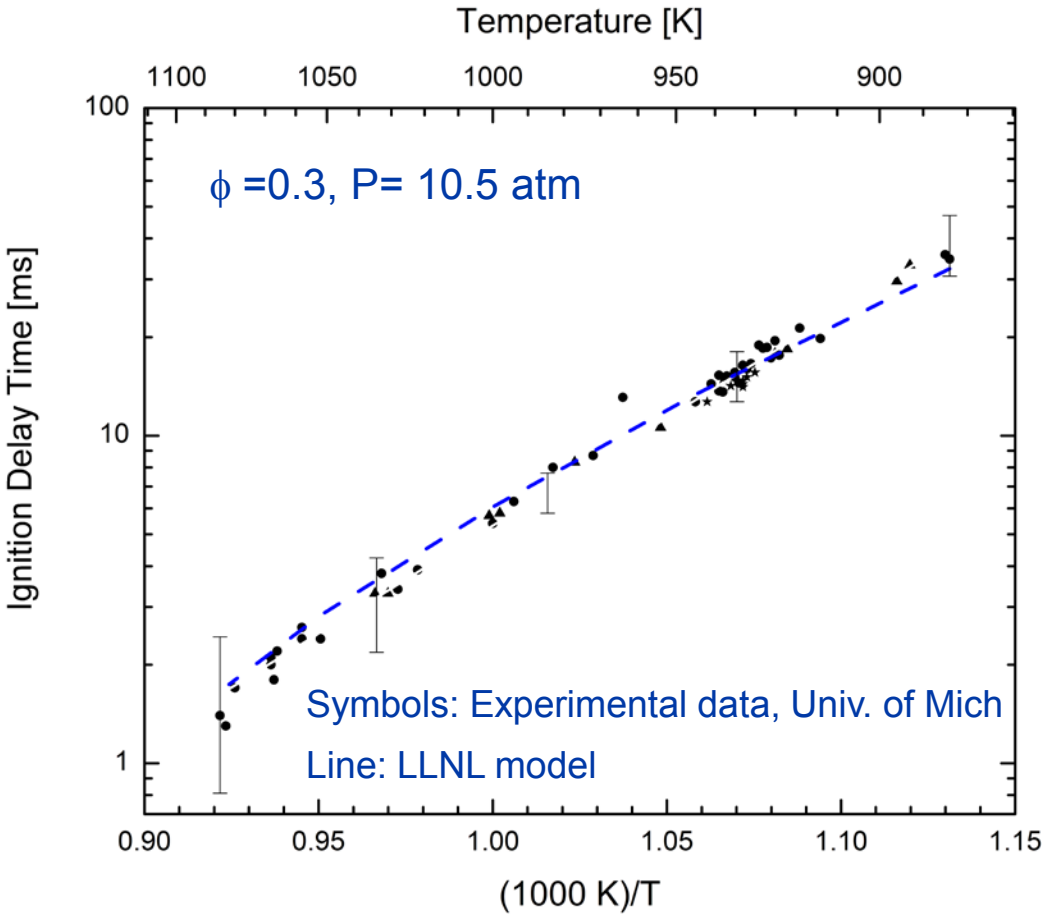
Squares: Stanford measurements

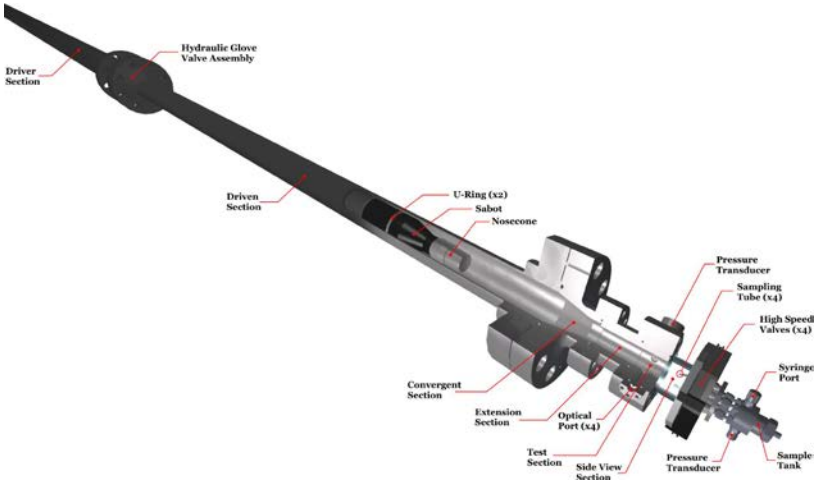
Experimental measurements by Campbell, Davidson and Hanson at Stanford University, 2011

