Lawrence Livermore National Laboratory

Fuel surrogate Mechanisms for Conventional and Biofuels

William J. Pitz, Marco Mehl, Charles K. Westbrook
Lawrence Livermore National Laboratory
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Acknowledgements

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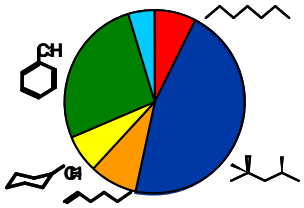
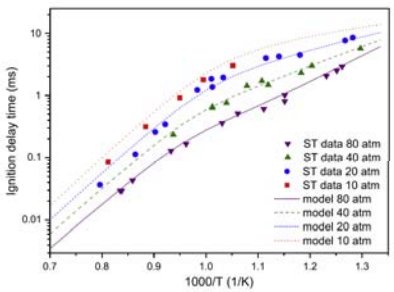
- Support from program manager Wade Sisk, Basic Energy Sciences, Department of Energy
- Support from program manager Sharon Beerman-Curtin, Office of Naval Research

Progress on surrogate fuels and biofuels

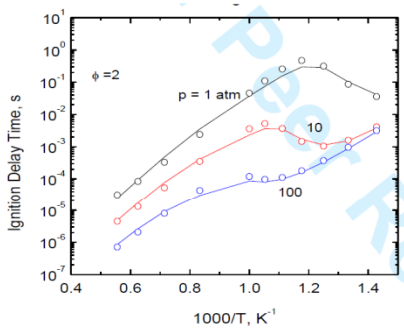
Defining surrogates for gasoline fuels:



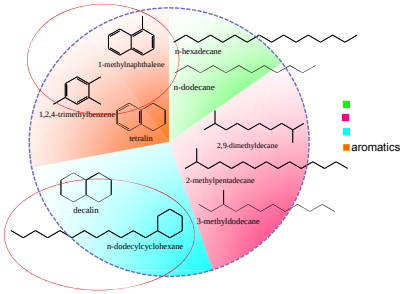
Improved, new models for large alcohols:



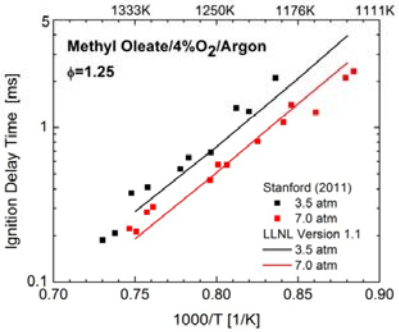
Reduced models for fuel surrogates for CFD engine simulations:



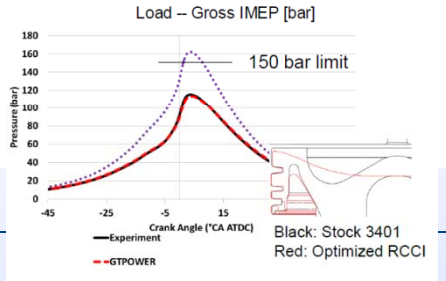
Detailed chemical kinetic models for surrogates components for diesel fuels:



Improved models for large methyl esters:



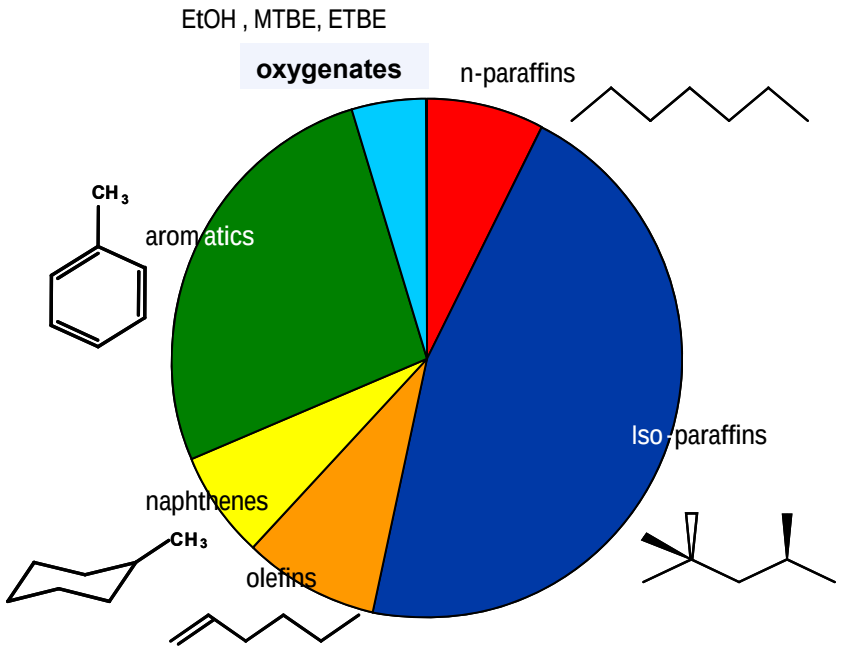
Future challenges



Why do we need surrogate fuels?

- **Real fuels are complex mixtures (100s of components)**
  - **We cannot simulate all those components**
- **Define simpler mixtures that represent properties of real fuels**

  => surrogates

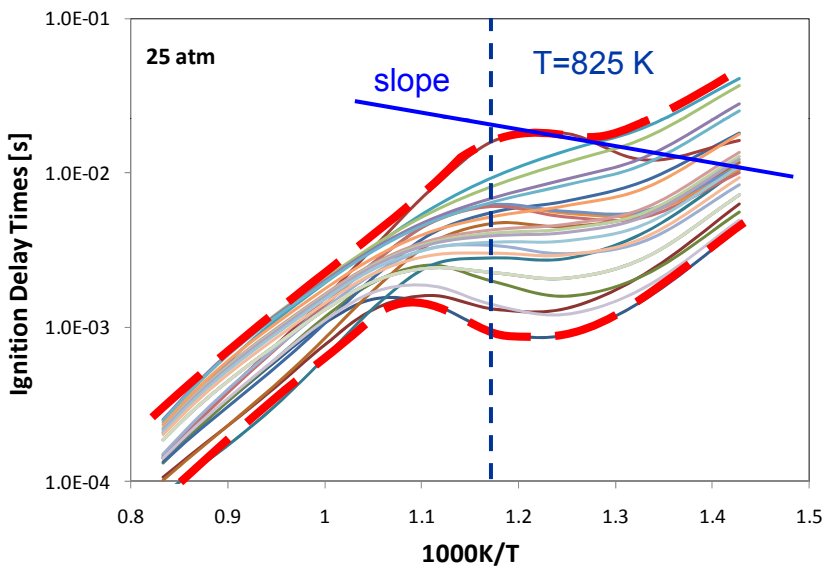


Chemical classes in gasoline with representative fuel components

Developed new procedure to formulate gasoline surrogates to match target gasoline fuels

