Lawrence Livermore National Laboratory

Chemical Kinetic Research on HCCI & Diesel Fuels

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

Washington, DC

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Overview

Timeline

- Ongoing project with yearly direction from DOE

Budget

- Funding received in FY08 and expected in FY09:
  - 800K (DOE)

Barriers

- 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 are critical for improved engine modeling and ultimately for engine design

Partners

- Interactions/ collaborations: DOE Working Group, National Labs, many universities, FACE Working group.

Relevance to DOE objectives

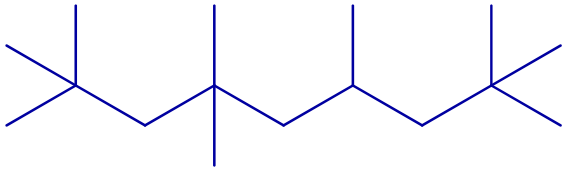
- Support DOE objectives of petroleum-fuel displacement by
  - Improving engine models so that further improvements in engine efficiency can be made
  - Developing models for alternative fuels (biodiesel, ethanol, other biofuels, oil-sand derived fuels, Fischer-Tropsch derived fuels) so that they can be better used to displace petroleum fuels while maximizing engine performance and efficiency and minimizing pollutant emissions

Approach

- Develop chemical kinetic reaction models for each individual fuel component of importance for fuel surrogates of gasoline, diesel, and alternative fuels including biofuels
- 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

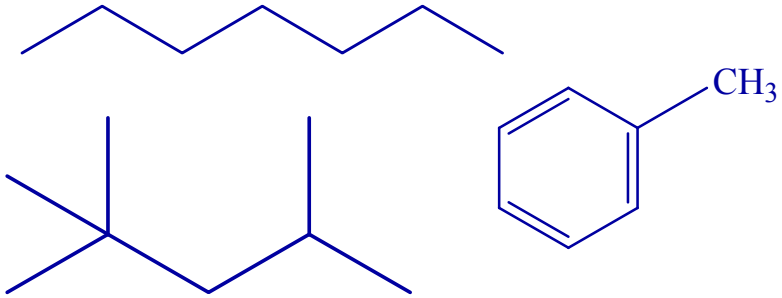
Objectives

- Improving models for diesel engines
  - Develop a model for n-heptamethylnonane: important fuel component for modeling diesel fuel

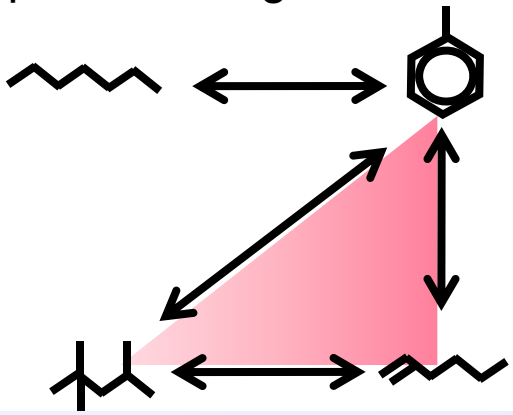


  - a primary reference fuel for diesel
  - Include both high and low temperature chemistry important to model low temperature combustion modes

- Improve component models for gasoline fuels, including n-heptane, iso-octane and toluene

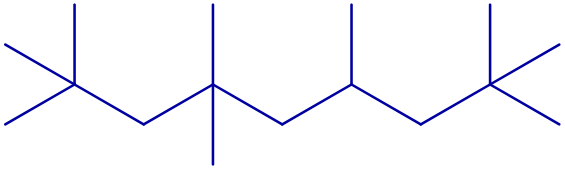


- Improve mixture models of components for gasoline fuels



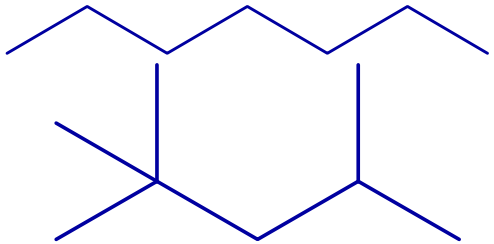
Technical Accomplishment Summary

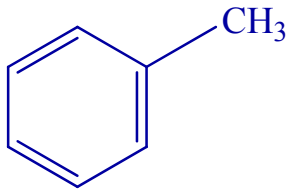
- Improving models for diesel engines
  - Completed development of high and low temperature model for heptamethyl nonane, important component and primary reference fuel for diesel



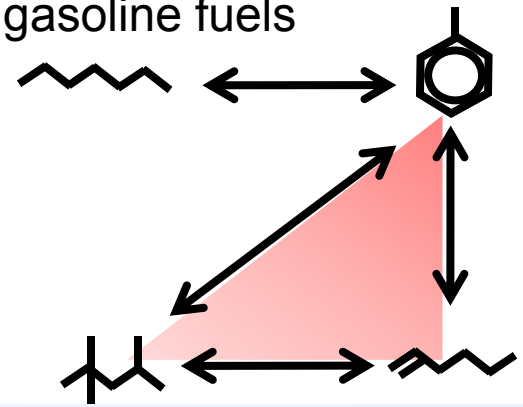
  - Milestones:
    - √ 5/9/09 High temperature mechanism
    - √ 9/9/09 Low temperature mechanism

- Improving models for gasoline-fueled engines:
  - Completed validation of component models for n-heptane, iso-octane and toluene, important components for gasoline fuels

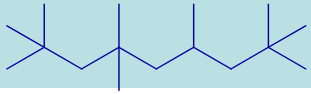




- Developed new surrogate models for gasoline fuels

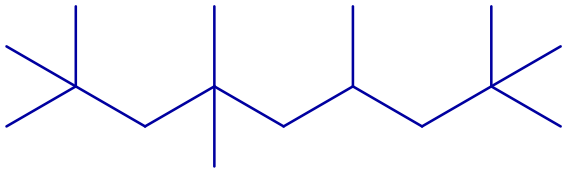


We have developed a model for heptamethylnonane, a primary reference fuel for diesel



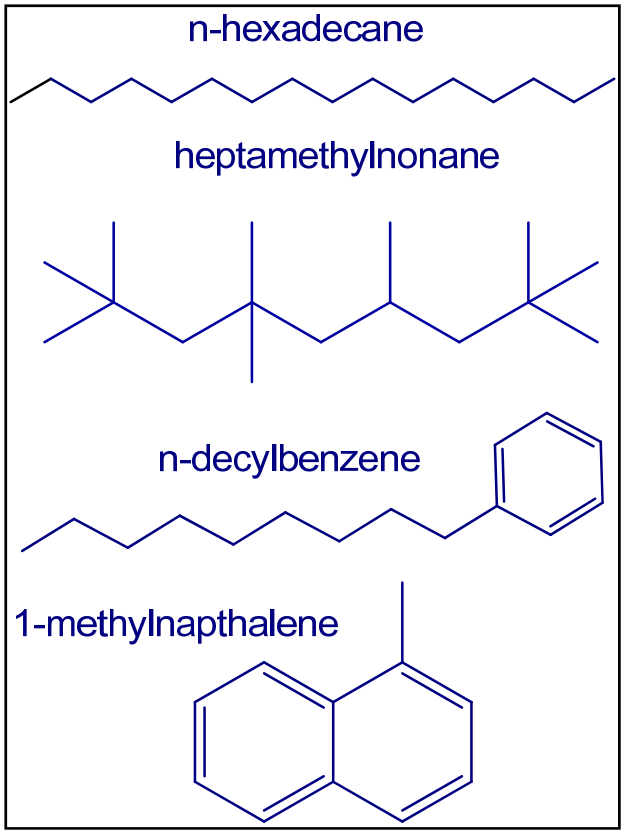
- One of the two primary reference fuels for diesel ignition properties (cetane number)
  - n-hexadecane

  - 2,2,4,4,6,8,8 heptamethylnonane

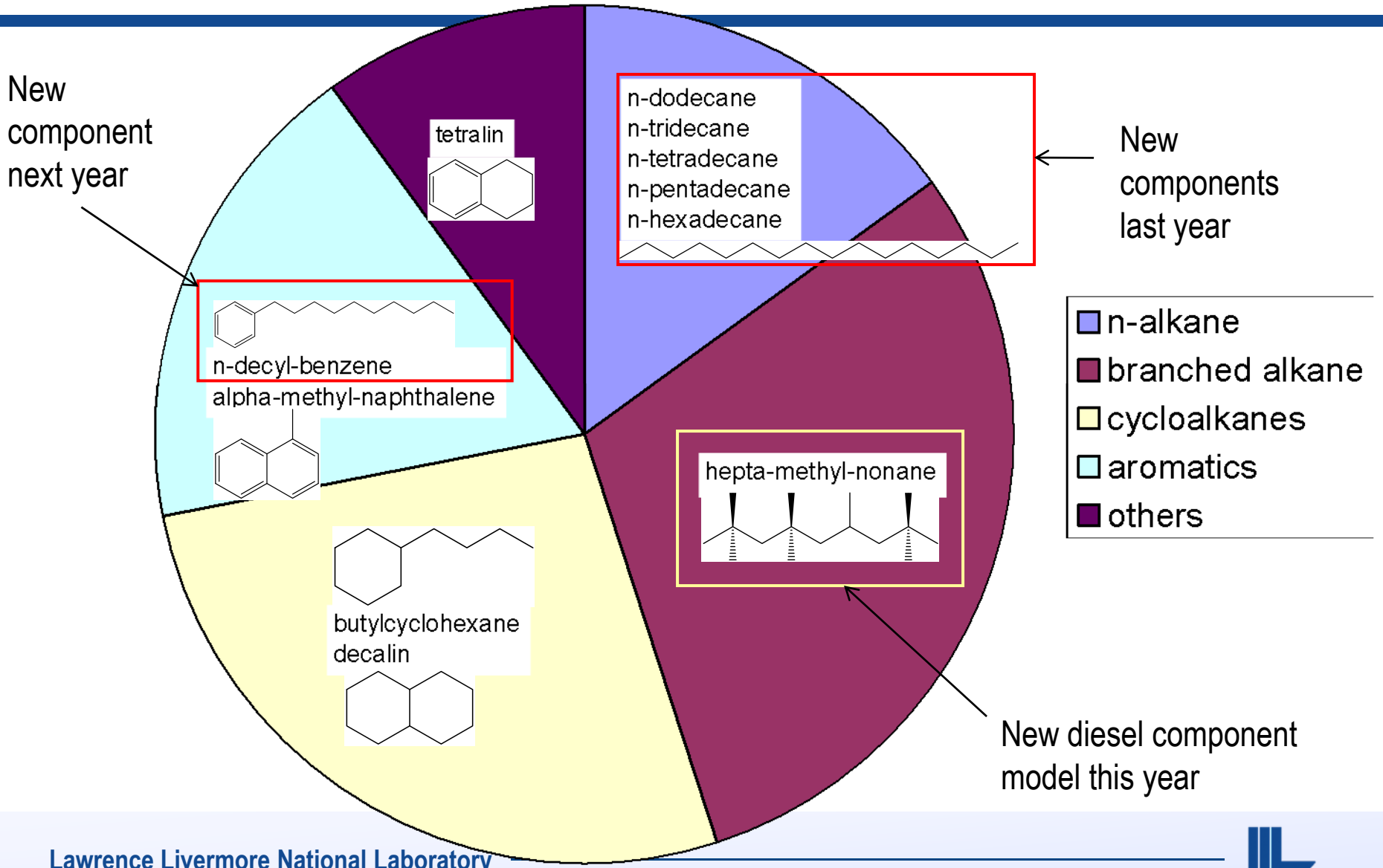


- **High and low temperature portion of the mechanism complete**
  - First-ever complete set of high and low temperature kinetic mechanisms for heptamethylnonane