Ignition of an unsaturated methyl ester in a rapid compression facility



3-methyl hexenoate

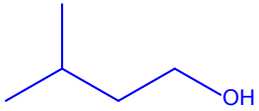




Univ. of Mich. rapid compression facility

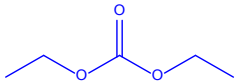
Experimental data: Wagnon and Wooldridge, University of Michigan, 2011

Chemical kinetic models for other biofuels

- isopentanol 

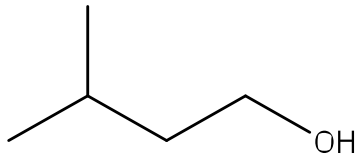
  - Exhibits intermediate temperature heat release needed to obtain high load operation with HCCI (Dec and Yang, 2010)
- 1-pentanol 

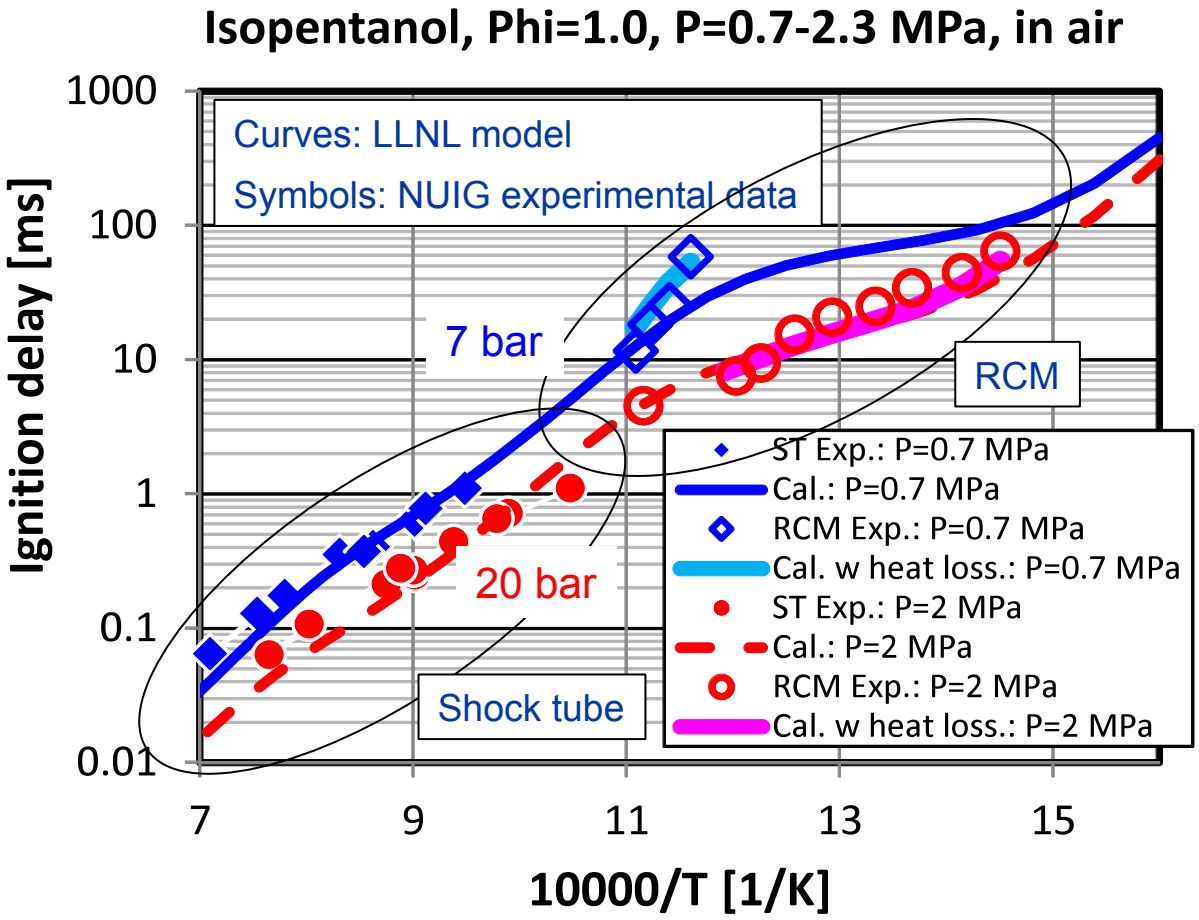
  - Higher energy density than ethanol
- 1-butanol 

