Lawrence Livermore National Laboratory

Chemical Kinetic Research on HCCI & Diesel Fuels

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Lawrence Livermore National Laboratory
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Project ID # ACE013

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-543385

Overview

Timeline

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

Budget

Project funded by DOE/VT:

- FY11: 500K
- FY12: 640K

Partners

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

Barriers/Targets

- Technical Barrier: 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
  - Chemical kinetic models for fuels are a critical part of engine models
- Targets: Meeting the targets below relies heavily on predictive engine models for optimization of engine design:
  - Fuel economy improvement of 25 and 40% for gasoline/diesel by 2015
  - 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 gasoline, diesel and next generation fuels so that simulations can be used to overcome technical barriers to low temperature combustion in engines and needed gains in engine efficiency and reductions in pollutant emissions

- FY12 Objectives:
  - Develop detailed chemical kinetic models for larger alkyl aromatics
  - Develop a reduced surrogate mechanism for diesel to be used for multidimensional CFD simulations
  - Develop more accurate surrogate kinetics models for gasoline
  - Develop a functional group method to represent cycloalkanes in diesel fuel
  - Validate and improve 2- and 3-methyl alkanes mechanisms with new data from shock tubes, jet-stirred reactors, counterflow flames, and premixed flames

Chemical kinetic milestones

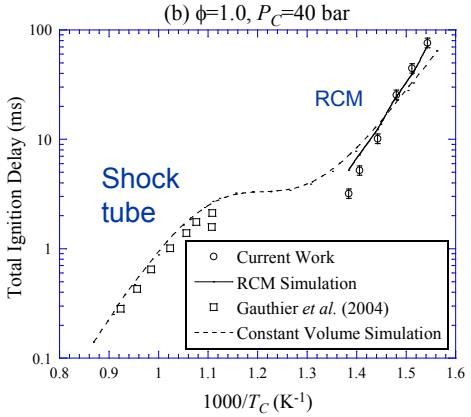
- ✓ January, 2012
  Develop more accurate surrogate kinetics models for gasoline
- June, 2012
  Develop a functional group method to represent cycloalkanes in diesel fuel
- June, 2012
  Develop detailed chemical kinetic models for larger alkyl aromatics
- September, 2012
  Develop a reduced surrogate mechanism for diesel to be used for multidimensional CFD simulations
- September, 2012
  Validate and improve 2- and 3-methyl alkanes mechanisms with new data from shock tubes, jet-stirred reactors, counterflow flames, and premixed flames

Approach

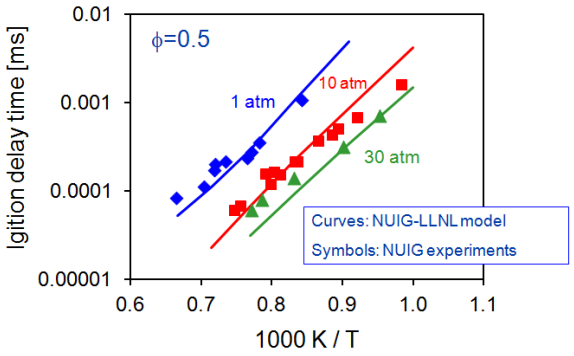
- Develop chemical kinetic reaction models for each individual fuel component of importance for fuel surrogates of gasoline, diesel, and next generation fuels
- Combine mechanisms for representative fuel components to provide surrogate models for practical fuels
  - diesel fuel
  - gasoline (HCCI and/or SI engines)
  - Fischer-Tropsch derived fuels
  - Biodiesel, ethanol and other biofuels
- 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