Recommended surrogate for diesel fuel (Farrell et al., SAE 2007):

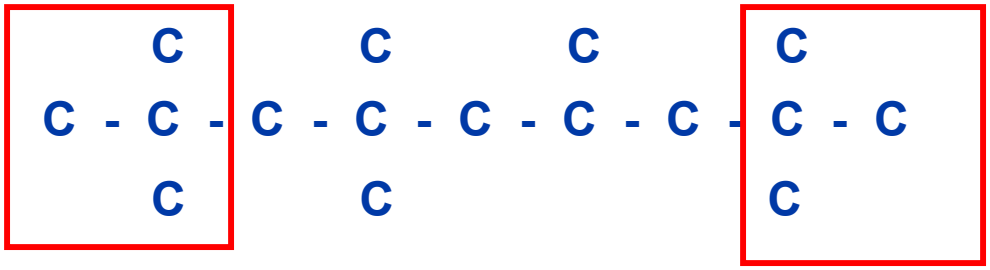


Diesel Fuel Surrogate palette:

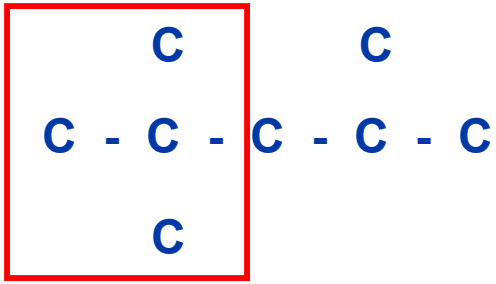


Heptamethylnonane (HMN) has a lot of structural similarities to iso-octane

HMN

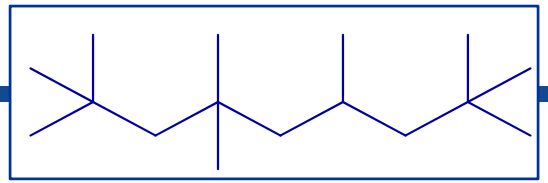


iso-octane



Site-specific reaction rates for HMN based largely on iso-octane

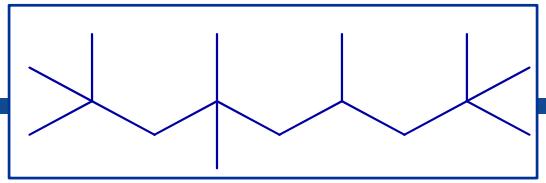
Development of detailed chemical kinetic mechanism for heptamethyl nonane (HMN)

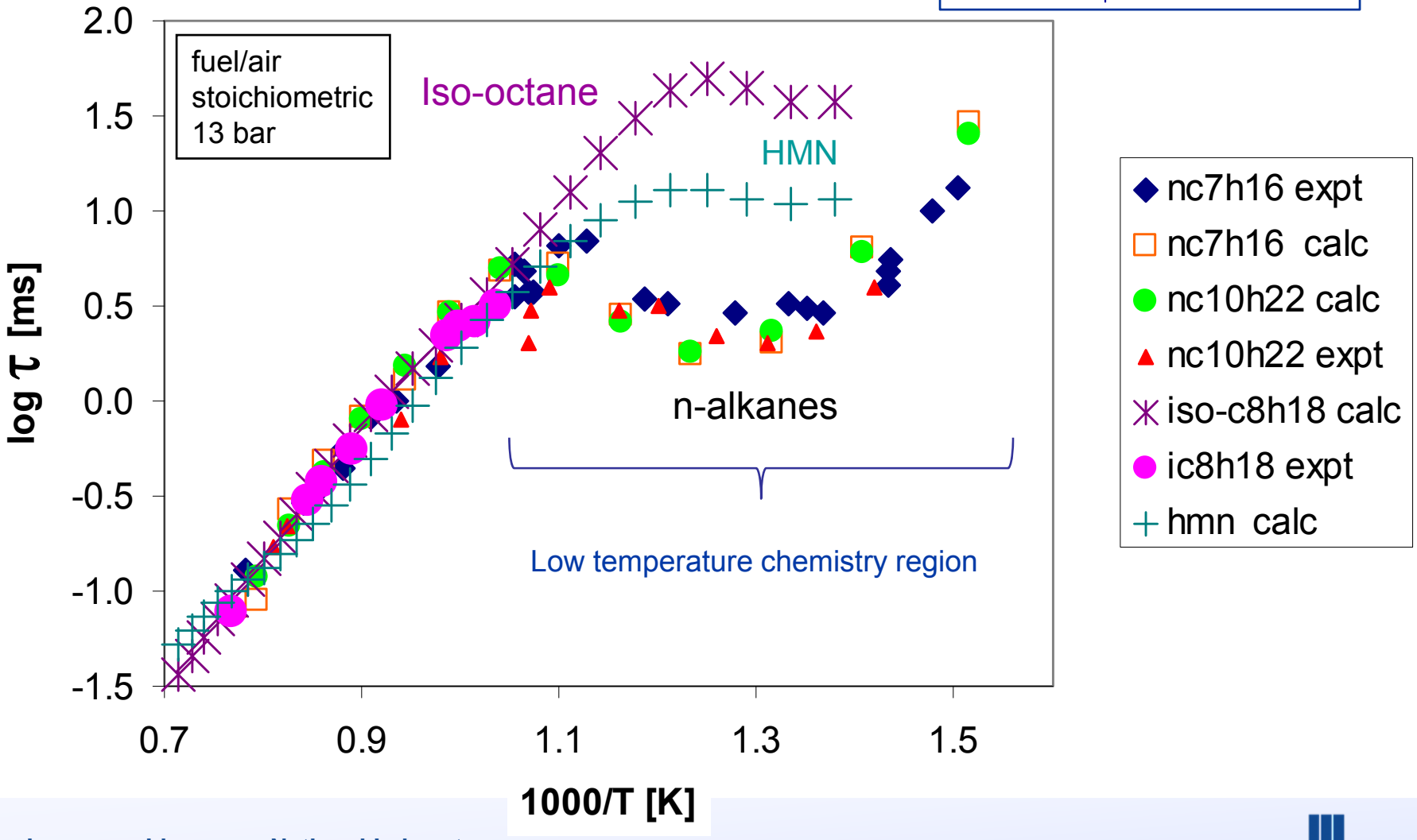


2,2,4,4,6,8,8 heptamethylnonane

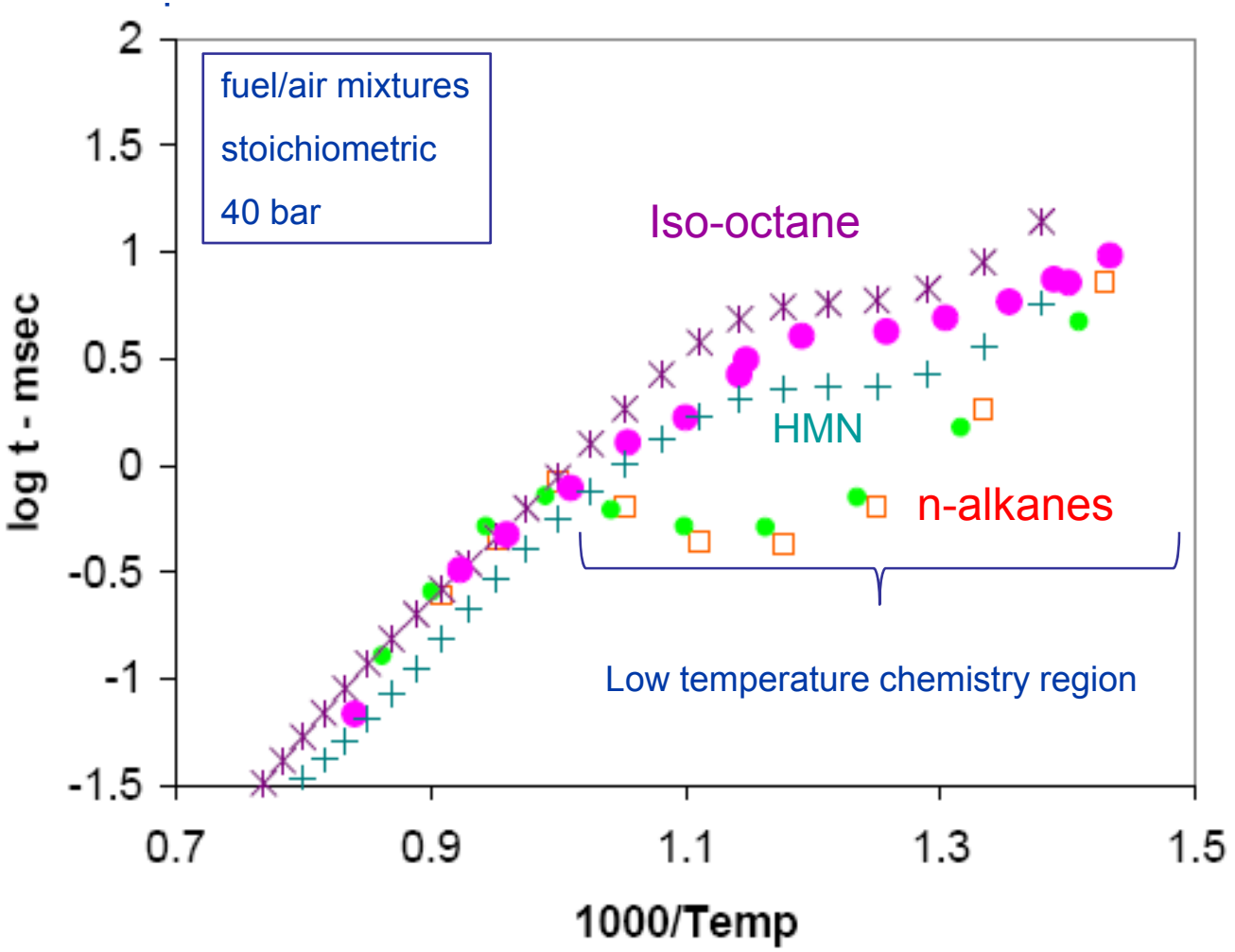
- Iso-octane and HMN are surrogate components useful for Fischer-Tropsch fuels that can be bio-derived
- Mechanism includes low and high temperature reactions => can examine low temperature combustion strategies in engines
- 1114 species
- 4468 reactions
- No fundamental laboratory experiments were originally available on HMN for mechanism validation

