Lawrence Livermore National Laboratory

Chemical Kinetic Modeling of Non-Petroleum Based Fuels

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Lawrence Livermore National Laboratory
May 10, 2011

Project ID # FT010

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

Washington, DC

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LLNL-PRES- 473455

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:

- FY10: 500K
- FY11: 438K

Partners

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

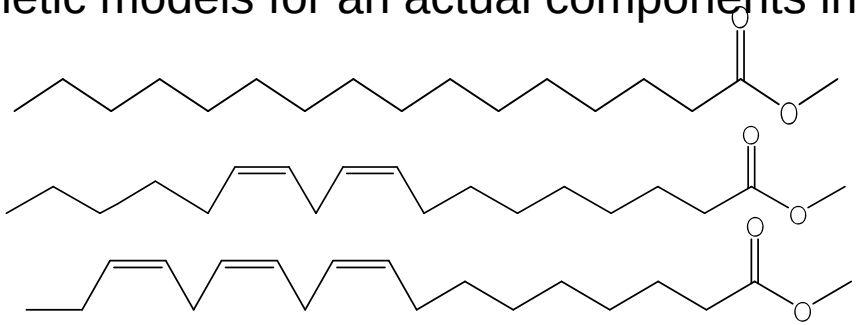
Barriers/Targets

- 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

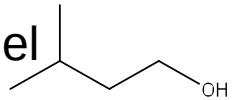
Objectives and relevance to DOE objectives

- 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

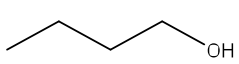
- FY11 Objectives:
  - Develop a chemical kinetic models for an actual components in biodiesel
    - Methyl palmitate
    - Methyl linoleate
    - Methyl linolenate

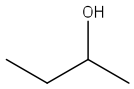


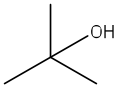
  - Develop a chemical kinetic model for iso-pentanol , a new biofuel

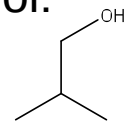


  - Develop chemical kinetic models for all four isomers of butanol:



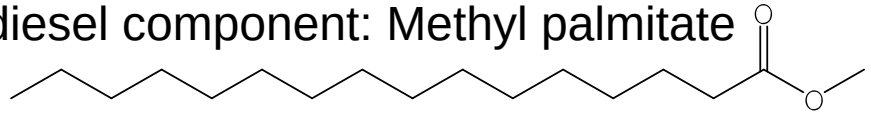




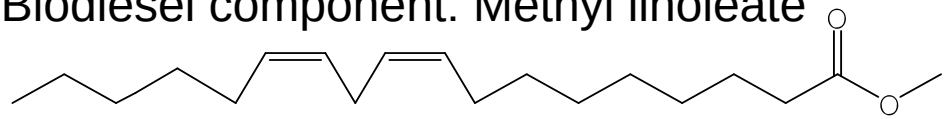


Milestones

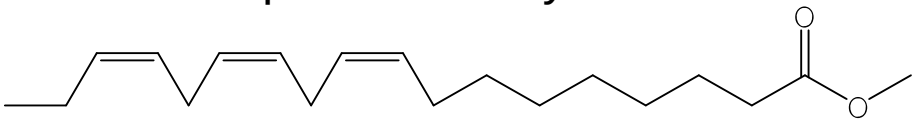
- ✓ December, 2010
  Develop chemistry model for actual Biodiesel component: Methyl palmitate



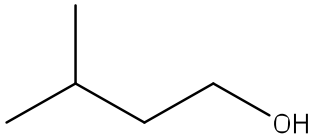
- ✓ February, 2011
  Develop chemistry model for actual Biodiesel component: Methyl linoleate



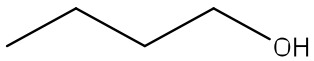
- ✓ May, 2011
  Develop chemistry model for actual Biodiesel component: Methyl linolenate

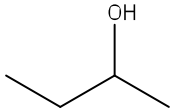


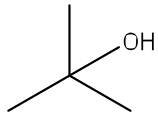
- ✓ March, 2011
  Develop a chemical kinetic model for iso-pentanol

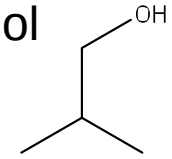


- September, 2011
  Develop a chemical kinetic model for all four isomers of butanol









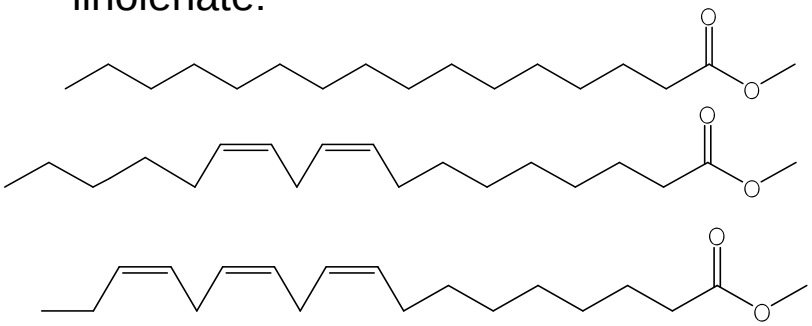
- September, 2011 Provide technical support for the Fuels for Advanced Combustion Engines (FACE) working group

Approach

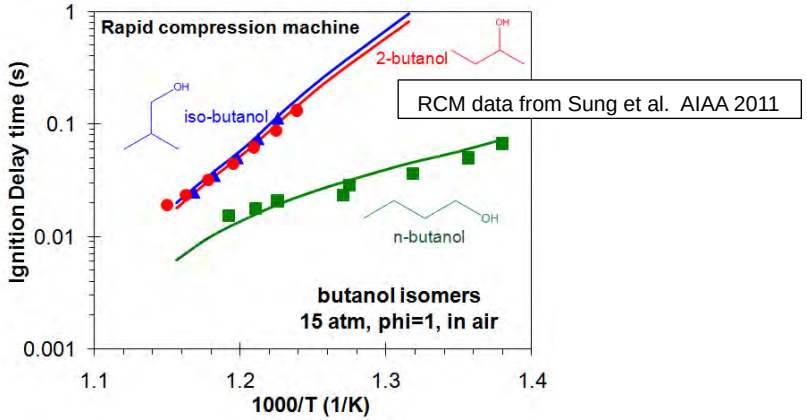
- Develop chemical kinetic reaction models for each individual fuel component of importance for advanced non-petroleum based fuels
- Combine mechanisms for representative fuel components to provide surrogate models for non-petroleum based fuels:
  - Biodiesel
  - New generation biofuels
  - Fuels from biomass
  - 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