Ignition delay at 825K correlates to octane number

Slope in NTC region correlates to octane sensitivity = RON - MON

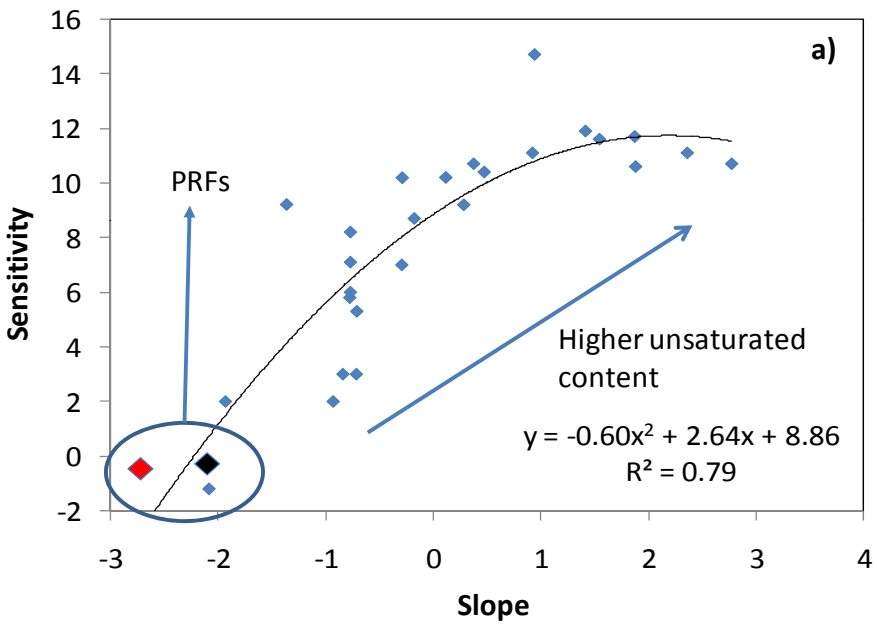


40 different gasoline surrogates were simulated

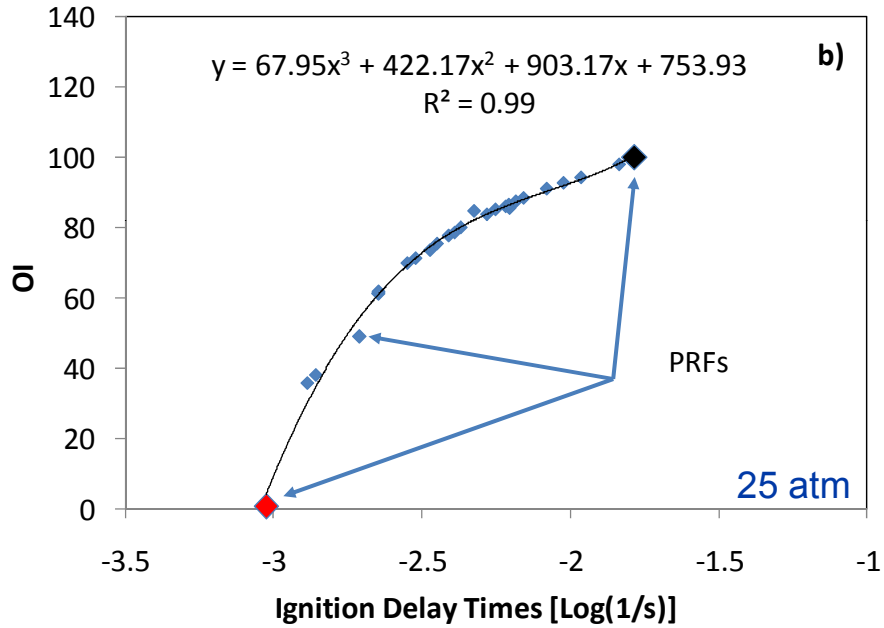
Experimental data: Personal communication and N.Morgan et al. Comb. & Flame

A correlation between the octane rating and the autoignition propensity of gasoline surrogate fuels has been identified

Sensitivity vs. Slope



Octane Index vs. Ignition Delay time @ 825K

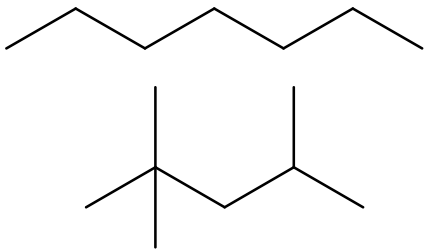


Starting from the analysis of 40 different fuel mixtures a general approach to the formulation of the gasoline surrogate has been developed on the basis of the key features of the ignition delay curves

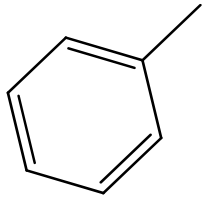
Matched gasoline properties with a surrogate

	Surrogate (%Vol)	RD387 Gasoline (%Vol)
i-Alkanes	0.57	0.731
n- Alkanes	0.16	
Aromatics	0.23	0.227
Olefins	0.04	0.042
A/F Ratio	14.61	14.79
H/C	1.925	1.946
Octane index	87	87
Sensitivity	4	4

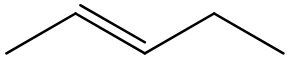
Alkanes



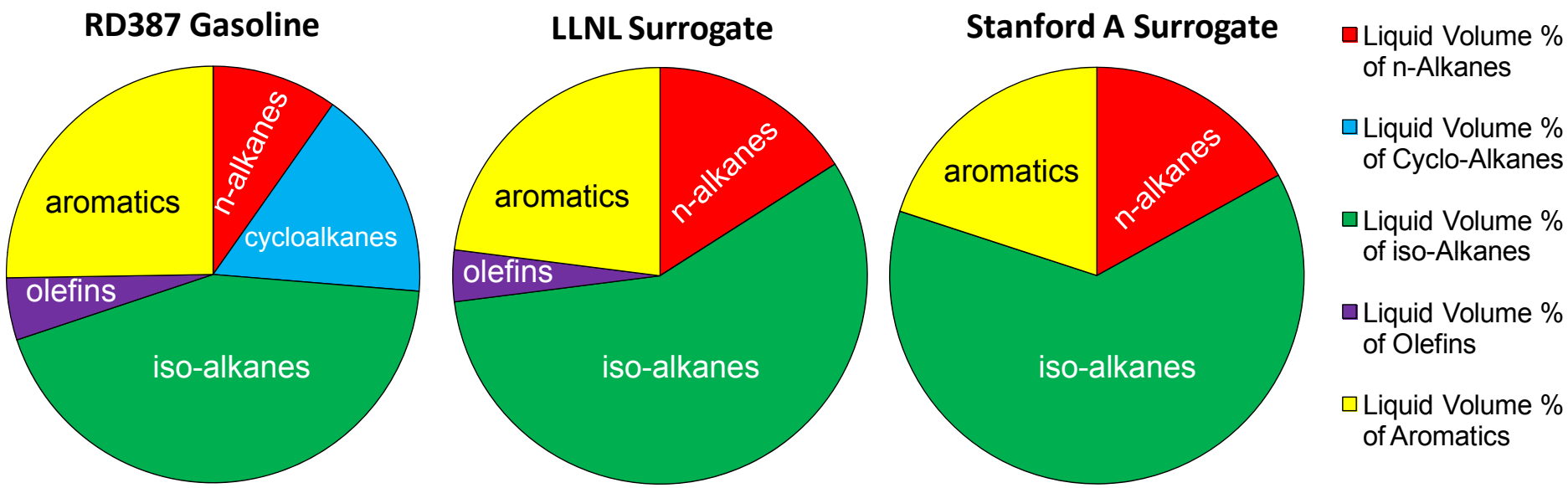
Aromatics



Olefins



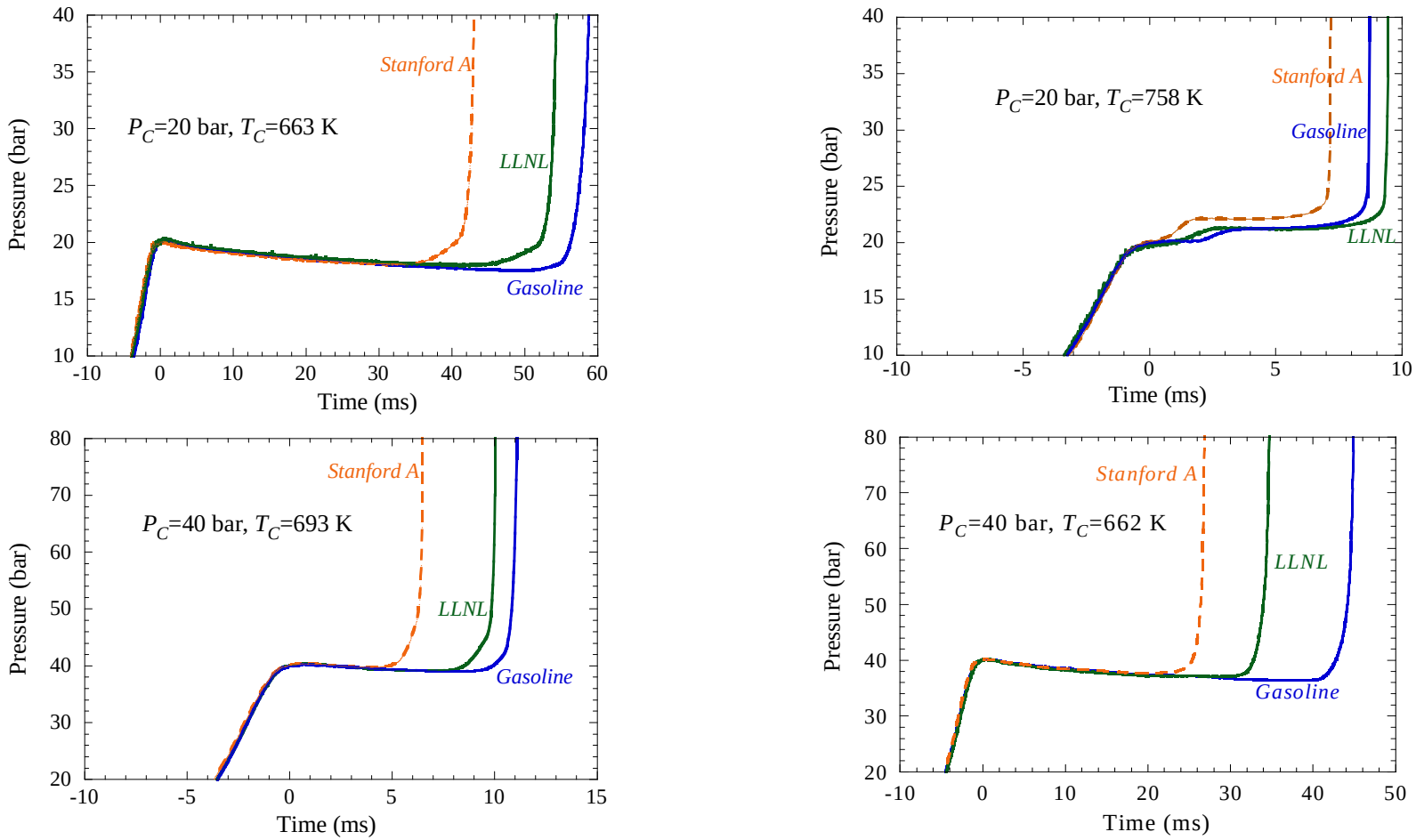
Three different fuels were tested in the UCONN Rapid Compression Machine