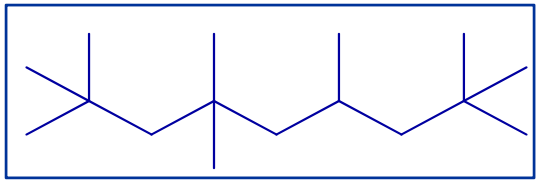
Reactivity for HMN is between those of iso-octane and large n-alkanes

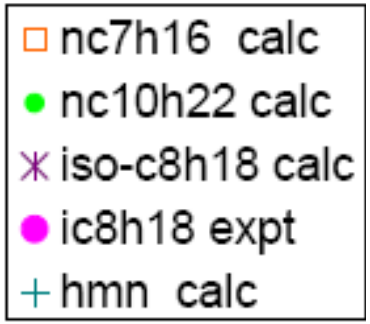




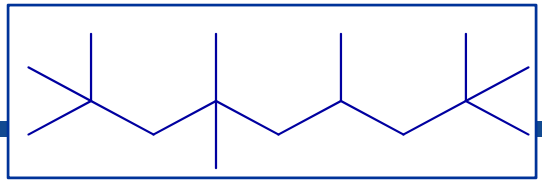
Similar behavior seen at 40 bar

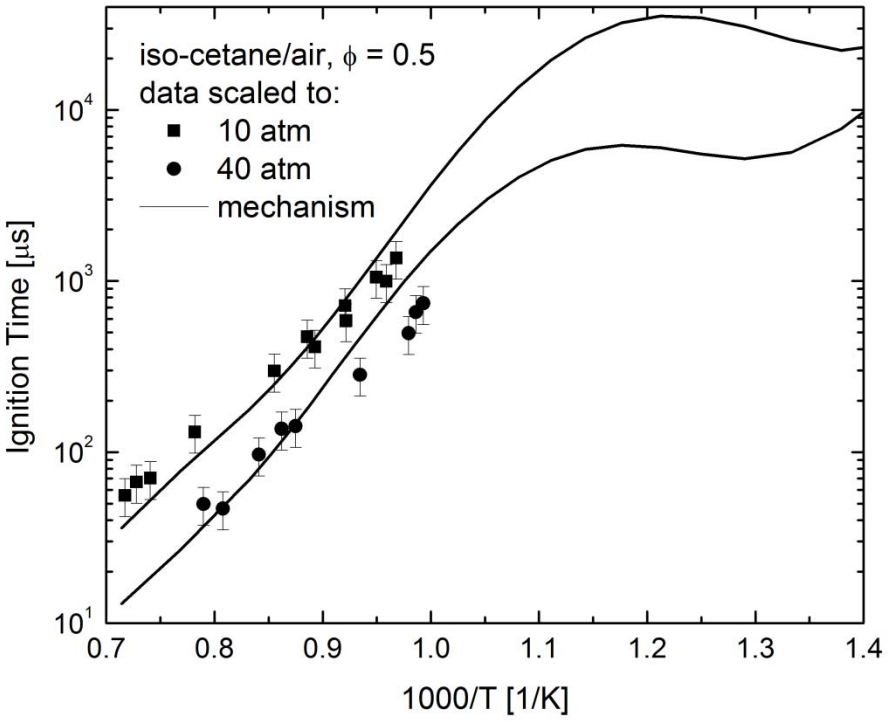


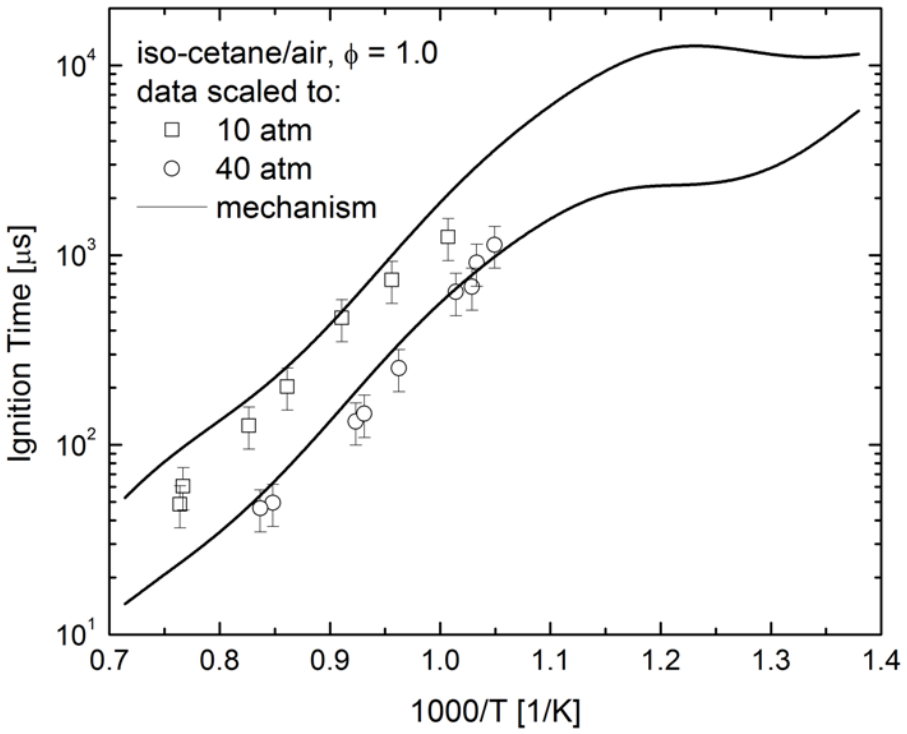




Recent experimental results show excellent agreement with modeling for HMN

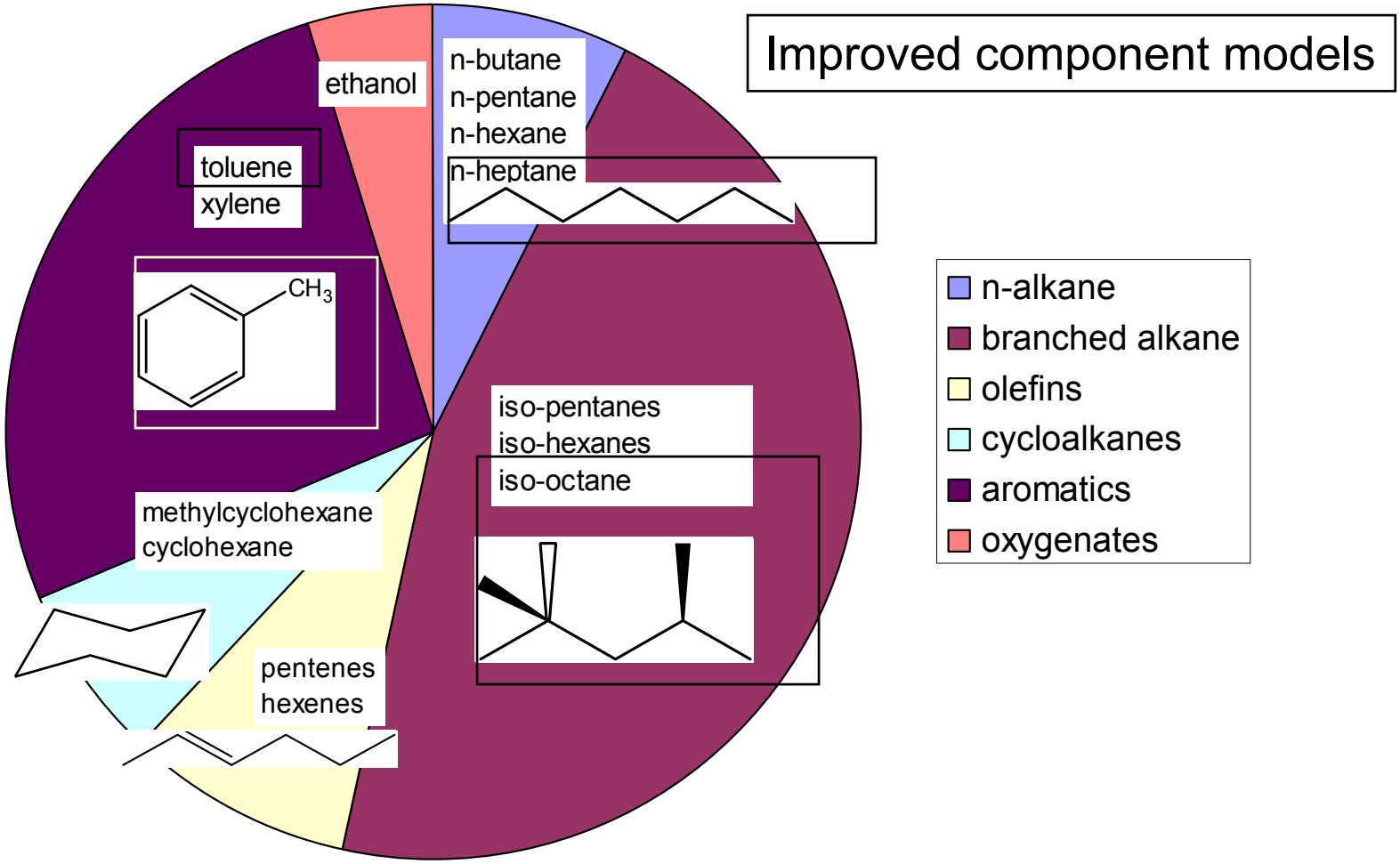




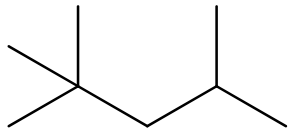


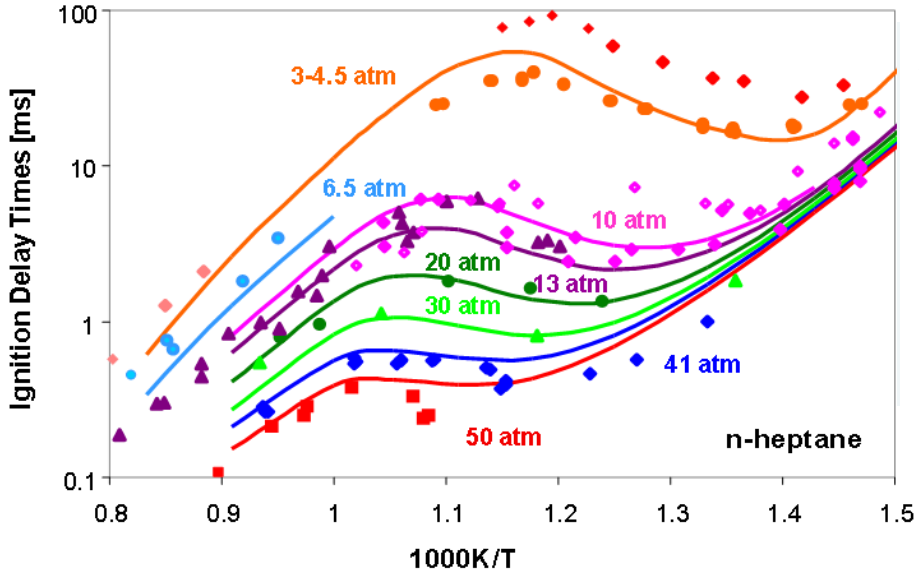
Experimental data shock tube data on iso-cetane (or HMN) from Oehlschlaeger et al, Rensselaer Polytechnic Institute, 2009

Recent improvements to fuel surrogate models: Gasoline



n-Heptane and iso-octane behave well over a wide pressure and temperature range





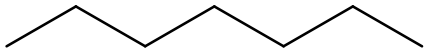
Shock tube and rapid compression machine validation of n-heptane & iso-octane mechanisms:

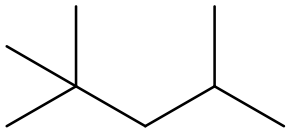
n-heptane:

P = 3 - 50 atm

T = 650K - 1200K