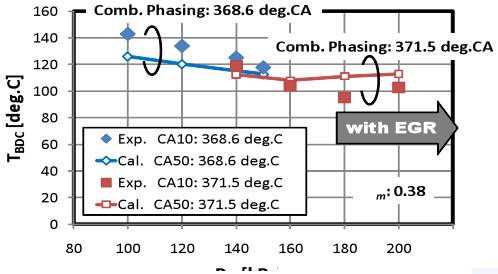
- Developed chemical kinetic model for actual biodiesel components: methyl palmitate, methyl linoleate and methyl linolenate:

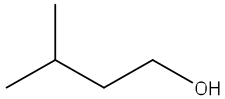


- Developed preliminary chemical kinetic model for all the isomers of butanol



- Developed chemical kinetic model for advanced biofuel iso-pentanol and compared computed results to HCCI engine experiments at Sandia

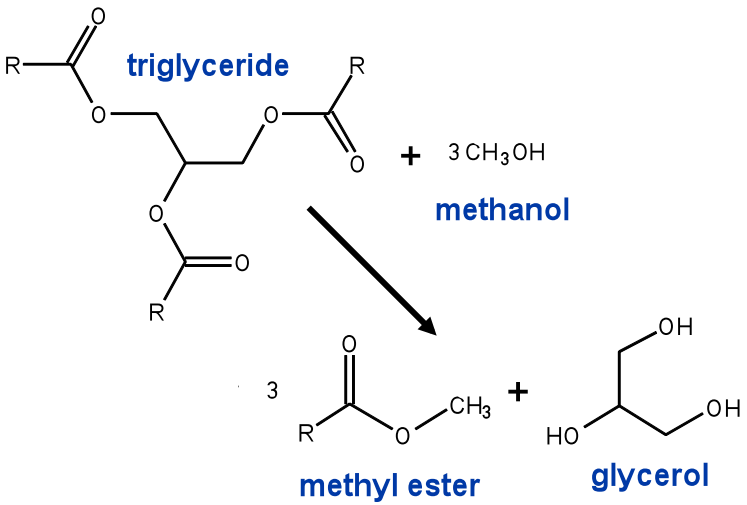


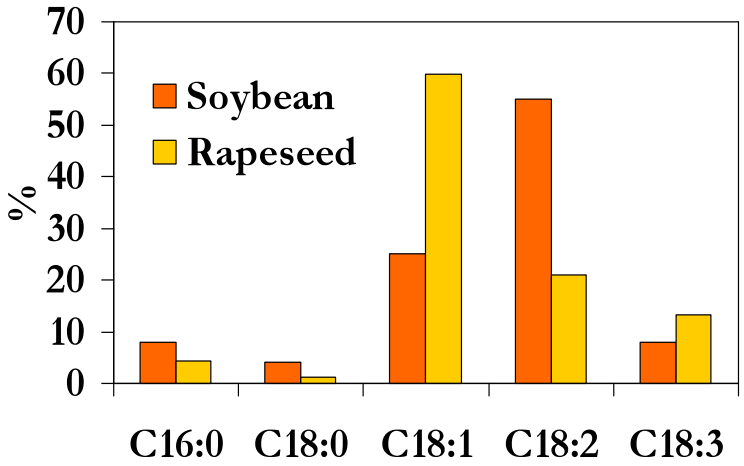


iso-pentanol

- Supported the FACE fuel effort through AVFL-18, “Surrogate fuels for kinetic modeling”:
  - W. J. Pitz and C. J. Mueller, "Recent progress in the development of diesel surrogate fuels," *Progress in Energy and Combustion Science (2011)*
  - C. J. Mueller, W. J. Cannella, T. J. Bruno, B. Bunting, H. Dettman, J. Franz, M. L. Huber, M. Natarajan, W. J. Pitz, M. A. Ratcliff and K. Wright, "A Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics," *(2011) In preparation*

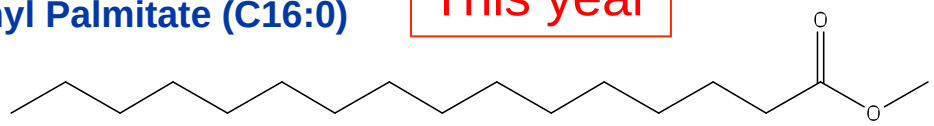
Soybean and rapeseed derived biodiesels have only 5 principal components



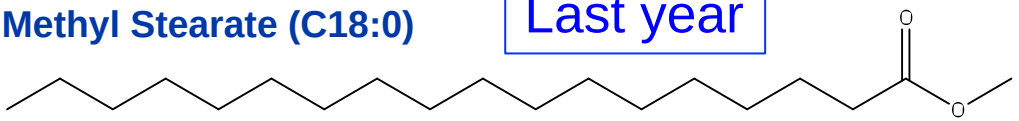


Fatty acid methyl esters (FAMEs):

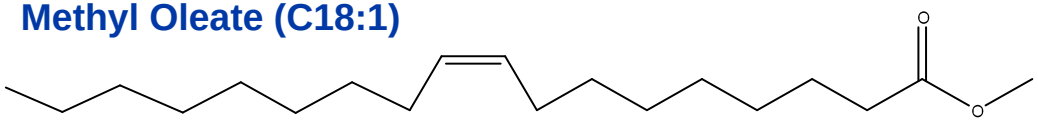
Methyl Palmitate (C16:0) This year



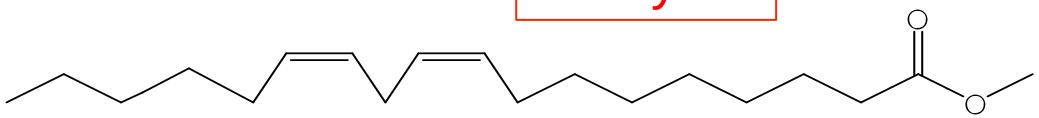
Methyl Stearate (C18:0) Last year



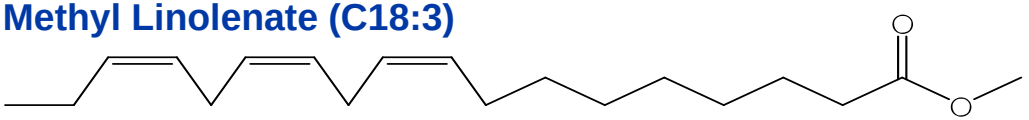
Methyl Oleate (C18:1)



Methyl Linoleate (C18:2) This year



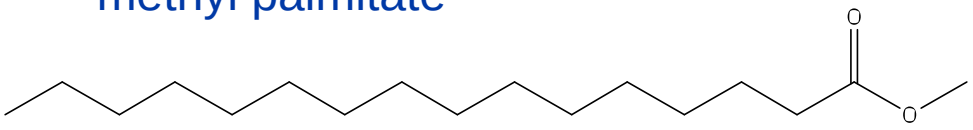
Methyl Linolenate (C18:3)



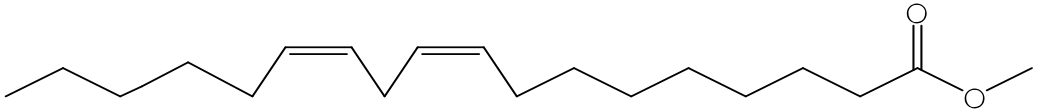
Model with all 5 components now published and available: Westbrook, Naik, Herbinet, Pitz, Mehl, Sarathy and Curran, "Detailed chemical kinetic reaction mechanisms for soy and rapeseed biodiesel fuels," Combustion and Flame, 2011.