- The Stanford A Surrogate has been formulated targeting high temperature shock tube data

From: Kukkadapu, Kumar, Sung, Mehl, and Pitz, Combust. Flame (2012)
Gauthier, Davidson, Hanson, Combustion and Flame (2004)

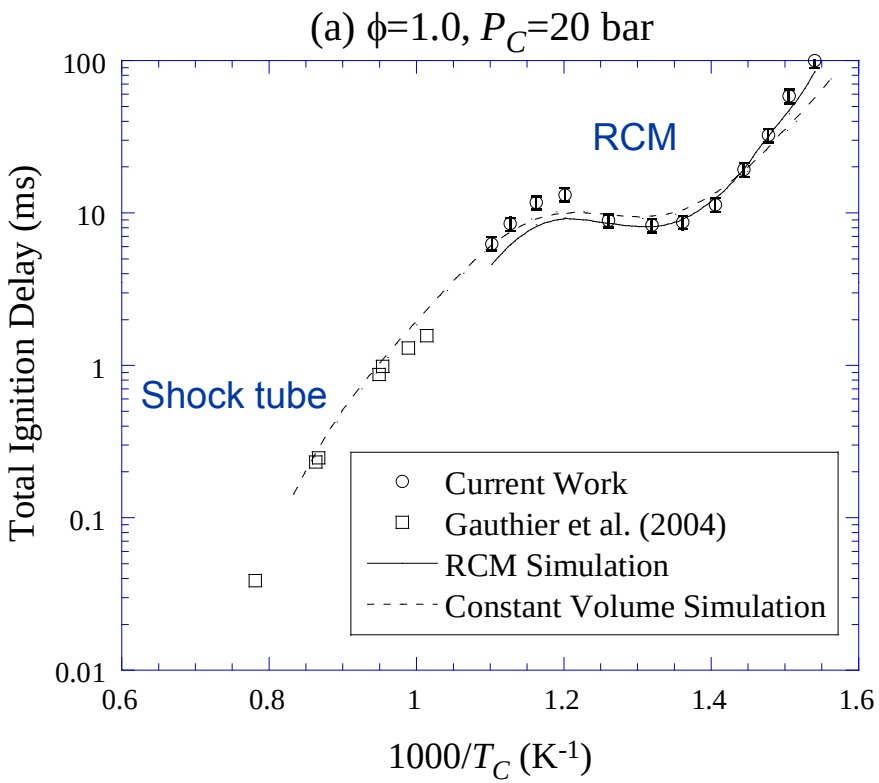
Comparison of experimentally-measured pressure histories in the RCM for 2 proposed surrogates and RD387 gasoline

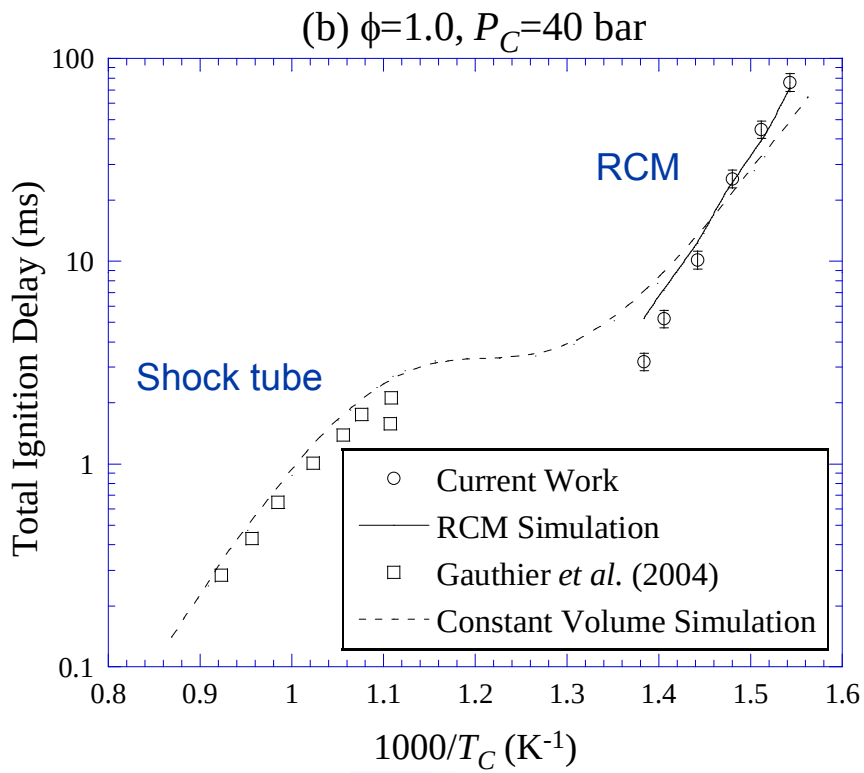


- The LLNL surrogate well reproduces the total ignition delay times and the heat release associated with the first stage ignition

From: Kukkadapu, Kumar, Sung, Mehl and Pitz, Proc. Combust. Inst.(2012)

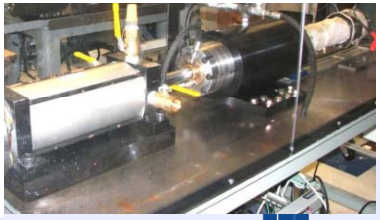
Simulations of real gasoline (RD387) experiments using LLNL surrogate model



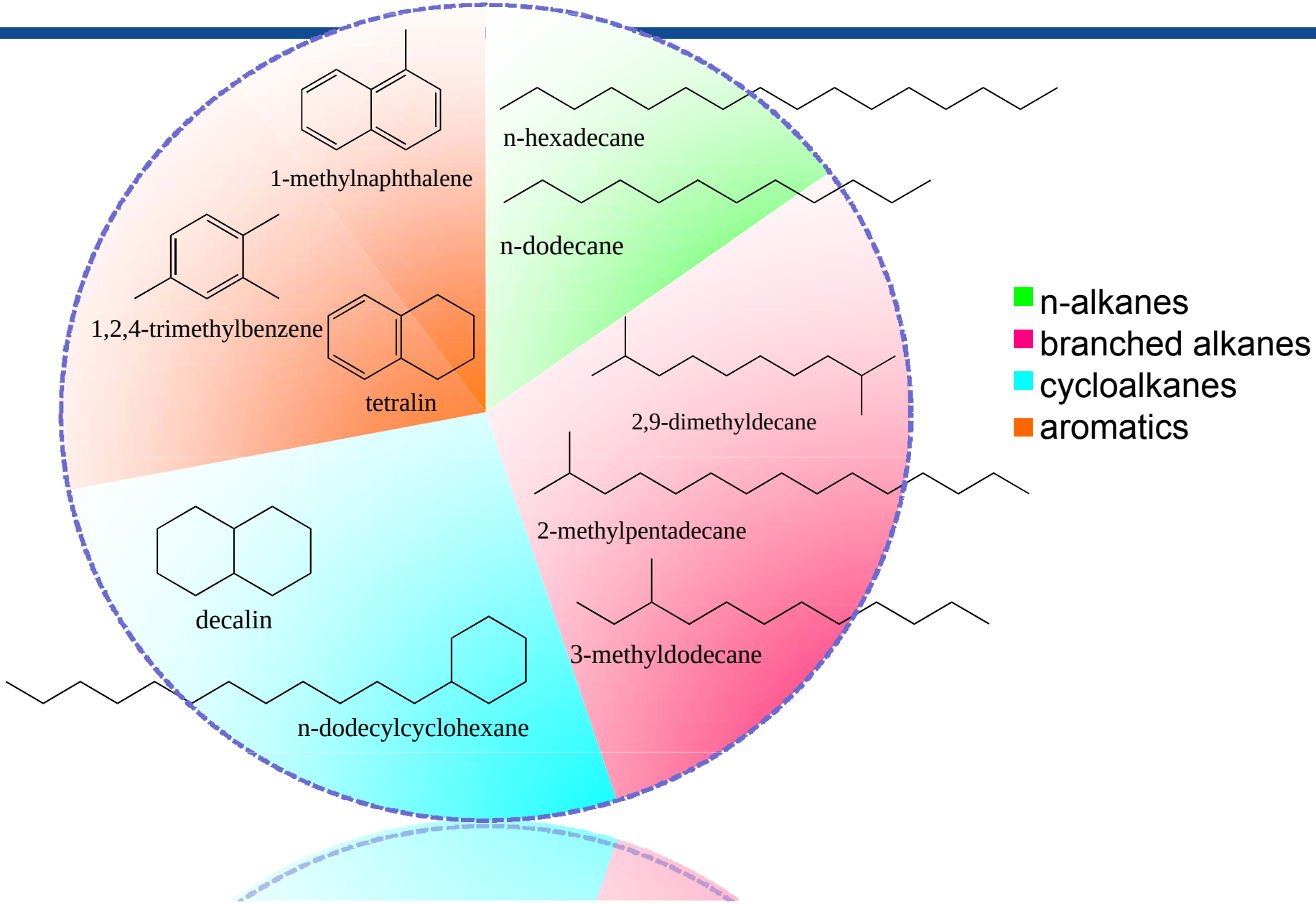


Kukkadapu, Kumar, Sung, Mehl, and Pitz, Combust. Flame (2012)