Φ= 1



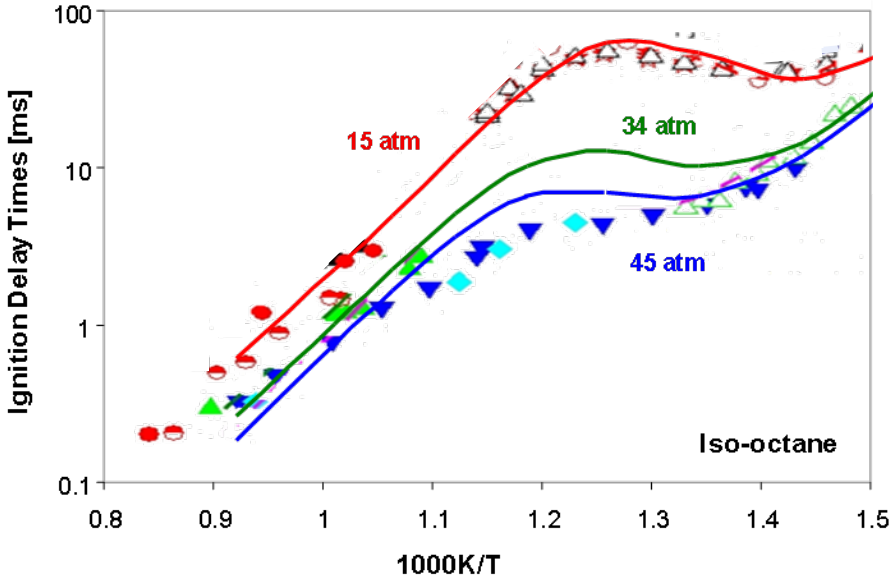


iso-octane:

P = 15 - 45 atm

T = 650K - 1150K

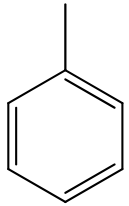
Φ= 1

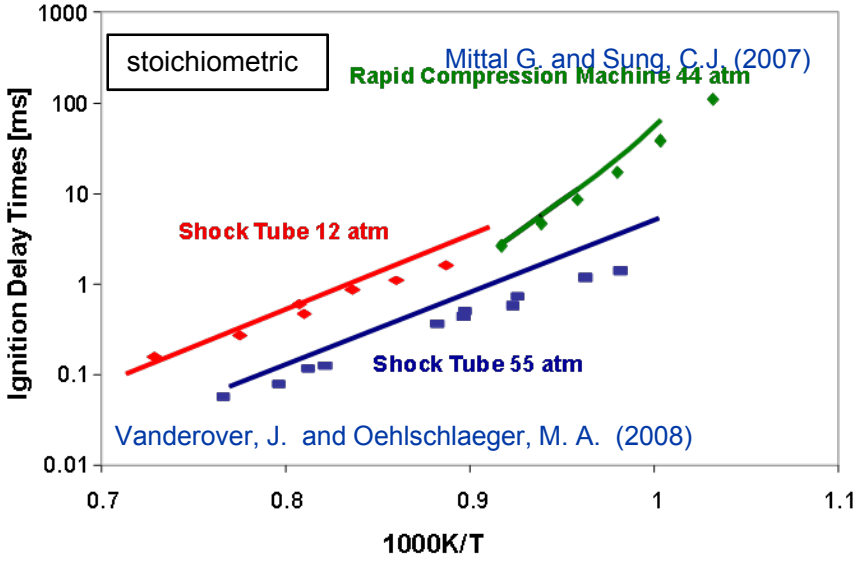


Significant improvements over the whole range of pressures

Minetti R., M. Carlier, M. Ribaucour, E. Therssen, L. R. Sochet (1995); H.K.Ciezki, G. Adomeit (1993); Gauthier B.M., D.F. Davidson, R.K. Hanson (2004); Mittal G. and C. J. Sung,(2007); Minetti R., M. Carlier, M. Ribaucour, E. Therssen, L.R. Sochet (1996); K. Fieweger, R. Blumenthal, G. Adomeit (1997).

After much development work, toluene mechanism behaves quite well

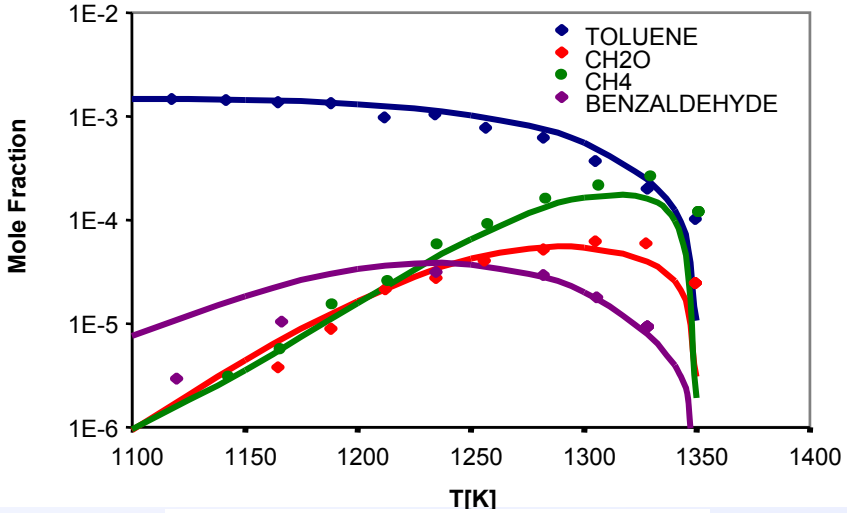




Good agreement with experimental measurements

The model explains the differences between the ignition delay times obtained in shock tube and rapid compression machine experiments

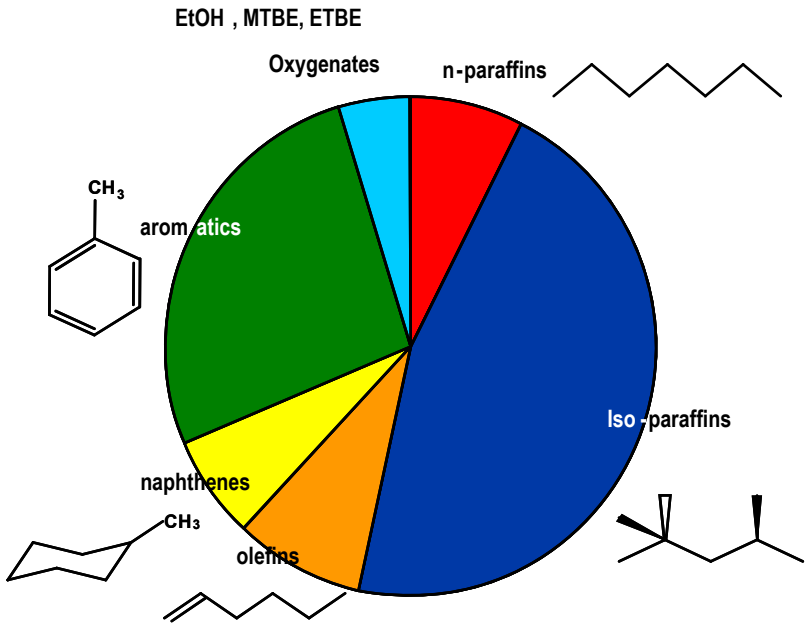
Species profiles measured in a jet stirred reactor are correctly reproduced as well
P = 1 atm
T = 0.1s