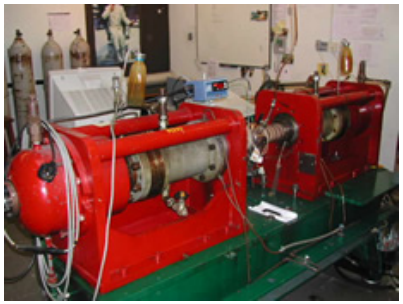
  - Has higher energy density than ethanol and can be mixed in fuel pipelines. Can be made from renewable sources
- diethylcarbonate 

  - Sugar cane in Colombia is converted to ethanol. The ethanol and CO_2 products are converted to diethyl carbonate. Diesel replacement fuel. (Hosted visiting student from Columbia.)

Iso-pentanol ignition in a shock tube and rapid compression machine





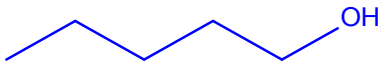


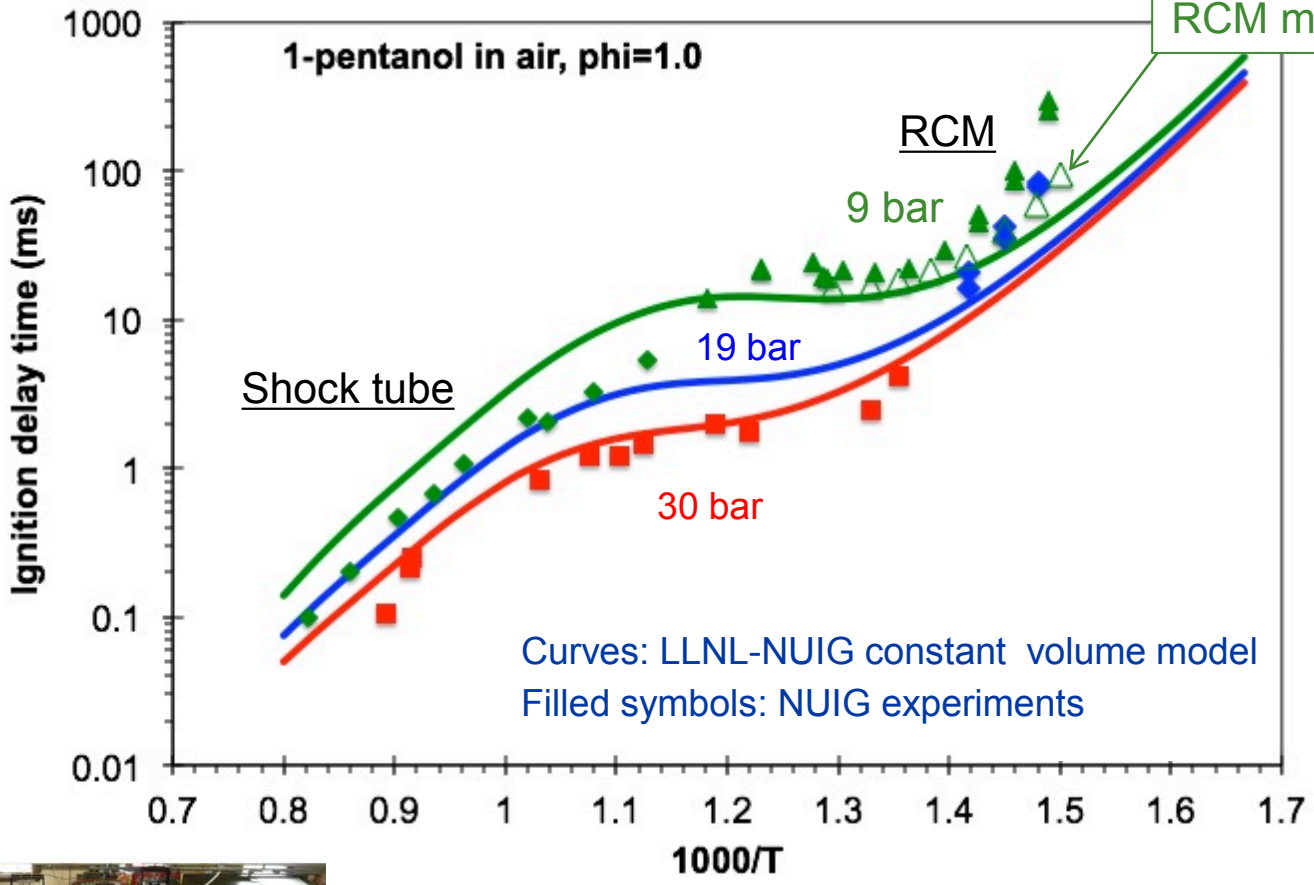
NUIG rapid compression machine (RCM)

