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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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:

- FY09: 400K
- FY10: 400K

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

- FY10 Objectives:
  - Development of high and low temperature mechanisms for selected higher molecular weight iso-alkanes
  - Development of improved toluene and benzene mechanisms
  - Development of a high and low temperature mechanism for a high molecular weight alkyl-benzene
  - Development of efficient software to create reduced mechanisms for use in multidimensional engine simulation codes

Chemical kinetic milestones

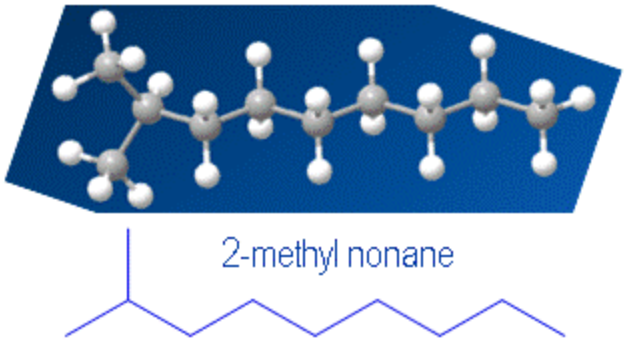
- ✓ December, 2009
  Development of improved toluene and benzene mechanisms
- ✓ May, 2010
  Development of a high and low temperature mechanisms for selected higher molecular weight iso-alkanes
- ▪ September, 2010
  Development of a high and low temperature mechanism for a high molecular weight alkyl-benzene
- ▪ September, 2010
  Development of efficient software to create reduced mechanisms for use in multidimensional engine simulation codes

Approach

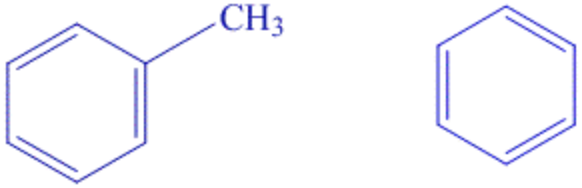
- Develop chemical kinetic reaction models for each individual fuel component of importance for fuel surrogates of gasoline, diesel, and alternative fuels
- Combine mechanisms for representative fuel components to provide surrogate models for practical fuels
  - diesel fuel
  - gasoline (HCCI and/or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

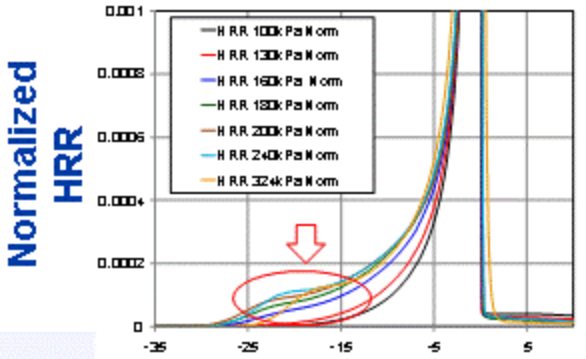
- Assembled high and low temperature model for a series of iso-alkanes, an important chemical class in gasoline and diesel fuels



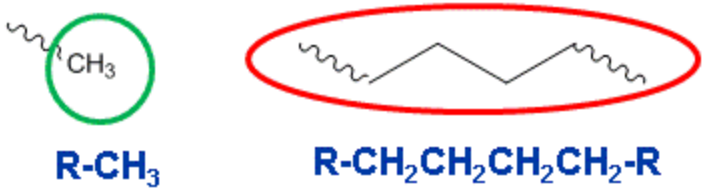
- Improved chemical kinetic models for toluene and benzene, important fuel component and intermediate species, respectively



- Successfully simulated intermediate heat release in Sandia HCCI engine, obtaining new understanding

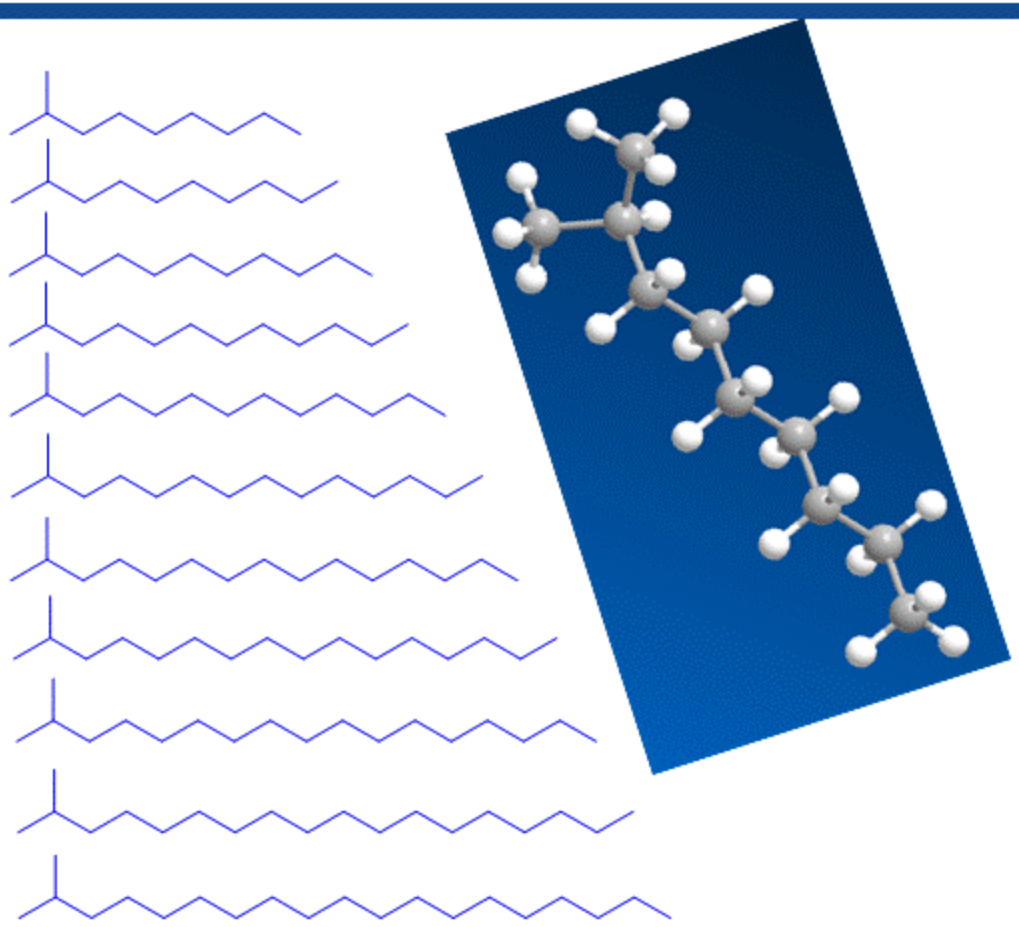


- Developed a functional-group kinetics modeling approach for n-alkanes that greatly reduces the size of the mechanism



n-cetane: 2100 species => 216 species

Assembled chemical kinetic model for a whole series of iso-alkanes to represent this chemical class in gasoline and diesel fuels