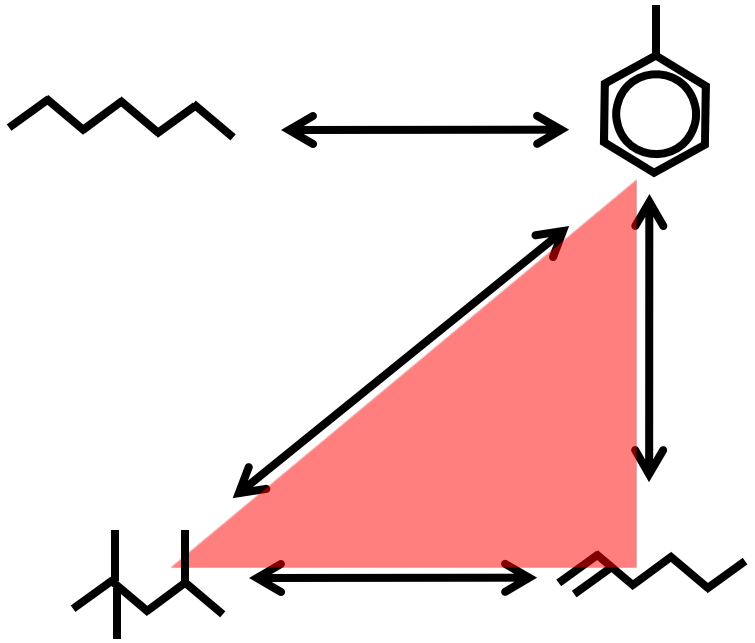


Dagaut, P., G. Pengloan, Ristori, A. (2002)

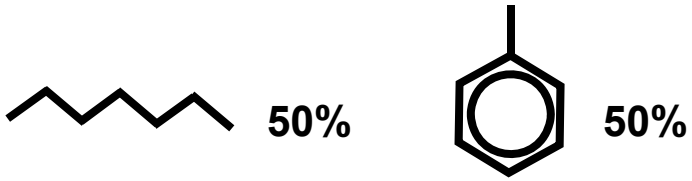
Examined binary and surrogate mixtures relevant to gasoline fuels

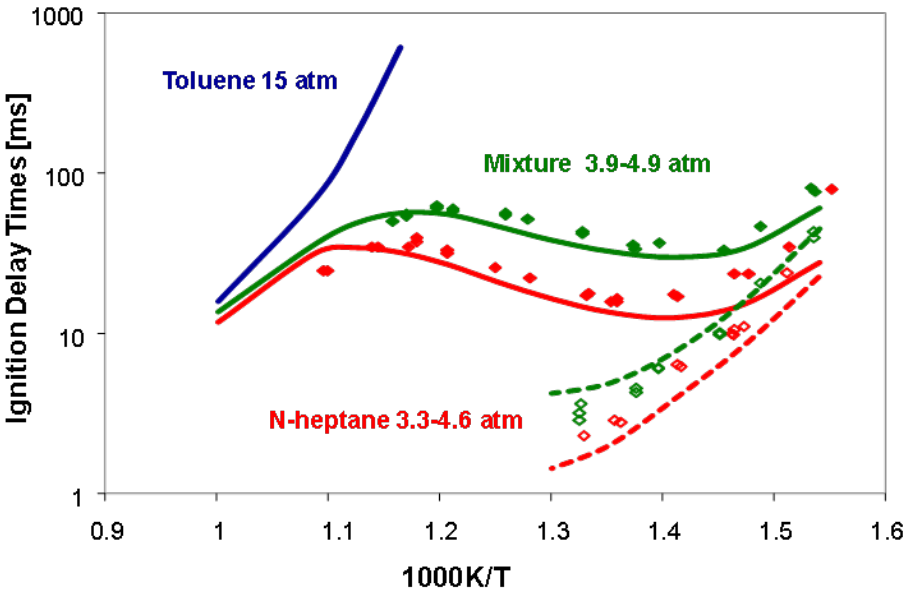
Gasoline fuel surrogate palette

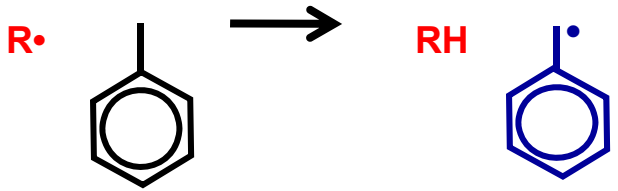




Mechanism simulates well n-heptane/toluene mixtures in a rapid compression machine





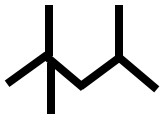


Allylic site on toluene depresses reactivity of mixture by formation of unreactive benzyl radicals

Toluene delays the low temperature heat release and high temperature ignition

Experiments: Vanhove, G., Minetti, R., Petit, G. (2006)

Iso-octane/toluene mixtures well simulated



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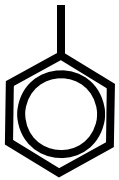

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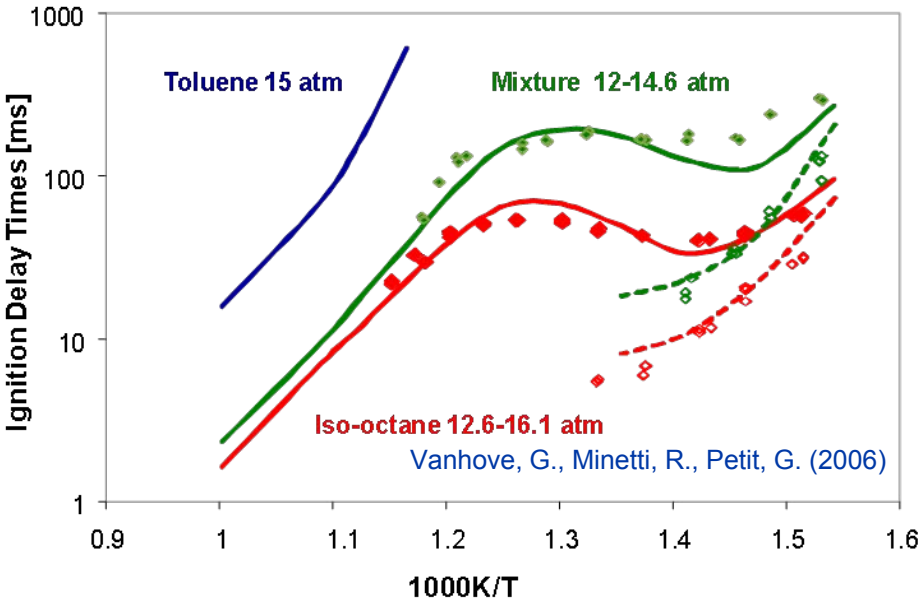
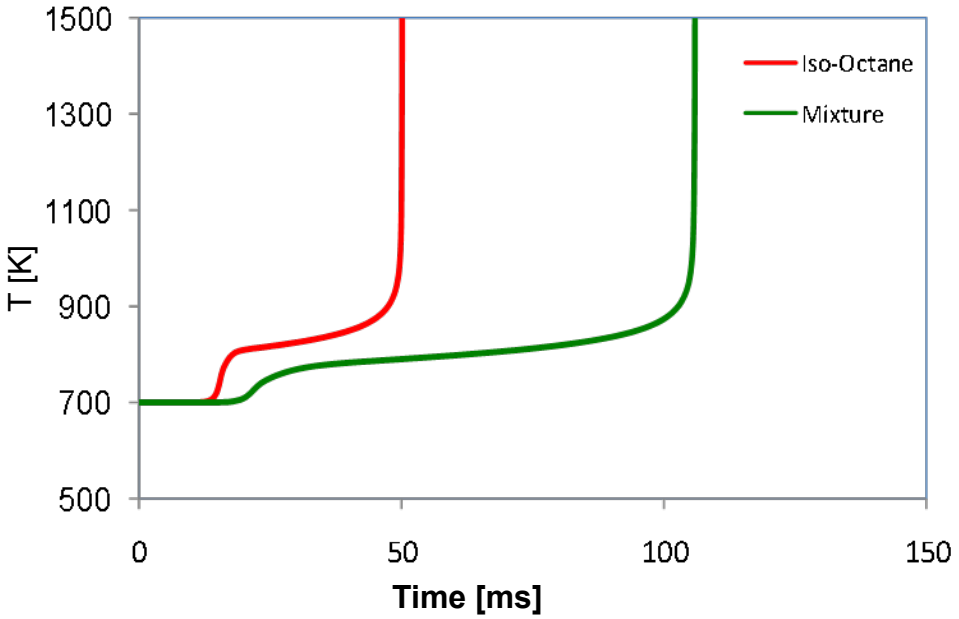
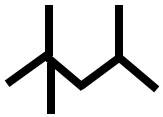




Interactions similar to those observed for n-heptane

Toluene addition lowers low temperature heat release and delays high temperature ignition

Iso-octane/1-hexene mixtures well simulated



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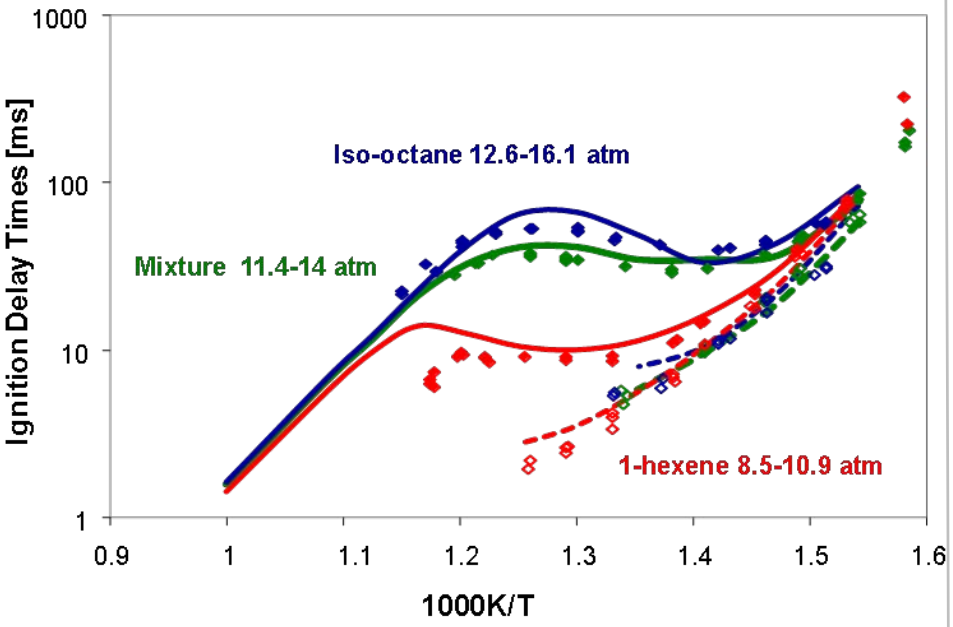
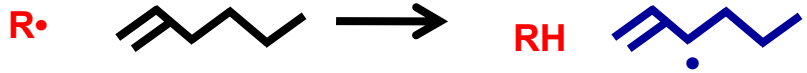
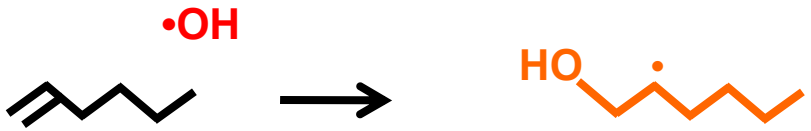