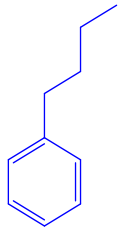
Technical Accomplishment Summary

- Validated approach and mechanism for gasoline surrogate fuels

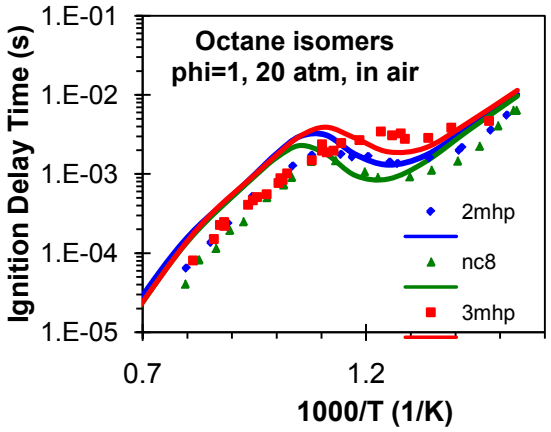


- Development of chemical kinetic model for larger aromatics

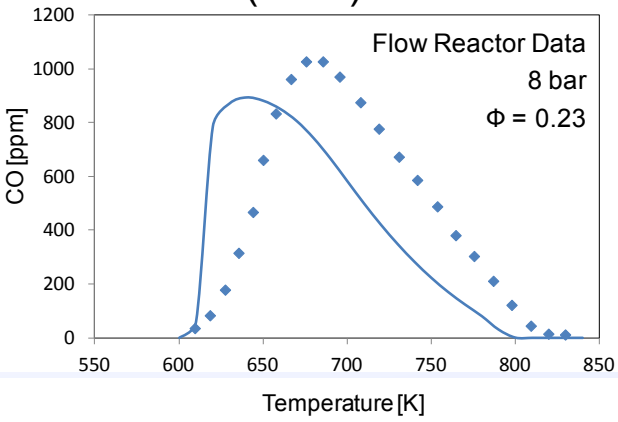




- Determined effect of branching for alkanes on ignition under engine conditions

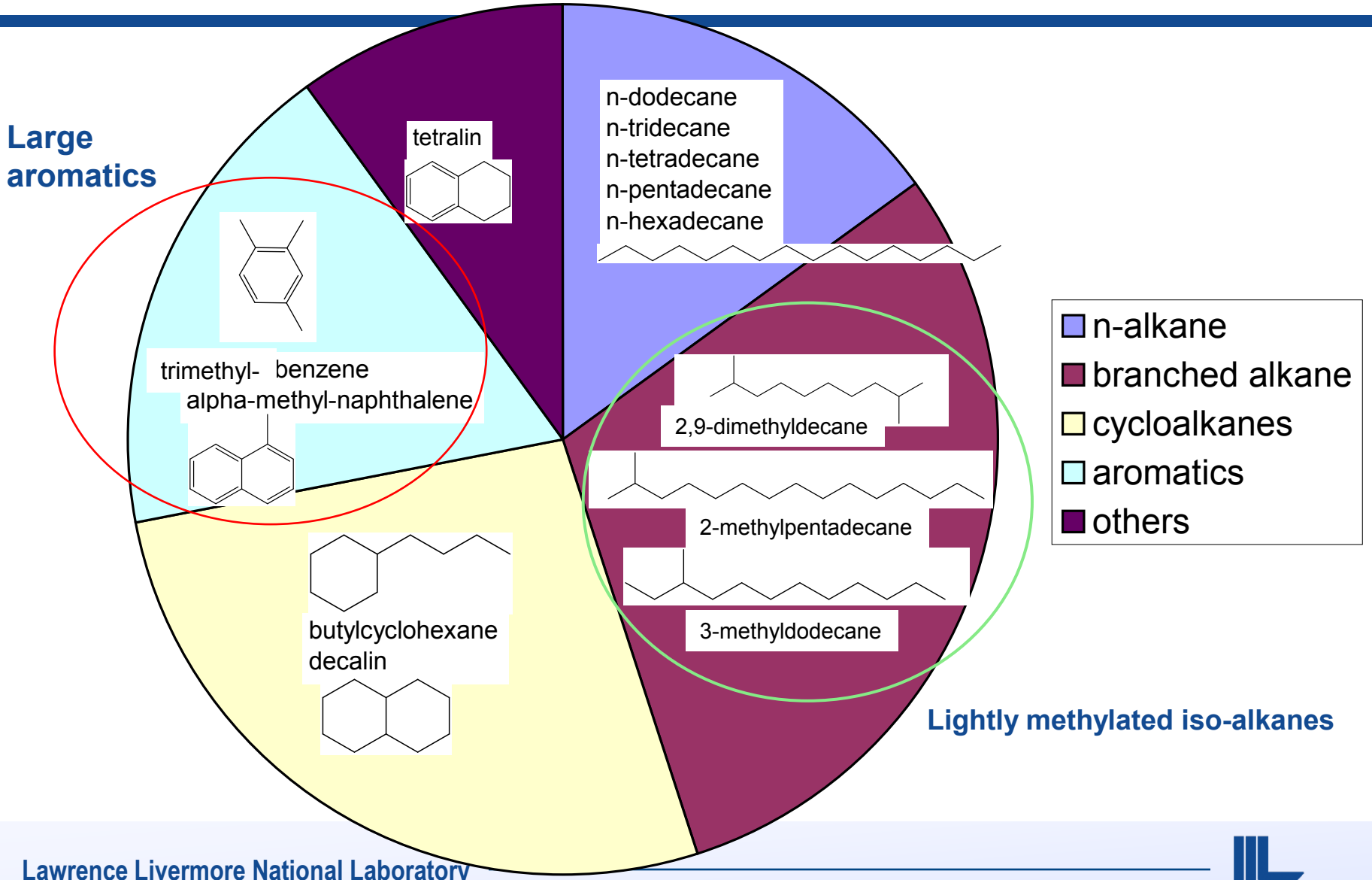


- Developing reduced chemical kinetic model for diesel for engine combustion network (ECN)



(23% m-xylene / 77% n-dodecane)

Need representative component models to fill out the diesel fuel surrogate palette:



Need to validate the fuel component and surrogate models

- Idealized chemical reactors with/without simplified transport phenomenon

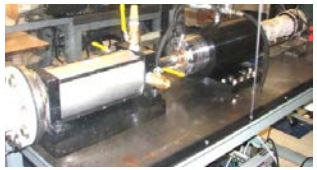
Jet Stirred Reactors

Premixed Laminar Flames

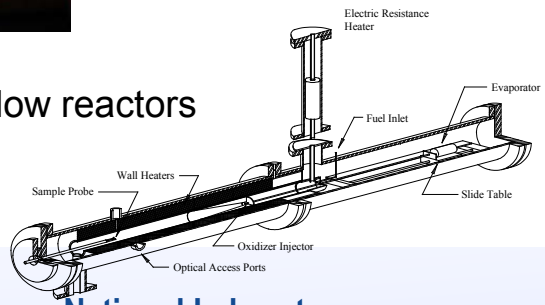
Shock tube

Non Premixed Flames

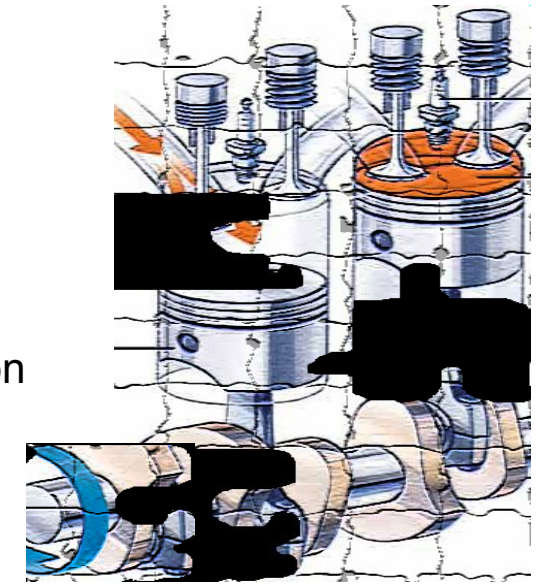
Rapid Compression Machine



High pressure flow reactors



Engine Combustion



Combustion Parameters

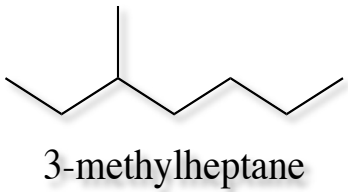
Temperature

Pressure

Mixture fraction (air-fuel ratio)