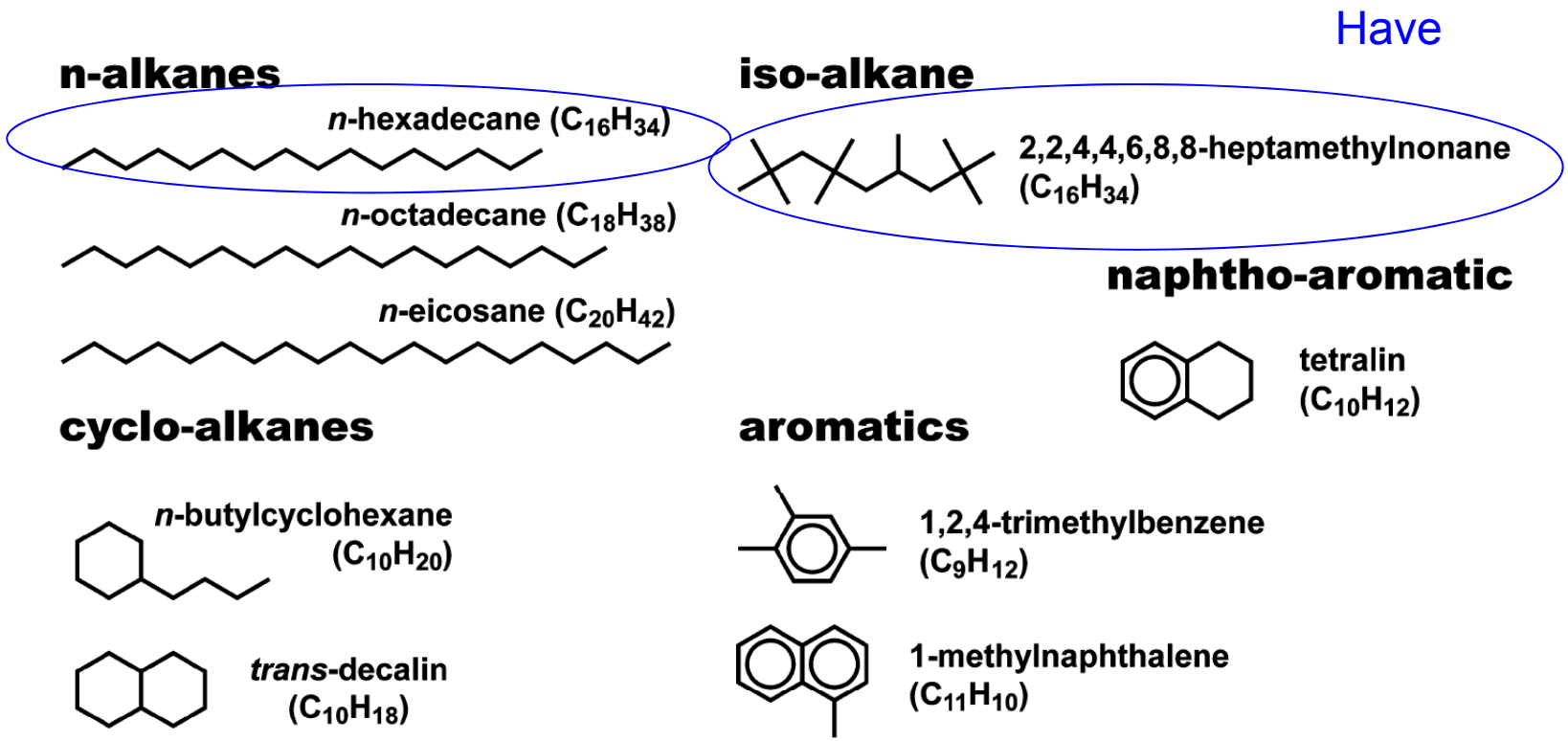
RCM



We are filling out components in the Diesel Fuel Surrogate Palette



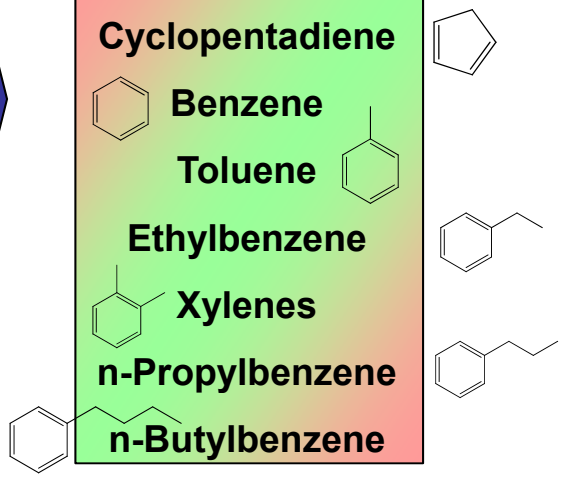
Diesel surrogate components selected by AVFL-18



Mueller, Cannella, Bruno, Bunting, Dettman, Franz, Huber, Natarajan, Pitz, Ratcliff and Wright, "Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics," *Energy & Fuels (2012)*

Comprehensive kinetic model for aromatics

LLNL	Galway/Princeton	Galway/Orleans/LLNL	Galway/LLNL
C0-C4 Version 49 (2009)	C0-C1 C2-C4	C0-C4 New! Version 54 (2012)	C0-C4 New! Version 54 (2012)
Cyclopentadiene Benzene Toluene Ethylbenzene Xylenes	Cyclopentadiene Benzene Toluene	Cyclopentadiene Benzene Toluene n-Propylbenzene n-Butylbenzene	Cyclopentadiene Benzene Toluene Ethylbenzene Xylenes n-Propylbenzene n-Butylbenzene



Objective: a new, fully internally coherent and comprehensive mechanism for aromatic species to be used for future developments and surrogates' simulations

The new mechanism core improves high temperature predictions (flame speeds, ignition, …)