Experimental data: Vanhove, G., Minetti, R., Petit, G. (2006)



Allylic site on 1-hexene depresses reactivity of mixture

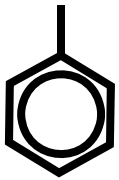
Some low temperature reactivity from 1-hexene



Radical Scavenging from the double bond

Reasonable agreement for toluene/1-hexene mixtures

30%



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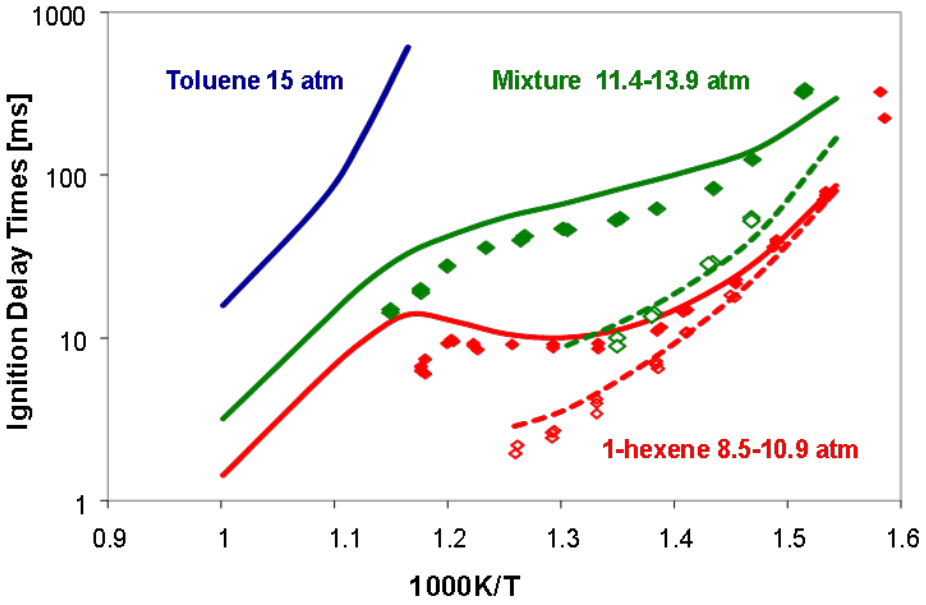
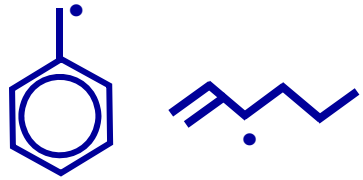


Experimental data: Vanhove, G., Minetti, R., Petit, G. (2006)

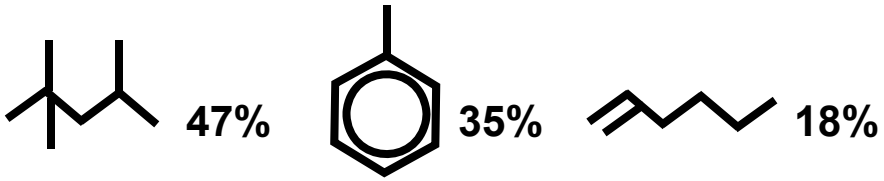


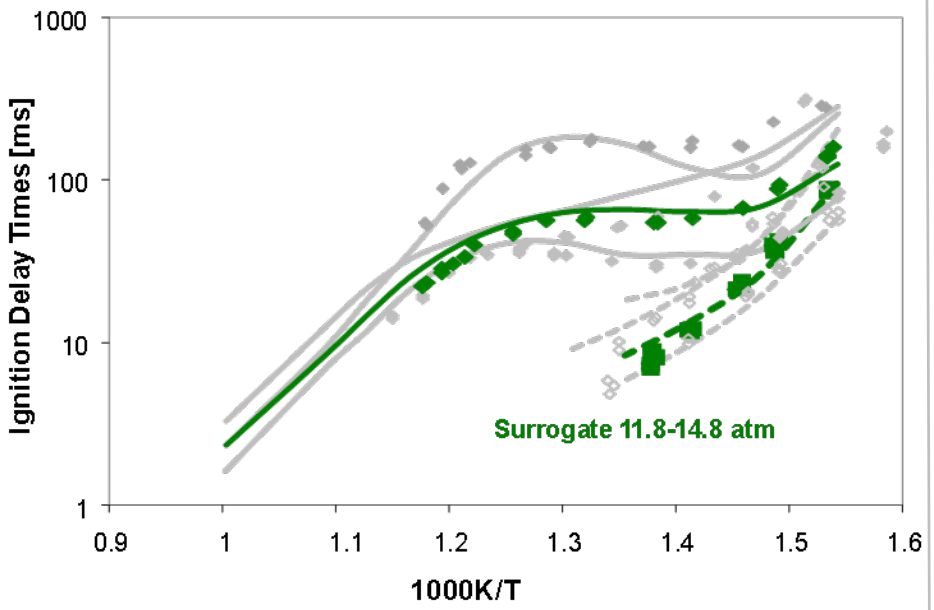
Formation of allylic radicals suppresses reactivity

Ketohydroperoxides + OH

Some low temperature reactivity from 1-hexene

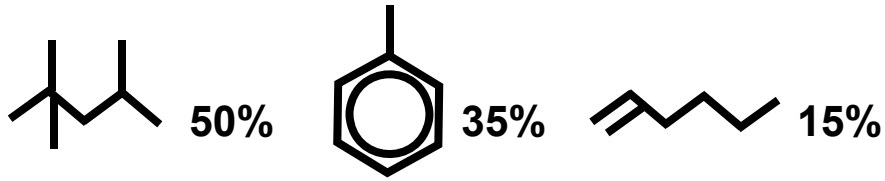
Gasoline surrogate well simulated

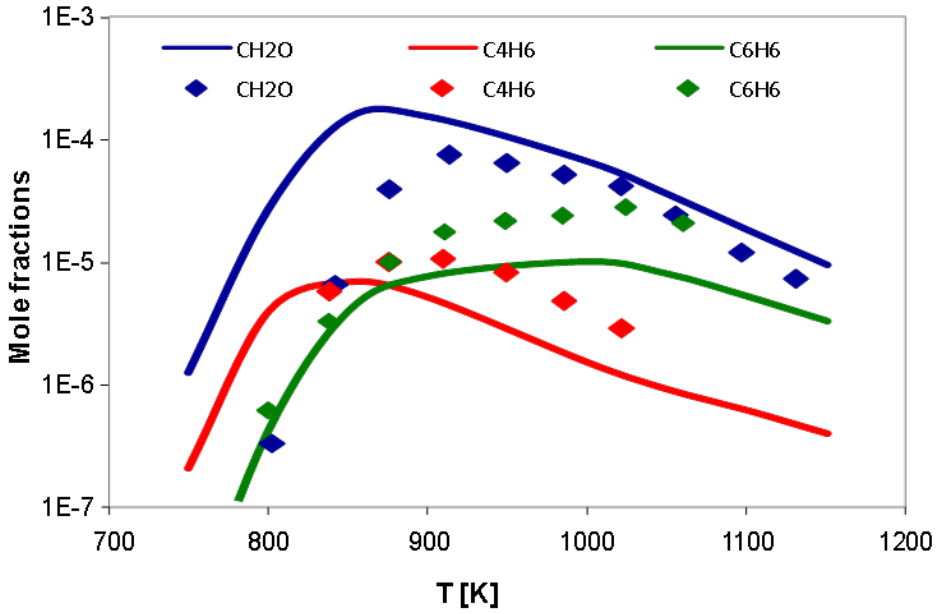




Rapid compression machine validation

Experiments: Vanhove, G., Minetti, R., Petit, G. (2006)



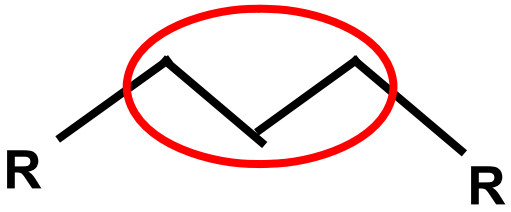


Jet stirred reactor validation: 10 atm, τ = 0.5 s

Experiments: M. Yahyaoui, N. Djebaïli-Chaumeix, P. Dagaut, C.-E. Paillard, S. Gail (2007)

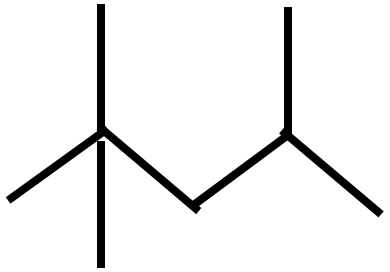
Key component interactions identified

n-alkane



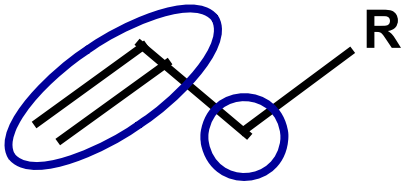
Long unsaturated chain promotes low temperature reactivity