Shock tube

Experimental data: Gillespie and Curran, National University of Ireland, Galway, 2011

Development of mechanism for 1-pentanol and validation with shock tube experiments



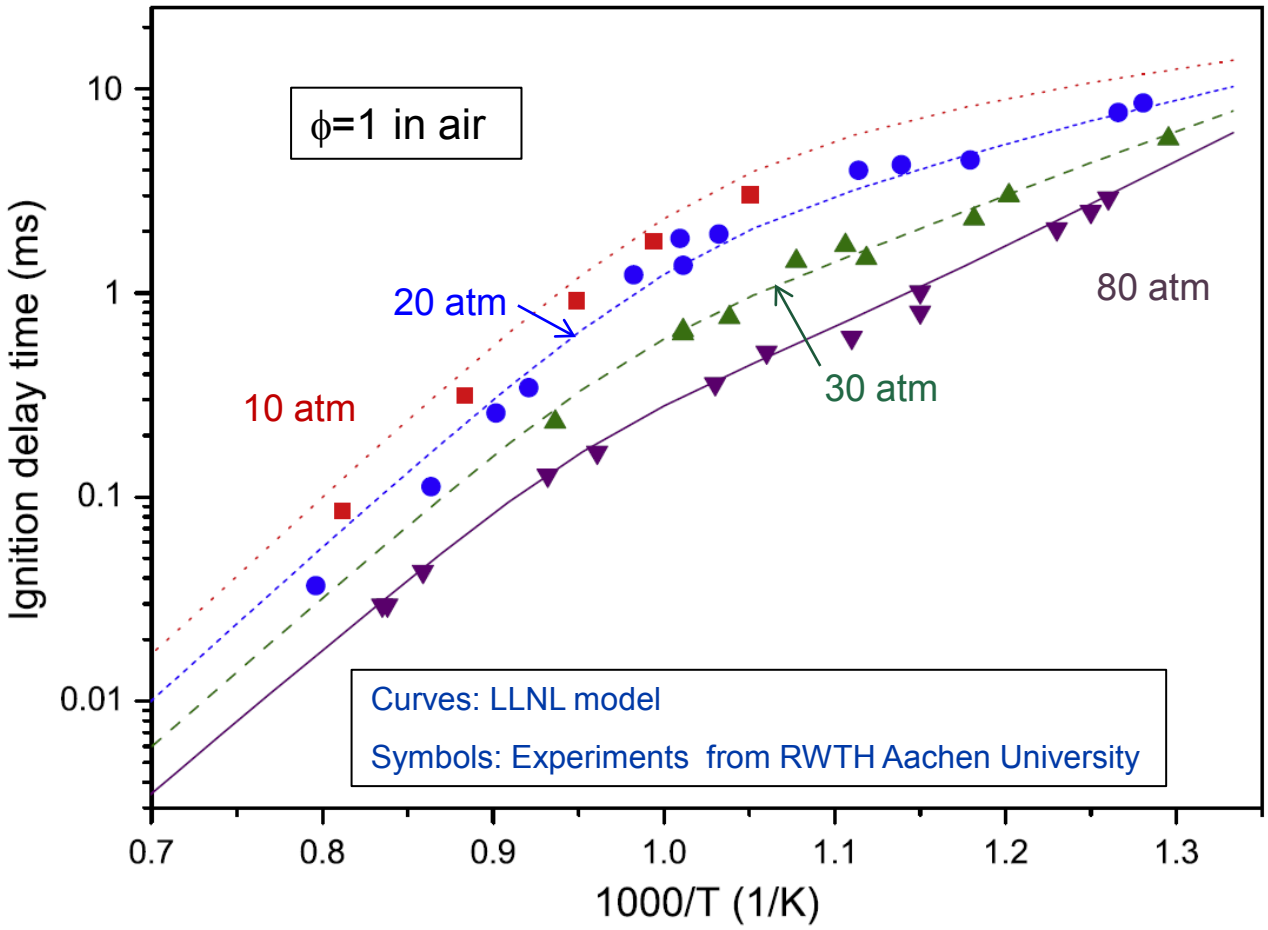


RCM

Shock tube

Experimental data: Heufer, Curran, National Univ. of Ireland