Chemical kinetic model validation

- Idealized chemical reactors with/without simplified transport phenomenon

Jet Stirred Reactors

Premixed Laminar Flames

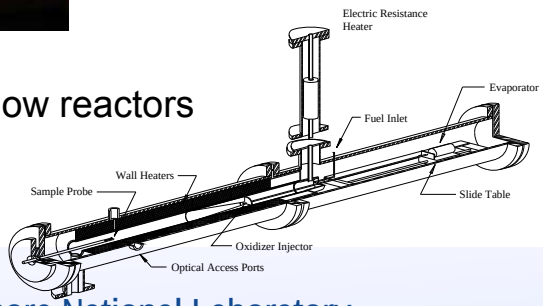
Twin premixed flames

Shock tube

Non Premixed Flames

Rapid Compression Machine

High pressure flow reactors



Engine Combustion

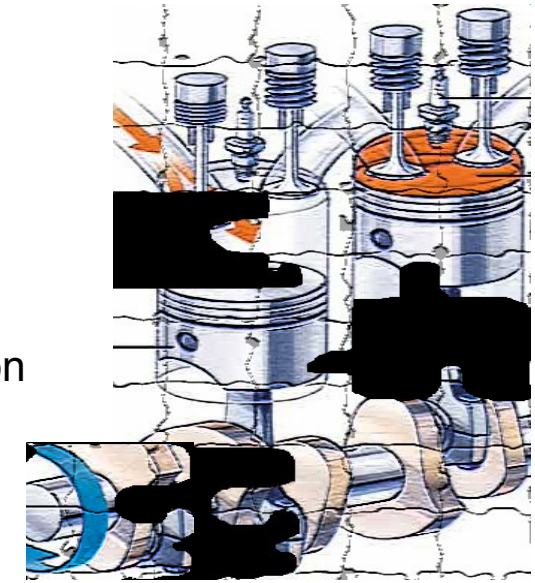
<u>Combustion Parameters</u>

Temperature

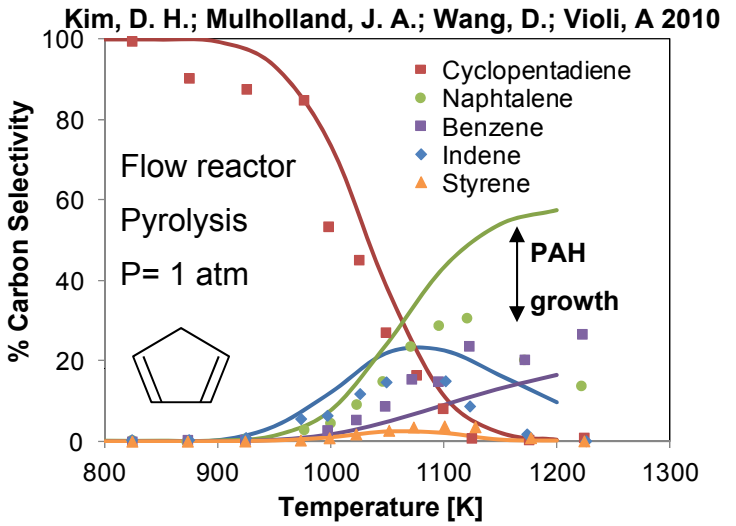
Pressure

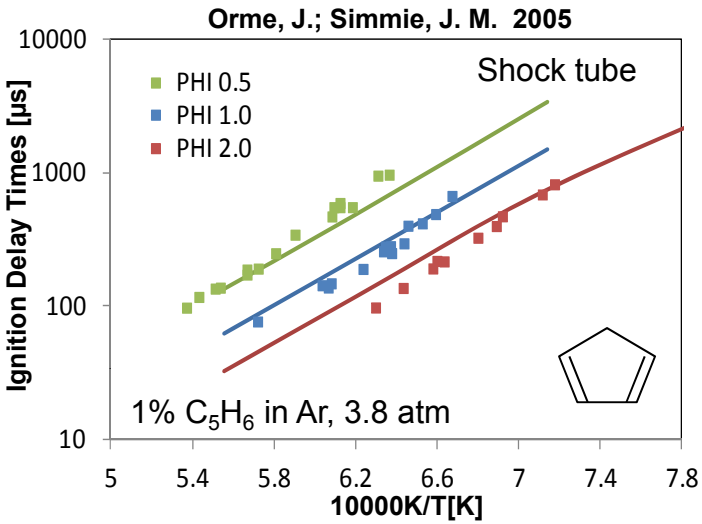
Mixture fraction (air-fuel ratio)

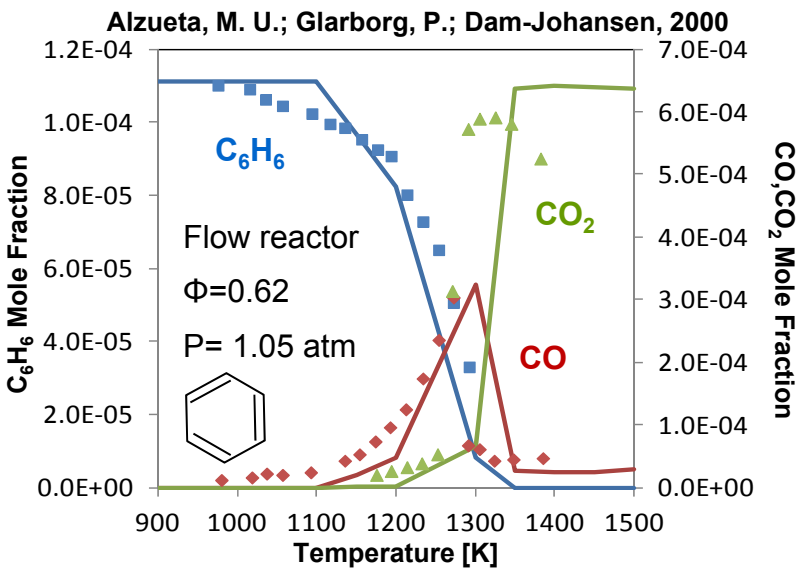
Mixing of fuel and air

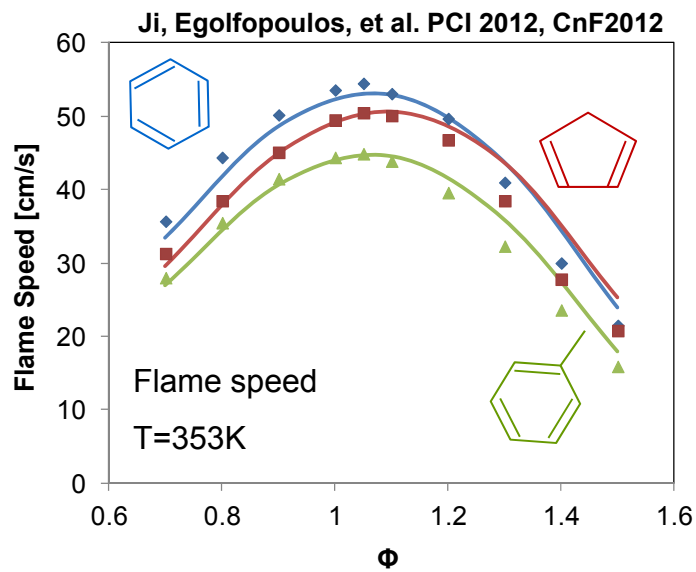


Validation of comprehensive aromatic model

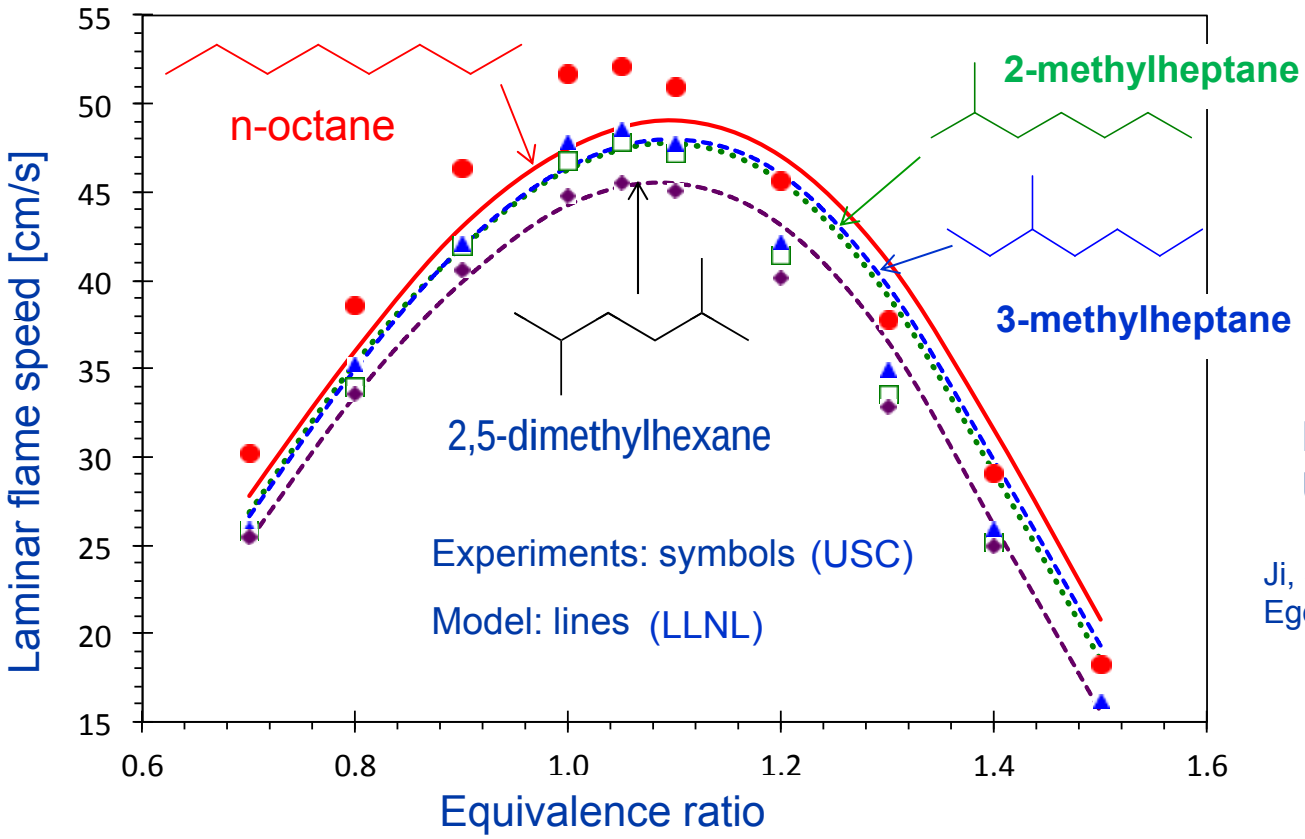








Progress on kinetic models for lightly-methylated iso-alkanes (present in diesel, jet, and hydrotreated renewable fuels)



