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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LLNL-PRES-472814

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:

- FY10: 400K
- FY11: 500K

Partners

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

- FY11 Objectives:
  - Develop a chemical kinetic mechanism for a new series of iso-alkanes to help represent the iso-alkane chemical class in diesel fuel
  - To provide validation of the chemical kinetic mechanisms of the 2-methyl alkane series
  - Develop chemical kinetic models to represent large aromatics in diesel fuel
  - Develop improved gasoline surrogate fuels for HCCI engines
  - Development of very efficient software to reduce the size of detailed chemical kinetic models for transportation fuels so that they can be effectively used in multidimensional engine simulation codes

Chemical kinetic milestones

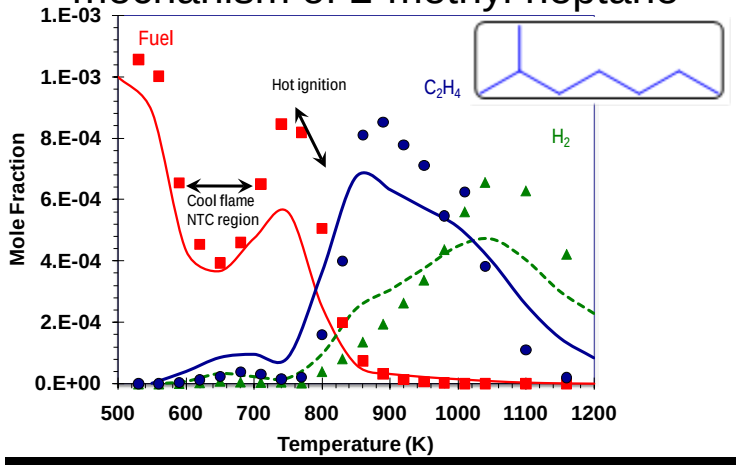
- ✓ December, 2010
  Validate the chemical kinetic mechanism of 2-methyl heptane
- May, 2011
  Development of a low and high temperature mechanisms for a new series of iso-alkanes for diesel fuel
- May, 2011
  Test surrogate mixture models for gasoline by comparison to HCCI engine and RCM experiments
- September, 2011
  Develop chemical kinetic model for a high molecular-weight aromatic
- September, 2011
  Develop a functional group method to represent iso-alkanes in diesel fuel

Approach

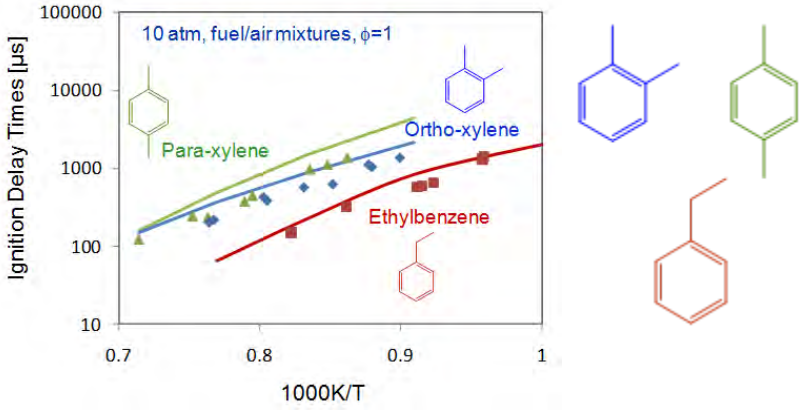
- Develop chemical kinetic reaction models for each individual fuel component of importance for fuel surrogates of gasoline, diesel, and next generation fuels
- Combine mechanisms for representative fuel components to provide surrogate models for practical fuels
  - diesel fuel
  - gasoline (HCCI and/or 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

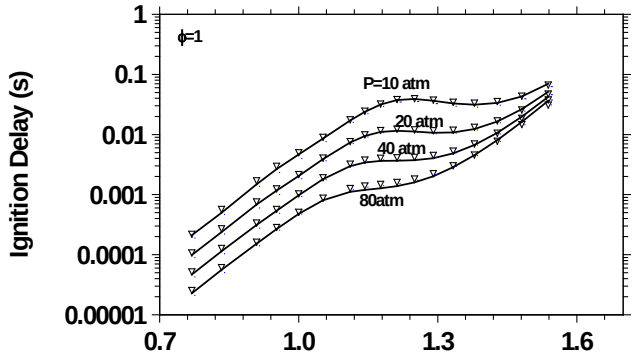
- Validated the chemical kinetic mechanism of 2-methyl heptane



- Development of chemical kinetic model for larger aromatics



- Developed new approach for formulating gasoline surrogate mixtures for real gasoline fuels
- Developed reduced mechanism for gasoline surrogate

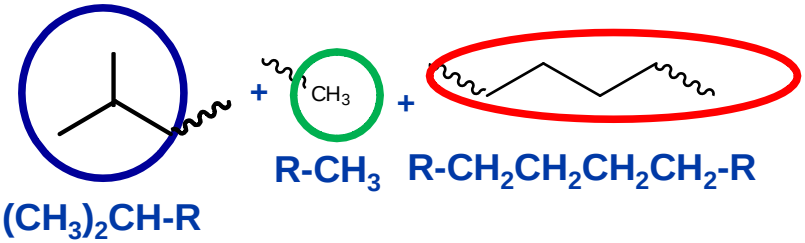


1500 species

↓

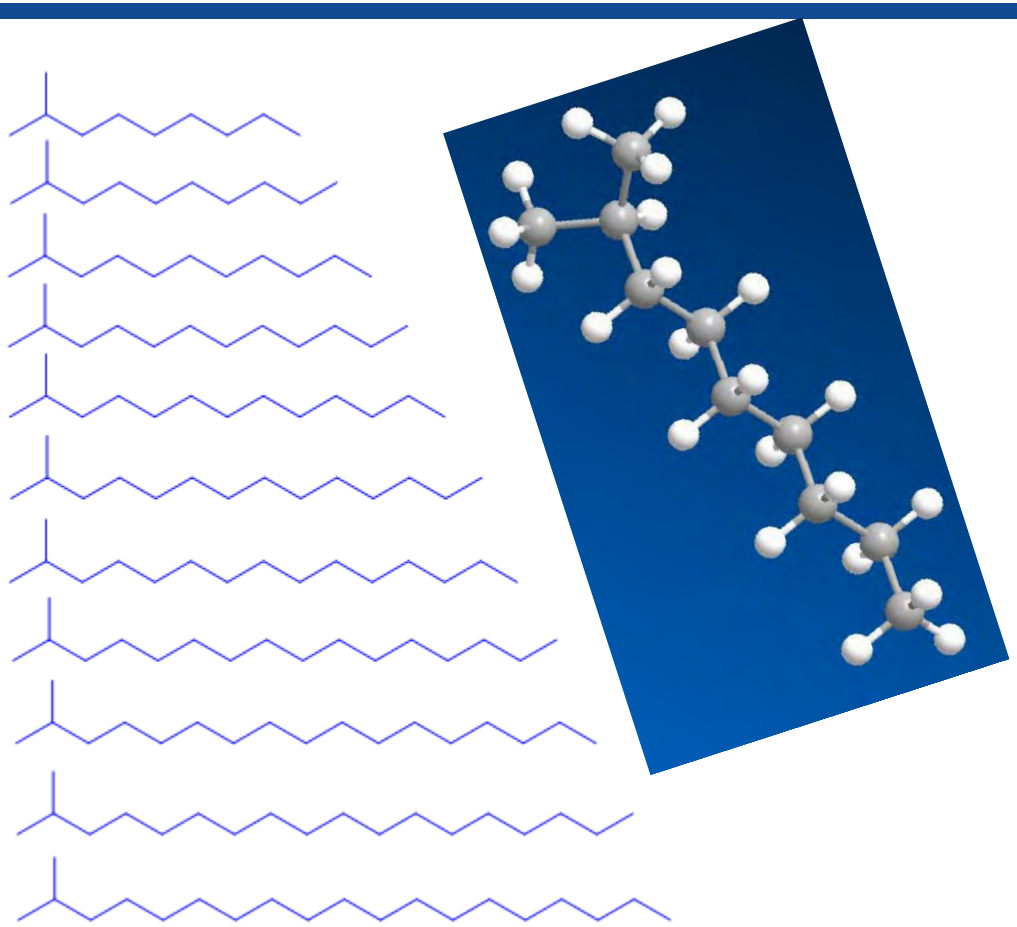
312 species

- Developed a functional-group kinetics modeling approach for iso-alkanes that greatly reduces the size of the mechanism



C8 to C20 mechanism: 7900 species => 280 species

Iso-alkanes: The chemical kinetic mechanism for 2-methylalkanes has been submitted for publication



Includes all 2-methyl alkanes up to C20 which covers the entire distillation range for gasoline and diesel fuels

Built with the same reaction rate rules as our successful iso-octane and iso-cetane mechanisms

7,900 species

27,000 reactions

Recently submitted mechanism for publication:

Sarathy, Westbrook, Mehl, Pitz, et al. (2011). "Comprehensive chemical kinetic modeling of the oxidation of C8 and larger n-alkanes and 2-methylalkanes." Combustion and Flame , Submitted.