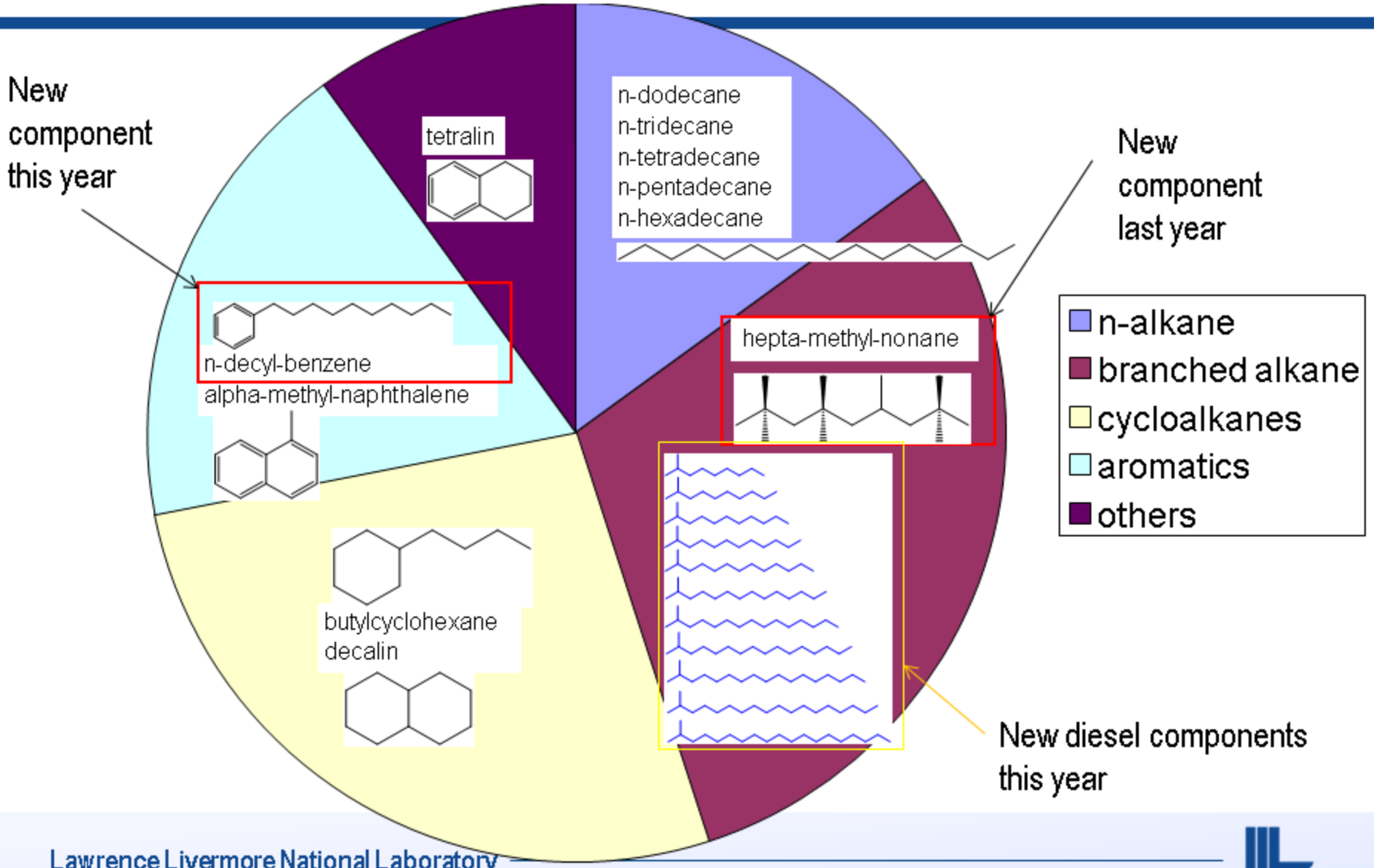
Includes all 2-methyl alkanes up to C20 which covers the entire distillation range for gasoline and diesel fuels

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

7,900 species

27,000 reactions

Diesel Fuel Surrogate palette:

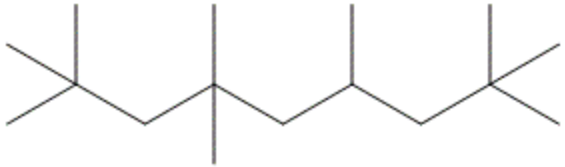


Have assembled primary reference fuel mechanism for diesel fuel

- Diesel PRF:
  - n-cetane

(n-hexadecane)