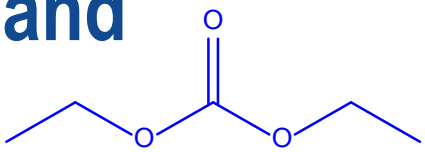
Shock tube ignition delay times for 1-butanol at engine-like pressures and temperatures



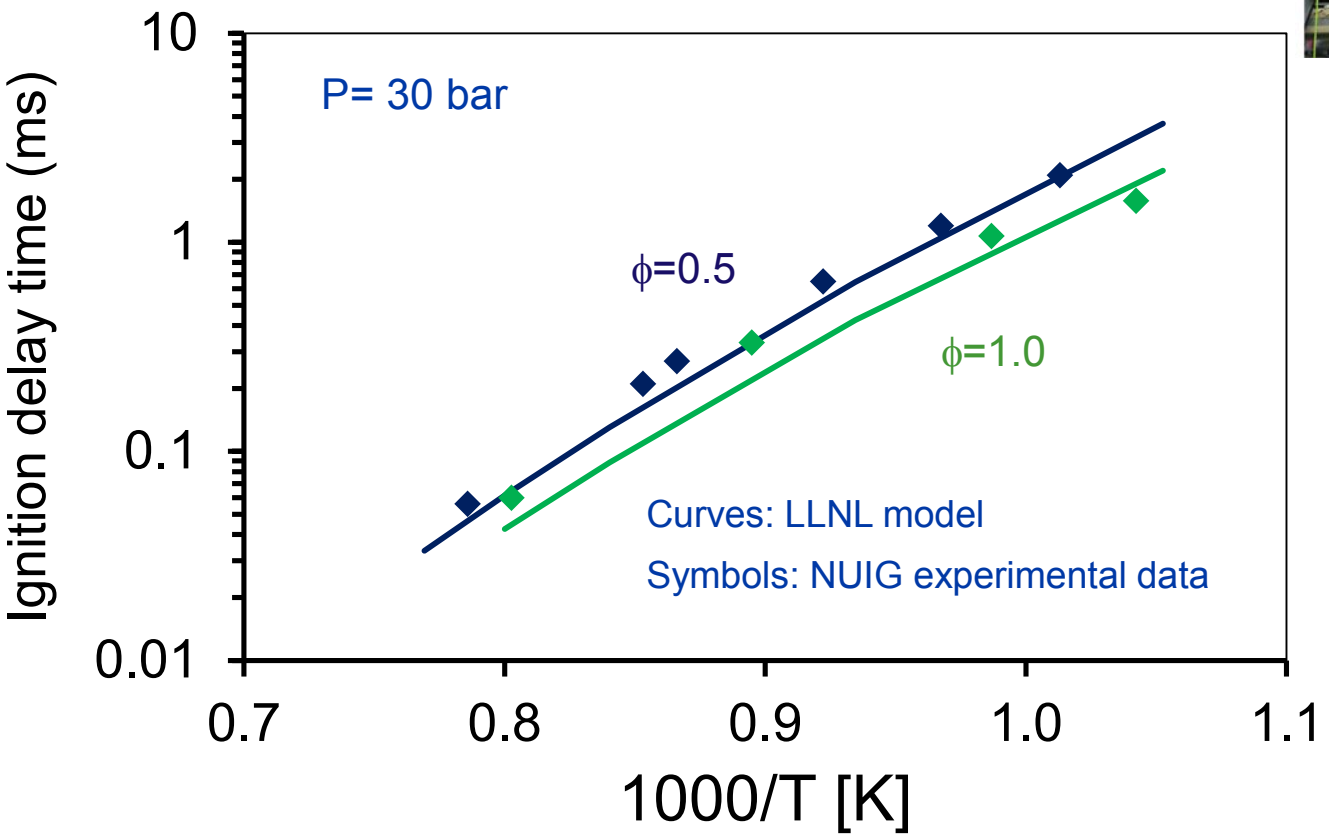
Shock tube

Experiments from Vranckx et al., Comb. Flame 2011 and Heufer et al. Proc. Combust. Inst. 2010