Validated iso-alkane mechanism using new experimental data from many different groups through collaborations

- Idealized chemically reacting flow systems with/without simplified transport phenomenon

Jet Stirred Reactors

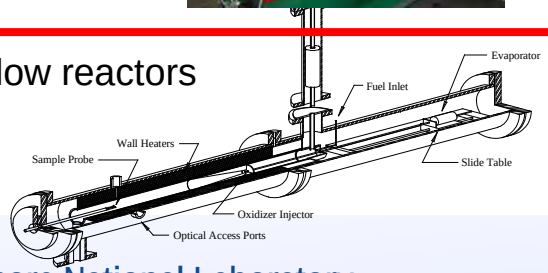
Premixed Laminar Flames

Non Premixed Flames

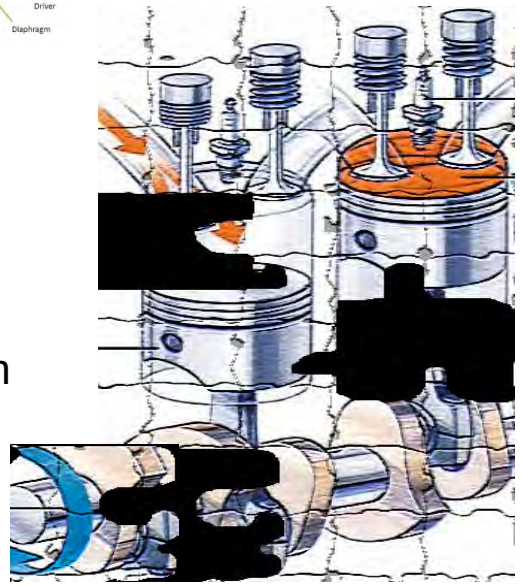
Rapid Compression Machines

Shock tube

High pressure flow reactors



Engine Combustion



Combustion Parameters

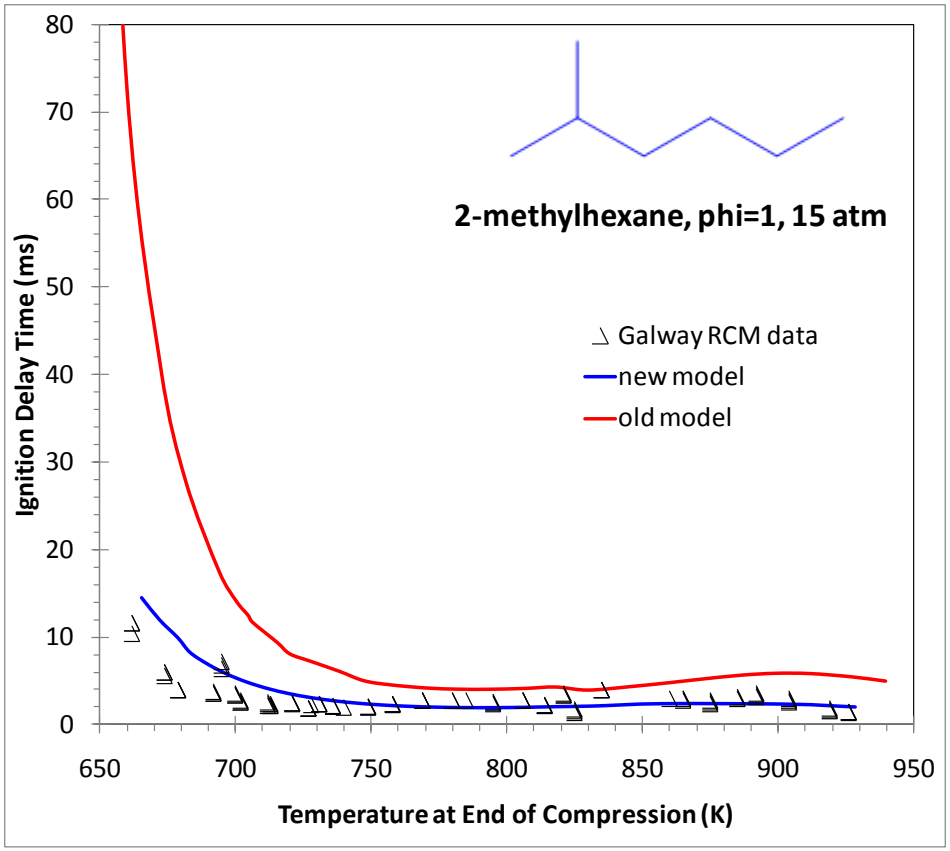
Temperature

Pressure

Mixture fraction (air-fuel ratio)

Mixing of fuel and air

Improved predictions for 2-methylhexane mechanism under engine conditions (RCM)

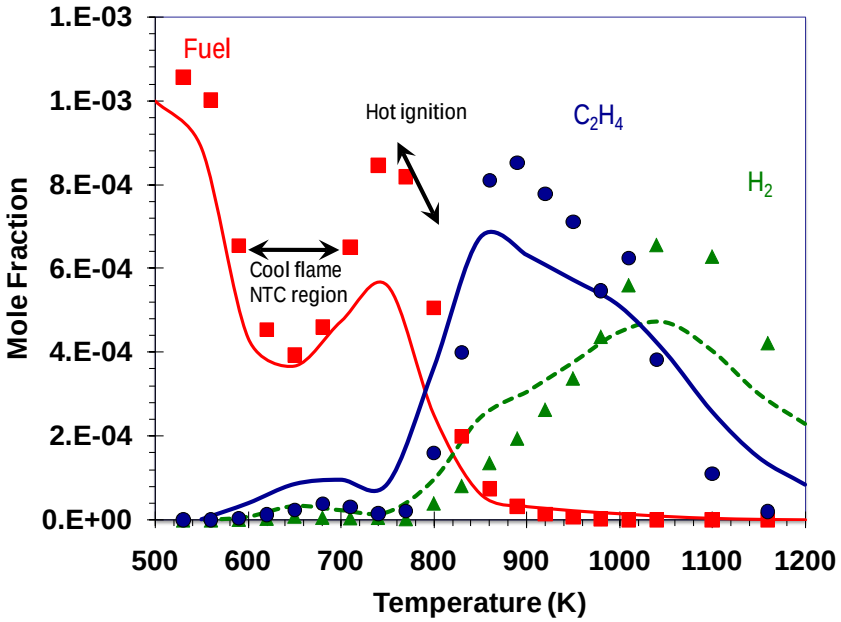


RCM experimental data:

Galway:
Silke et al. Proc. Comb. Inst. (2005)

Reaction rules were updated on the basis of our latest work on n-heptane leading to significant improvements

2-methylheptane model agrees well species profiles measured in a JSR at elevated pressure

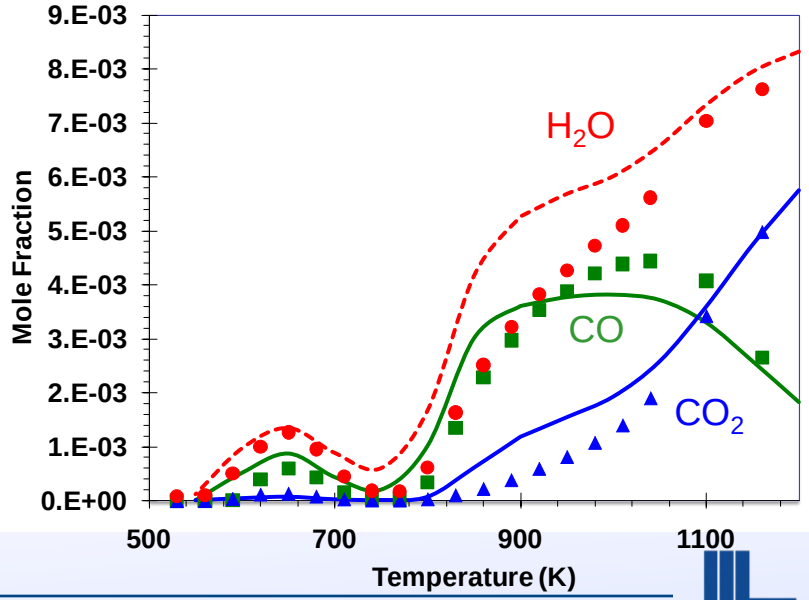


Experiments: Dagaut et al. CNRS (2011)

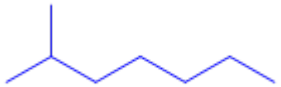
Φ = 1, 10 atm, τ= 0.7s

Good prediction of low T and high T reactivity

Jet stirred reactor (JSR)