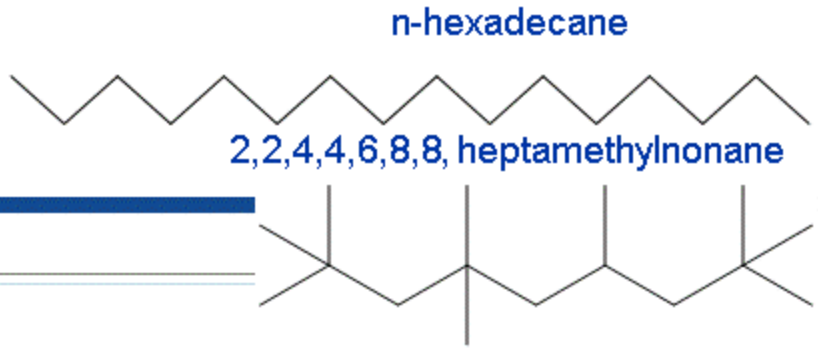
  - iso-cetane

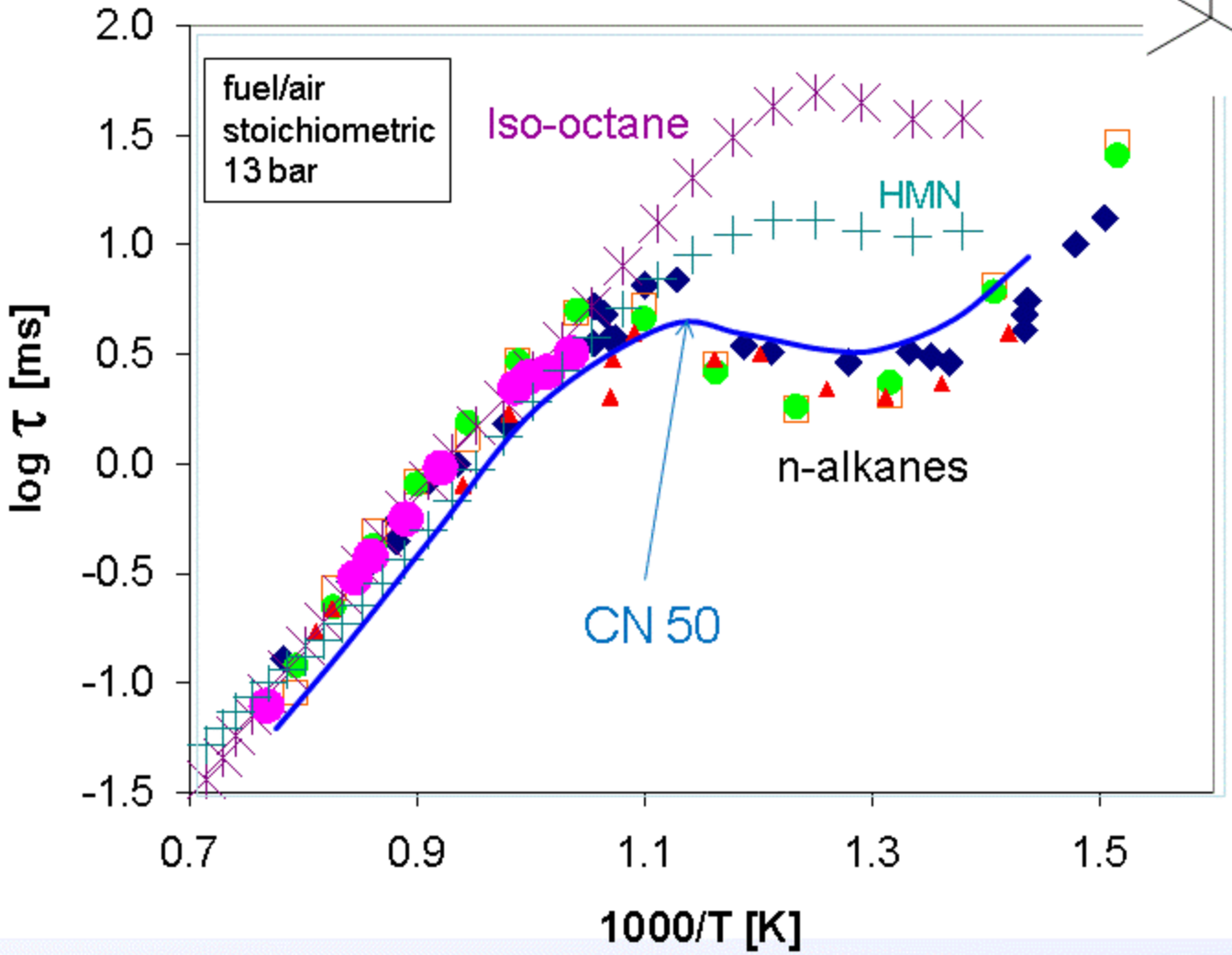


(2,2,4,4,6,8,8-heptamethylnonane)

- PRF for Diesel mechanism:
  - 2,837 species
  - 10,719 reactions

PFR Ignition results at 13 bar:

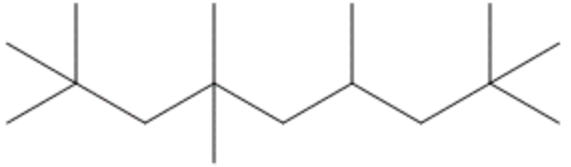


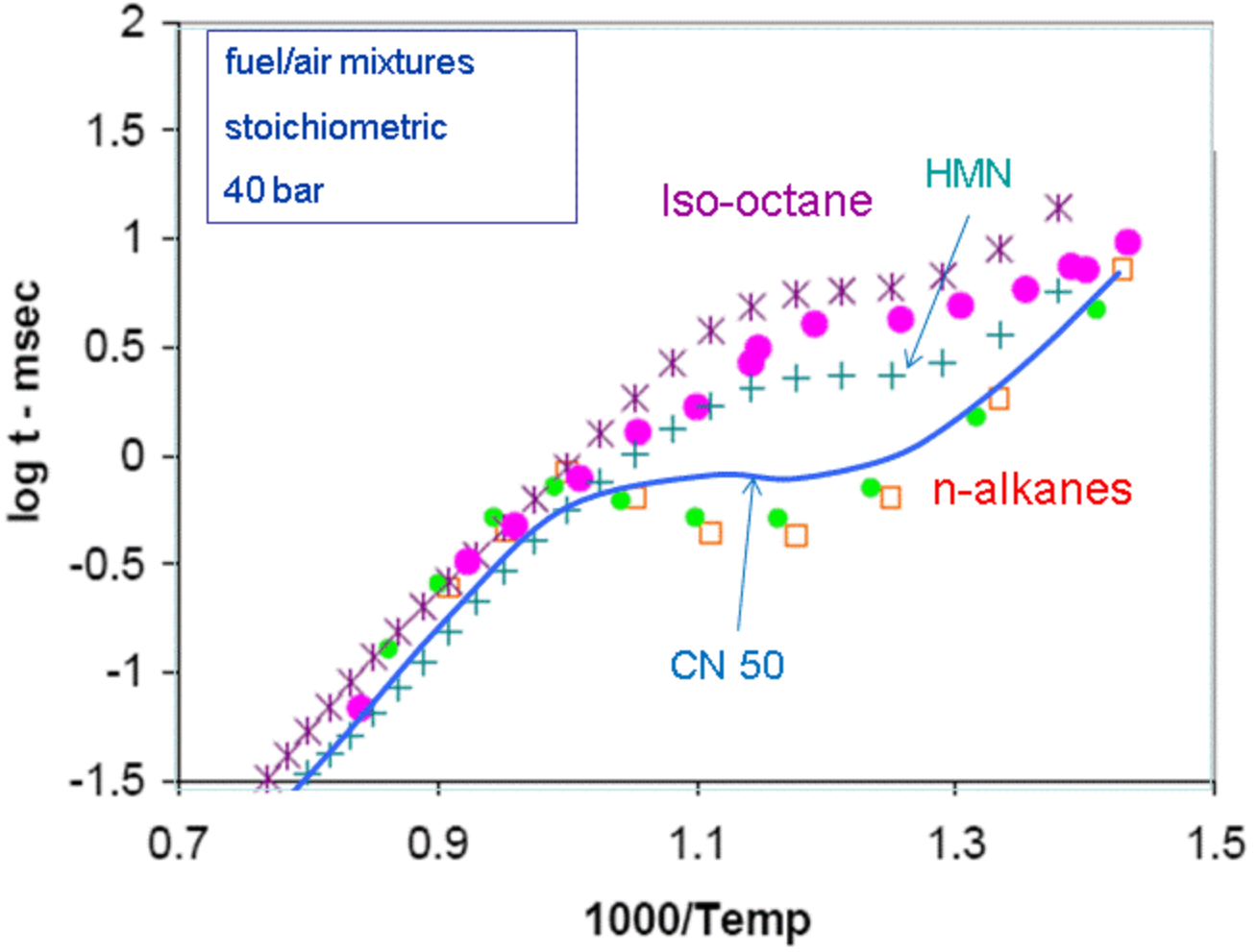


PFR Ignition results at 40 bar:

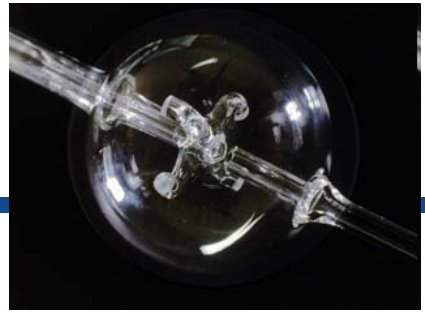
n-hexadecane

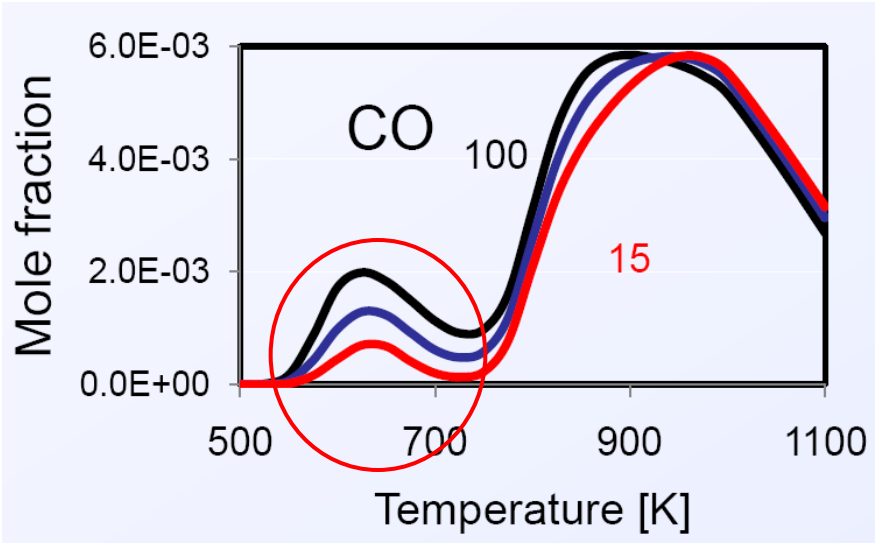
2,2,4,4,6,8,8, heptamethylnonane





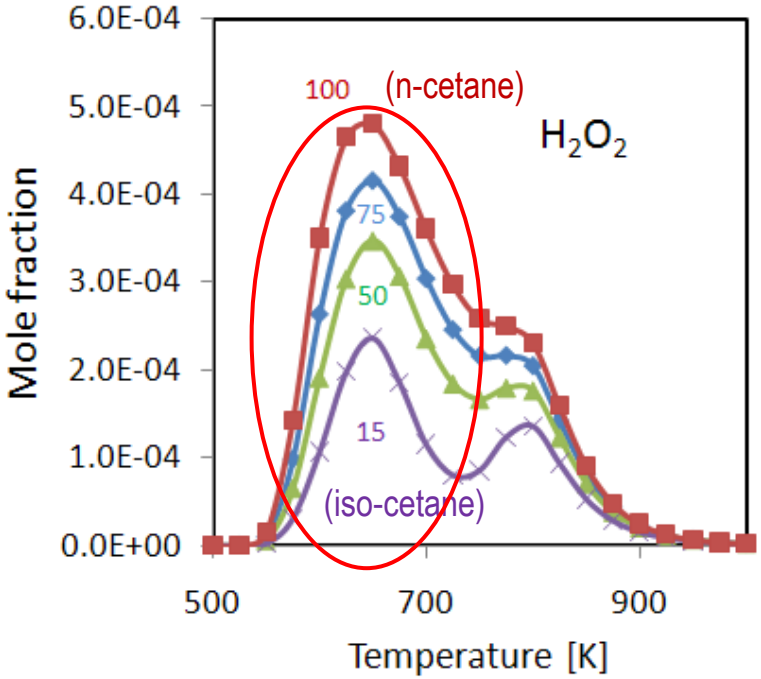
Diesel PRFs: Cetane number has a big effect at low temperatures



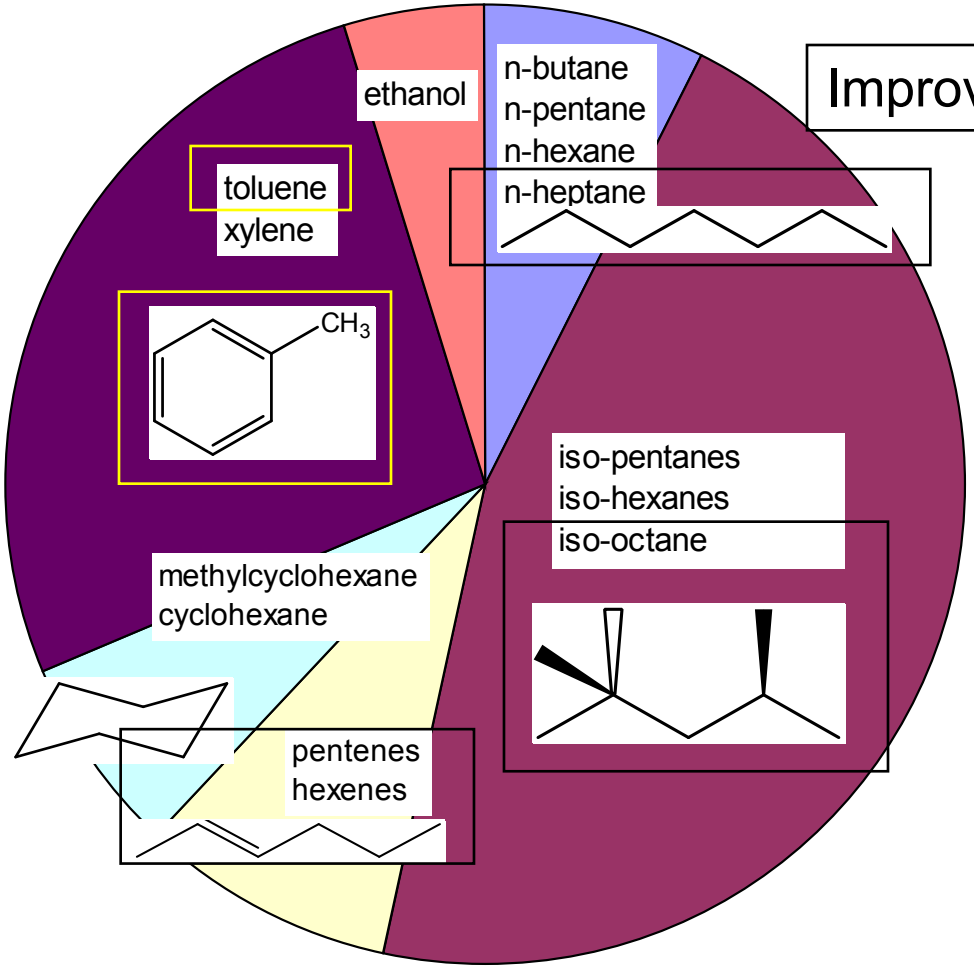


Perfectly stirred reactor
stoichiometric mixtures
10 atm

High cetane PRFs lead to more H2O2 which decomposes to reactive OH radicals



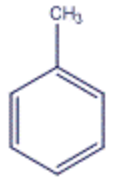
Recent improvements to fuel surrogate models: Gasoline