Iso-alkane



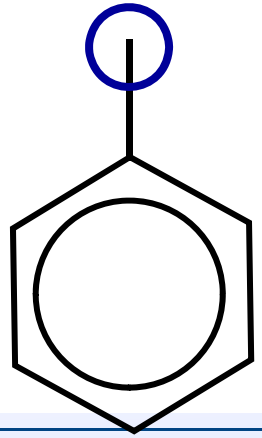
Primary sites reduce reactivity – substitutions on the chain interfere with isomerizations

n-alkene



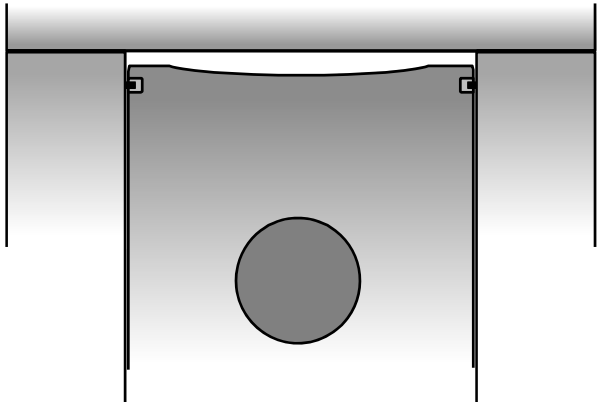
Double bonds act as radical scavenger – allylic sites depress reactivity

toluene

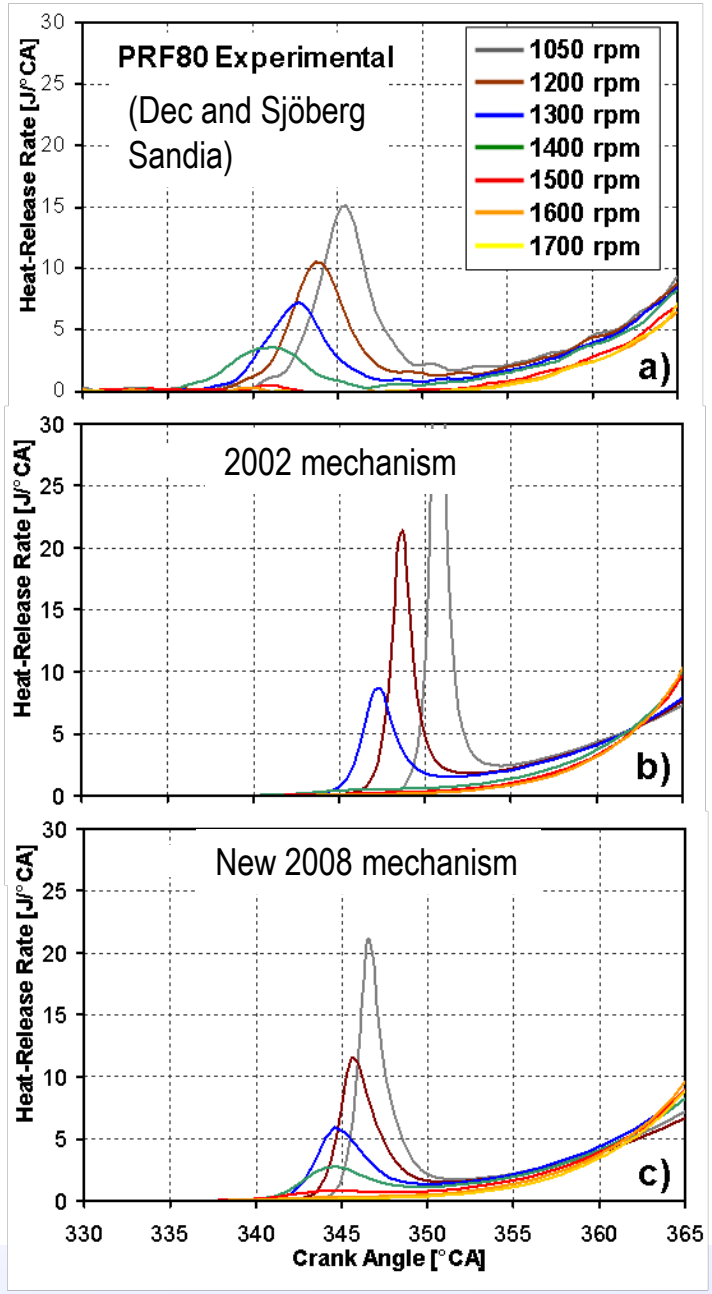


Abstraction on the benzylic site generates stable radicals – suppresses reactivity

HCCI engine results:



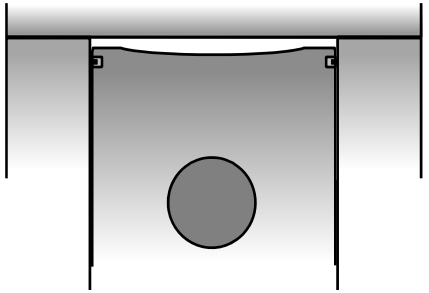
Better simulation of heat release rate



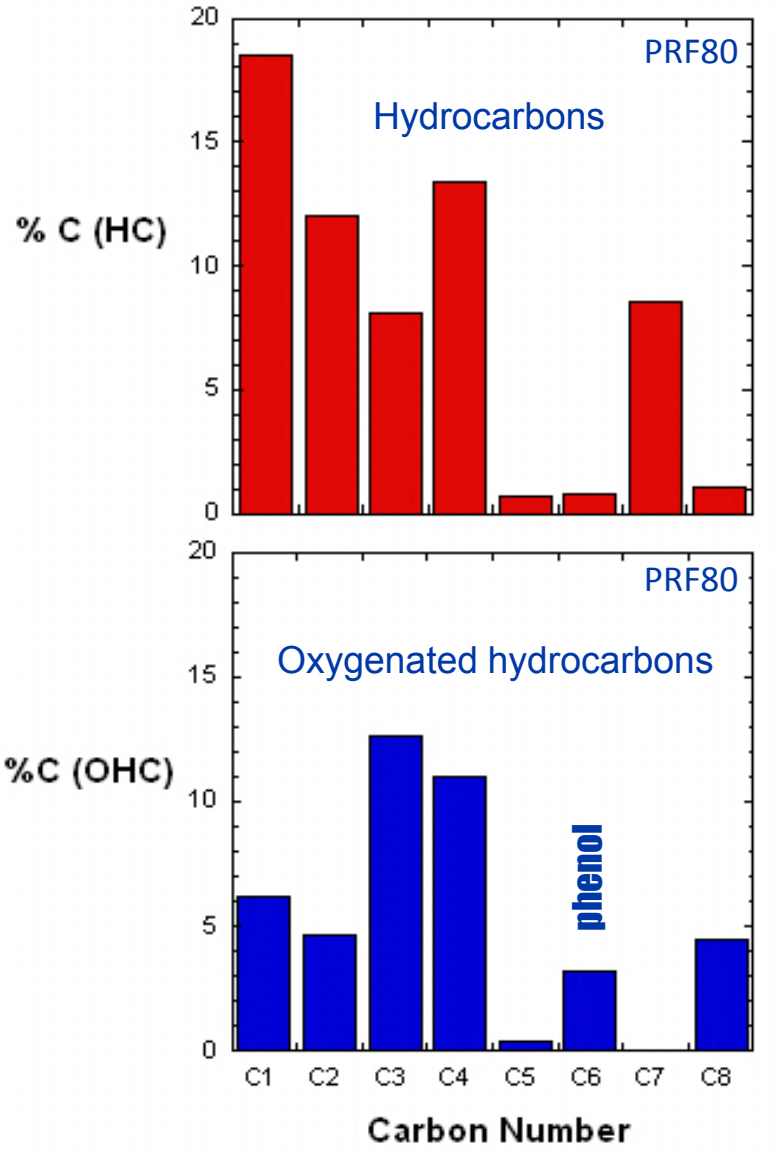
PRF80 fueling

We have obtained engine speciation data for validation of HCCI KIVA multizone model with detailed chemical kinetics

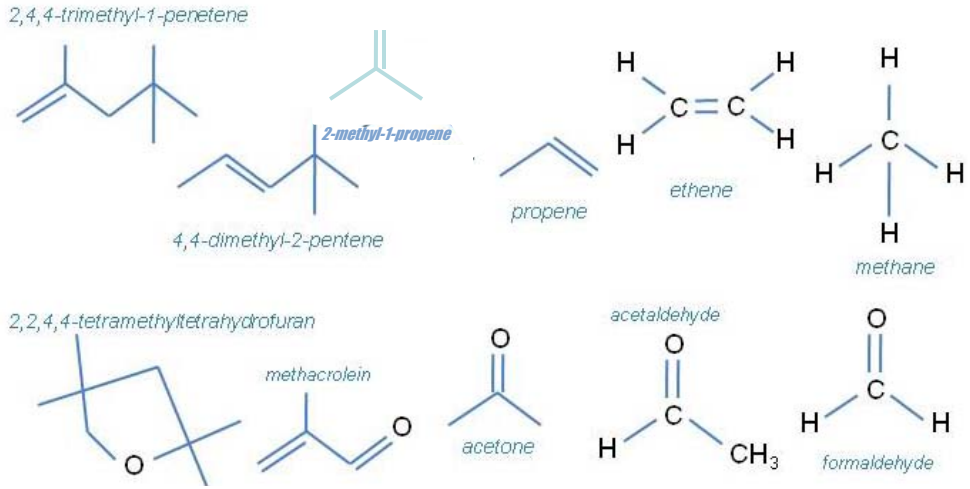
- Lee Davisson (LLNL) in collaboration with John Dec and Magnus Sjöberg, Sandia
- Expanded sample standards to 25 neat materials, including oxygenated hydrocarbons
- Developed HPLC method for derivatized C1-C5 aldehydes and ketones
- Collected and measured HCCI exhaust species using PRF80 fuel in Sandia engine
  - Pre-mix phi sweep from 0.32 to 0.08 equivalence ratio
  - Collected several at near misfire conditions
  - Analytical work 95% complete
  - Data analysis ongoing
    - e.g., comparison to previous gasoline and isooctane results



PRF80 Initial Species Results



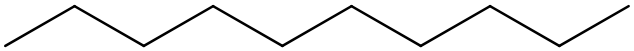
- Greater than 50 identifiable species in the exhaust
- Similarity to results from iso-octane and Chevron-Phillips Reference Gasoline
  - Many species in common, but relative amount varies
- Larger distribution of oxygenated species in near-misfire exhaust conditions