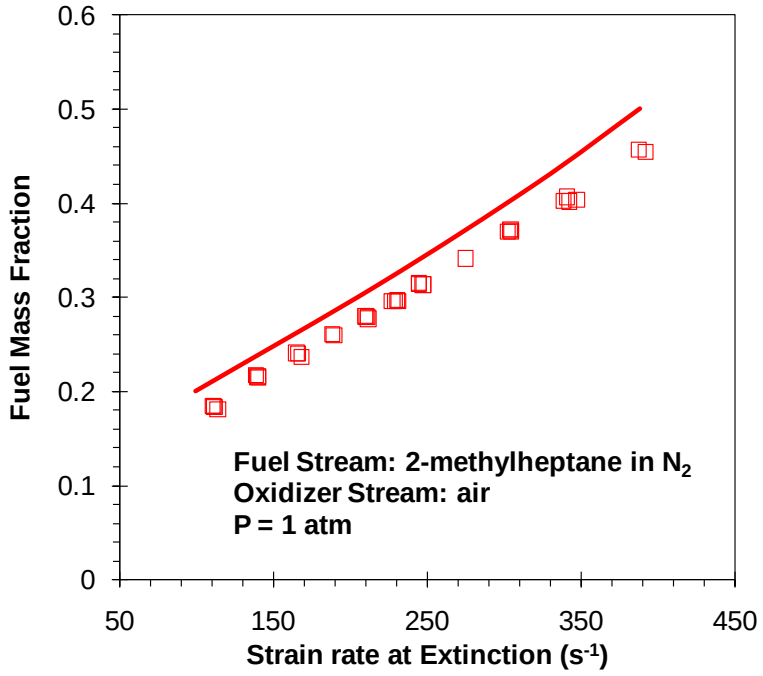


Reduced chemical kinetic models for 2-methyl heptane well simulates extinction and ignition in a counterflow flame

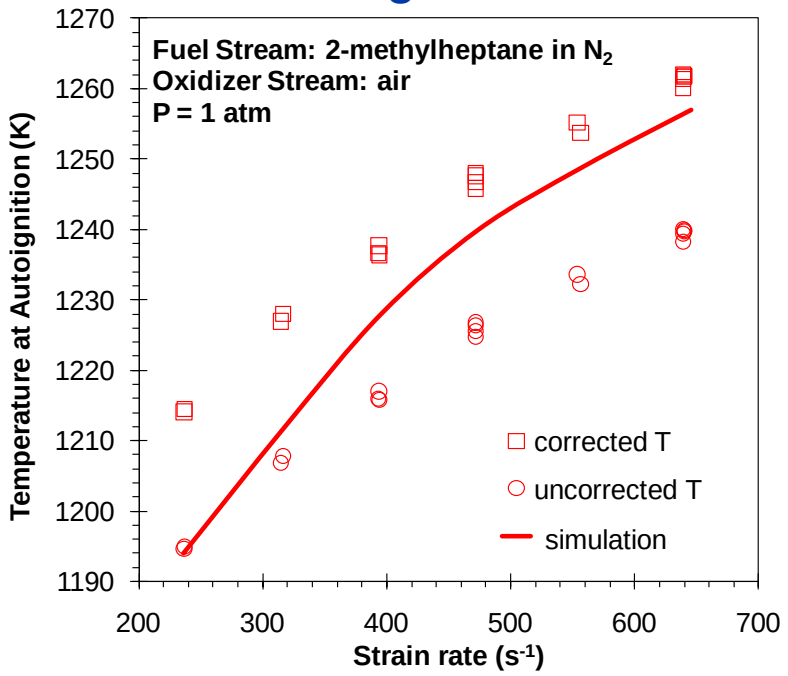


Experiments:
K. Seshadri,
Univ. of California, San Diego, 2011

Extinction

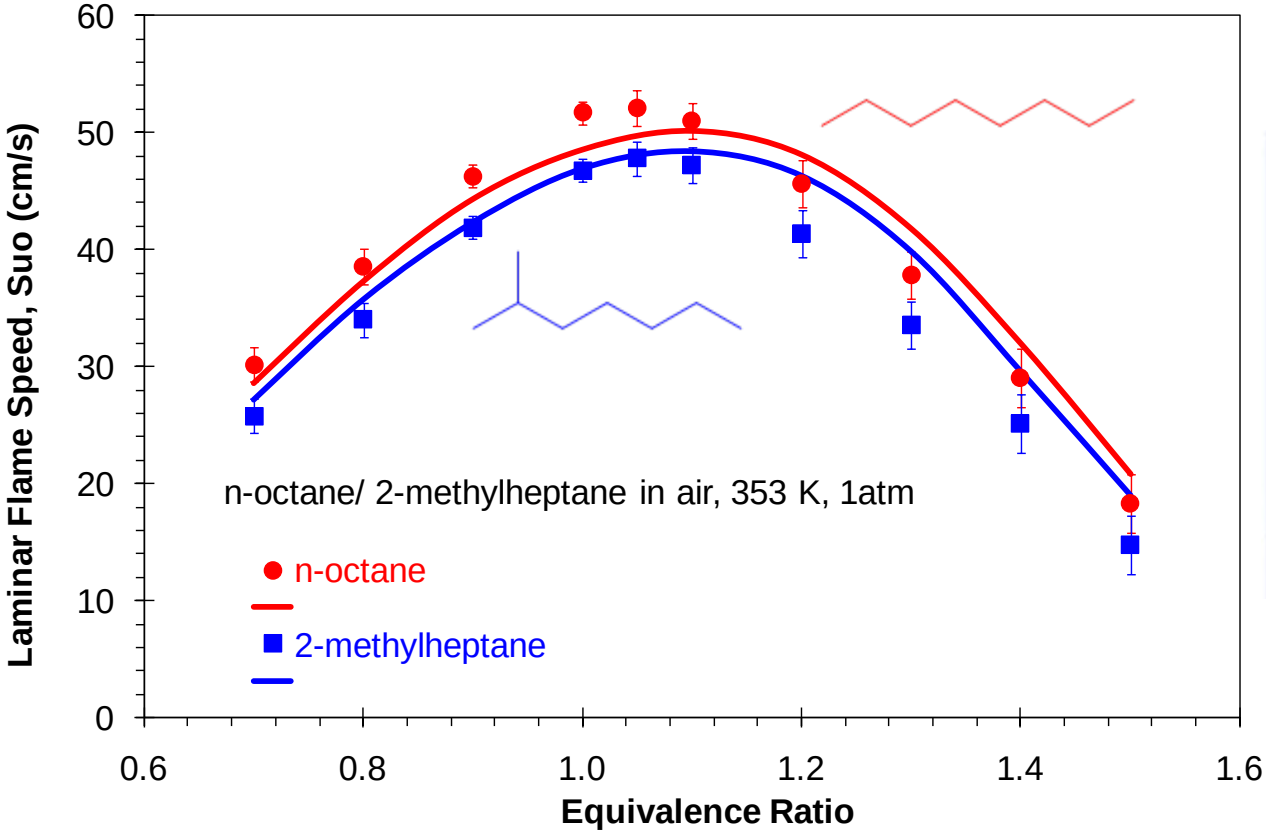


Ignition



<u>To perform these reacting flow simulations</u>: Mechanism reduced from 714 to151 species using directed relational graph method.
(Collaboration with T. Lu at Univ. of Connecticut)

Laminar flame speeds of n-octane and 2-methylheptane are well predicted by the model