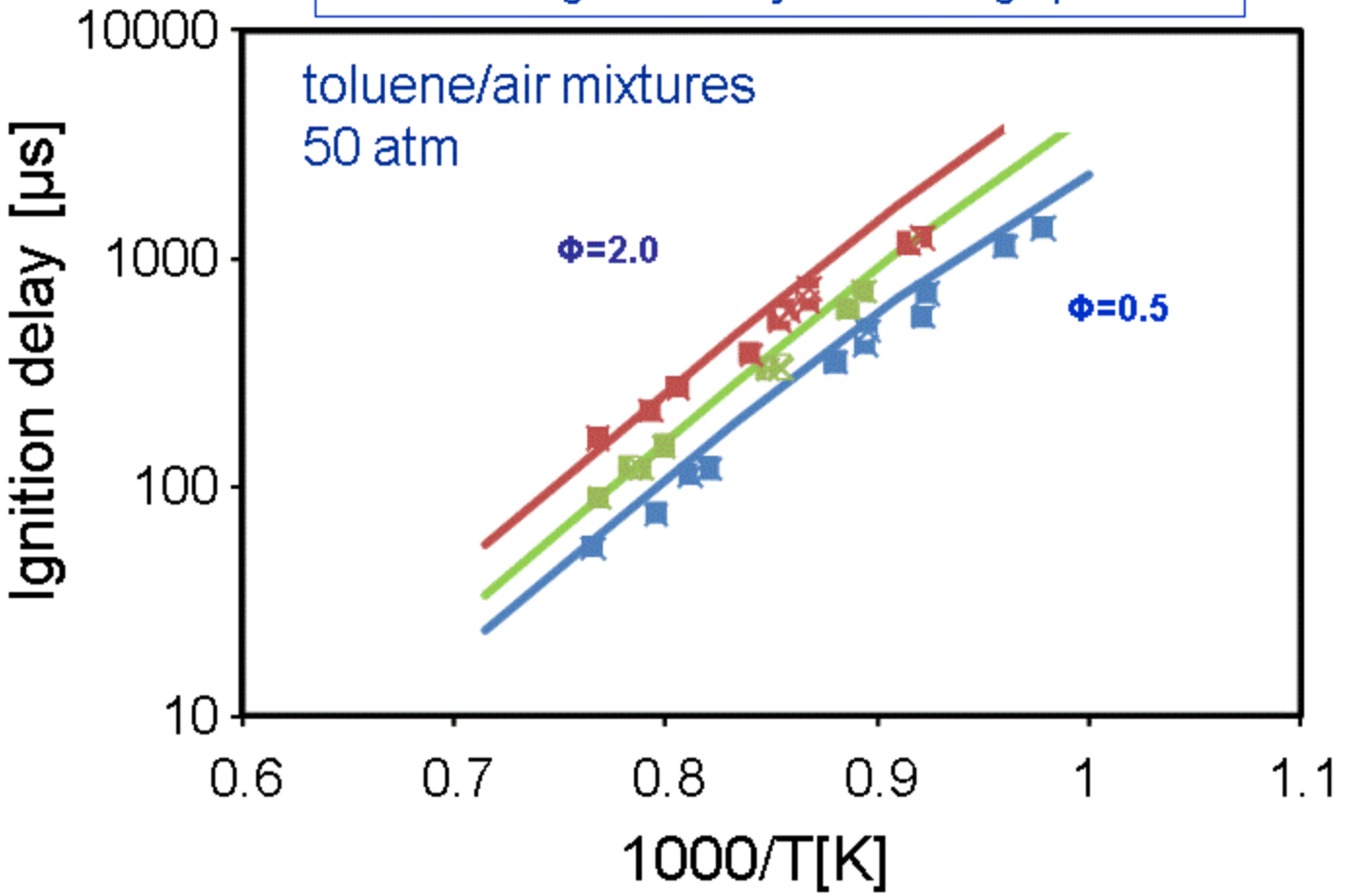
Improved component models

- n-alkane
- branched alkane
- olefins
- cycloalkanes
- aromatics
- oxygenates

Improved toluene model well predicts ignition at high pressure

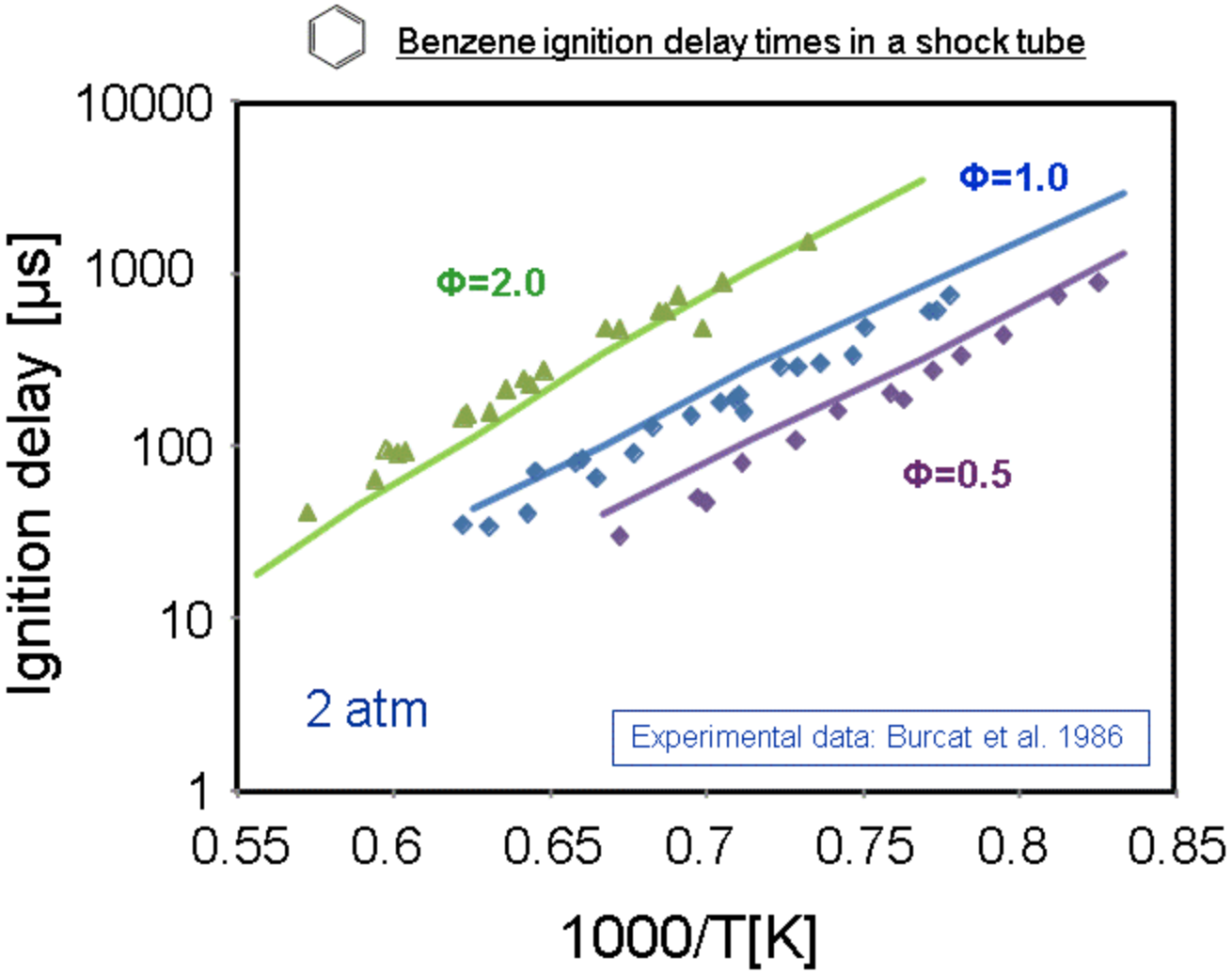


Shock tube ignition delay times at high pressure

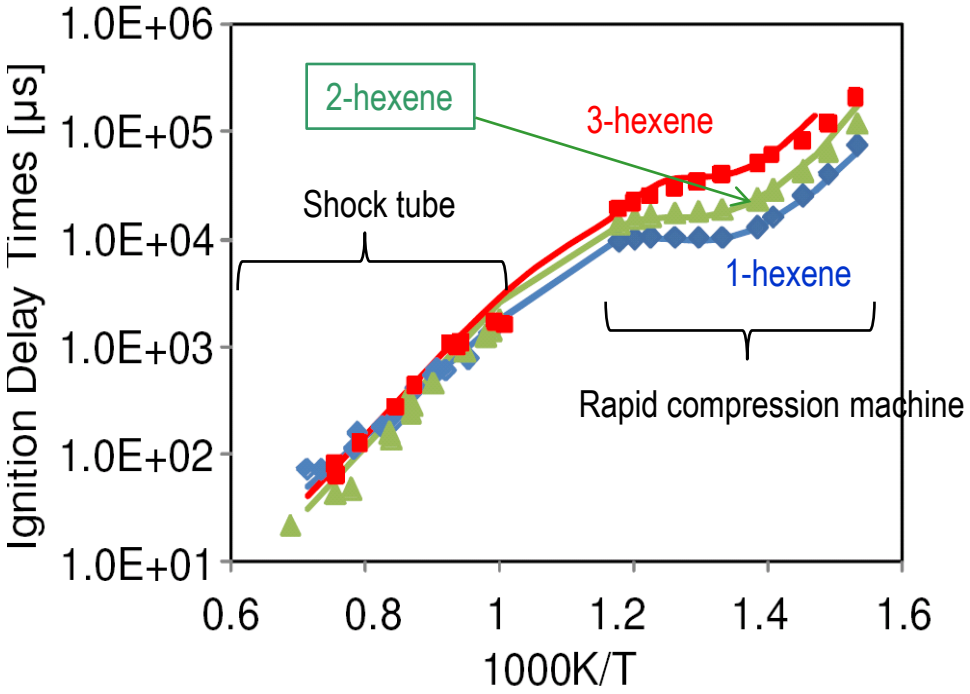


Experimental data: Shen, Vanderover and Oehlschlaeger (2009)

Improving building blocks for toluene: benzene



Improved the predictive behavior of hexenes and pentenes mechanisms over the entire temperature range