Twin premixed flames

Experiments performed at USC, Los Angeles

Ji, Sarathy, Veloo, Westbrook and Egolfopoulos, Combust. Flame (2012)

- **Important to properly predict flame speeds for gas turbine applications**
- **Location of single methyl branch has minimal effect on flame speed**

Biofuels

Camelina Sativa

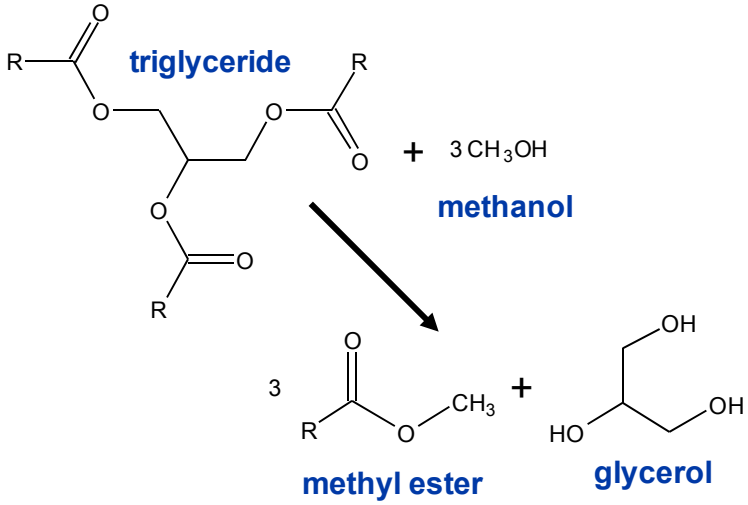
Sustainable Feedstock

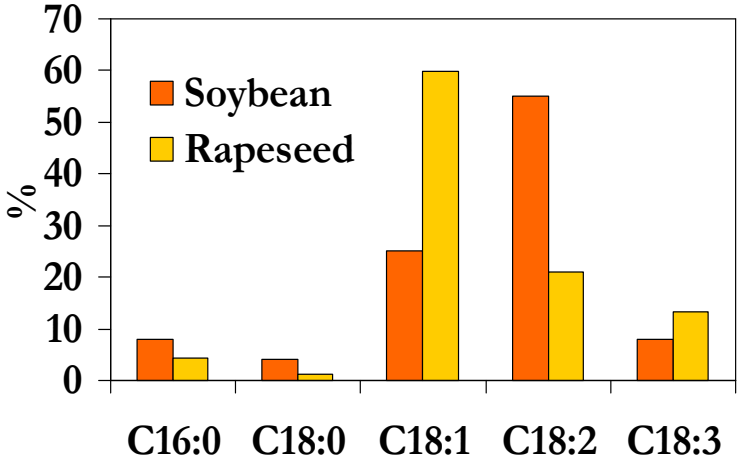
algal pilot scale bioreactor

rapeseed

sugarcane

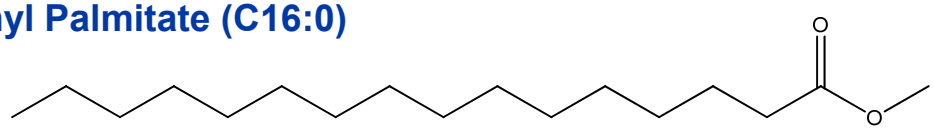
For the first time, experimental validation data are available for main components in biodiesel



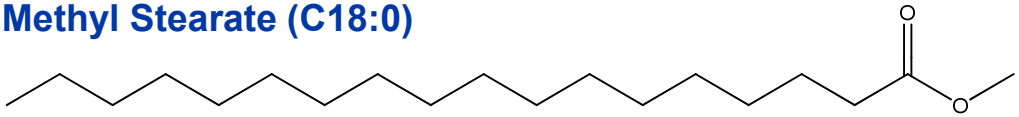


Fatty acid methyl esters (FAMEs):

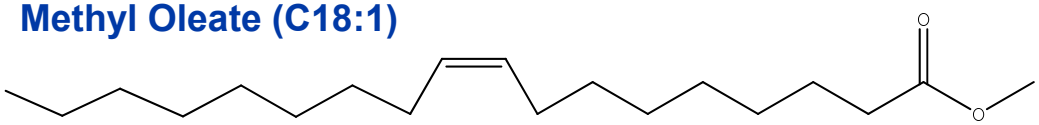
Methyl Palmitate (C16:0)



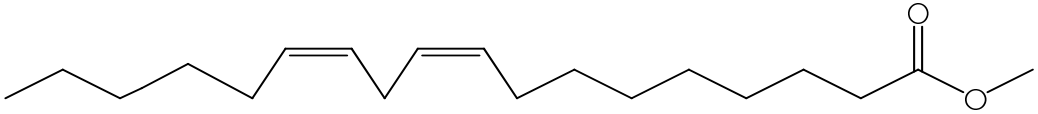
Methyl Stearate (C18:0)



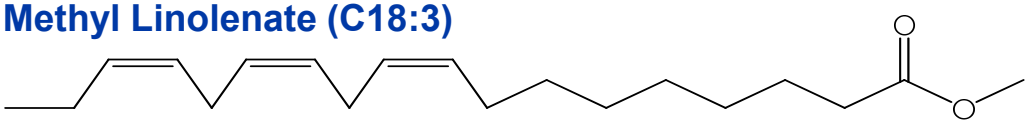
Methyl Oleate (C18:1)



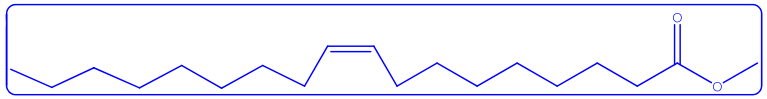
Methyl Linoleate (C18:2)



Methyl Linolenate (C18:3)

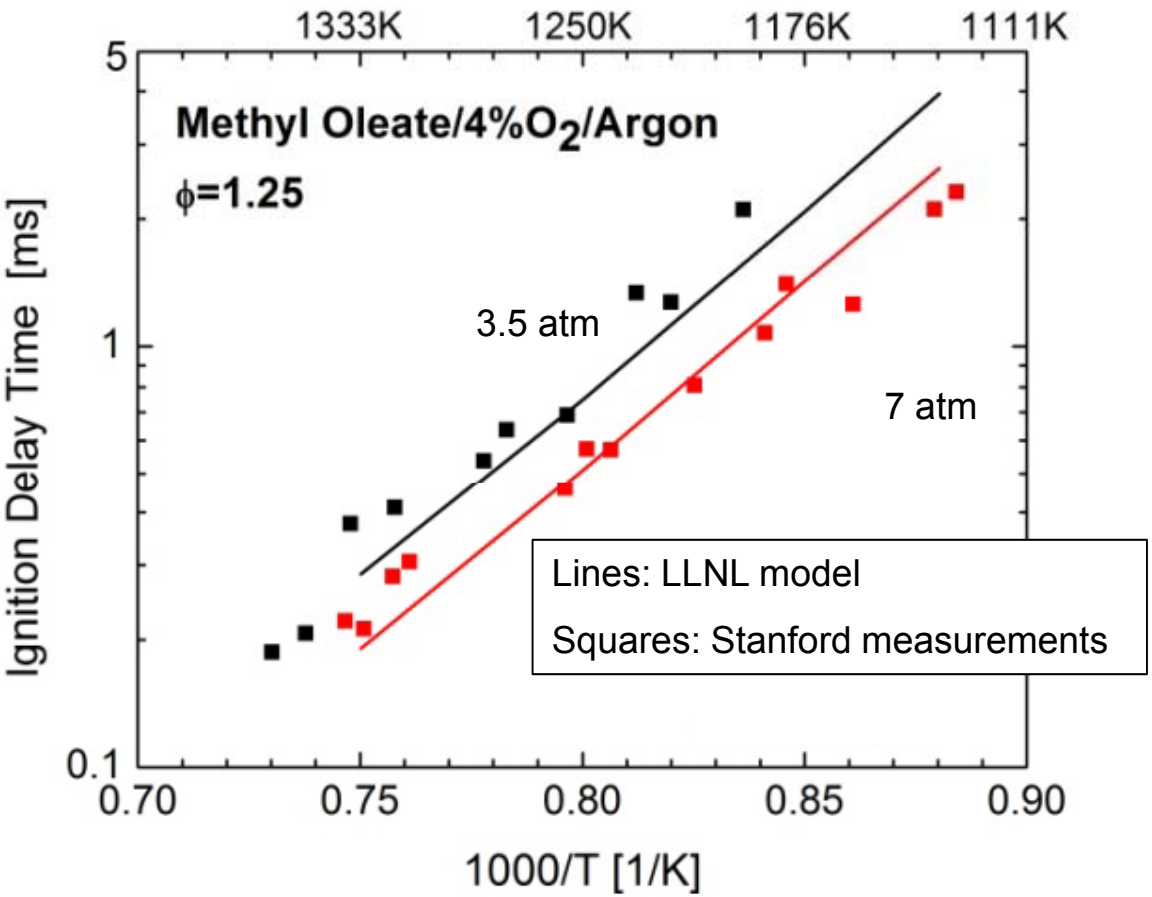


Methyl oleate model compares well to shock tube ignition experiments at elevated pressures