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

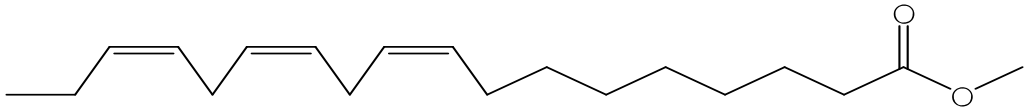
methyl palmitate



methyl linoleate



methyl linolenate

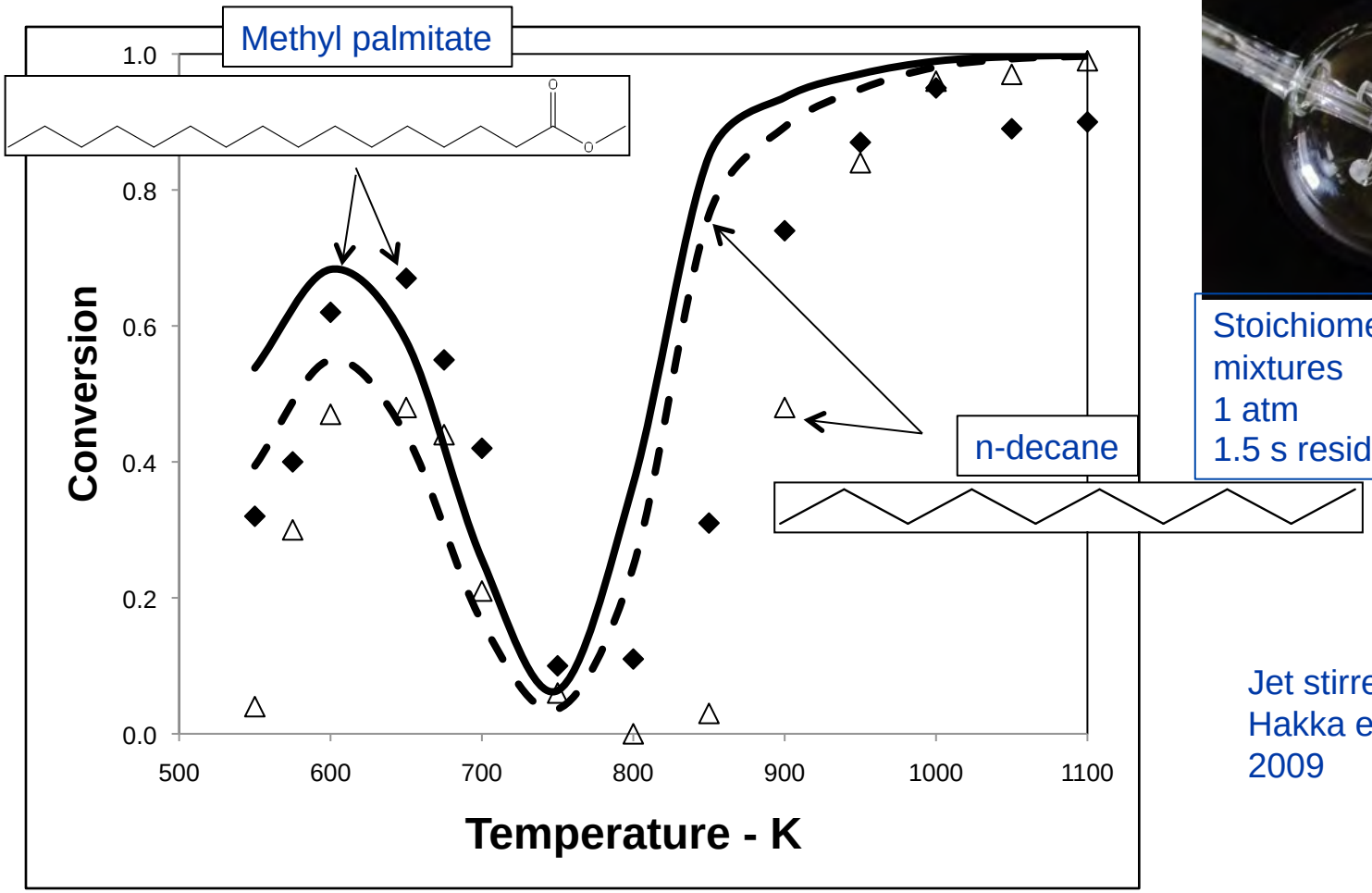


Built with the same reaction rate rules as our successful methyl decanoate and methyl decenoate mechanism