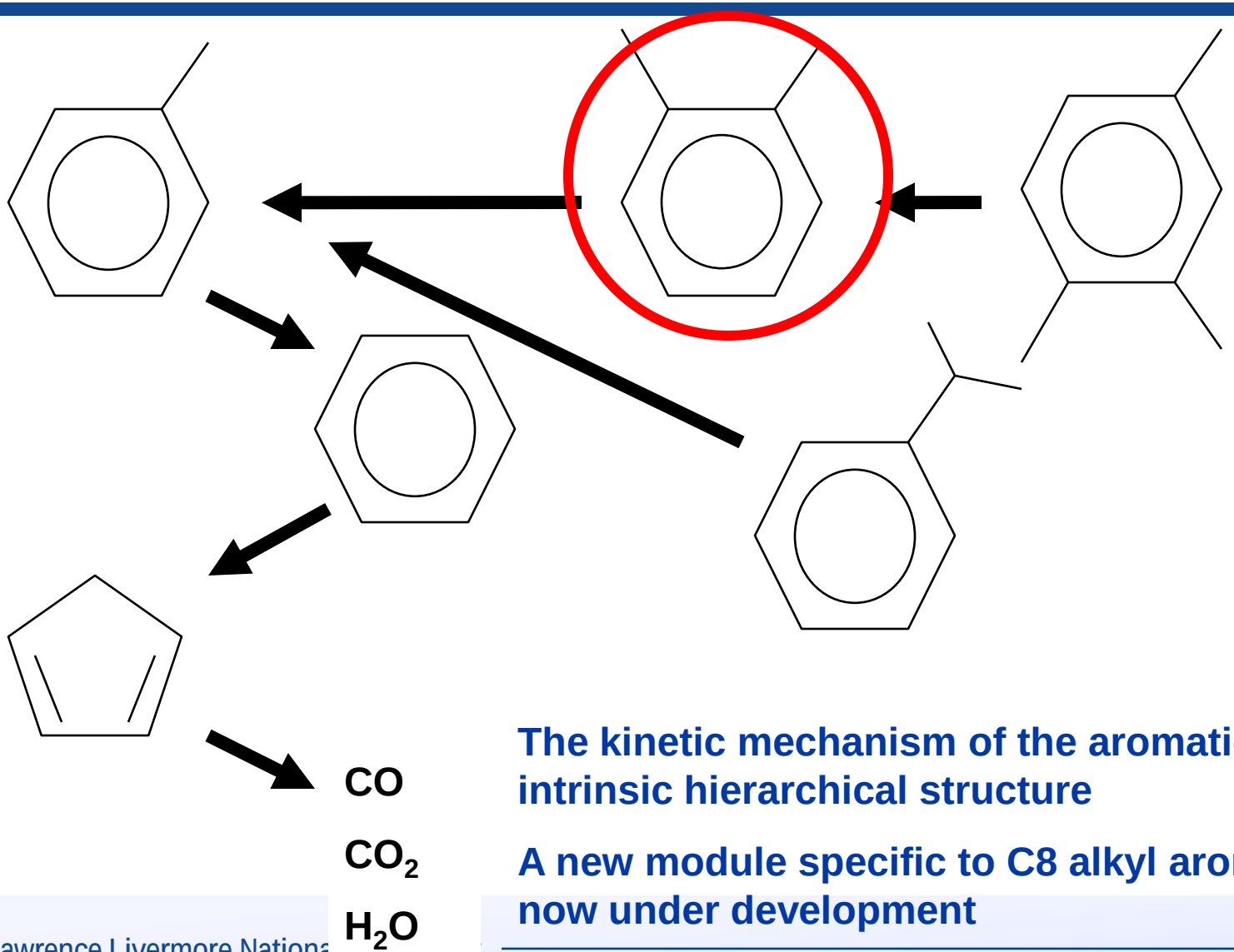


Flame speed measurements: Egolfopoulos et al. 2011 USC

Twin premixed counterflow flames

Flame speeds of 2-methyl alkanes are slightly slower than n-alkanes' ones: Chemical effect due to the formation of resonantly stabilized radicals by iso-alkanes

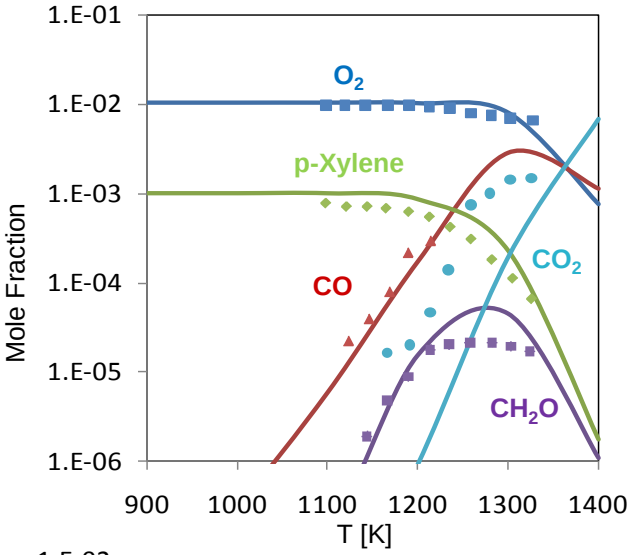
Chemical kinetic mechanism for larger aromatics

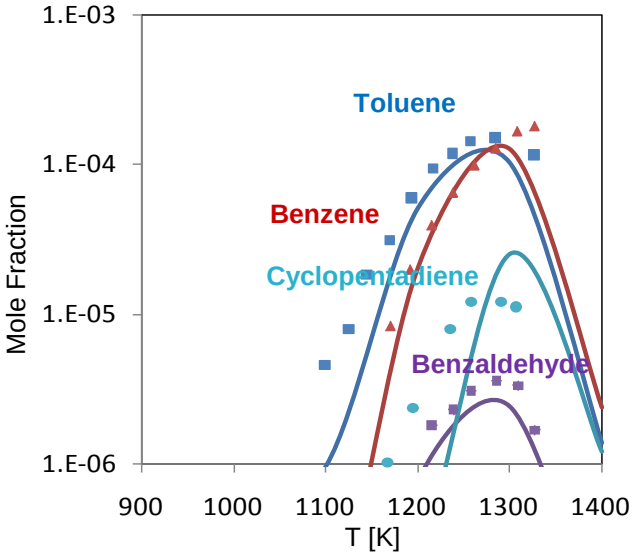


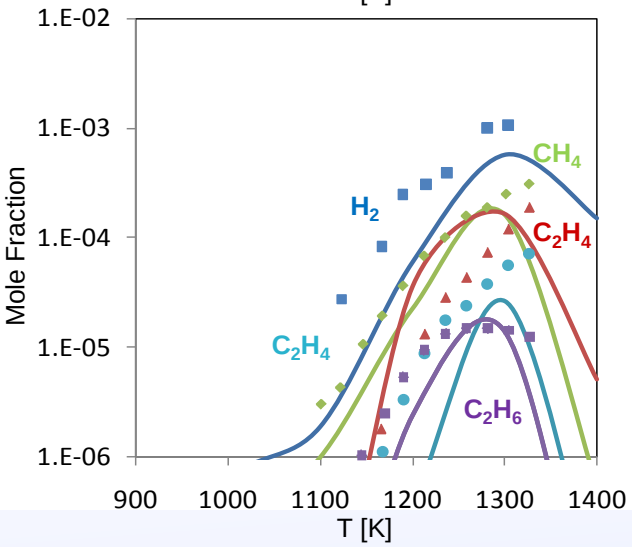
The kinetic mechanism of the aromatics has an intrinsic hierarchical structure