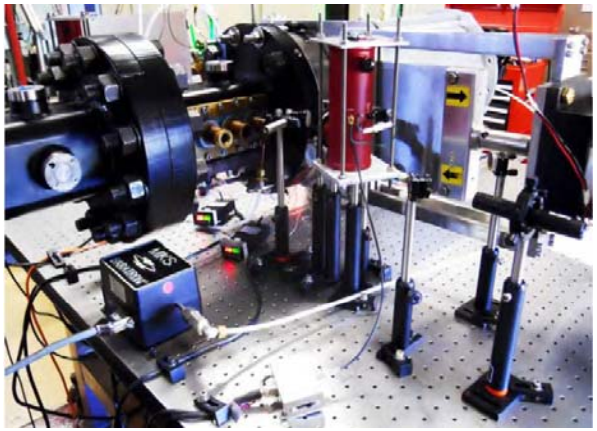
methyl oleate:

Real biodiesel methyl ester



Lines: LLNL model

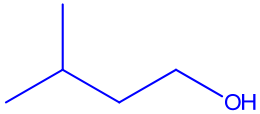
Squares: Stanford measurements



Stanford aerosol shock tube

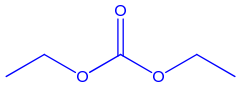
Campbell, Davidson, Hanson and Westbrook, Proc. Combust. Inst (2012)

Chemical kinetic models for other biofuels

- isopentanol 

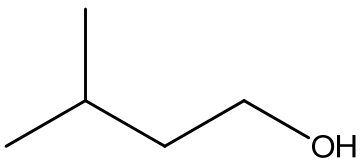
  - Exhibits intermediate temperature heat release needed to obtain high load operation with HCCI (Dec and Yang, 2010)
- 1-pentanol

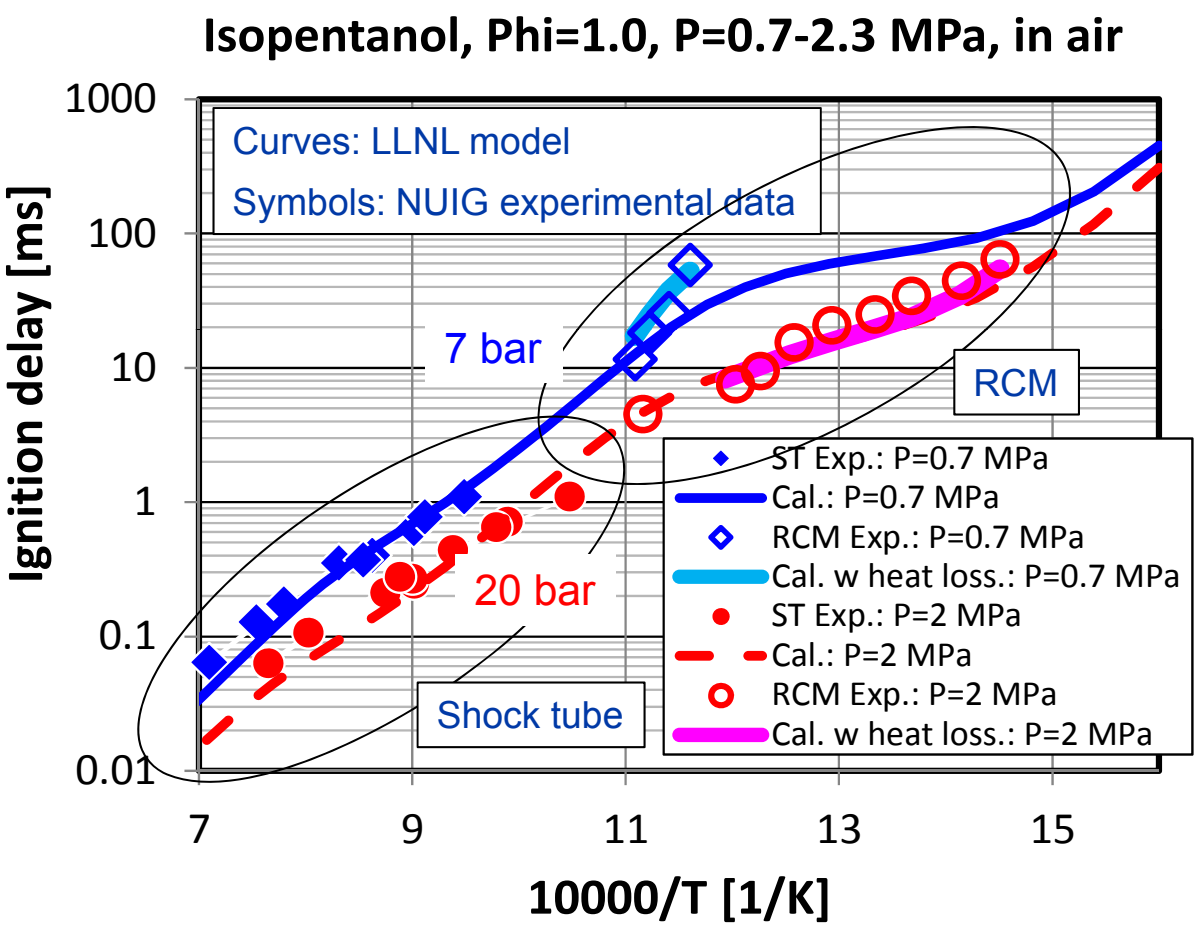
  - Higher energy density than ethanol
- 1-butanol

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

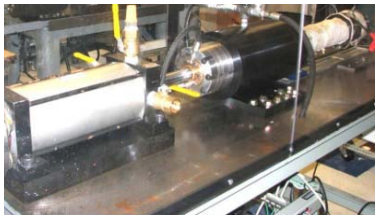
  - Sugar cane in Colombia is converted to ethanol. The ethanol and CO_2 products are converted to diethyl carbonate. Diesel replacement fuel. (Hosted visiting student from Columbia.)