5 component mechanism, approximately

5,000 species
20,000 reactions

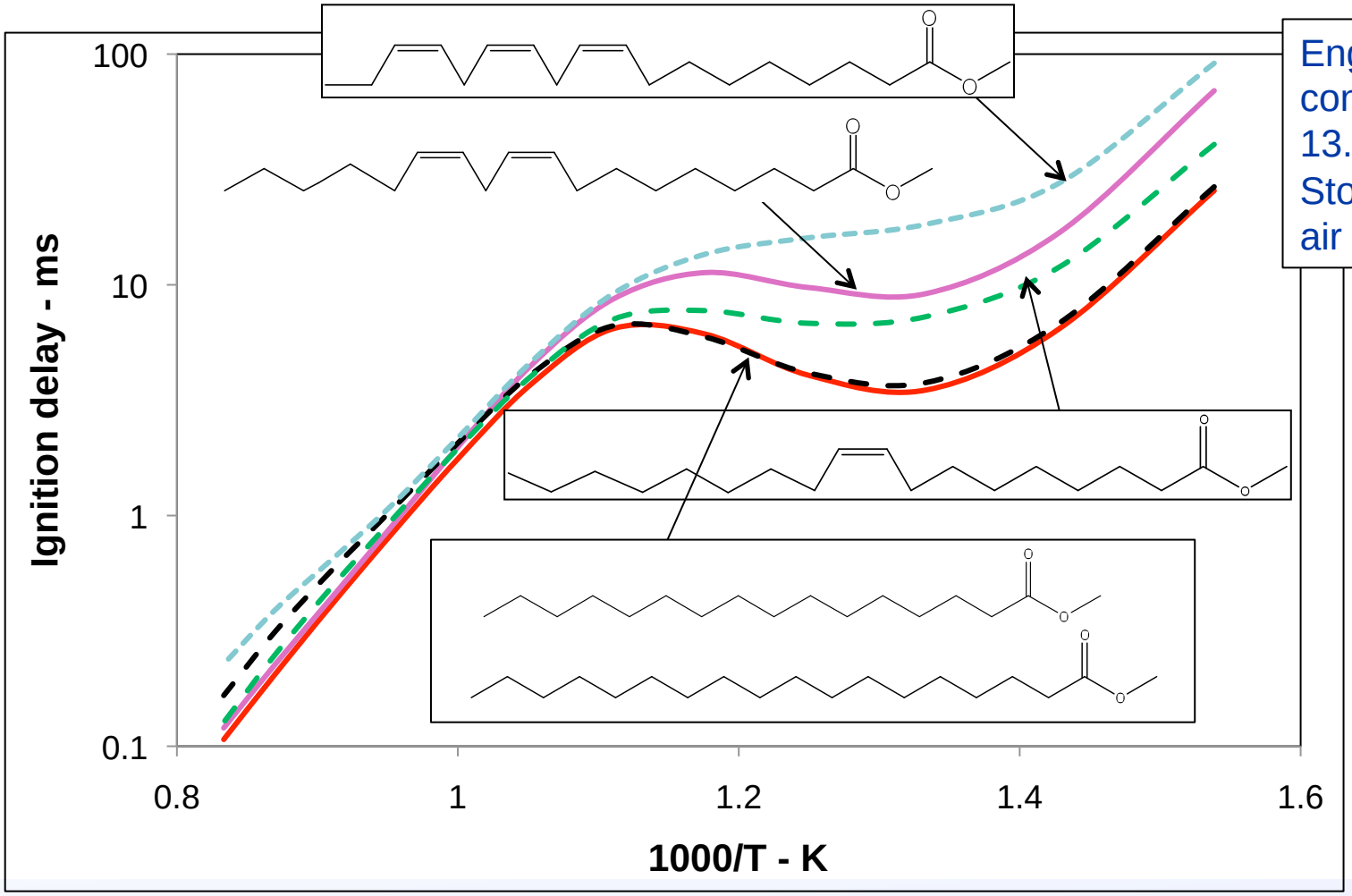
New biodiesel model reproduces oxidation of n-decane/ methyl palmitate mixture in jet stirred reactor



Stoichiometric fuel/O_2/He mixtures
1 atm
1.5 s residence time

Jet stirred reactor data: Hakka et al. Comb Flame 2009

Biodiesel component ignite in order of number of double bonds

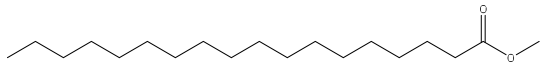


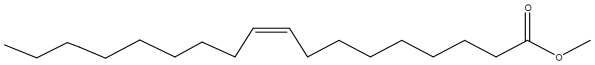
Engine-like conditions:
13.5 bar
Stoichiometric fuel/ air mixtures

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, Φ=2 (Fuel: 200 ppm, residence time = 0.05 s)

Stearate CN101

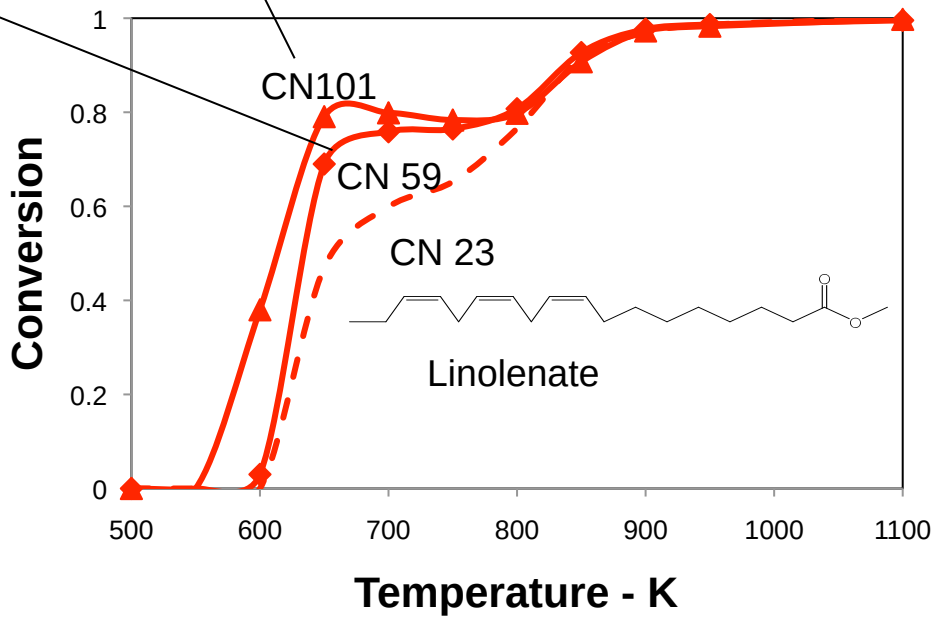




Oleate CN 59

Jet stirred reactor

Simulated conversions of biodiesel components



Derived cetane numbers from Knothe (2010)

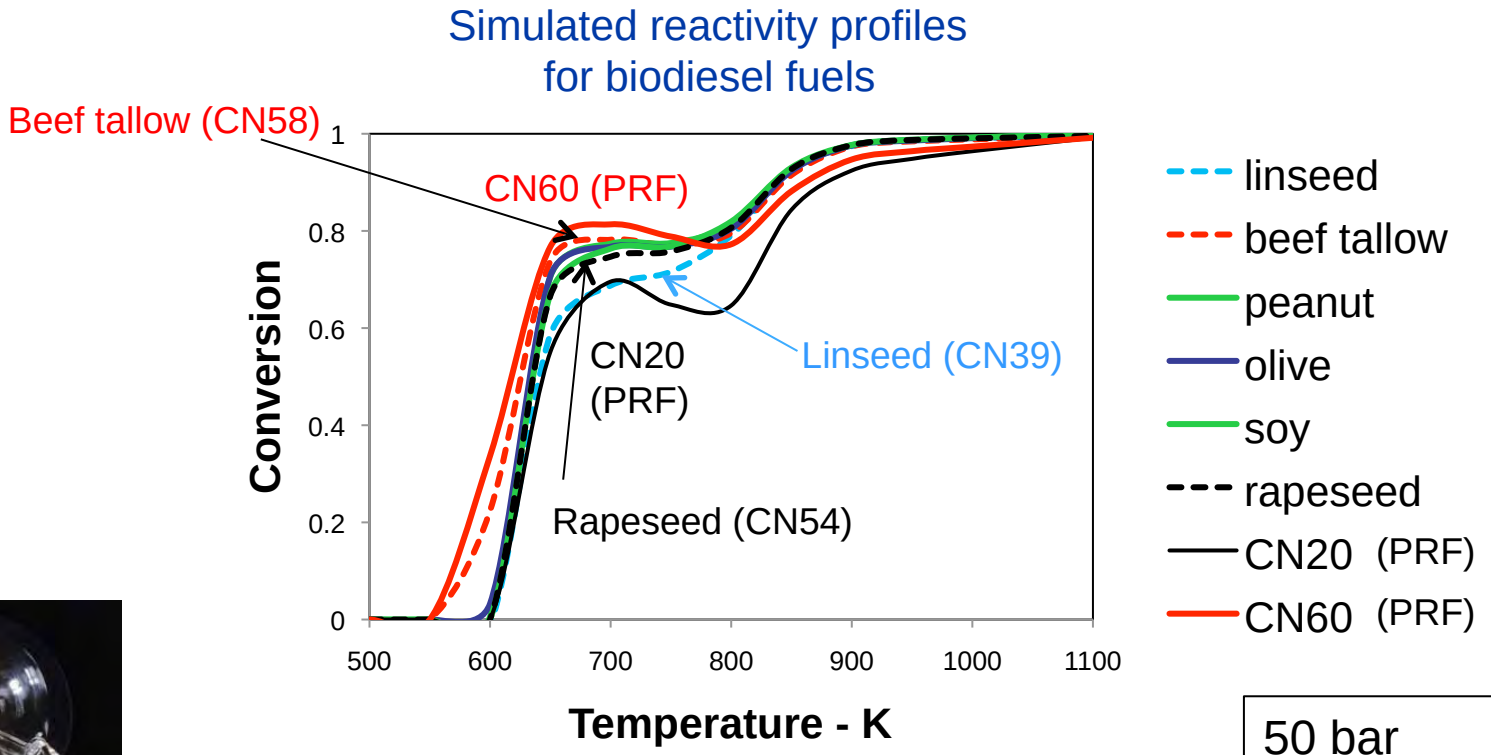
Plant and animal fat oils have different fatty acid profiles that affect reactivity in a diesel engine

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

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 !

Diesel PRF scale allows assessment of the reactivity of biodiesel from different sources



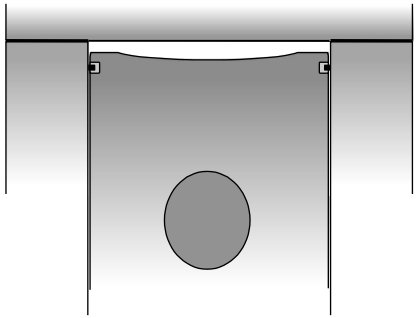
Jet stirred reactor

Diesel PRF mixtures:
n-hexadecane and 2,2,4,4,6,8,8-heptamethylnonane

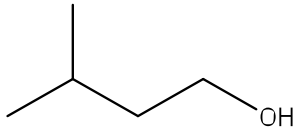
50 bar
Φ=2
fuel: 200 ppm
τ=0.05s

Developed chemical kinetic model for new biofuel iso-pentanol and compared it to experiments in Sandia HCCI engine

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



Iso-pentanol mechanism

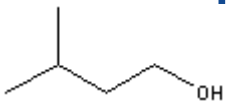


New generation biofuel proposed by DOE Joint BioEnergy Institute (JBEI)

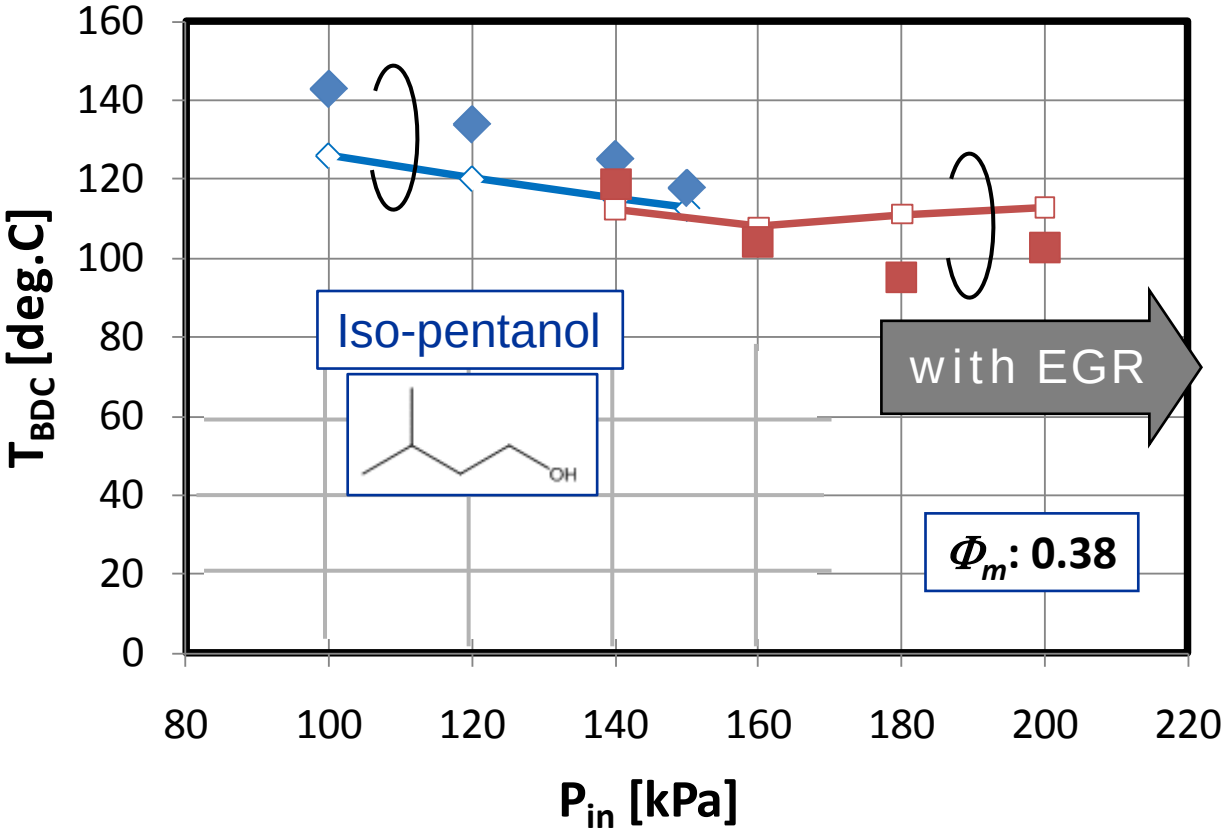
Reaction rate rules on successful iso-octane because it has some similar structures