Diethylcarbonate is made from ethanol and displaces petroleum-derived diesel



Results from new diethylcarbonate model compare well with shock tube ignition experiments

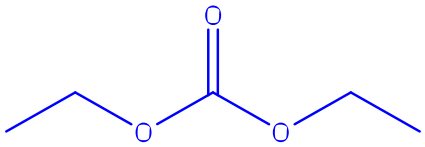


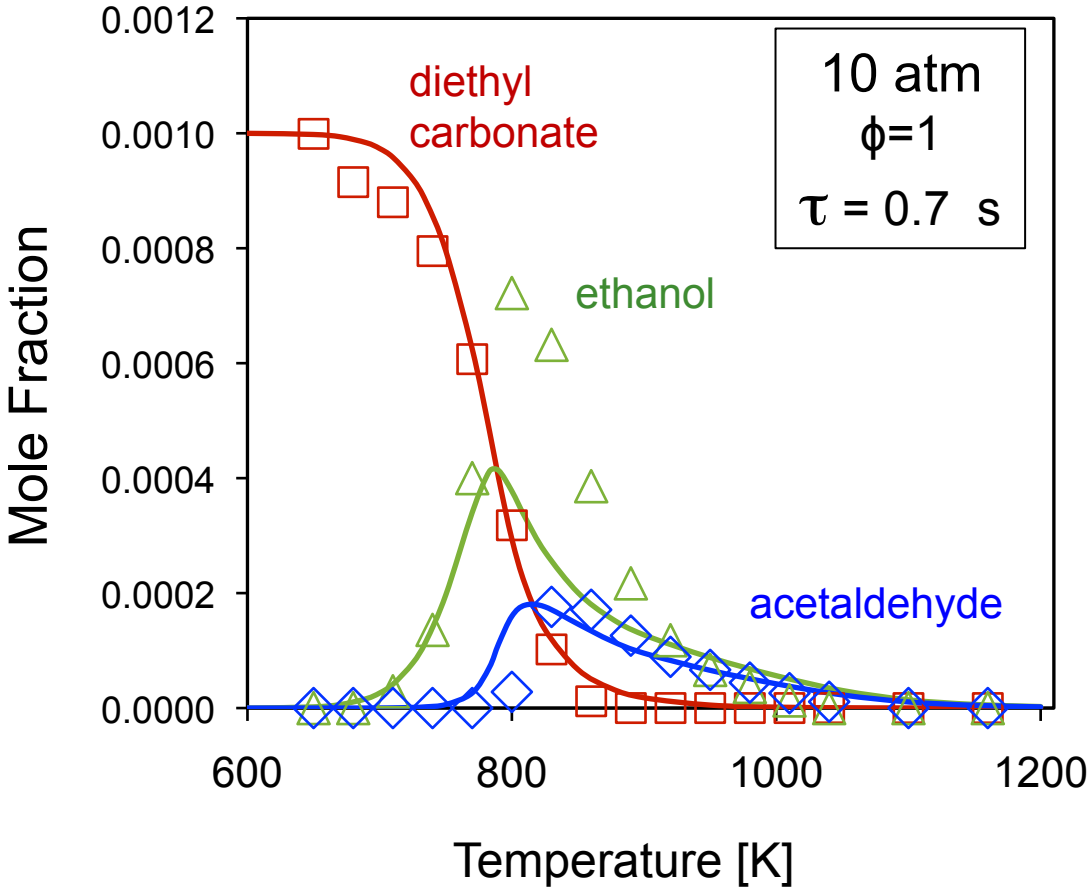
Shock tube

Visiting student,
Angel Polo
University of Antioquia, Colombia

Experimental data: Nakamura and Curran, National University of Ireland, Galway

Validated diethyl carbonate model under jet stirred reactor conditions



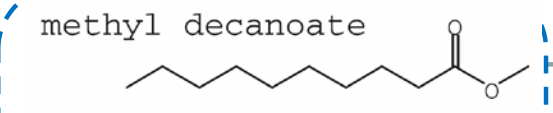


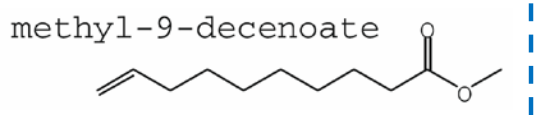
Experiments performed at CNRS, Orleans (P. Dagaut and C. Togbe)