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





R
C
M

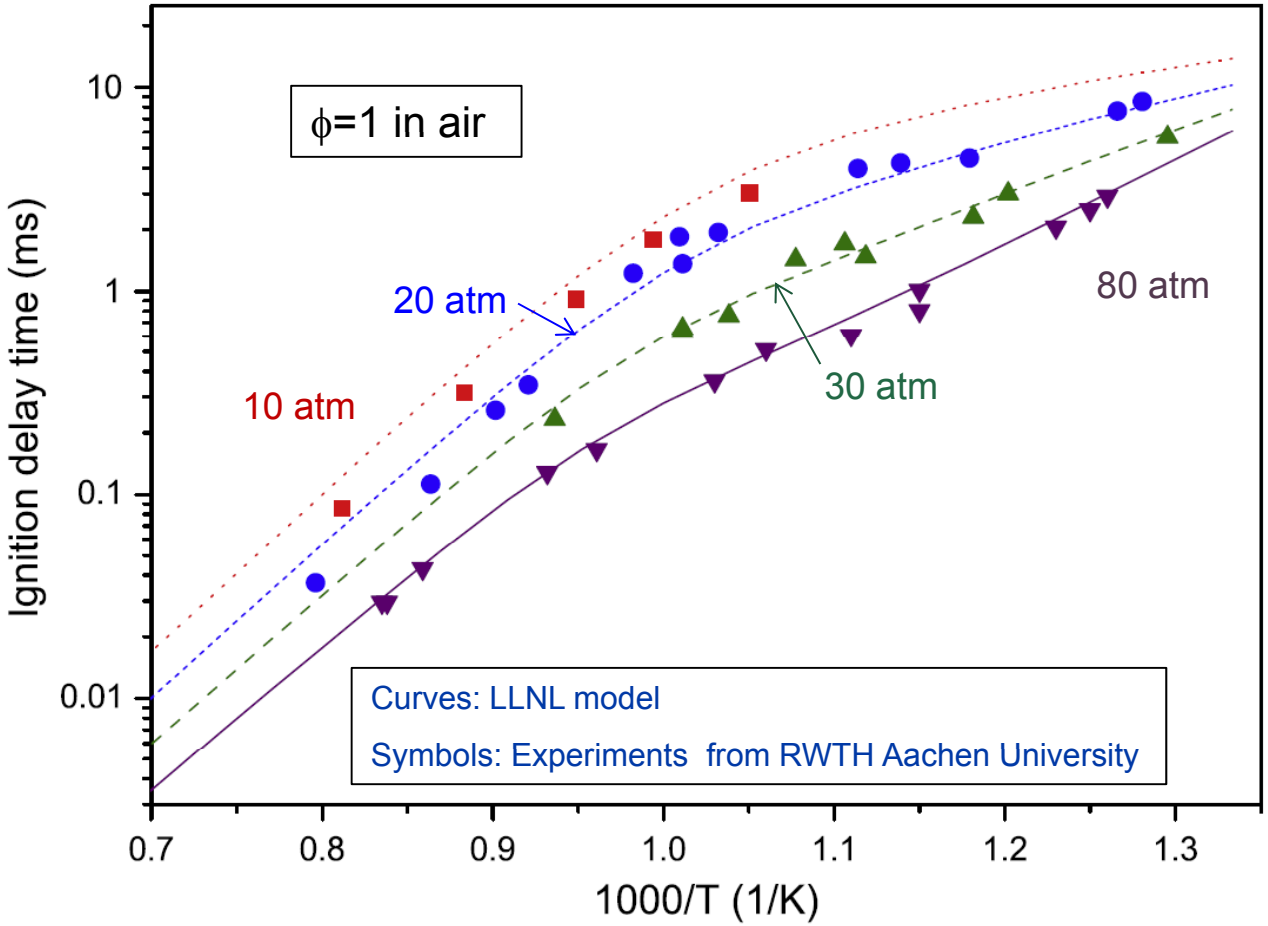


Rapid compression machine
Experimental data: UConn

Shock tube
Experimental data: NUIG

From: Tsujimura, Pitz, Gillespie, Curran, Weber, Zhang and Sung, Energy & Fuels (2012)

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



Shock tube

From: Sarathy, Vranckx, Yasunaga, Mehl, Oßwald, Metcalfe, Westbrook, Pitz, Kohse-Höinghaus, Fernandes, and Curran, Combust. Flame (2012)

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

Mechanisms are available on LLNL website and by email

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

- Ethanol
- Butanol isomers
- 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
- Gasoline Surrogate
- 2-Methyl Alkanes

Combustion Chemistry

Go Directly to Mechanisms...

The central feature of the Combustion Chemistry project at LLNL is our development, validation, a application of detailed chemical kinetic reaction mechanisms for the combustion of hydrocarbon other types of chemical fuels. For the past 30 years, our group has built hydrocarbon mechani fuels from hydrogen and methane through much larger fuels including heptanes and octanes classes of fuels for which models have been developed include flame suppressants such as h organophosphates, and air pollutants such as soot and oxides of nitrogen and sulfur.

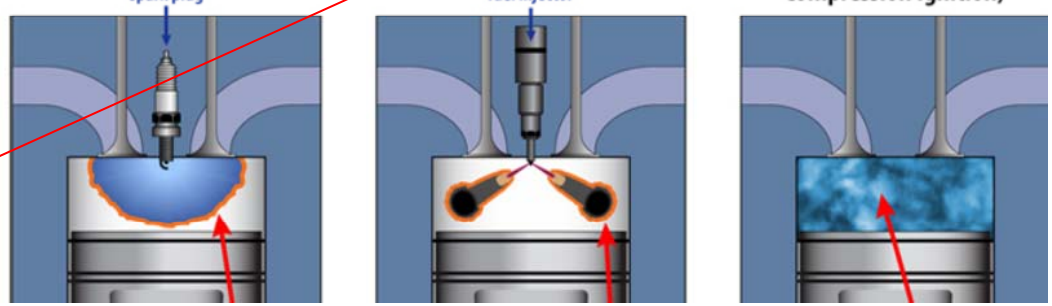
Reaction mechanisms have been tested and validated extensively through comparisons betw computed results and measured data from laboratory experiments (e.g., shock tubes, lami rapid compression machines, flow reactors, stirred reactors) and from practical systems (e.g., engines, spark-ignition engines, homogeneous charge, compression ignition (HCCI) engines). W used these kinetic models to examine a wide range of combustion systems.

Gasoline Surrogate

Gasoline Engine (Spark Ignition) — spark plug

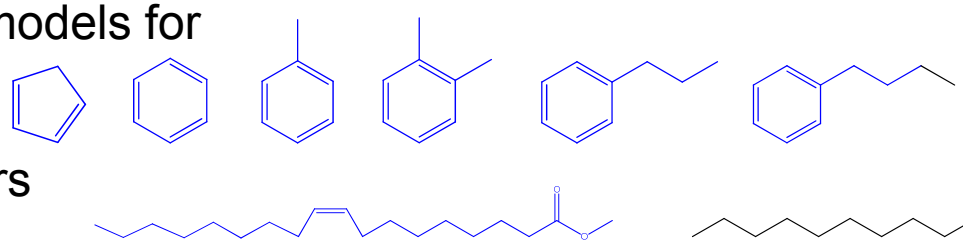
Diesel Engine (Compression Ignition) — fuel injector

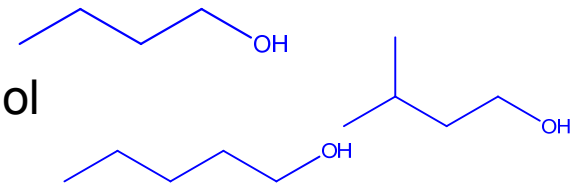
HCCI Engine (Homogeneous Charge Compression Ignition)



Summary: Improved/new models for many different fuel components

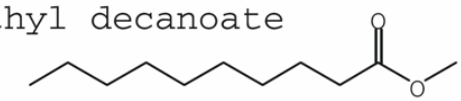
- Improved/new models for
  - Aromatics
  - Methyl esters
  - Alcohols
    - Butanol
    - Iso-pentanol
    - n-pentanol



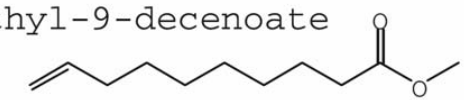


- Reduced models for use in CFD engine codes:

methyl decanoate



methyl-9-decenoate



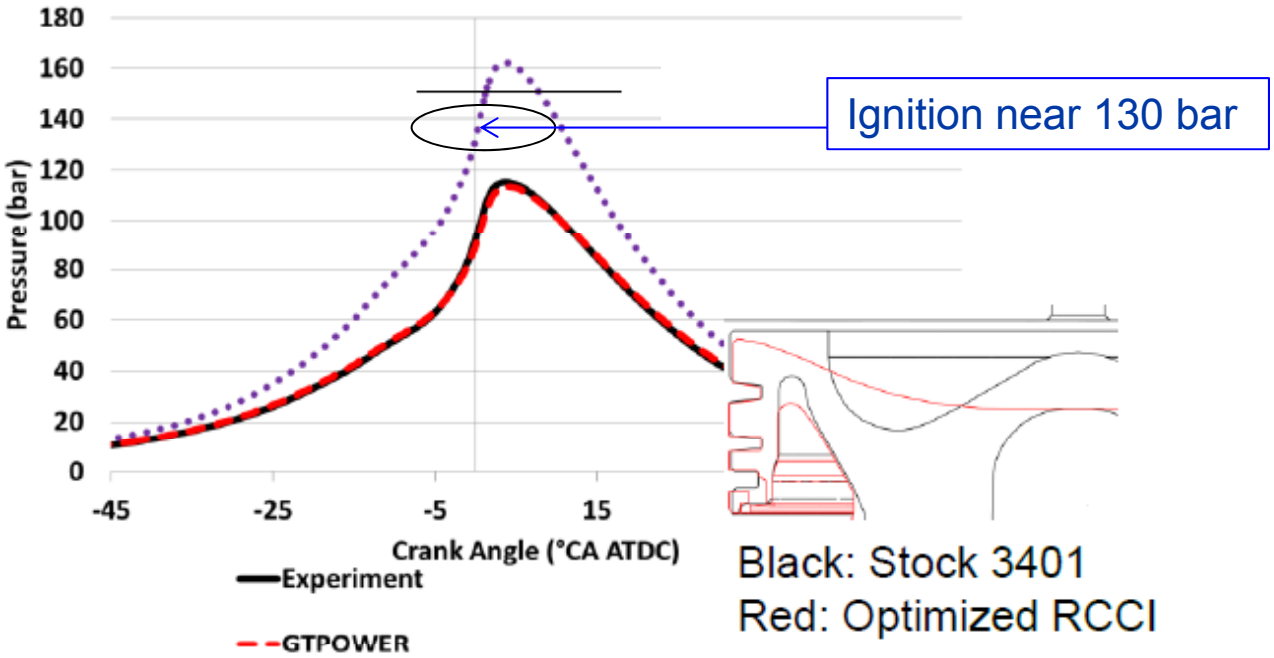
n-heptane, n-C_7H_{16}

n-dodecane

Challenges for kinetic model development for surrogate fuels for IC engines: Higher pressures

- Need experimental validation data at 100-200 bar with EGR (dilution by H_2O and CO_2) for advanced diesel engine combustion regimes

Reactivity Controlled Compression Ignition (RCCI) Engine:



Black: Stock 3401
Red: Optimized RCCI

Reitz et al., 2012, www.annualmeritreview.energy.gov