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



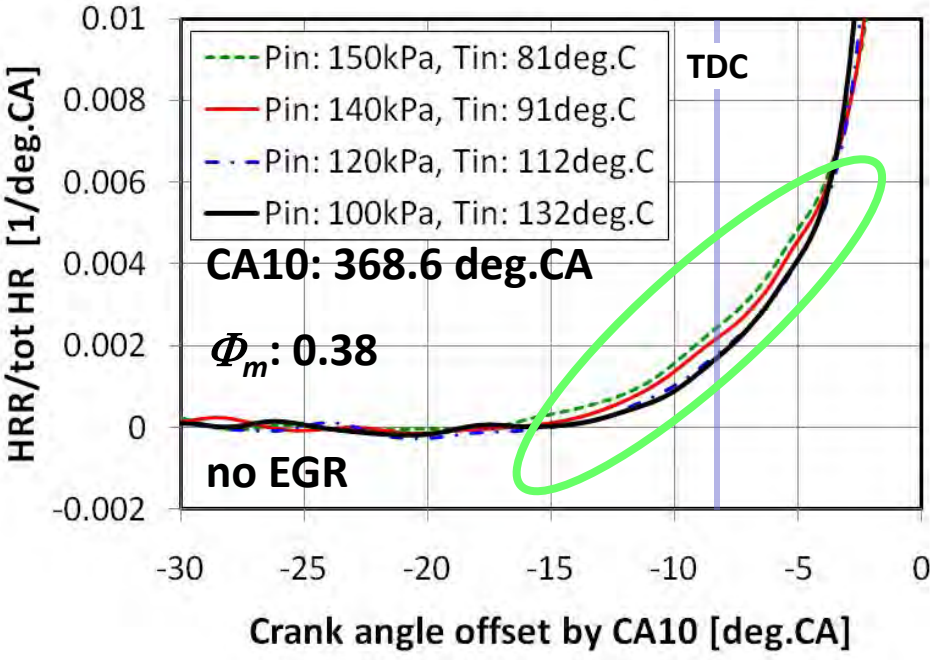
Experiments and Calculations:
Required T_{BDC} for constant combustion phasing



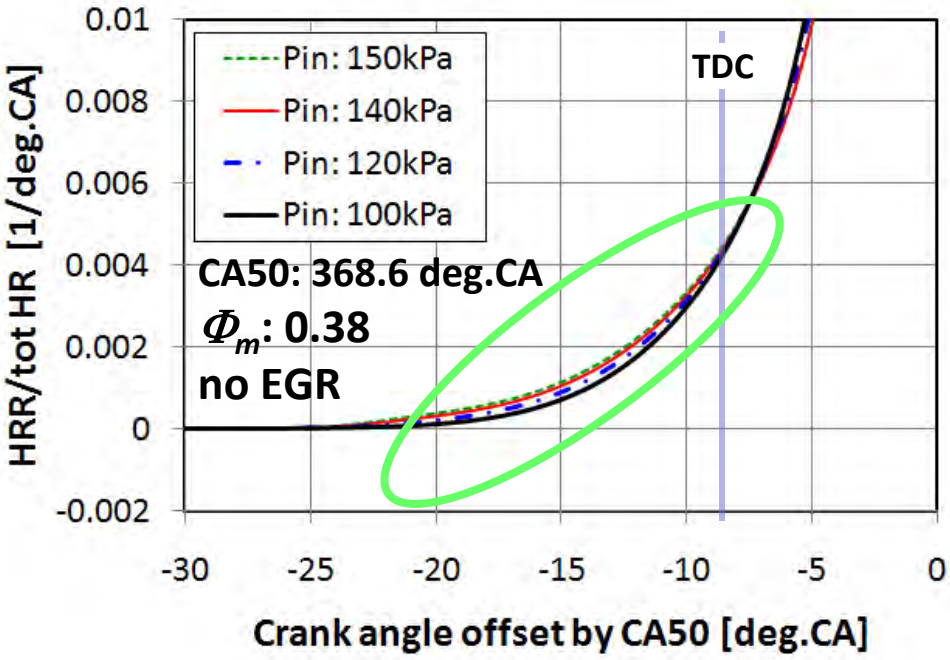
Iso-pentanol model predicts intermediate heat release that allows high load operation for HCCI

Iso-pentanol

Experiments



Calculations



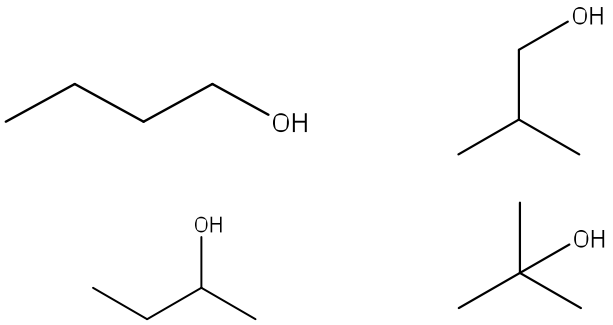
HCCI engine experiments:
Yi and Dec, Sandia, SAE 2010