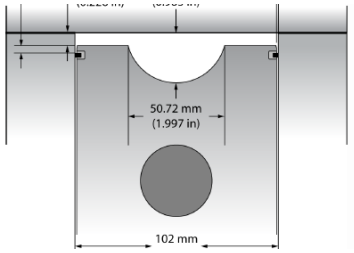


RCM experiments: Vanhove et al. 2007

Shock tube experiments: Yasunaga and Curran, 2010

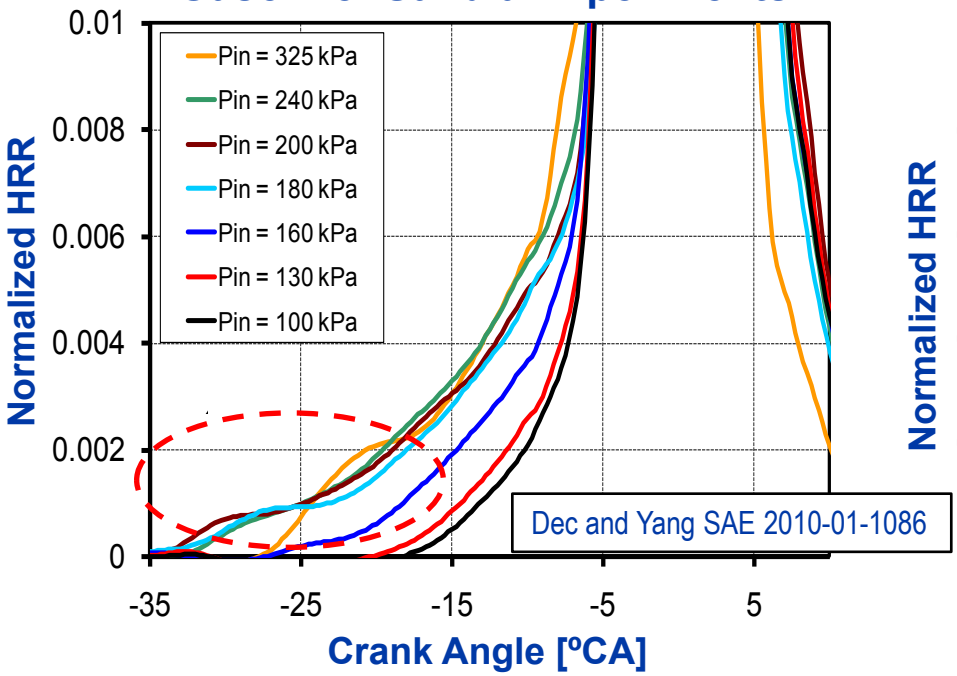
Mehl, Pitz, Westbrook, Yasunaga and Curran, The 33rd International Symposium on Combustion, 2010.

Successful simulation of intermediate heat release in HCCI engine using gasoline surrogate blends

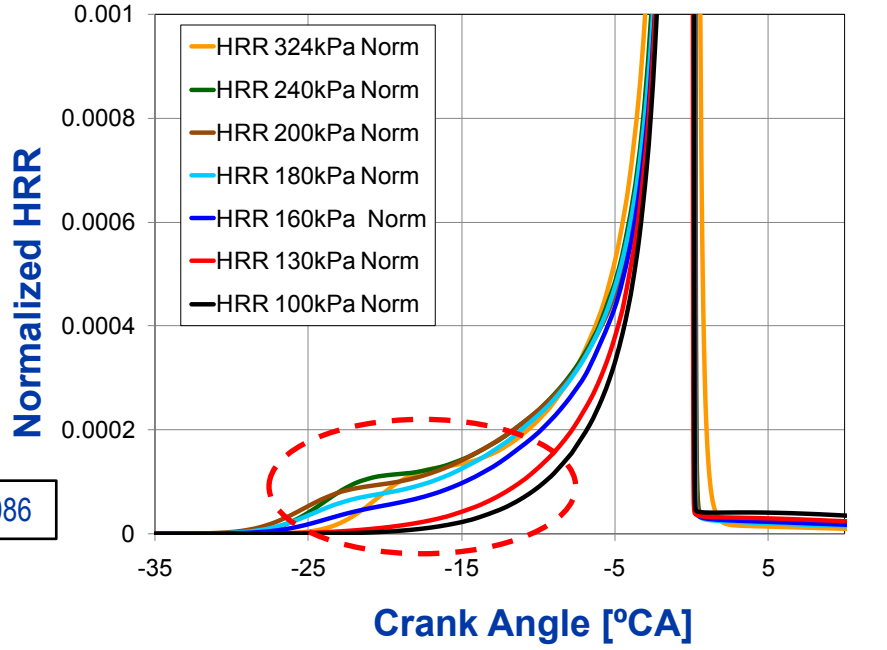


Dec and Yang, 2010: Intermediate heat release allows highly retarded combustion phasing and high load operation with gasoline

Gasoline: Sandia Experiments

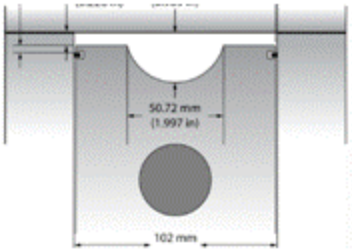


Gasoline Surrogate: Calculations



(Curves are aligned by time of peak heat release and normalized by total heat release)

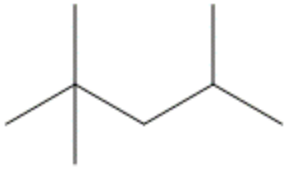
4-component gasoline surrogate: Matched gasoline composition targets and reactivity



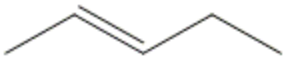
Gasoline surrogate:

n-heptane (n-alkanes)

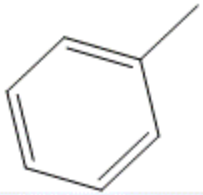
iso-octane (iso-alkanes)



2-hexene (olefins)



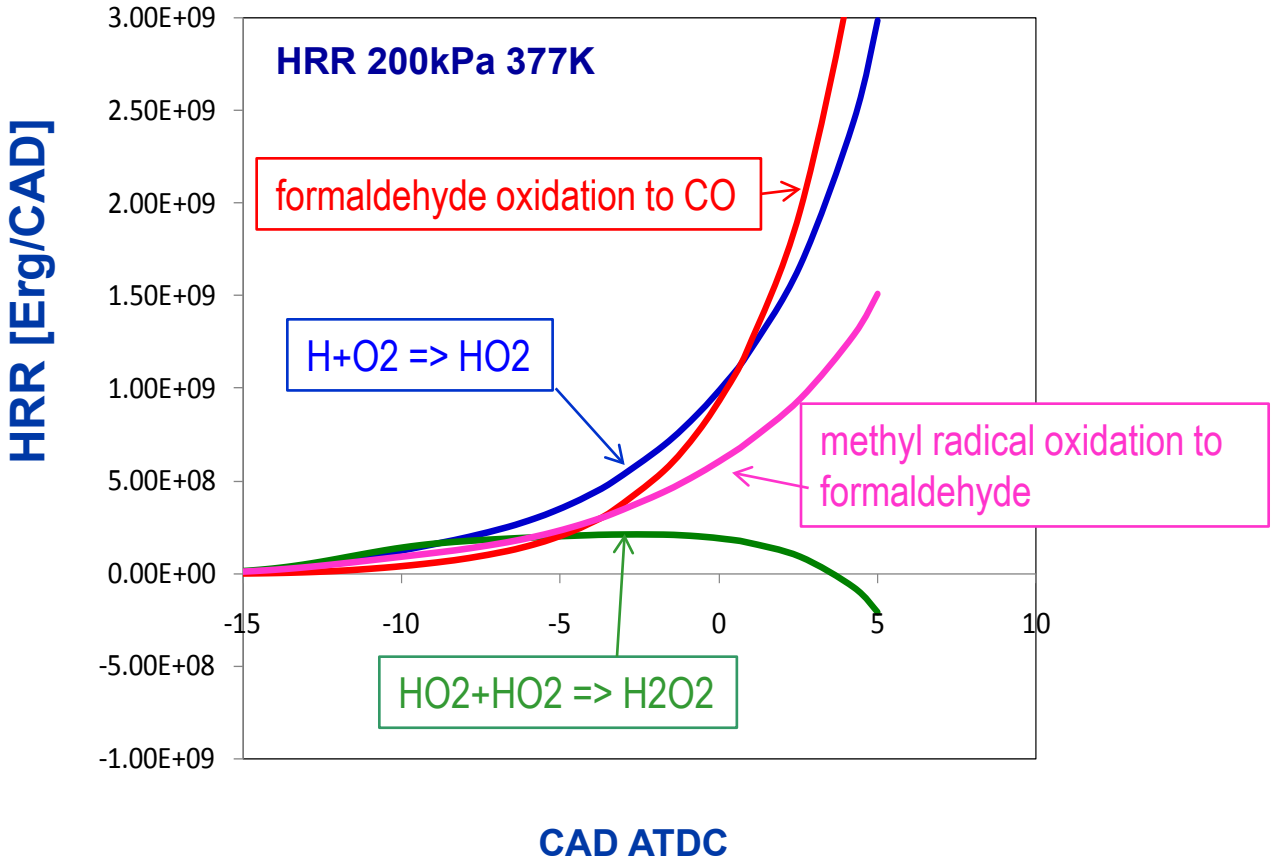
toluene (aromatics)



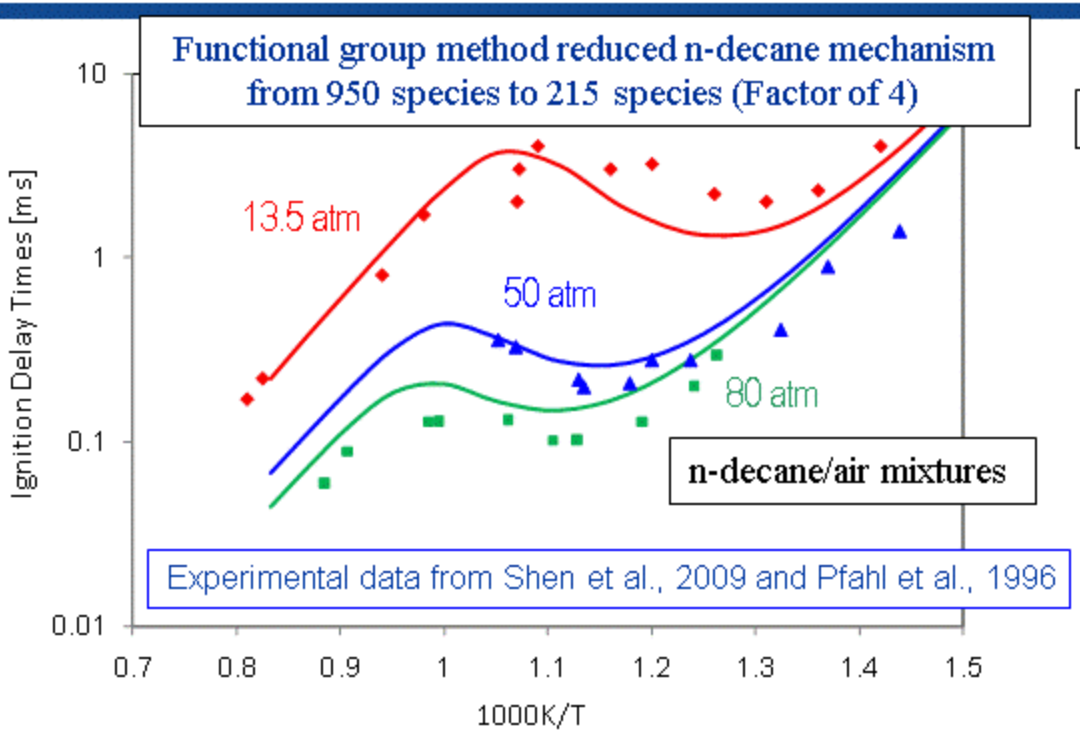
	Surrogate (%Vol)	Gasoline (%Vol)
n-alkanes	0.16	0.731
iso- alkanes	0.57	
olefins	0.04	0.04
aromatics	0.23	0.23
A/F Ratio	14.60	14.79
H/C	1.92	1.95

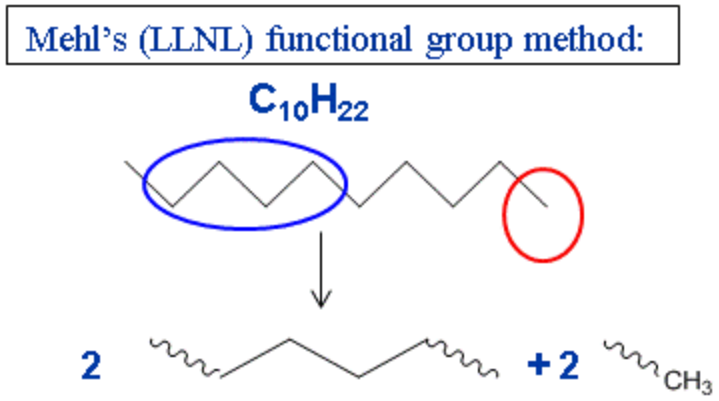
Matched the reactivity of a mixture having the same RON and MON as the gasoline

Reaction contributions to intermediate heat release rate



With the newly available mechanism reduction tools, LLNL mechanisms are being reduced for use in reacting flow codes:





LLNL mechanism	Researchers	Reduction method	Total number species before reduction	Species reduction factor	CPU Speed-up factor
n-cetane	Mehl et al., 2010	Functional group	2116	10	
n-decane	Niemeyer et al., 2010	Directed relational graph	940	5	
PRF for gasoline (n-heptane & iso-octane)	He et al., 2010	On-the-fly			20
n-heptane	Lu and Law, 2009 Prager et al., 2009	Directed relational graph, lumping, QSSA Computational Singular Perturbation	561 561	11 9	
Methyl decanoate (biodiesel surrogate)	Sarathy et al., 2010	Directed relational graph	3034	5	

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

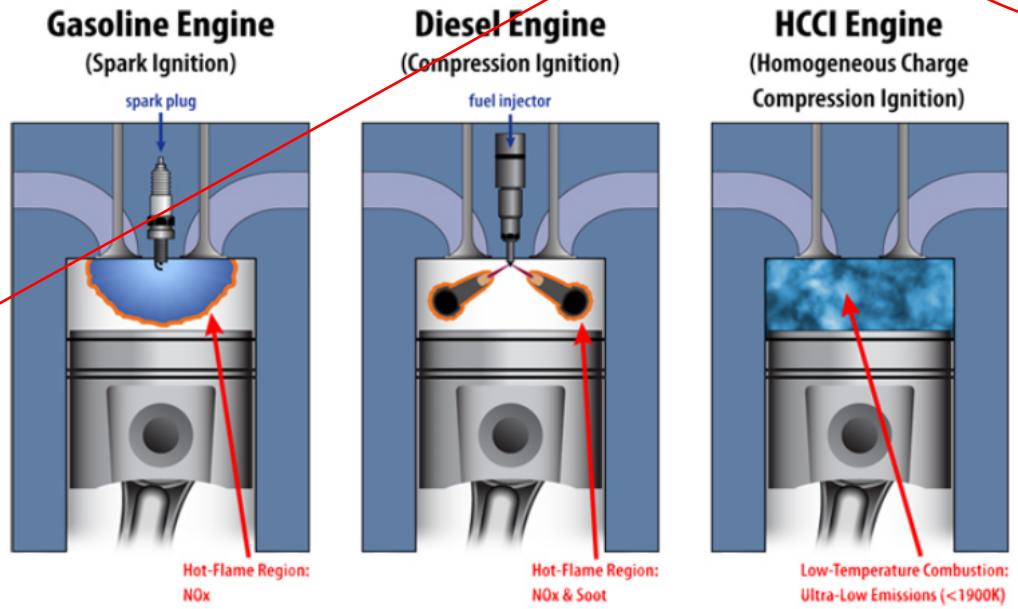
Combustion Chemistry

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.

2,2,4,4,6,8,8-Heptamethylnonane



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, Univ. of Wisc., U. of Mich.)
  - Collaboration with John Dec and Magnus Sjöberg at Sandia on HCCI engine experiments
- 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 Prof. Ranzi's group, Milan, Italy on toluene
  - Collaboration with Prof. Lu, U. of Conn. on mechanism reduction
- Participation in other working groups with industrial representation
  - Fuels for Advanced Combustion Engines (FACE) Working group

Special recognitions and awards during FY10

Charles Westbrook:

- Wilhelm Jost Memorial Lectureship from the Deutsche Bunsengesellschaft fur Physikalische Chemie
- President of the Combustion Institute

William J. Pitz:

- Best paper of the year award 2009: Combustion Society Japan

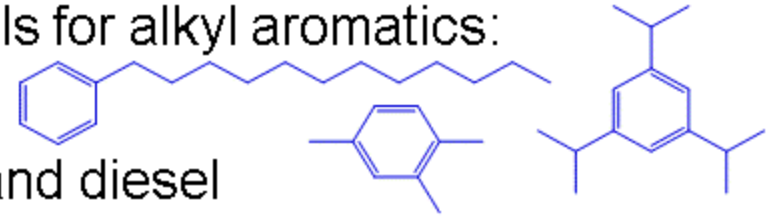
S. M. Sarathy:

- Postdoctoral fellowship from Natural Sciences and Engineering Research Council of Canada

Activities for Next Fiscal Year

- Develop detailed chemical kinetic models for another series iso-alkanes: 3-methyl alkanes

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



- More accurate surrogates for gasoline and diesel
- Further develop mechanism reduction using functional group method

n-decylbenzene - Diesel Fuels

Summary

- Approach to research
  - Continue development of surrogate fuel mechanisms to improve engine models for HCCI and diesel engines
- Technical accomplishments:
  - Assembled reaction mechanism for the high and low temperature oxidation of a series of 2-methyl alkanes that covers the entire distillation range of gasoline and diesel
- 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:
  - Whole series of 3-methyl alkanes
  - Alkyl aromatics class of fuels