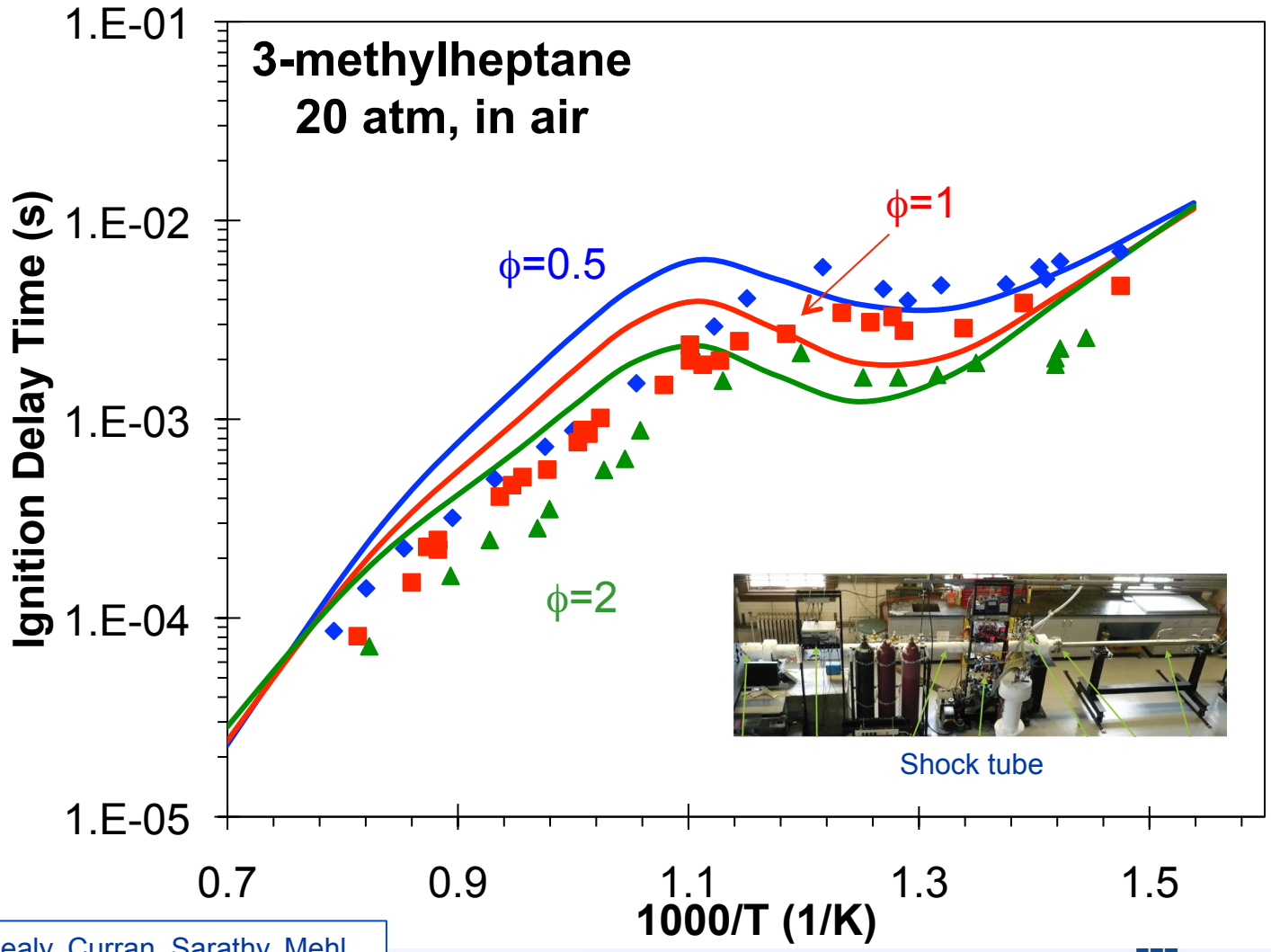
Mixing of fuel and air

Modeling of 3-methylheptane Ignition



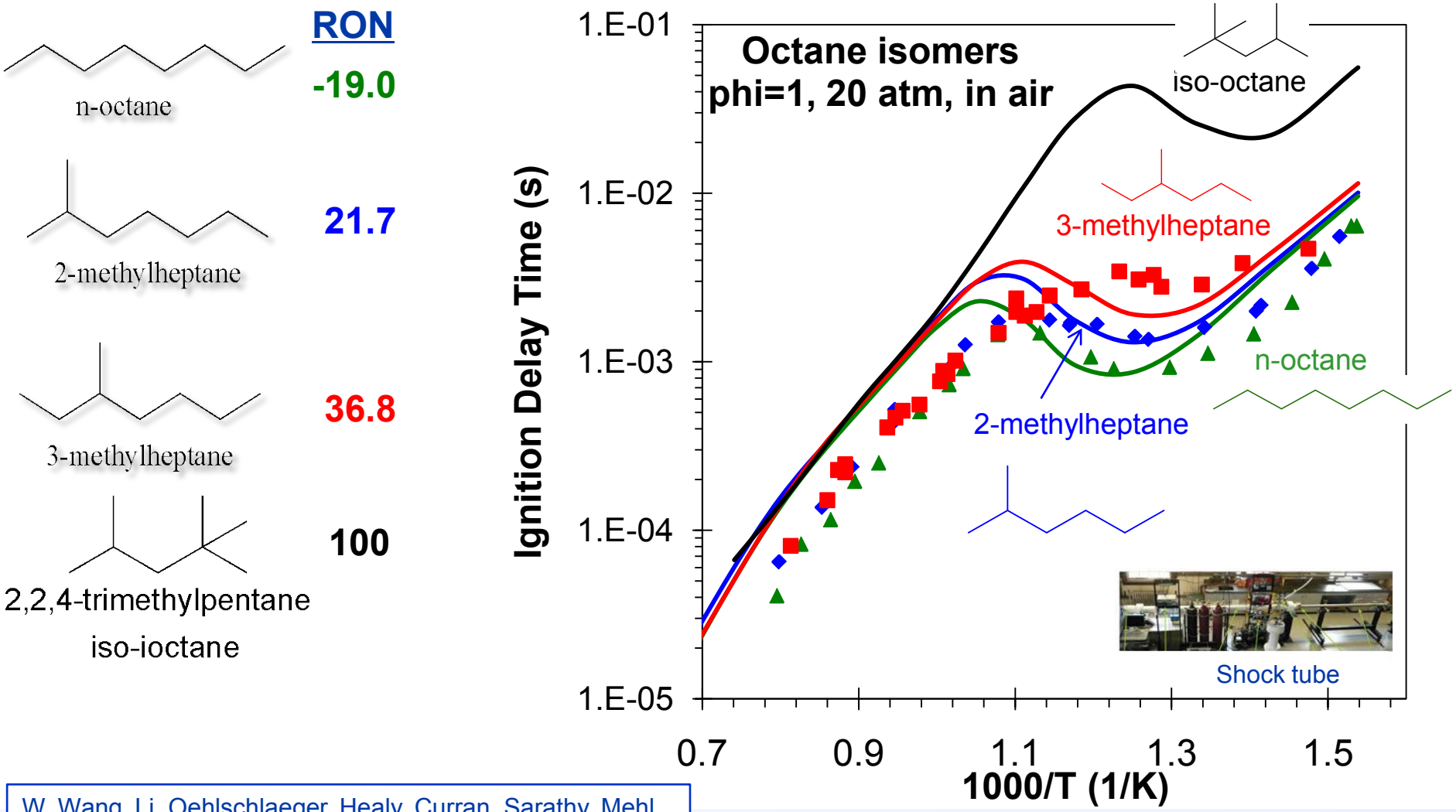
Model is generally within a factor of 1.5-2 of the experimental data.

Model slightly faster than shock tube data in the NTC region



W. Wang, Li, Oehlschlaeger, Healy, Curran, Sarathy, Mehl, Pitz, Westbrook, Proc. Combust. Inst. (2012).

Modeling the effect of branching on ignition

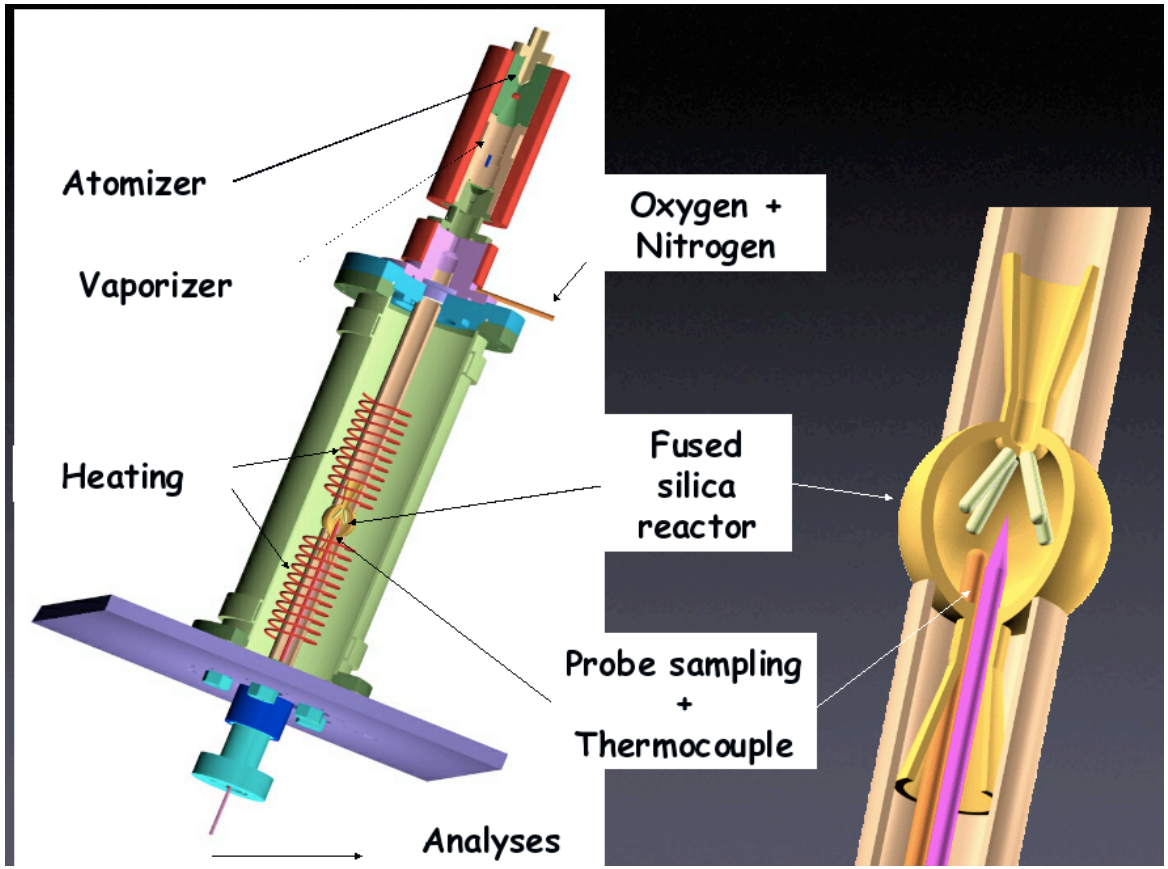


W. Wang, Li, Oehlschlaeger, Healy, Curran, Sarathy, Mehl, Pitz, Westbrook, Proc. Combust. Inst. (2012).

Jet Stirred Reactor (JSR)