New capability of modeling reacting sprays for biodiesel

T= 1000 K, ρ=23 kg/m^3

Biodiesel Surrogate mixture

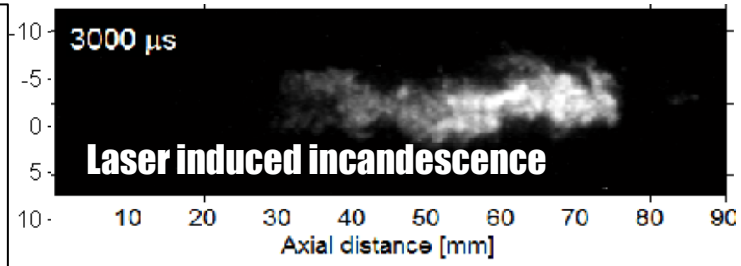




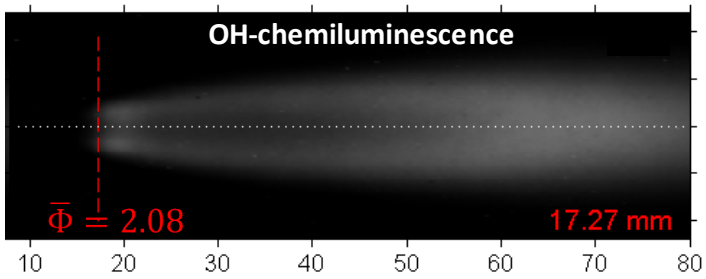
n-heptane, n-C_7H_{16}

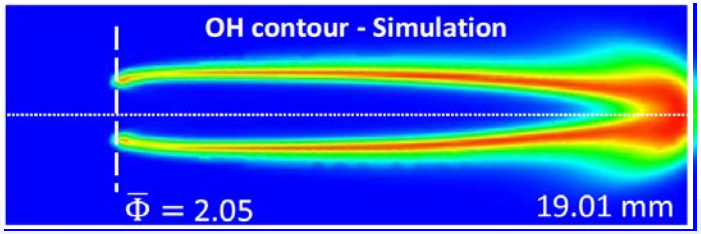
115 species and 460 reaction mechanism

Soot



OH chemiluminescence





Detailed mechanism captures:

- ✓ Ignition delay
- ✓ Flame lift-off length
- ✓ Equivalence ratio distribution
- ✓ Emission characteristics

- ➢CFD simulations: Sibendu Som, Argonne National Laboratory
- ➢Biodiesel surrogate: LLNL
- ➢Mechanism reduction, Luo and Lu, University of Connecticut
- ➢Experiments with soy biodiesel: Lyle Pickett et al., SNL