A new module specific to C8 alkyl aromatics is now under development

p-Xylene mechanism well reproduces species profiles in jet stirred reactor







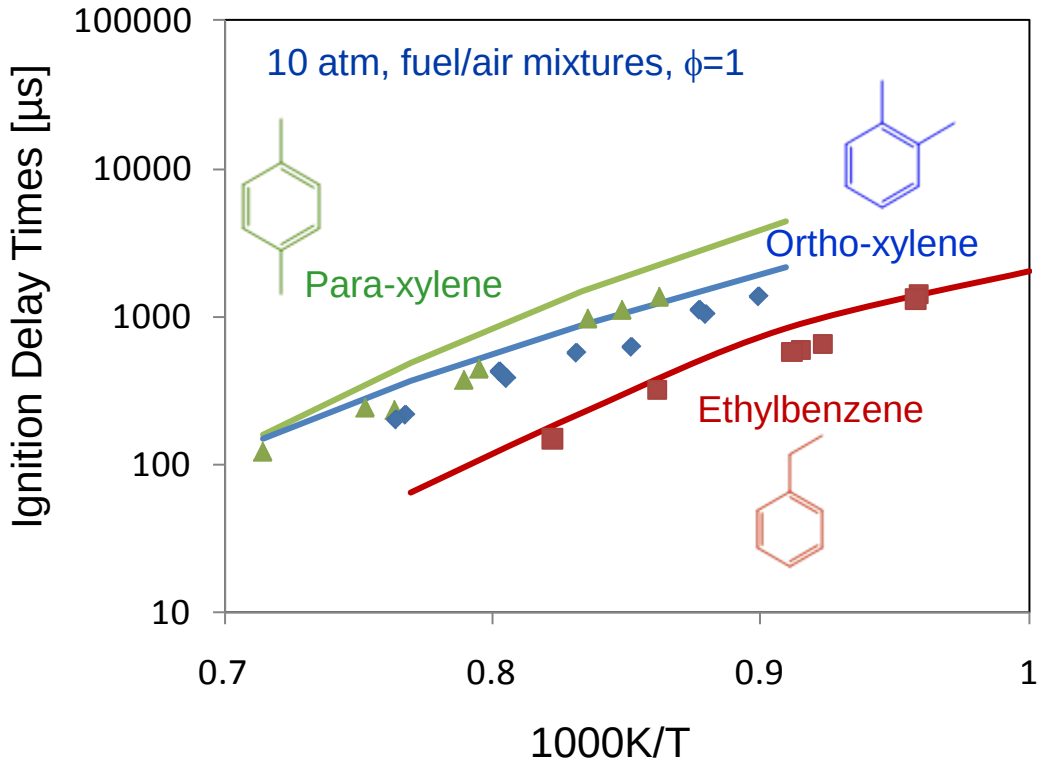
Jet stirred reactor

P = 1 atm, Φ = 1, τ = 0.1s

Experiments: Gail and Dagaut Combustion and Flame 2005

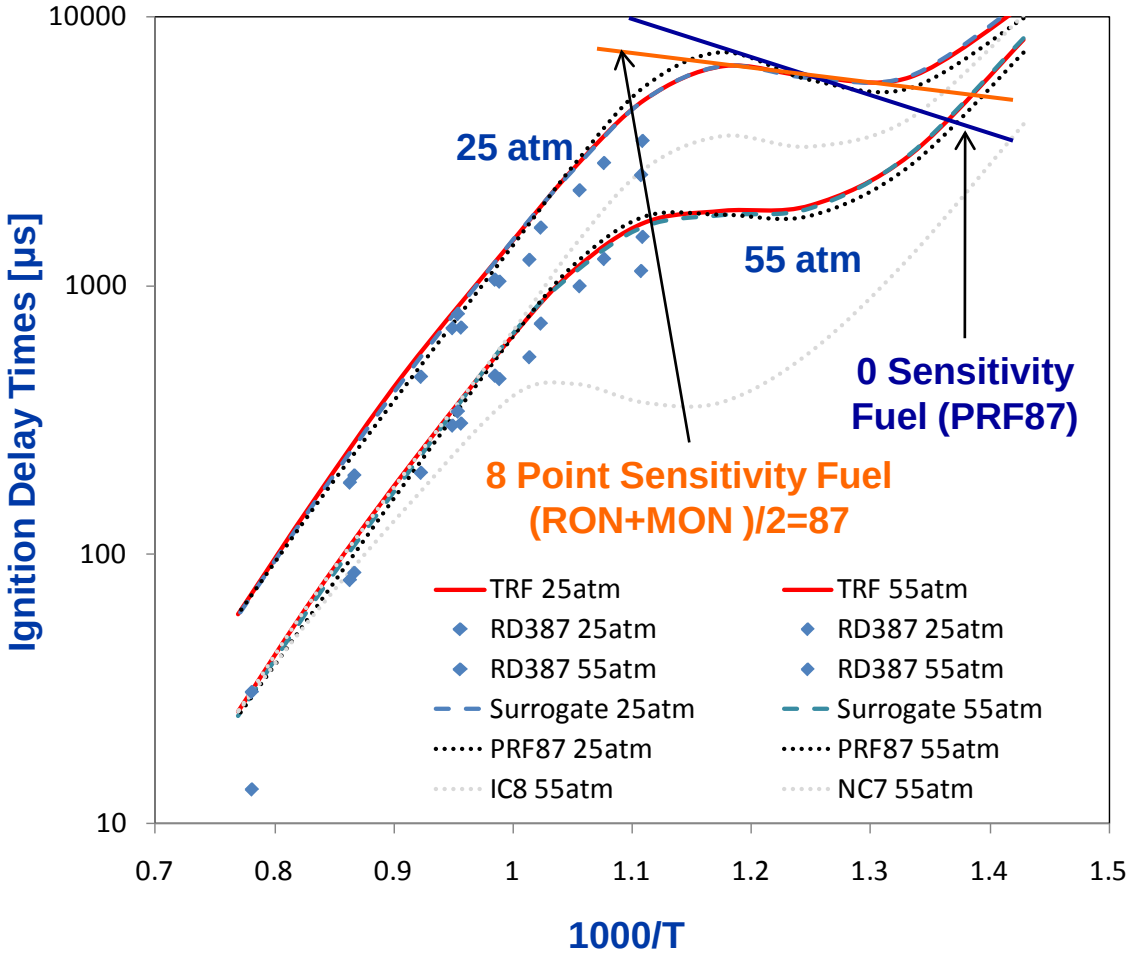
Ortho-, para- and ethyl-benzene models compare well to ignition delay times measured at pressure and temperatures relevant to engines

Ignition delay times in a shock tube for aromatics



Shock tube experimental data: Shen and Oehlschlaeger, Combustion and Flame 2009

Gasoline surrogates: New methodology for matching gasoline surrogate properties to real fuel

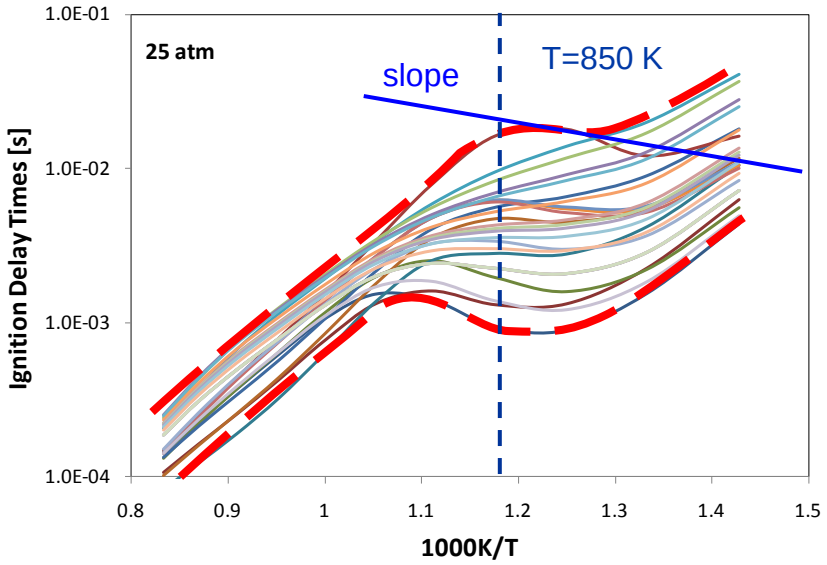


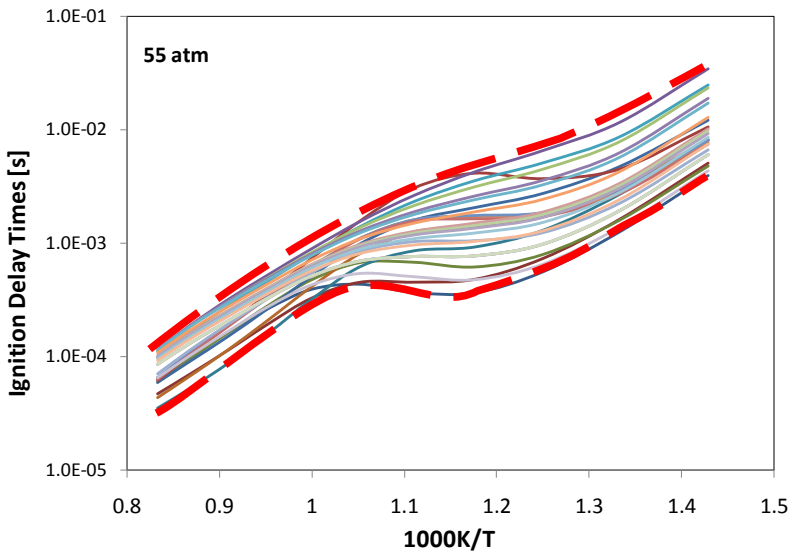
Octane sensitivity is correlated to slope in the NTC region

Experimental data for RD387 gasoline: Gauthier, Davidson, R.K. Hanson, 2004

40 different gasoline surrogates were simulated to obtain key features of their ignition curves

Key feature of their ignition curves were correlated with their octane index (OI) and sensitivity



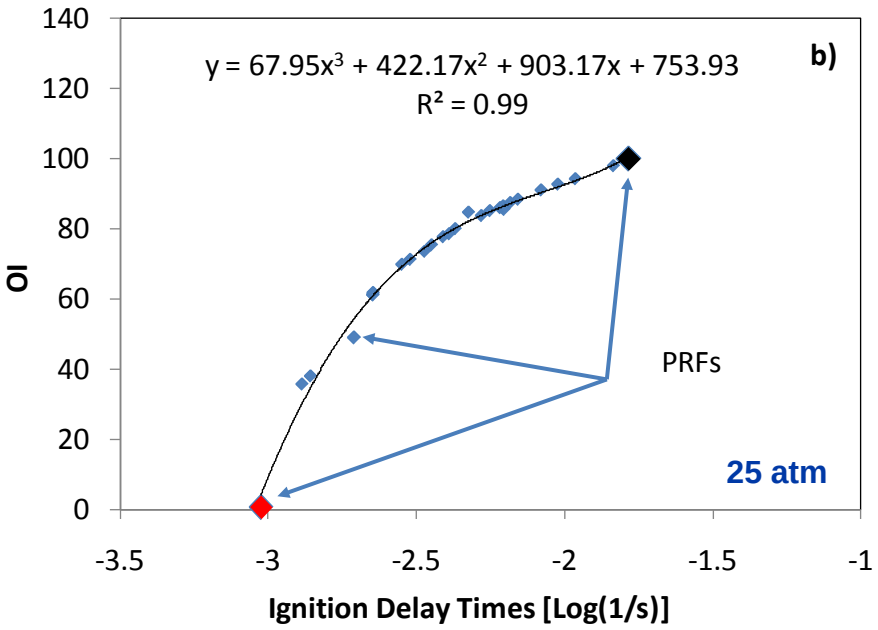


The slope in the NTC region is found to be proportional to the sensitivity while the ignition delay time at a specified T correlates with the OI

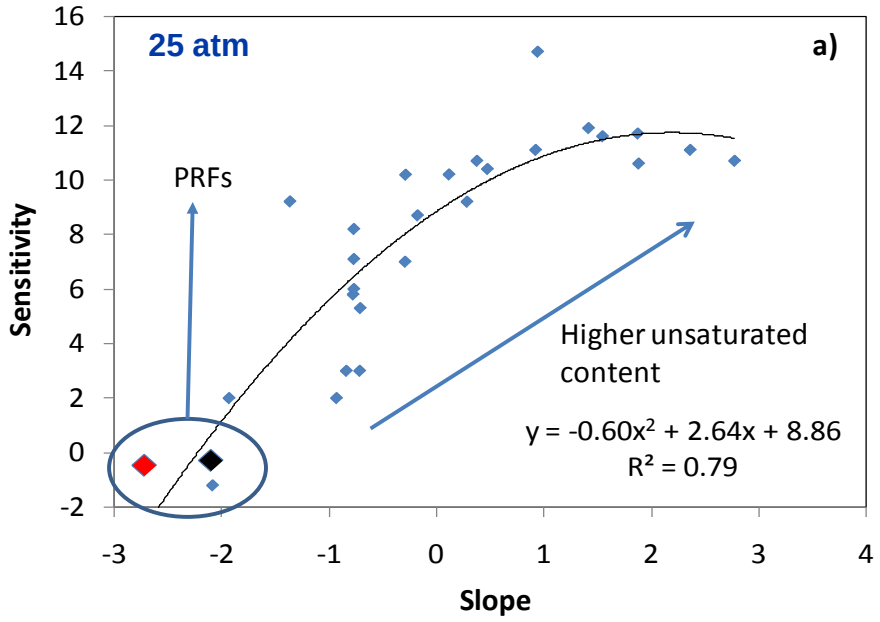
Experimental data: Personal communication and N.Morgan et al. Comb. & Flame