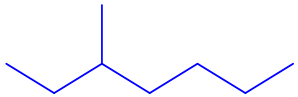
3-methylheptane

CNRS Orleans, France



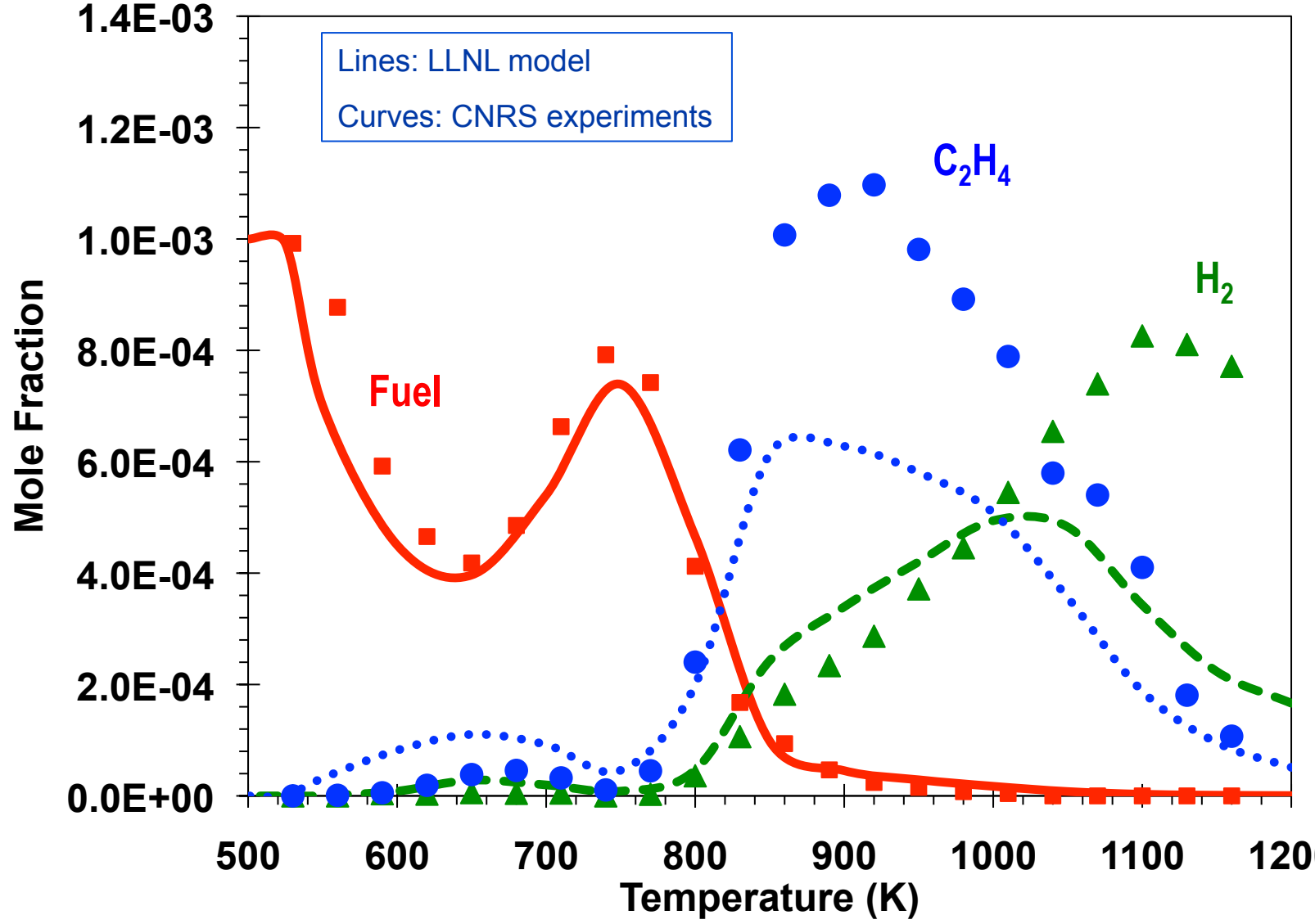
- The zero dimensional perfectly system is ideal for modeling.
- The products species profiles are dependent on chemical kinetics due to the perfectly mixed homogeneous environment.

JSR 3-Methylheptane Results



Dagaut et al. CNRS (2010)

Experiments performed at CNRS, Orleans (F. Karzenty, C. Togbe G. Dayma, P. Dagaut)



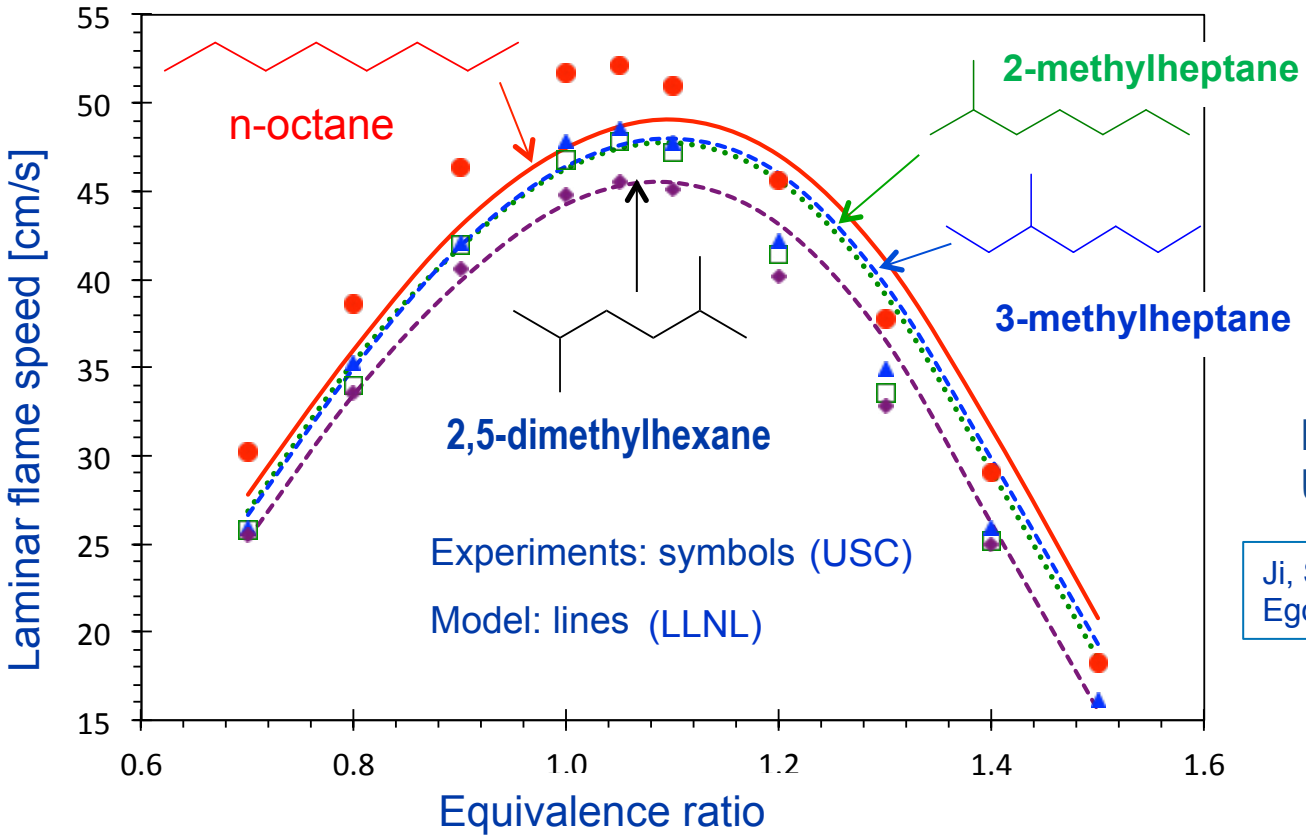
10 atm

$\phi = 1$

$\tau = 0.7$ sec

Good prediction of low T and high T reactivity

Model simulations and experiments show decrease in laminar flame speeds with branching for octane isomers



Twin premixed flames

Experiments performed at USC, Los Angeles

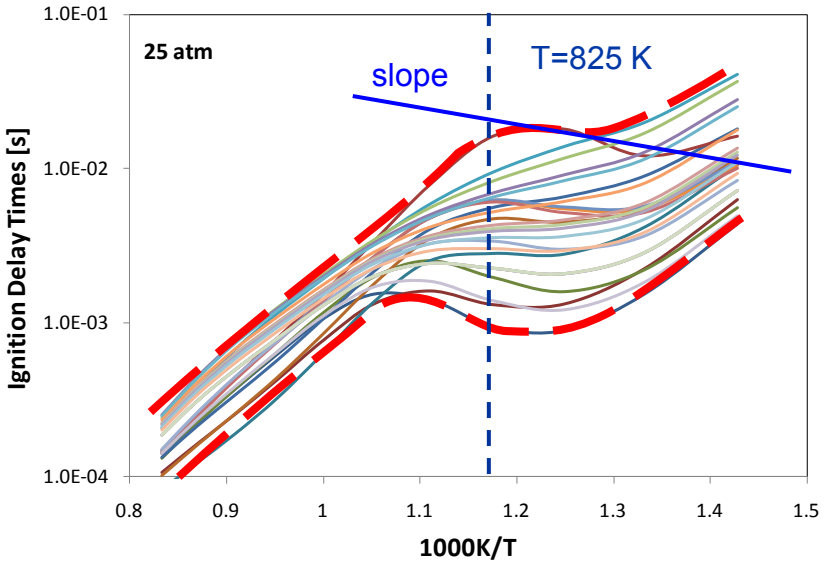
Ji, Sarathy, Veloo, Westbrook and Egolfopoulos, Combust. Flame (2012)