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

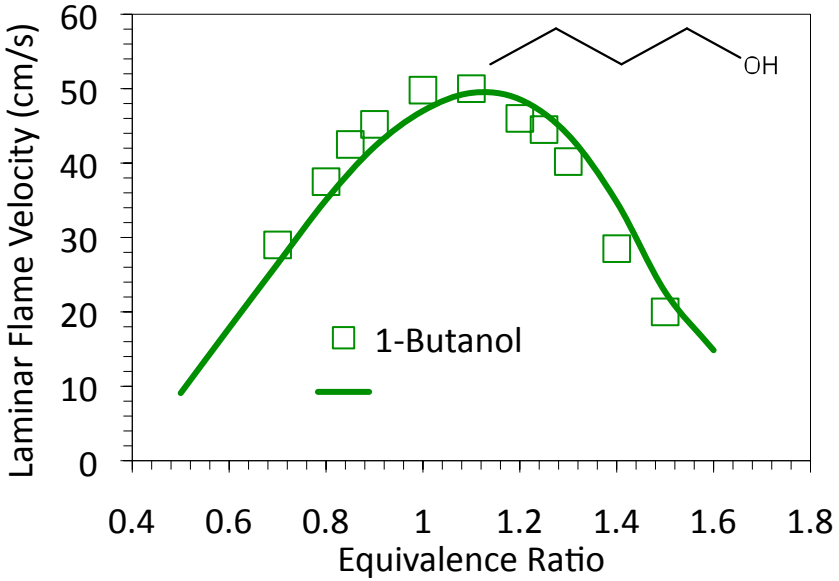


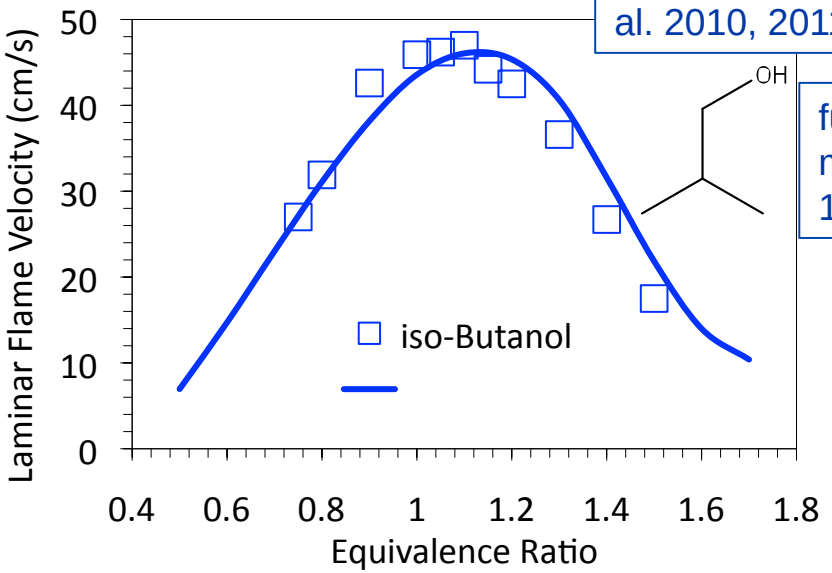
Iso-butanol is a new type of biofuel that can be made directly from cellulose using bacteria

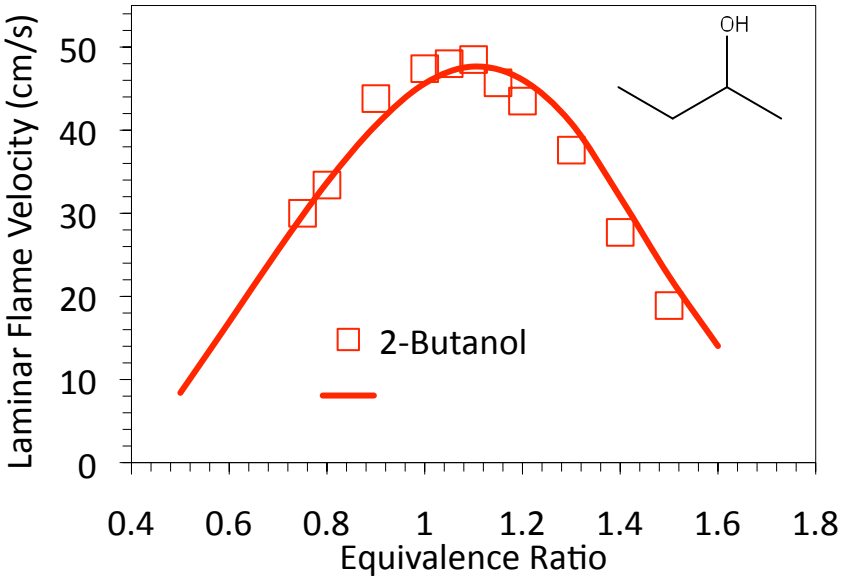
Butanol mechanism accurately simulates flame speeds important for predicting spark ignition engine combustion

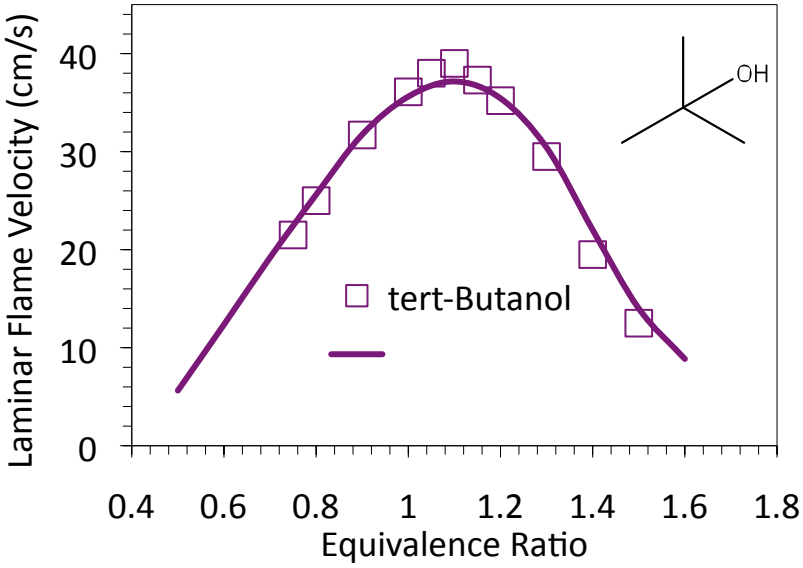
Experimental data: Veloo, Egolfopoulos et al. 2010, 2011