Octane index correlates with ignition delay time and octane sensitivity correlates with slope in the NTC

Octane Index vs. Ignition Delay time @ 850K



Sensitivity vs. Slope

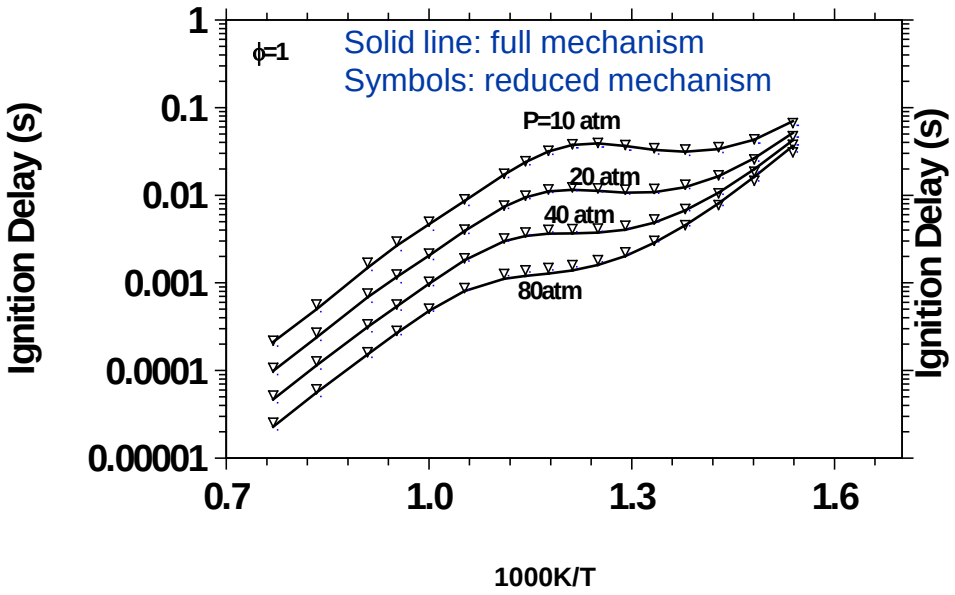


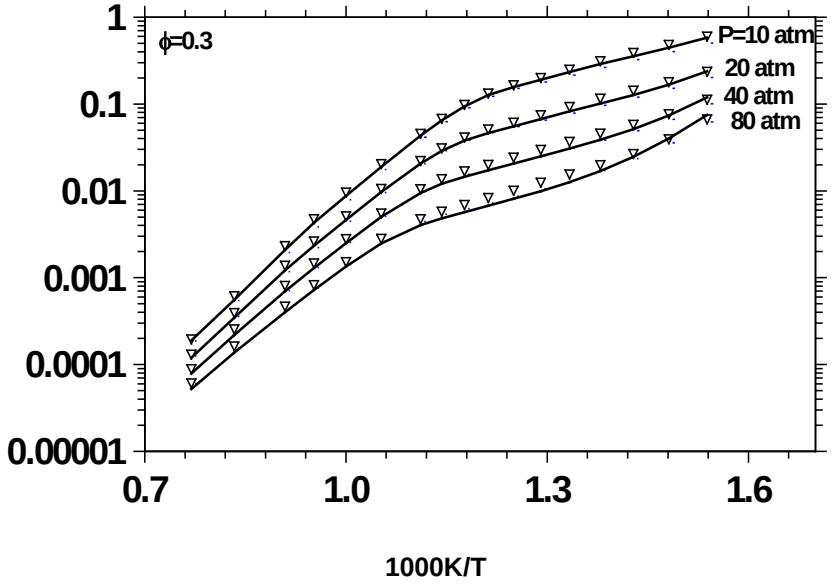
Correlated parameters of octane rating with characteristics of ignition curve for 40 different surrogates

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

Gasoline surrogate mechanism has been reduced for use in engine simulations

Comparison of ignition delay times for detailed and reduced mechanism:

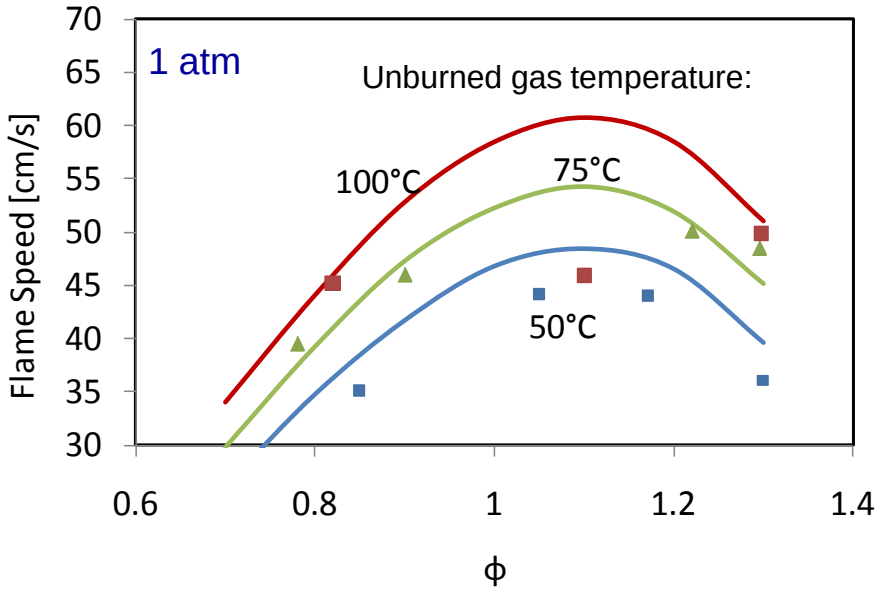




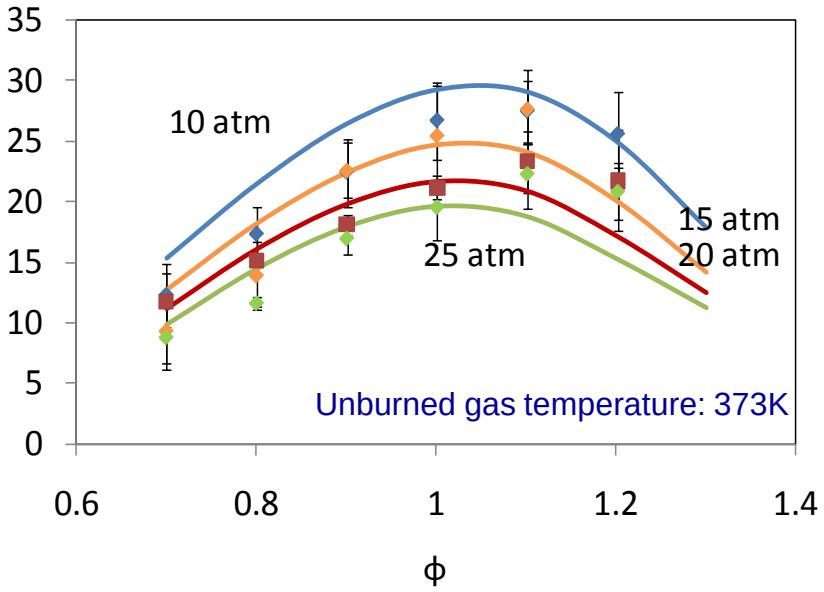
Reduction: 1500 species to 312 species

Collaboration with J.Y. Chen, U. C. Berkeley

Reduced gasoline surrogate mechanism has also been validated against experimental flame speed data for gasoline



Experimental data: Tian et al. Energy & Fuels 2010

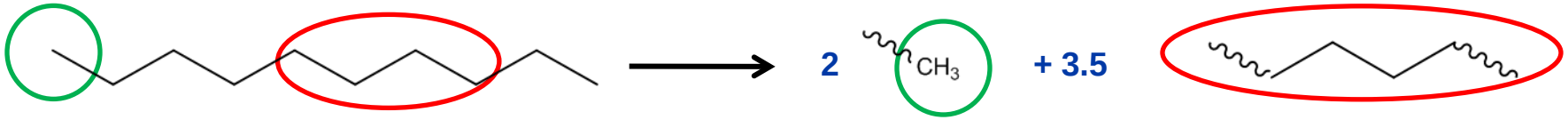


Experimental data: Jerzembeck & Peters SAE 2007

Prediction of flame speed important for spark ignition engine simulations

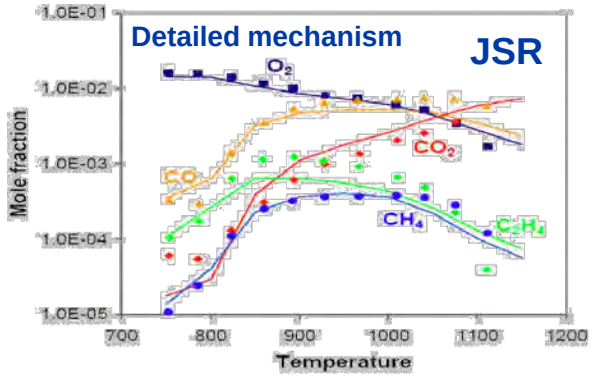
We have developed a novel functional group approach that greatly reduces the size of chemical kinetic mechanisms