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

Developed new procedure to formulate gasoline surrogates

Ignition delay at 825K correlates to octane number

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



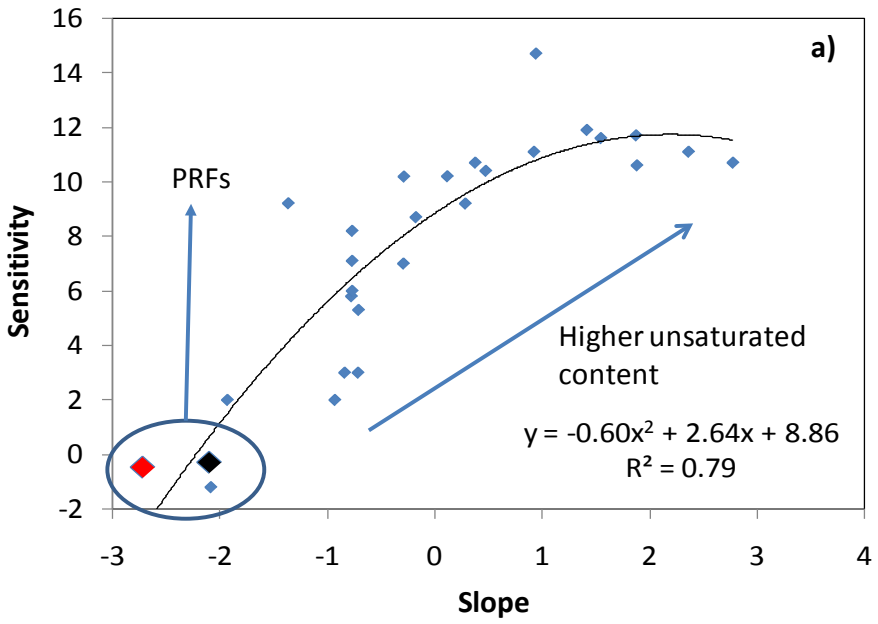
40 different gasoline surrogates were simulated

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

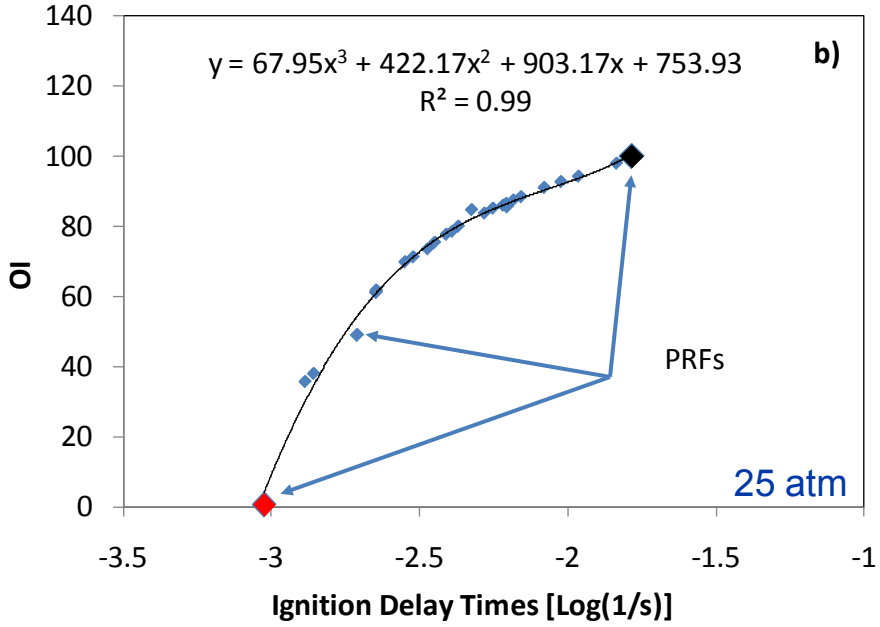
A correlation between the octane rating and the autoignition propensity of gasoline surrogate fuels has been identified

FY2011

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

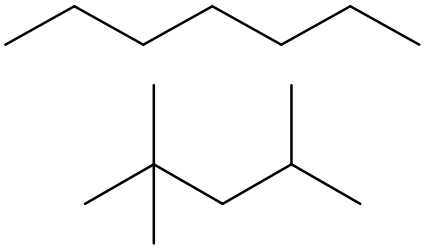
Composition:

	Surrogate (%Vol)	RD387 Gasoline (%Vol)
i-Alkanes	57	73
n- Alkanes	16	
Aromatics	23	23
Olefins	4.0	4.2

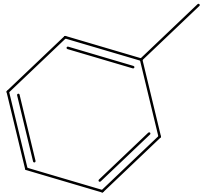
Other properties:

A/F Ratio	14.6	14.8
H/C	1.93	1.95
Octane index	87	87
Sensitivity	8.0	7.6

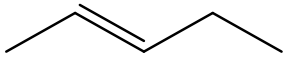
Alkanes



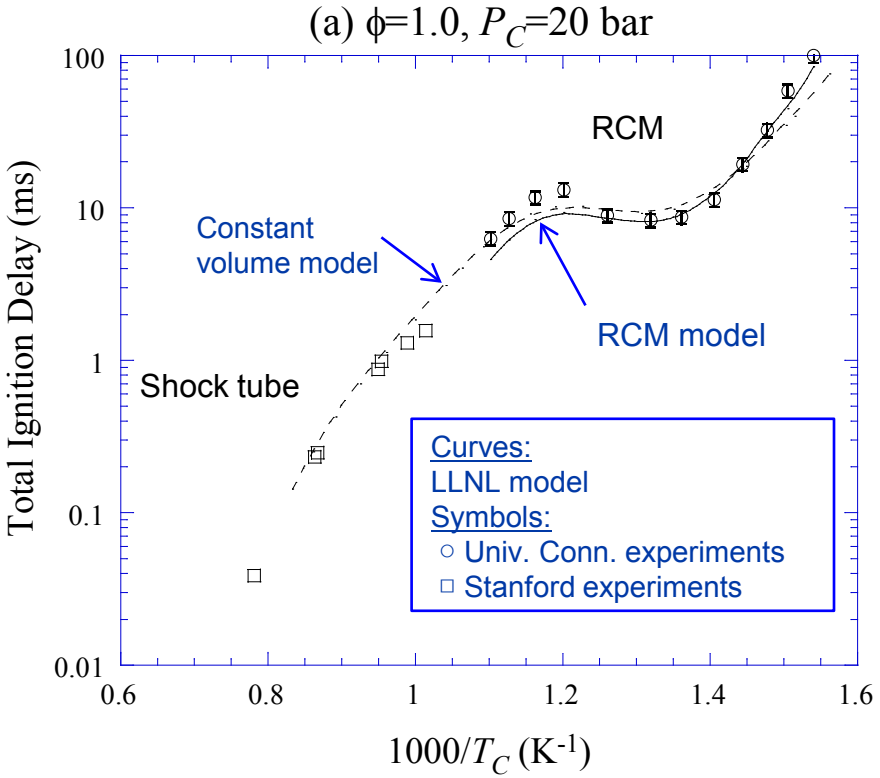
Aromatics

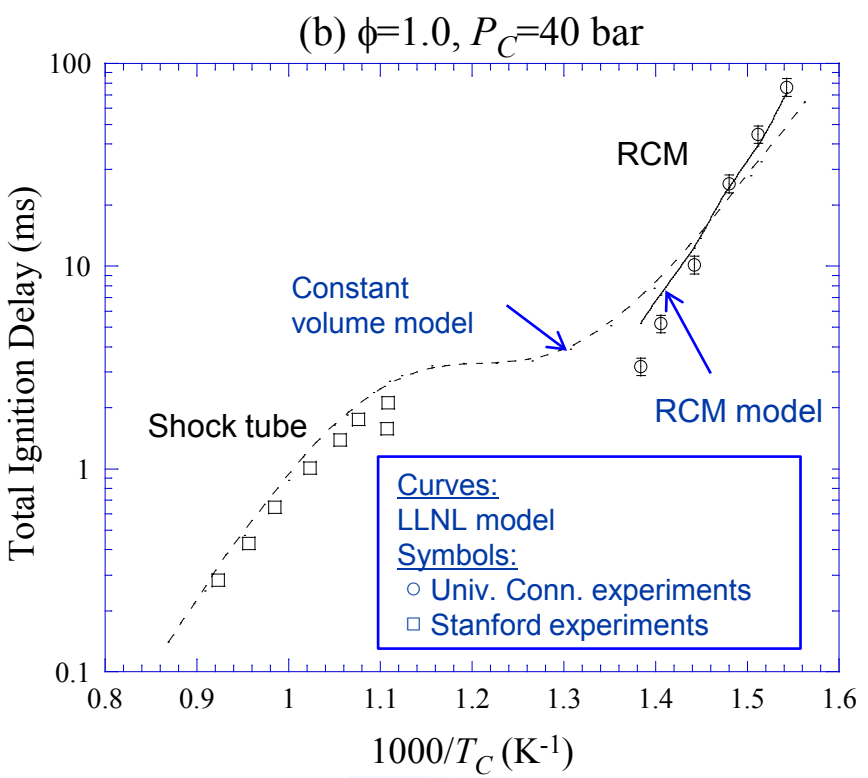


Olefins

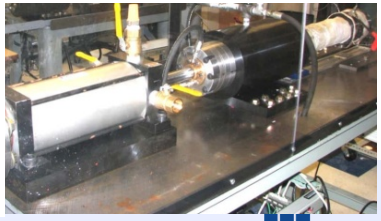


Simulations of real gasoline (RD387) experiments using LLNL surrogate model

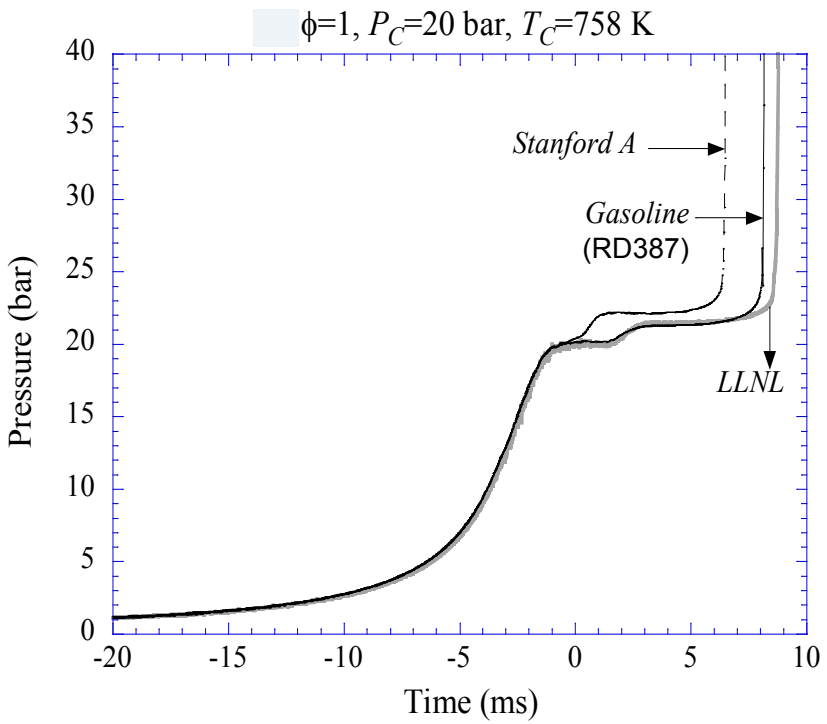


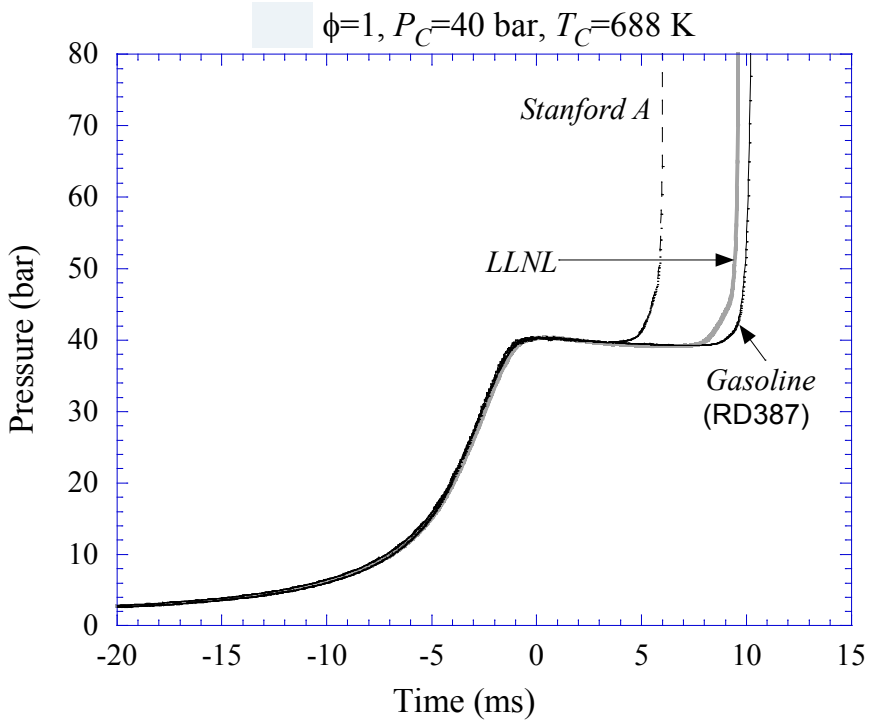


RCM experiments: G. Kukkadapu, K. Kumar, C.-J. Sung, Univ. of Connecticut
Shock tube experiments: Gauthier, Davidson and Hanson, 2004



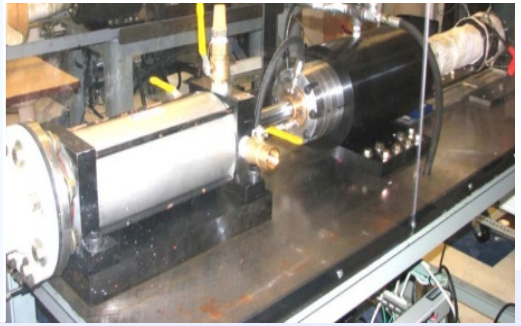
Purely experimental comparisons of LLNL and Stanford surrogate formulation with real gasoline: LLNL formulation matches well real gasoline





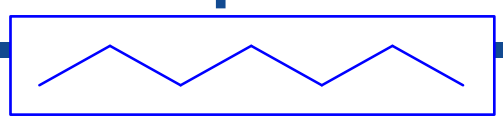
RCM experiments:

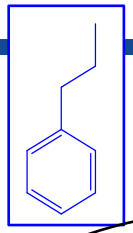
G. Kukkadapu, K. Kumar, C.-J. Sung, Univ. of Conn.



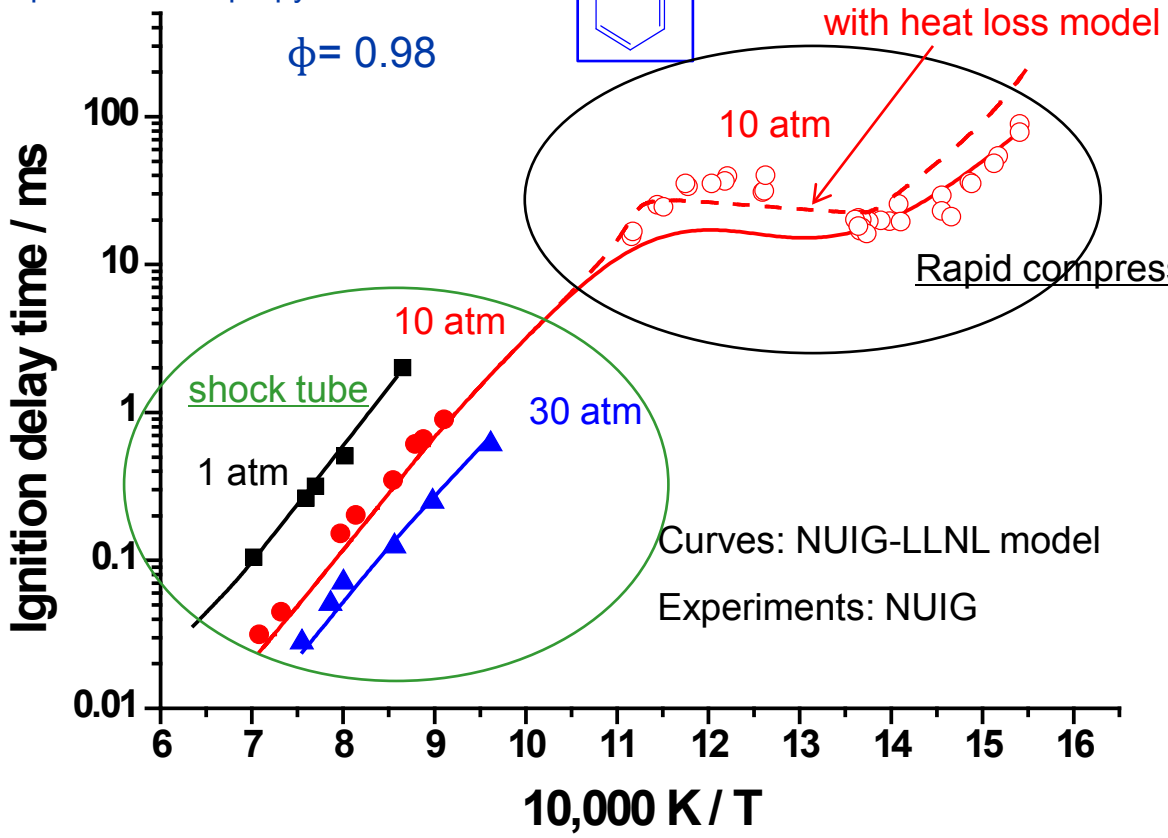
RCM

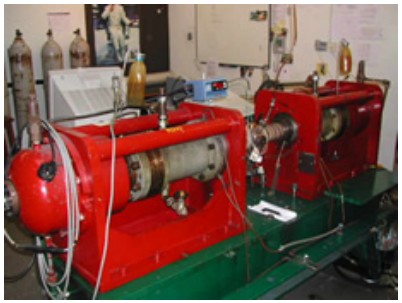
Surrogate for larger alkyl aromatics: n-heptane + n-propylbenzene





43% n-heptane /57% n-propylbenzene in air



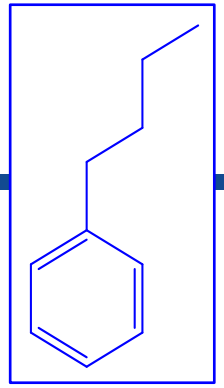


Shock tube

Shock tube study: Darcy, Mehl, Simmie, Wurmel, Metcalfe, Pitz and Curran, Proc. Combust. Inst. (2012)

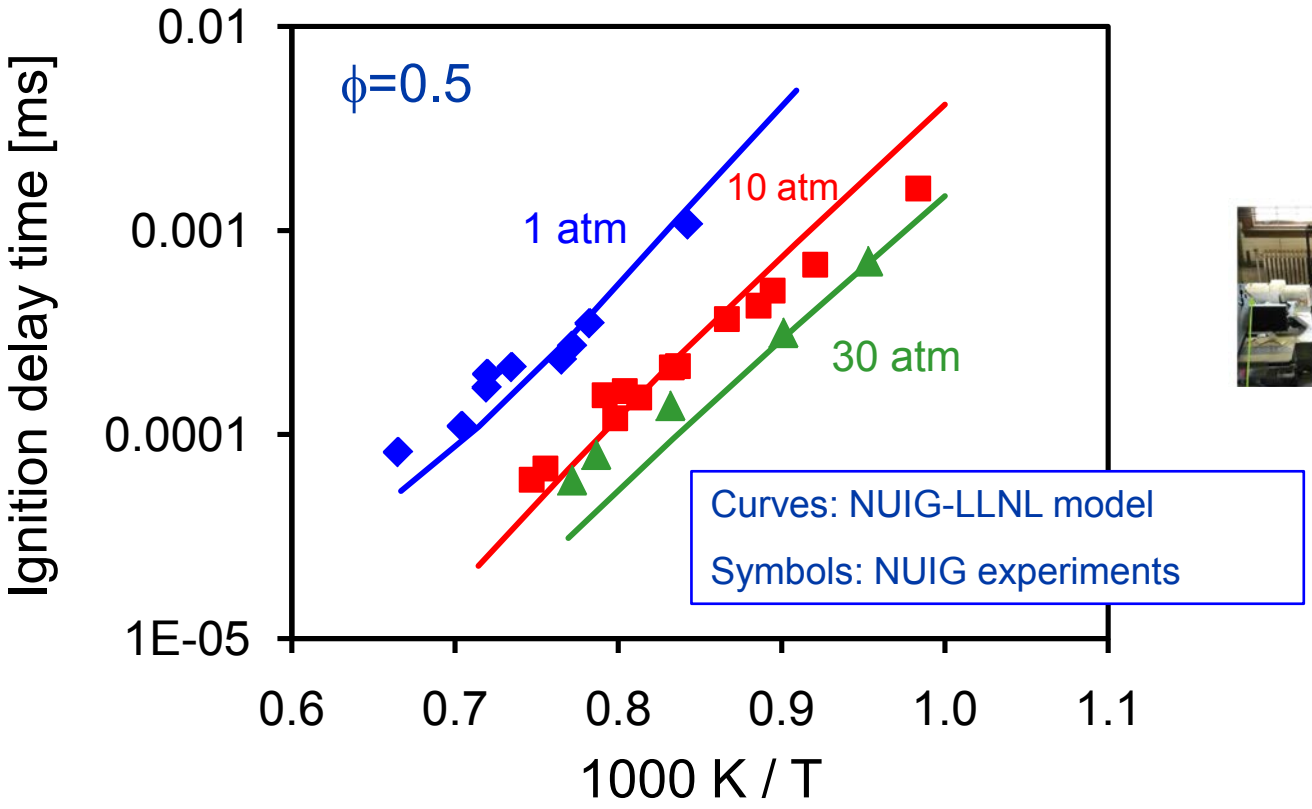
Experimental RCM data: Darcy and Curran, NUIG, 2011

Larger aromatics: Shock tube ignition of n-butyl benzene at high pressure



n-butylbenzene

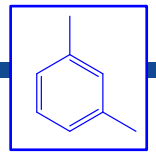
Shock tube



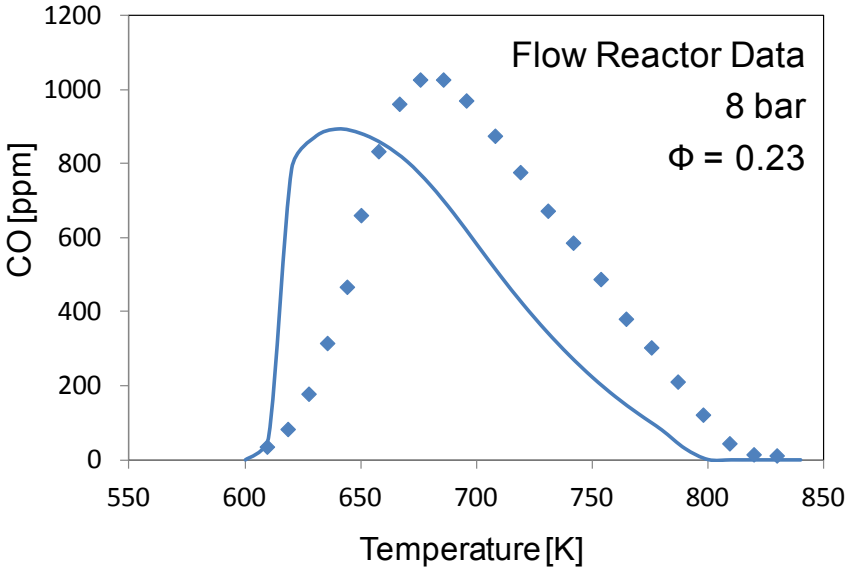
Experiments: Tobin,Yasunaga and Curran, NUIG, Ireland (Combust. Flame 2011)

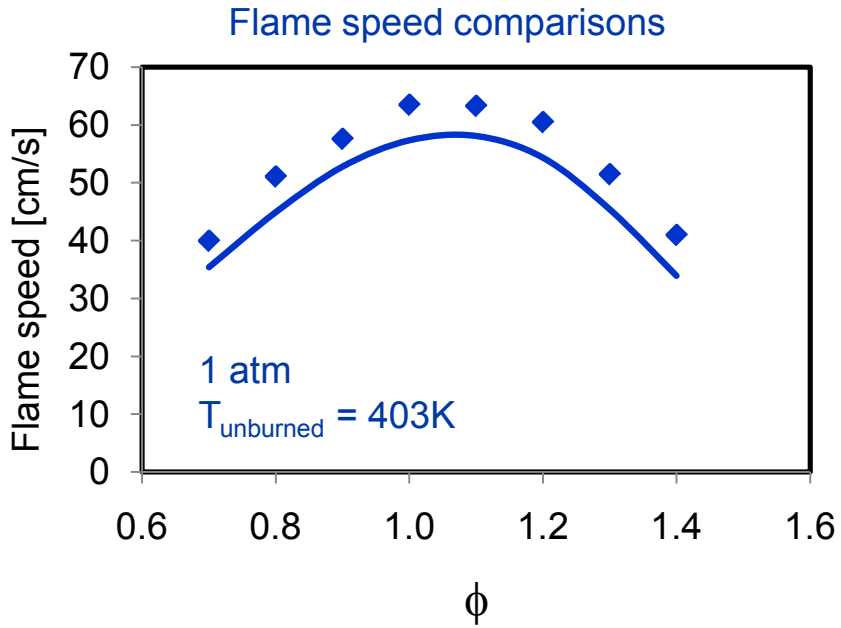
Developing reduced model for diesel surrogate for Engine Combustion Network (ECN)

(23% m-xylene / 77% n-dodecane)
(by liquid volume)



LLNL detailed model results:





CO formation is a good index of the reactivity of the mixture

Good predictions on the peak value, but shifted by 40K

Reasonable agreement on the flame speed measurements

Flow reactor data: Natelson, Kurman, Johnson, Cernansky, and Miller, Combust. Sci. Tech. (2011)
Flame data: Ji, Moheet, Wang, Colket, Wang, Egolfopoulos, Combustion Meeting, 2011

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
- 2-Methyl Alkanes
- 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

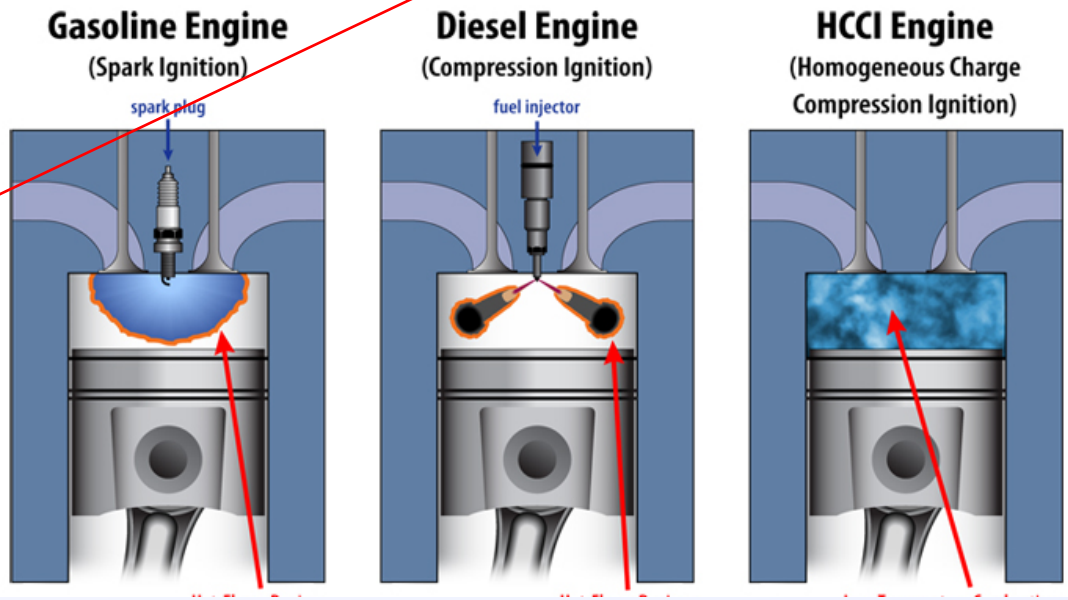
Combustion Chemistry

Go Directly to Mechanisms...

The central feature of the Combustion Chemistry project at LLNL is our development, vali 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 bu hydrocarbon mechanisms for fuels from hydrogen and methane through much larger fue including heptanes and octanes. Other classes of fuels for which models have been dev include flame suppressants such as halons and organophosphates, and air pollutants su soot and oxides of nitrogen and sulfur.

Reaction mechanisms have been tested and validated extensively through comparisons bet 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.

2-Methyl Alkanes



Collaborations

- 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, U. of Wisc., U. of Mich.)
  - Collaboration with John Dec at Sandia on HCCI engine experiments with gasoline
  - Collaboration with Sibendu Som at Argonne on diesel reacting sprays
- Second interaction is collaboration with many universities
  - Prof. Sung's group, U of Conn. on gasoline surrogates
  - 2-methyl, 3-methyl and dimethyl alkanes:
    - Prof. Oehlschlaeger at RPI, shock tube ignition at engine pressures
    - Prof. Egolfopoulos at USC flame speed, ignition and extinction
    - Prof. Seshadri at UC San Diego: flame ignition and extinction
    - Dr. Dagaut, CNRS, Orleans, France
  - Dr. Curran at Nat'l Univ. of Ireland on 2-methyl, 3-methyl heptane, n-propyl benzene and n-butyl benzene in RCM and shock tube
  - Prof. Lu, U. of Conn. on mechanism reduction
- Participation in other working groups with industrial representation
  - Fuels for Advanced Combustion Engines (FACE) Working group and AVFL-18 (Surrogate fuels for kinetic modeling)
  - Engine combustion network (ECN)

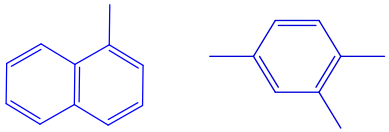
Activities for Next Fiscal Year

- Develop detailed chemical kinetic models for:
  - larger alkyl aromatics 
  - larger n-alkanes (above C16)(important to get end of distillation curve) 

  (both coordinated with CRC AVFL-18, “Surrogate fuels for kinetic modeling”)
- Modeling of engine combustion with reduced models for diesel surrogate fuels for the Engine Combustion Network
- Gasoline surrogate work with Prof. Sung (UConn) for RCM ignition and Egolfopoulos (USC) for flame speeds
  - Look at the effect of EGR

Summary

- Approach to research
  - Continue development of surrogate fuel mechanisms to improve engine models for HCCI and diesel engines
- Technical accomplishments:
  - We validated our 3-methyl, 2-5-dimethyl alkane, and alkylated aromatics mechanisms by comparison to experimental data at engine-like pressures and temperatures
- Collaborations/Interactions
  - Collaboration through AEC working group and FACE working group with industry. Many collaborators from national labs and universities
- Plans for Next Fiscal Year:
  - Larger alkyl aromatics:



  - Reduced models for engine combustion network (ECN)
  - Validate gasoline surrogate mechanism with experiments including EGR