Fuels, 2012 submitted

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

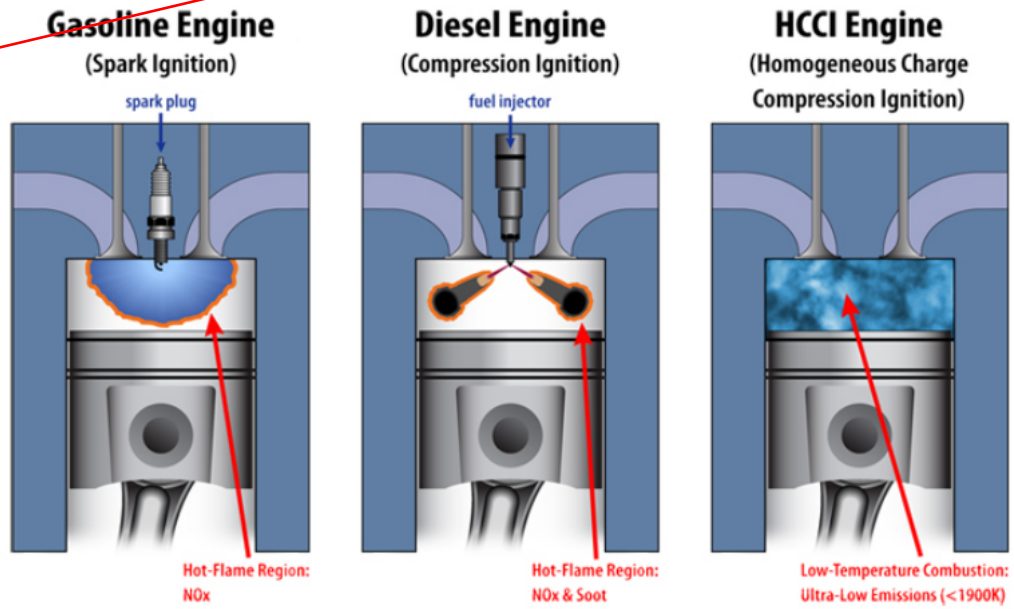
Combustion Chemistry

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 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 halons and 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



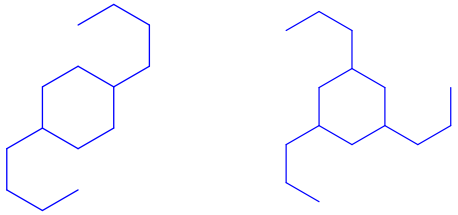
Collaborations

- 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 Sjoberg on ethanol-gasoline mixtures
  - Collaboration with John Dec at Sandia on HCCI engine experiments on many fuels (e.g. iso-pentanol, gasoline)
  - Collaboration with Sibendu Som at Argonne on CFD simulation of biodiesel engine combustion
- Second interaction is participation with many universities
  - Prof. Hanson, Stanford on methyl oleate
  - Prof. Oehlschaeger, RPI on iso-pentanol and large methyl esters
  - Prof. Wooldridge, U. Mich. on 3-methyl hexanoate in the shock tube.
  - Prof. Egolfopoulos on ethanol-gasoline mixtures
  - Dr. Curran, National Univ. of Ireland on many fuels (iso-pentanol, n-pentanol, n-butanol)
  - Prof. Sung, Univ. of Conn. on iso-pentanol
  - Prof. Lu, Univ. of Conn. on mechanism reduction
  - University of Antioquia in Columbia on diethylcarbonate
- Participate in Fuels for Advanced Combustion Engines (FACE) Working group (Industry, National Labs) including AVFL-18, Surrogate fuels for kinetic modeling
- Participating in the Engine Combustion Network that includes members from national labs, academia and industry

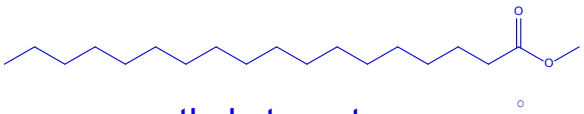
Activities for Next Fiscal Year

- Large alkyl cyclohexane to represent cycloalkane class in diesel and alternative fuels (AVFL-18)

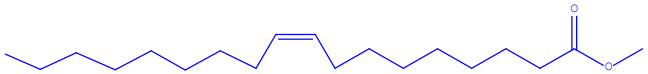
Example C14 and C15 cycloalkanes:



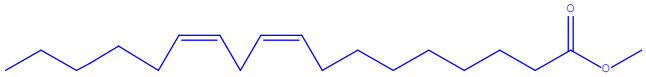
- Continue validation of large ester models by comparison to new high-pressure shock tube data from Oehlschlaeger at RPI:



methyl stearate



methyl linoleate



methyl linolenate

- Further improvements on a reduced model for biodiesel for CFD applications
- Validate gasoline-ethanol surrogate model
- Effect of double bond on ignition characteristics

Summary

- Approach to research
  - Continue development of surrogate fuel mechanisms for non-petroleum based fuels to obtain predictive models that can optimize fuel formulations
- Technical accomplishments:
  - Validated chemical kinetic models for real biodiesel components and alcohols at engine-like conditions
- Collaborations/Interactions
  - Collaboration through AEC working group and FACE working group (AVFL18) with industry. Many collaborations with national labs and universities
- Plans for Next Fiscal Year:
  - Develop model for a larger cycloalkane
  - Further validated chemical kinetic models for real biodiesel components
  - Validate gasoline-ethanol surrogate model
  - Look at the effect of double bond on ignition characteristics