$C_{10}H_{22}$ (Diesel Surrogate):



Traditional Approach:

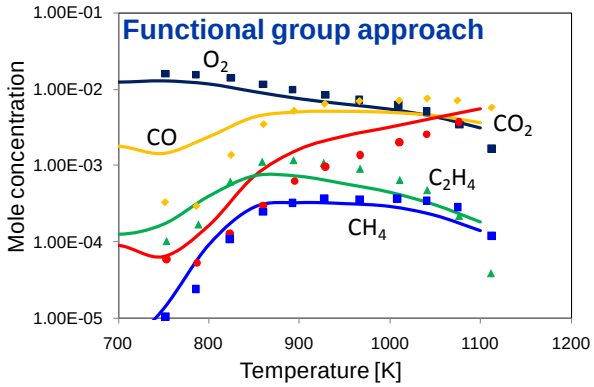
2100 Species 8150 Reactions



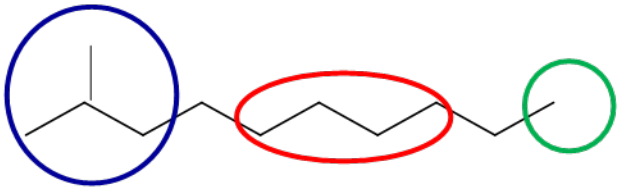
Experimental data:
10 atm, ϕ=1, 0.5s,
0.1% n-decane
Jet Stirred Reactor
Dagaut et. al. 1994

Proposed Approach:

250 Species 1400 Reactions

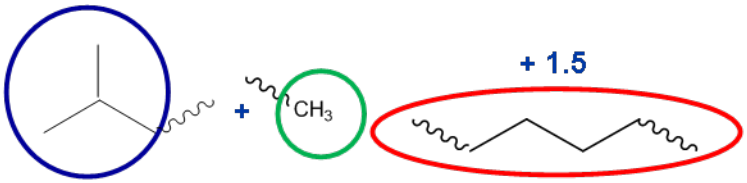


C8 to C20 iso-alkanes:



Traditional Approach:

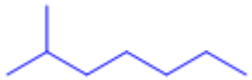
7900 Species 27000 Reactions



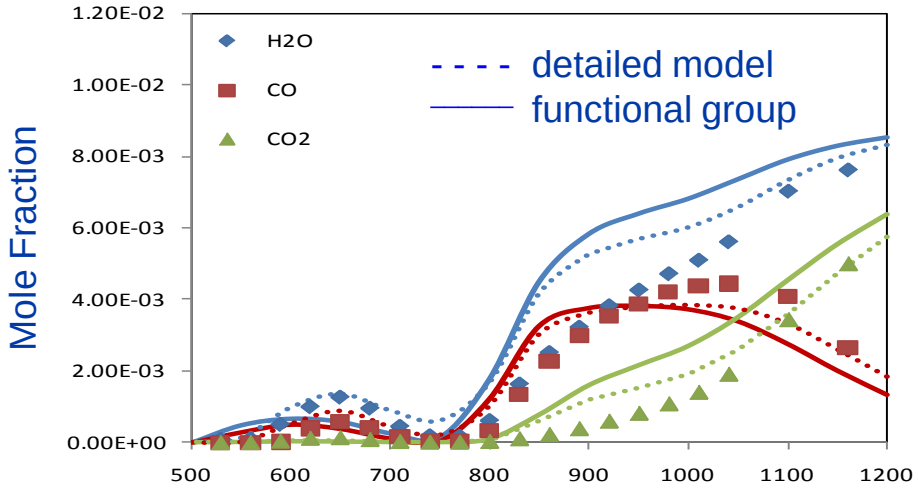
Proposed Approach:

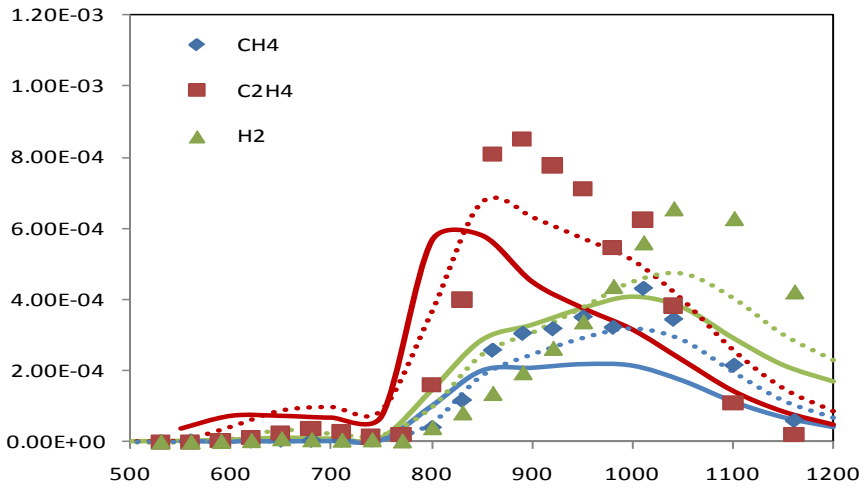
280 Species 1500 Reactions

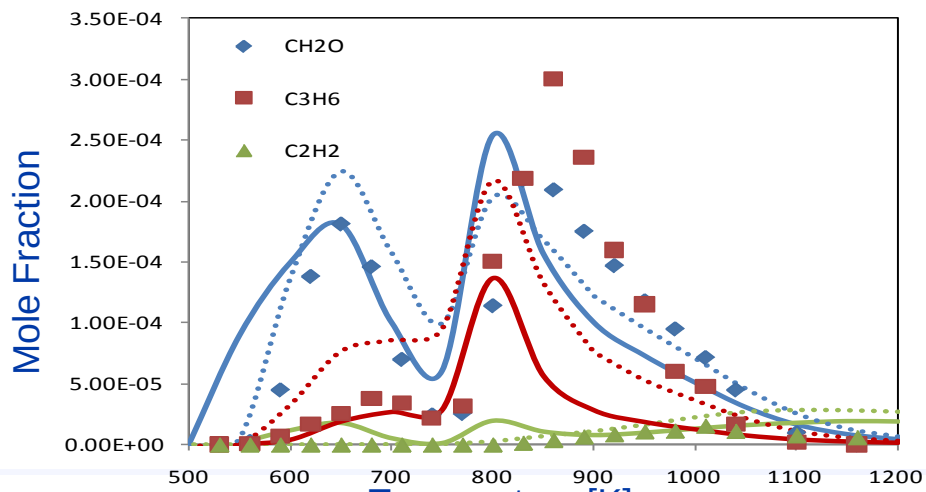
Functional group approach has been successfully extended to 2-methylalkanes and validated in a JSR (2- methyl heptane)