fuel/air mixtures 1 atm

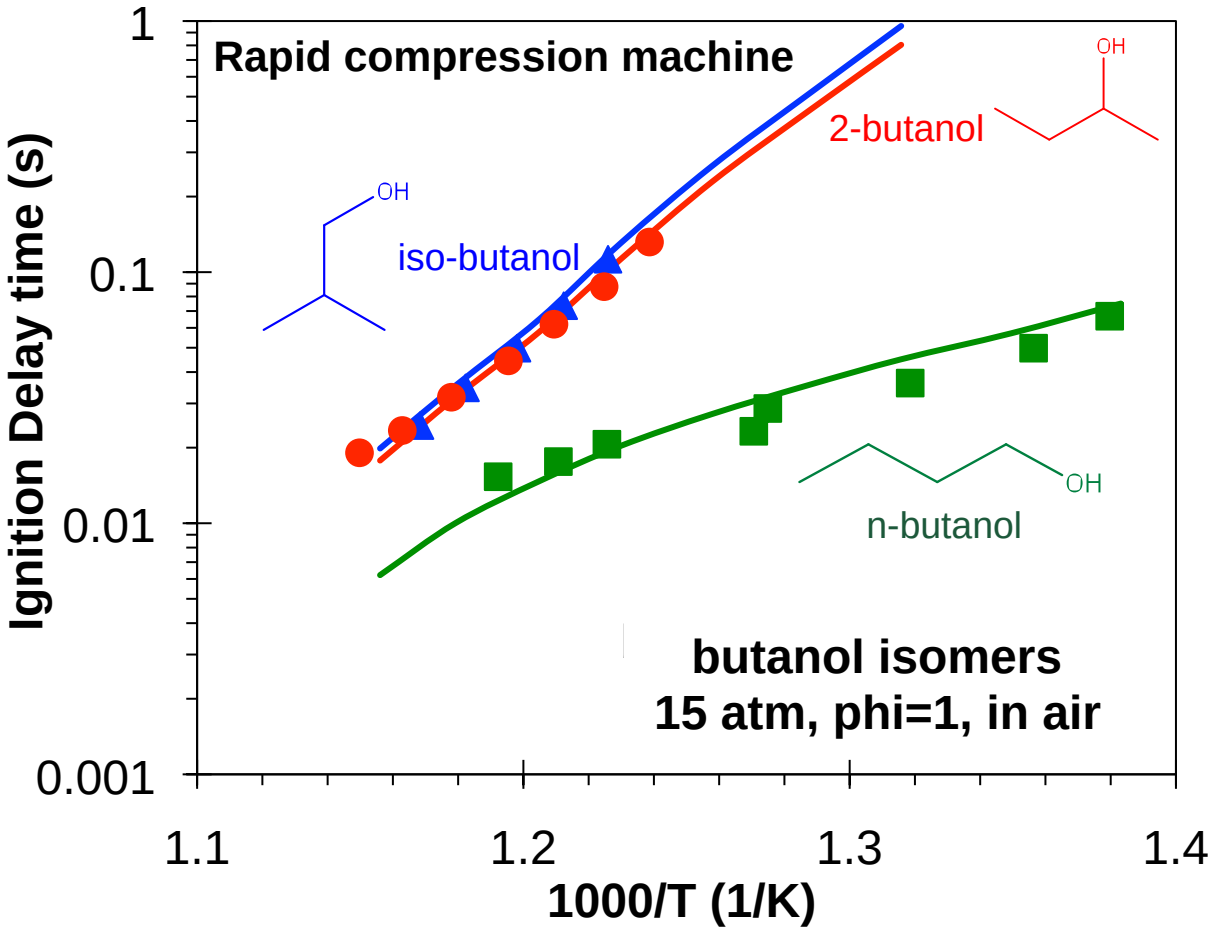




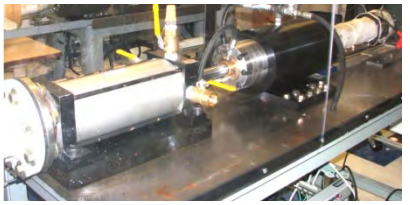




Butanol model well predicts ignition delay times at pressures and temperatures found in IC engines



Symbols:
experimental data
Sung et al.,
AIAA paper, 2011



Rapid compression machine
University of Connecticut

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

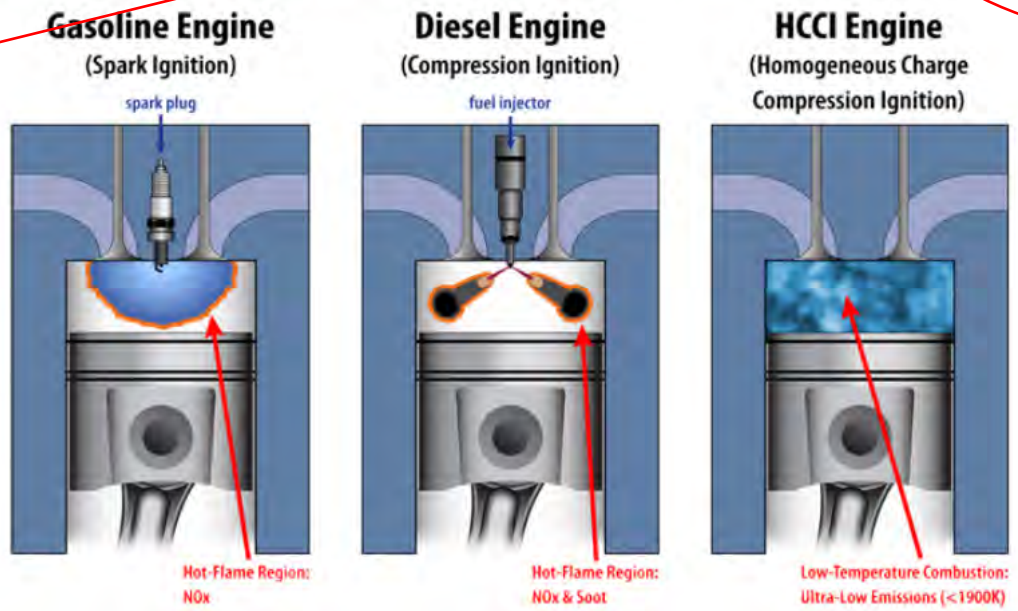
Combustion Chemistry

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 John Dec at Sandia on HCCI engine experiments on many fuels (e.g. iso-pentanol, gasoline)
- Second interaction is participation with many universities
  - Collaboration with Curran at National Univ. of Ireland on many fuels (iso-pentanol, butanol)
  - Collaboration with Prof. Sung at Univ. of Conn. on iso-pentanol
  - Collaboration with Prof. Lu, U. of Conn. on mechanism reduction
  - Collaboration with Prof. Oehlschaeger at RPI on iso-pentanol and methyl esters
- Participate in Fuels for Advanced Combustion Engines (FACE) Working group (Industry, National Labs) including AVFL-18, Surrogate fuels for kinetic modeling

Special recognition during FY11

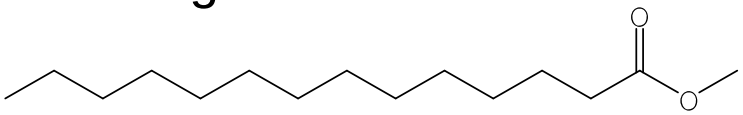
Charles Westbrook:

- Honorary Doctorate Degree from Polytechnic Institute of Lorraine, Nancy, France

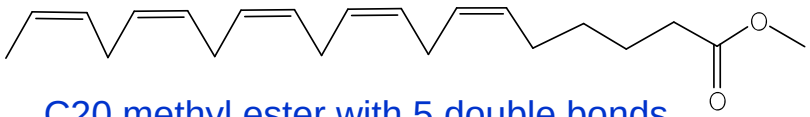
Activities for Next Fiscal Year

- Develop detailed chemical kinetic models algal derived fuels:

Algal pilot scale bioreactor in Lawrence, Kansas

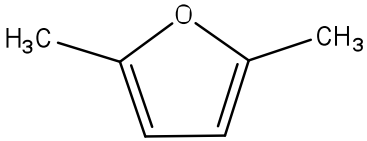


C14 methyl ester

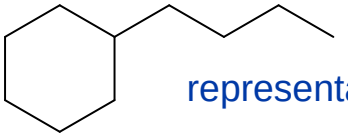


C20 methyl ester with 5 double bonds

- Biomass fuel:

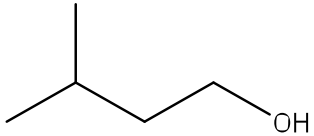


dimethylfuran



representative cycloalkanes

- Further validation of iso-pentanol mechanism in flames:



(iso-pentanol)

- Further validation of mechanisms for large methyl esters:
  - New ignition data in high pressure shock tube (Oehlschlaeger, RPI)

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:
  - Developed chemical kinetic model for the 3 remaining actual biodiesel components
- 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 chemical kinetic models for algal-derived fuels and other new biofuels