Major exhaust species besides unburned fuel

We collaborate with others to reduce our models for use in reacting flow codes

n-decane

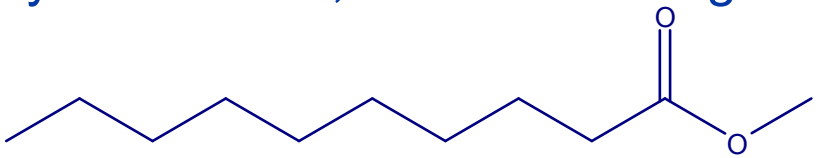


940 species
3887 reactions

⇒

211 species
794 reactions

Methyl-decanoate, biodiesel surrogate

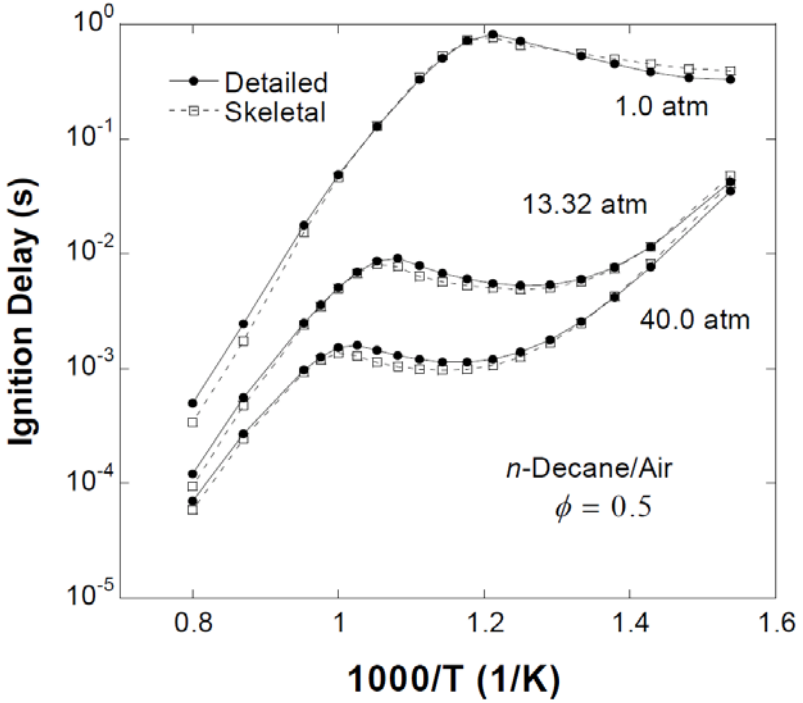


3036 species
8555 reactions

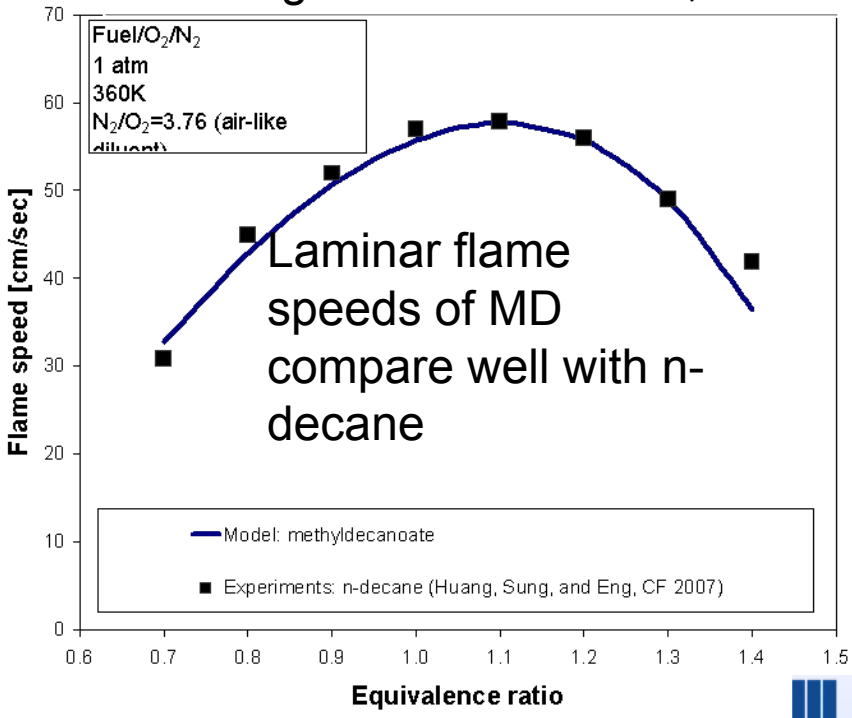
⇒

125 species
712 reactions

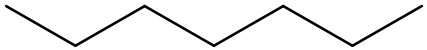
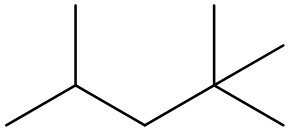
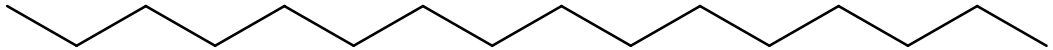
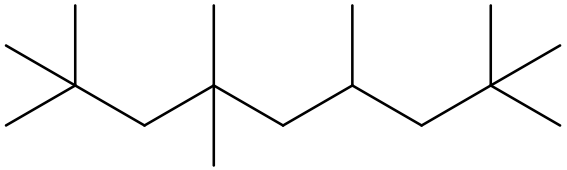
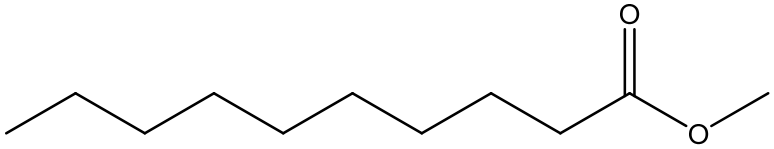
Niemeyer, Raju and Sung, *2009*



Tianfeng Lu and C. K. Law, 2009



We now have state-of-the-art, chemical kinetic models for transportation fuels

- Gasoline
  - n-heptane 
  - iso-octane 
- Diesel
  - n-cetane 
  - iso-cetane 
- Biodiesel 

Mechanisms are available on LLNL website and by email

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

- Hydrogen
- 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
- Dimethyl Carbonate
- Heptane, Detailed Mechanism
- Heptane, Reduced Mechanism
- iso-Octane
- Primary Reference Fuels: iso-Octane / n-Heptane Mixtures
- Organophosphorus Compounds under Incineration Conditions
- Organophosphorus Compounds in Propane Flames
- Organophosphorus Compounds Effect on Flame Speeds

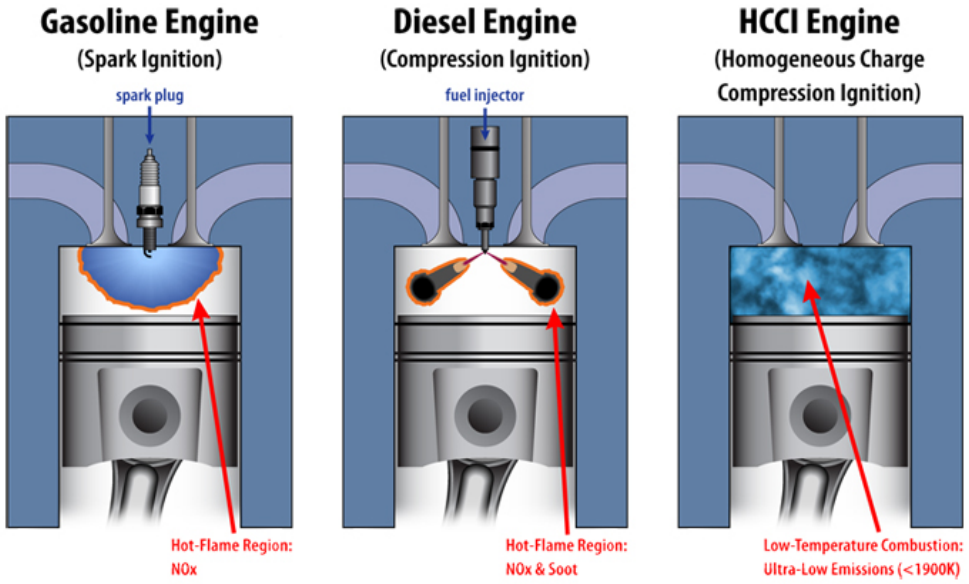
Combustion Chemistry

Go Directly to Mechanisms...

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

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

C8-C16 n-Alkanes



Industry Collaboration

- 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, Univ. of Wisc.)
  - Collaboration with Magnus Sjöberg and John Dec at Sandia on HCCI engine experiments
  - Collaboration with Randy Hessel at Univ. of Wisconsin on CFD simulations.
- Second interaction is participation with universities
  - Collaboration with Curran at National Univ. of Ireland on many fuels
  - Collaboration with Prof. Oehlschaeger at RPI on large alkanes
  - Collaboration with C. K. Law's group, Princeton University on mechanism reduction
  - Collaboration with Prof. Koshi at Univ. of Tokyo on toluene
- Participation in other working groups with industrial representation
  - Fuels for Advanced Combustion Engines (FACE) Working group

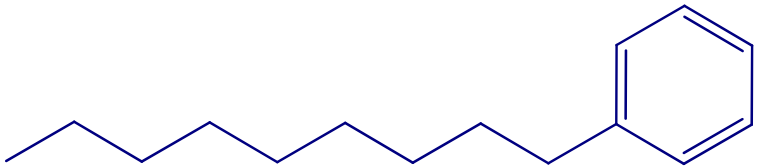
Special recognitions and awards during FY09

- Charles K. Westbrook: Elected to the 2008-2009 Class of Fellows of the Society of Automotive Engineers (SAE).
- Charles K. Westbrook: 2008 Bernard Lewis Gold Medal award by the Combustion Institute.
- Charles K. Westbrook: 2008 - 2012 President of the Combustion Institute.
- William J. Pitz, "Progress in Chemical Kinetic Modeling for Surrogate Fuels," Invited Plenary Lecture, The 7th COMODIA International Conference on Modeling and Diagnostics for Advanced Engine Systems, Sapporo, Japan, July, 2008.

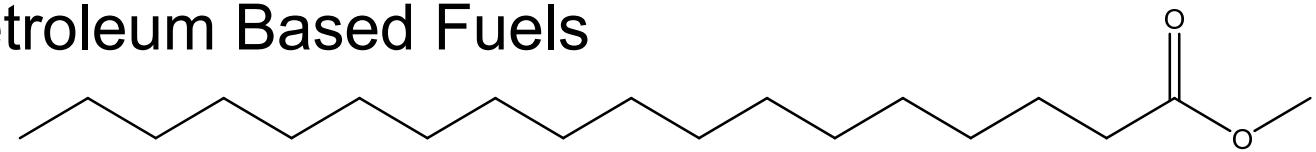
Activities for Next Fiscal Year

Develop detailed chemical kinetic models for:

- large alkyl benzene, important component for diesel fuel

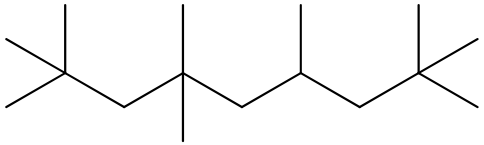


- gasoline surrogate with ethanol
- larger olefins in present gasoline (C5, C6 branched olefins, nC7 olefins) for Advanced Petroleum Based Fuels
- actual biodiesel component (methyl stearate) for Non-Petroleum Based Fuels



Summary

- Approach to research
  - Continue development of surrogate fuel mechanisms to improve engine models for HCCI and diesel engines
- Technical accomplishments:
  - Completed reaction mechanism for the high and low temperature oxidation of heptamethylnonane



- 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:
  - Large alkyl benzene, important component for diesel
  - Gasoline surrogate with ethanol