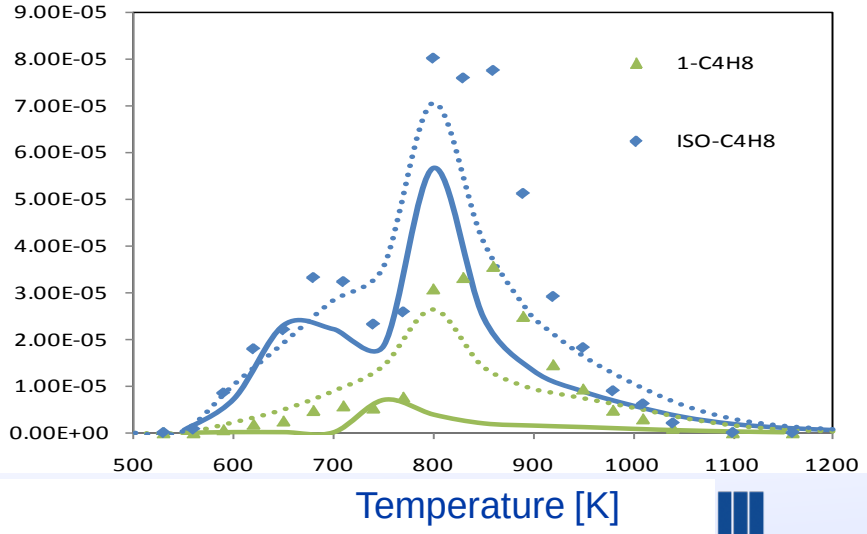


10 atm, ϕ=1, τ=0.7s, 0.1% initial fuel

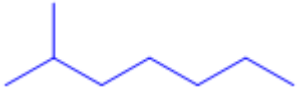


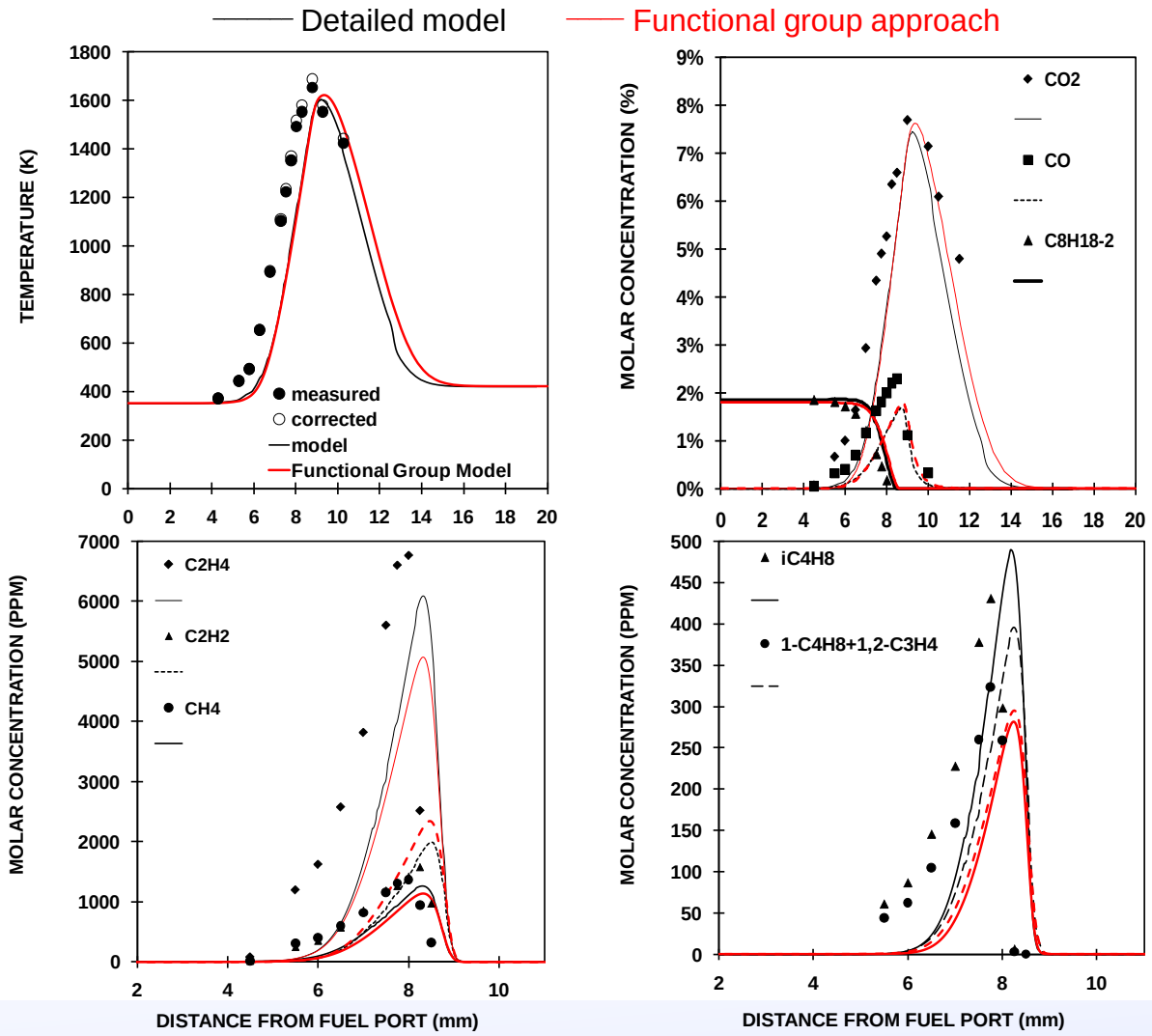






Validation of functional group approach in counter flow flame (2- methyl heptane)





The model successfully reproduces the flame temperature profile as well as the flame structure

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

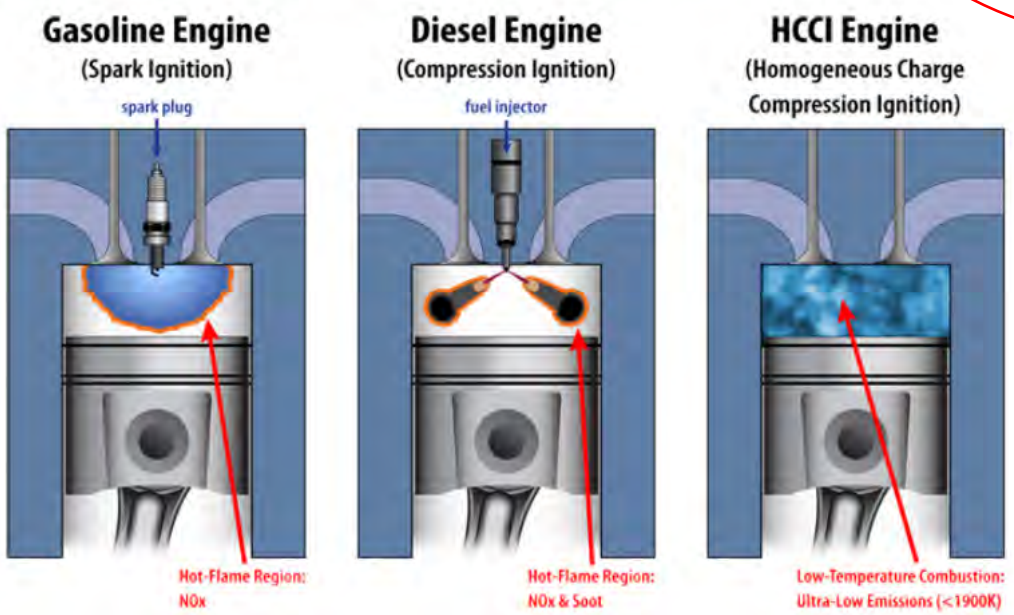
Combustion Chemistry

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.

C8-C16 n-Alkanes

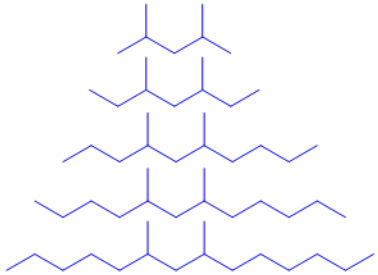


Collaborations

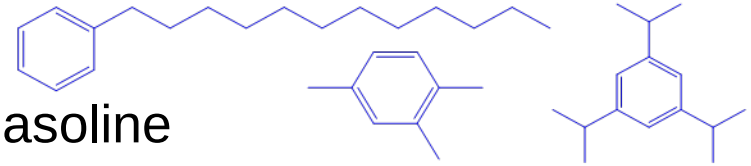
- Our major current industry collaboration is via the DOE working groups on HCCI and diesel engines
  - All results presented at Advanced Engine Combustion Working group meetings (Industry, National labs, U. of Wisc., U. of Mich.)
  - Collaboration with John Dec at Sandia on HCCI engine experiments
- Second interaction is collaboration with many universities
  - Dr. Curran at Nat'l Univ. of Ireland on 2-methyl heptane & other fuels
  - Prof. Egolfopoulos at USC on 2-methyl heptane
  - Prof. Seshadri at UC San Diego on 2-methyl heptane and toluene
  - Prof. Oehlschaeger at RPI on large alkanes
  - Prof. Sung's group, U of Conn. on gasoline surrogates
  - Prof. Lu, U. of Conn. & Prof. Chen, UCB 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)

Activities for Next Fiscal Year

- Develop detailed chemical kinetic models for another series iso-alkanes: di-methyl alkanes

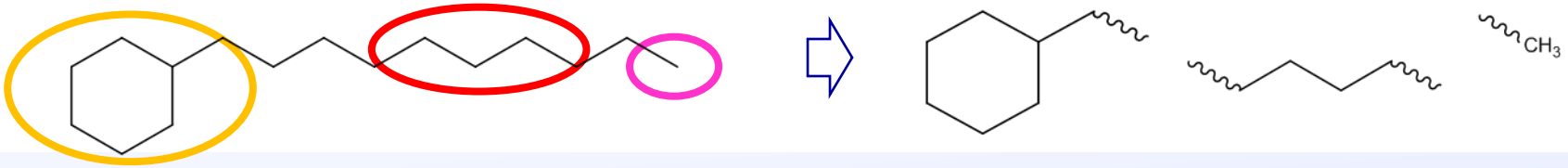


- Validation of 2 and 3-methyl alkanes mechanisms with new data from shock tubes, jet-stirred reactors, and counterflow flames
- Develop detailed chemical kinetic models for larger alkyl aromatics:



- Develop more accurate surrogates for gasoline
- Further develop mechanism reduction using functional group method

n-decyl-cyclohexane - Diesel fuels



Summary

- Approach to research
  - Continue development of surrogate fuel mechanisms to improve engine models for HCCI and diesel engines
- Technical accomplishments:
  - We validated our 2-methyl alkane mechanism on a wide set of experimental data and improved the model
- 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: