Lawrence Livermore National Laboratory

Multidimensional simulation and chemical kinetics development for high efficiency clean combustion engines

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Our team develops chemical kinetic mechanisms and applies them to simulating engine combustion processes

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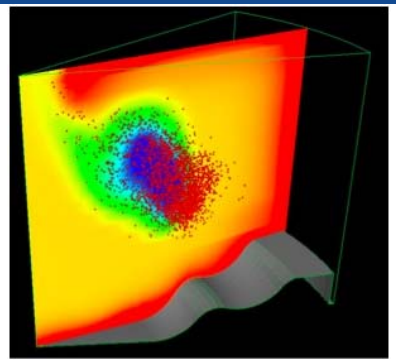
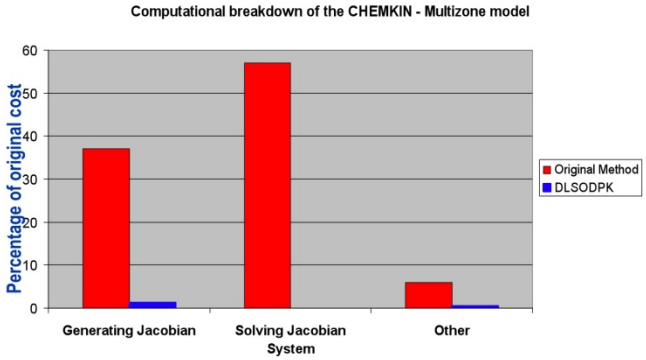
Partners

- DOE working groups
- Sandia Livermore
- Oak Ridge
- Los Alamos
- International
- UC Berkeley
- University of Wisconsin
- University of Michigan
- Chalmers University
- FACE working group
- National Univ. of Ireland
- RPI
- Princeton University
- Univ. of Tokyo

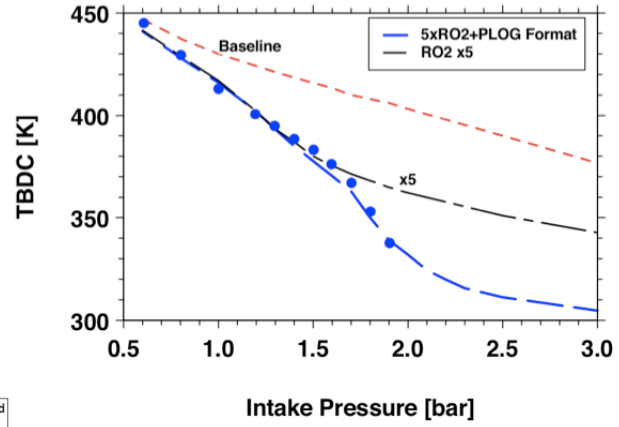
We apply simulations methodologies to gain insight into advanced combustion regimes



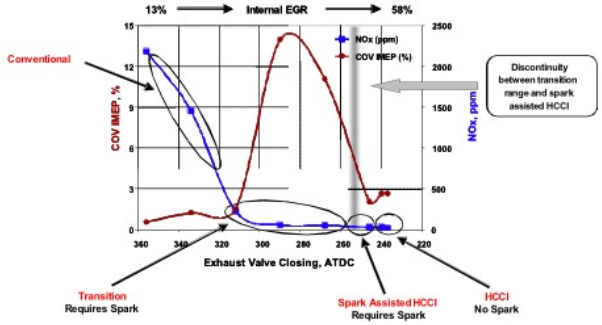
Prediction of partially stratified combustion with kiva3v-multizone



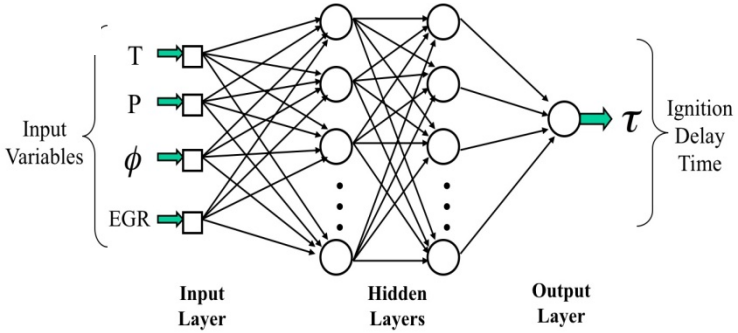
Improved kinetic solver numerics



Improved surrogate chemical kinetic model for gasoline



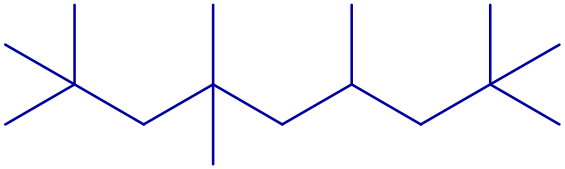
Simulating SI-HCCI transition with ORNL



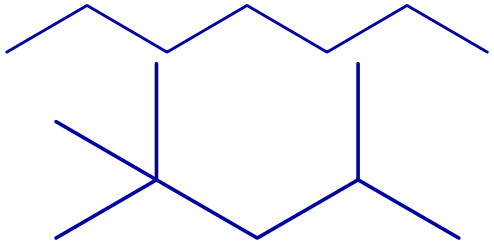
Prediction of PCCI combustion with an artificial neural network-based chemical kinetic model

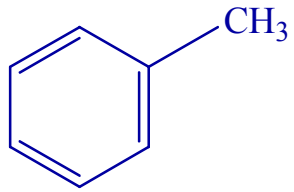
We continue to expand and improve chemical kinetic mechanisms for diesel and gasoline components

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

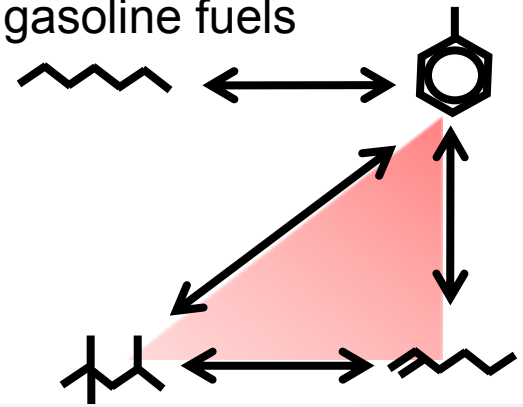


- Improving models for gasoline-fueled engines:
  - Completed validation of component models for n-heptane, iso-octane and toluene, important components for gasoline fuels

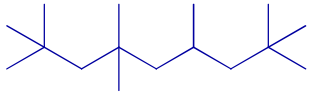




- Developed new surrogate models for gasoline fuels

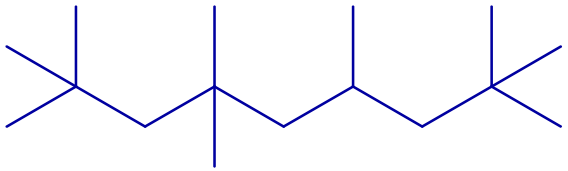


We have developed a model for heptamethylnonane, a primary reference fuel for diesel



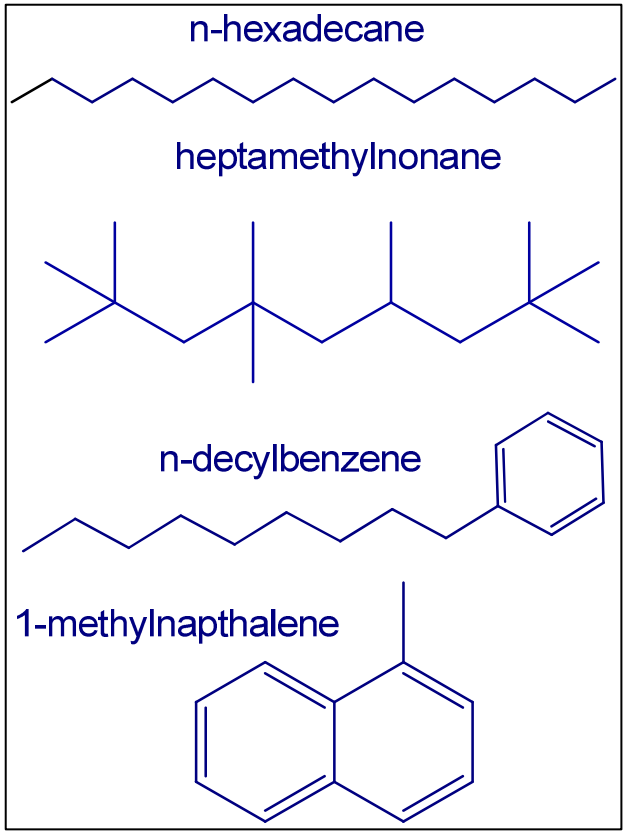
- One of the two primary reference fuels for diesel ignition properties (cetane number)
  - n-hexadecane

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

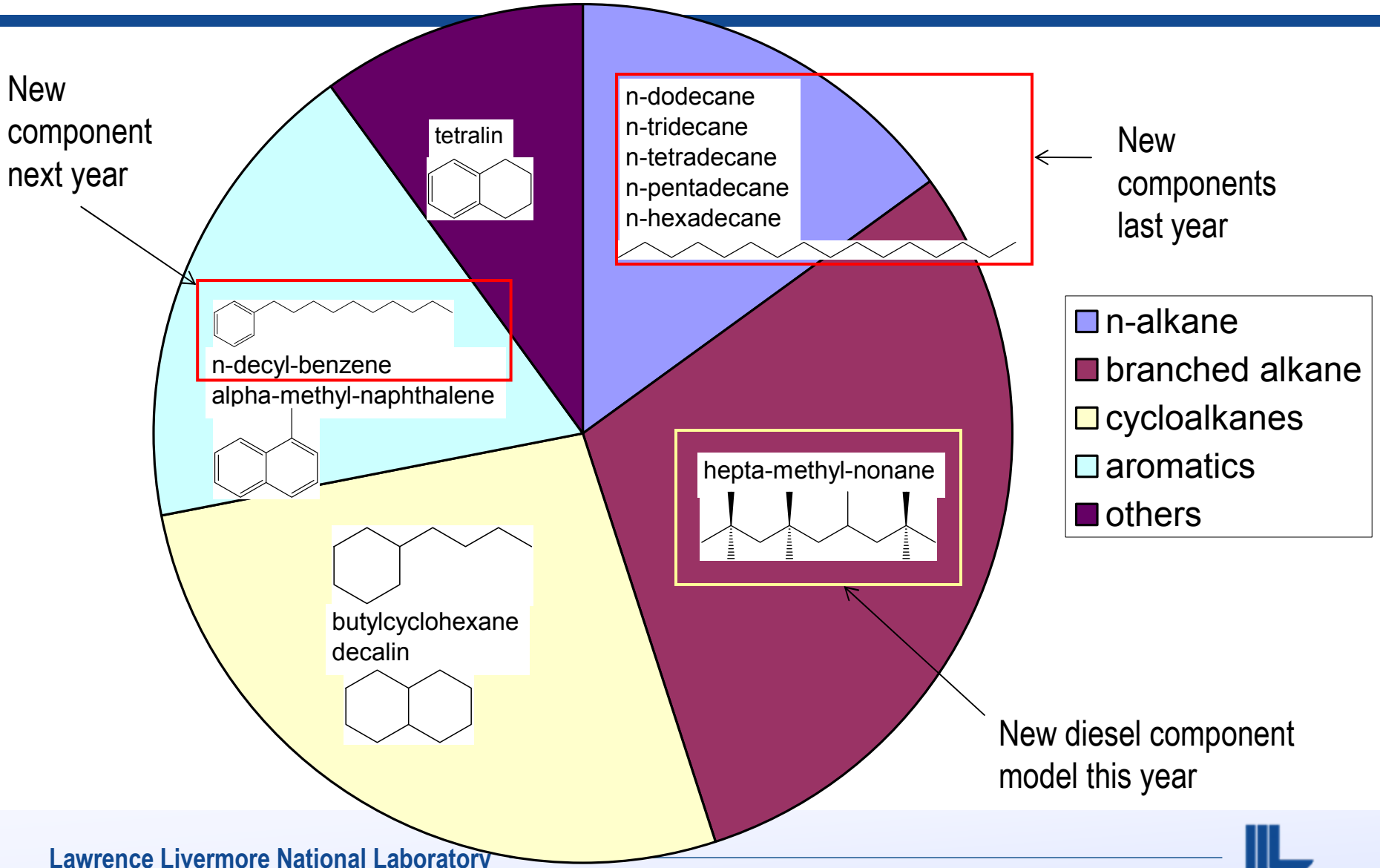


- **High and low temperature portion of the mechanism complete**
  - First-ever complete set of high and low temperature kinetic mechanisms for heptamethylnonane

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

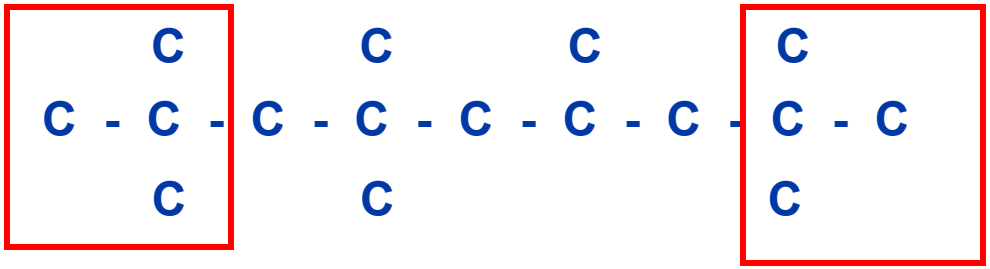


Diesel Fuel Surrogate palette:

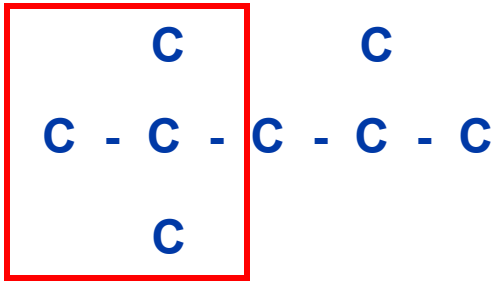


Heptamethylnonane (HMN) has a lot of structural similarities to iso-octane

HMN

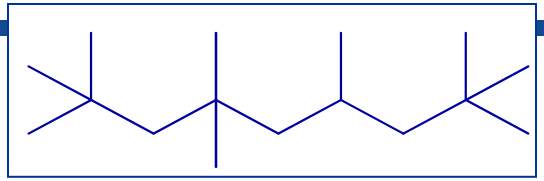


iso-octane



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

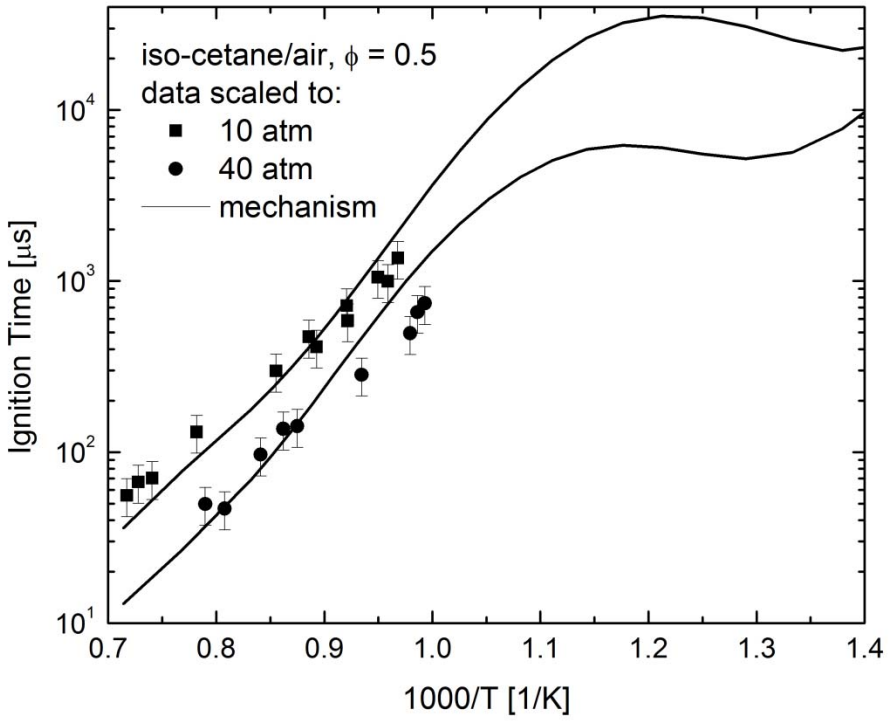
Heptamethyl nonane (HMN) detailed chemical kinetic mechanism contains 1114 species 4468 reactions

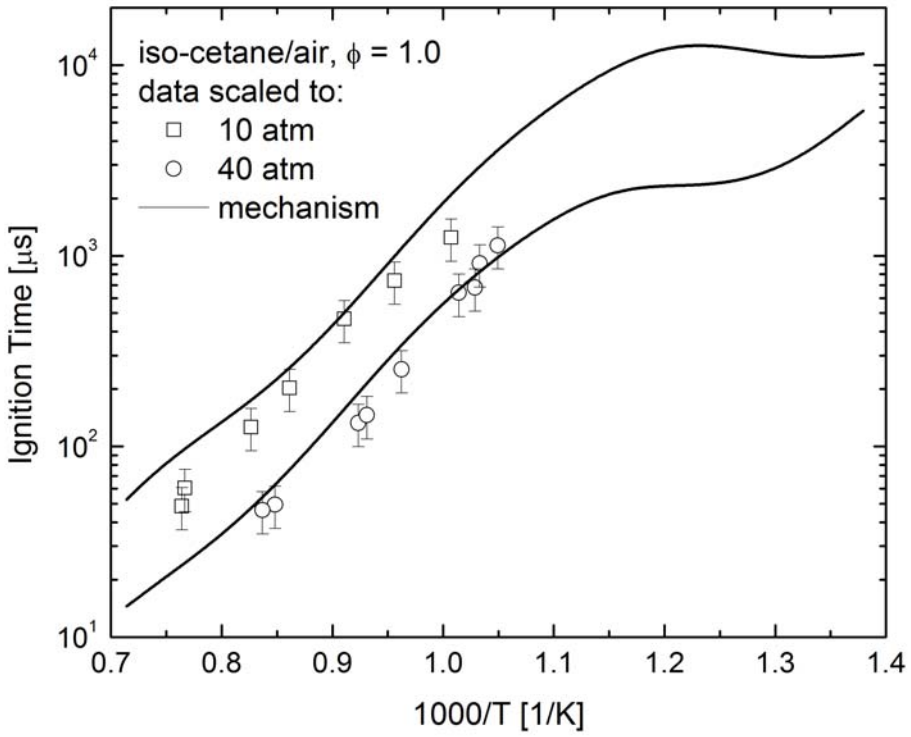


2,2,4,4,6,8,8 heptamethylnonane

- 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
- Recent experiments now available on HMN for mechanism validation

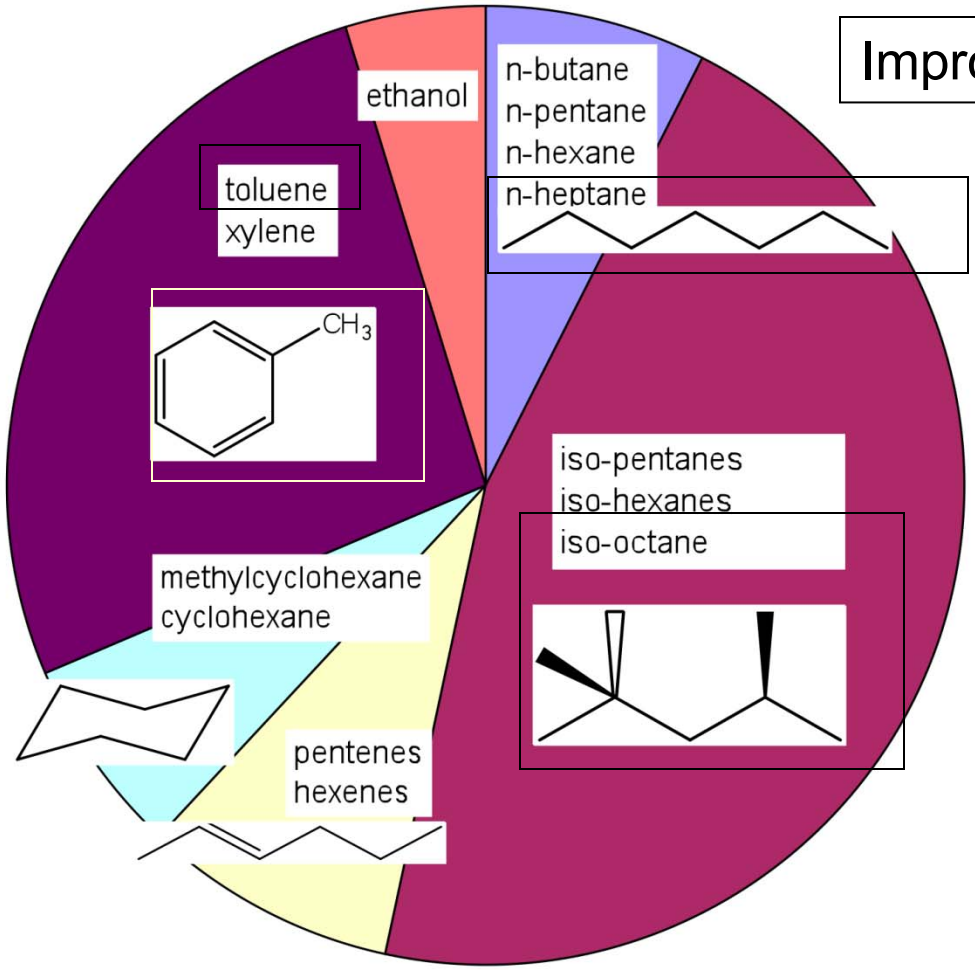
Recent experimental results show excellent agreement with modeling for HMN





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

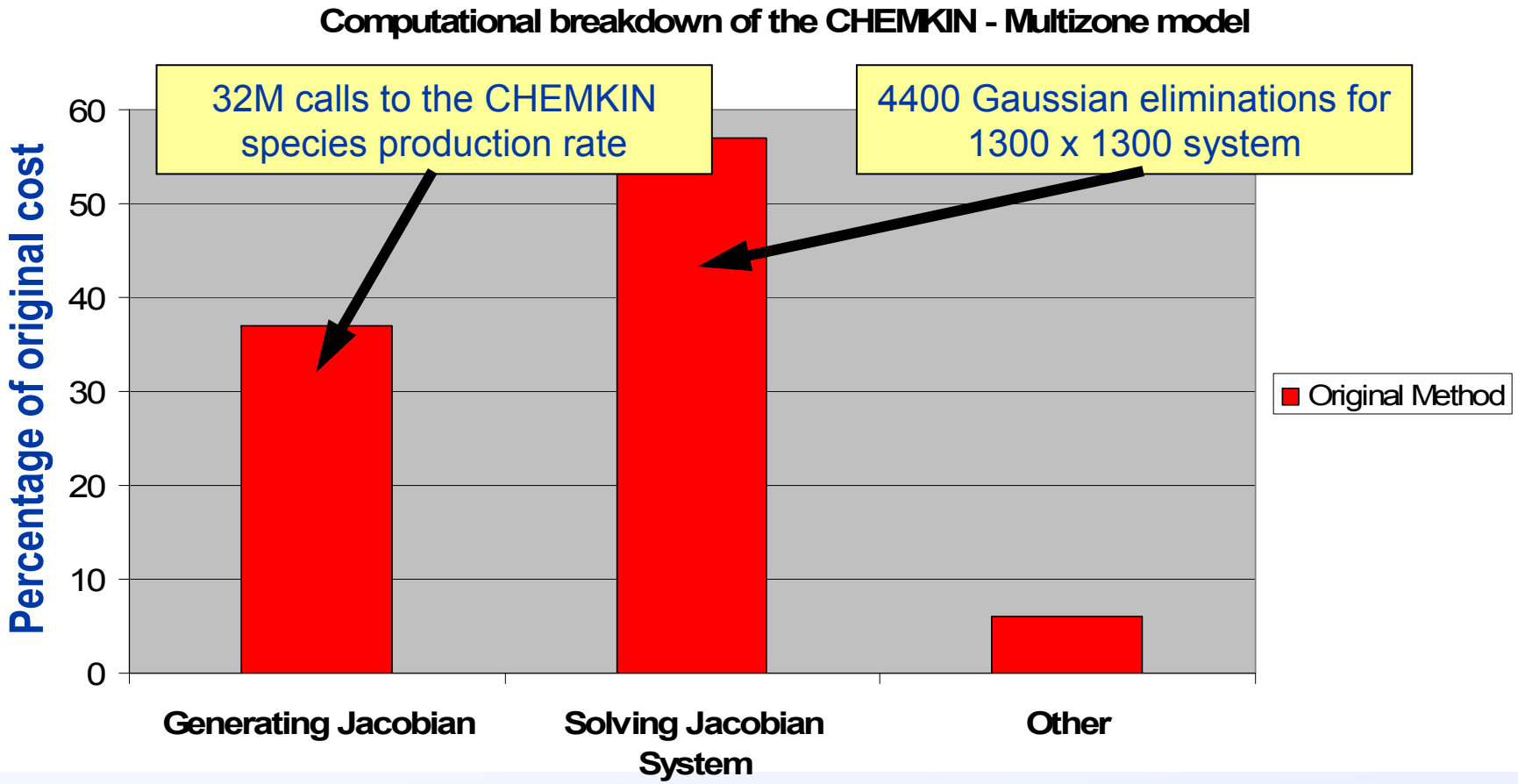


Improved component models

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

Improving numerics: Processing the Jacobian is the most computationally expensive part of CHEMKIN-Multizone

- 94% of the total computational cost solving kinetic ODEs is spent generating the Jacobian and solving the associated linear system.

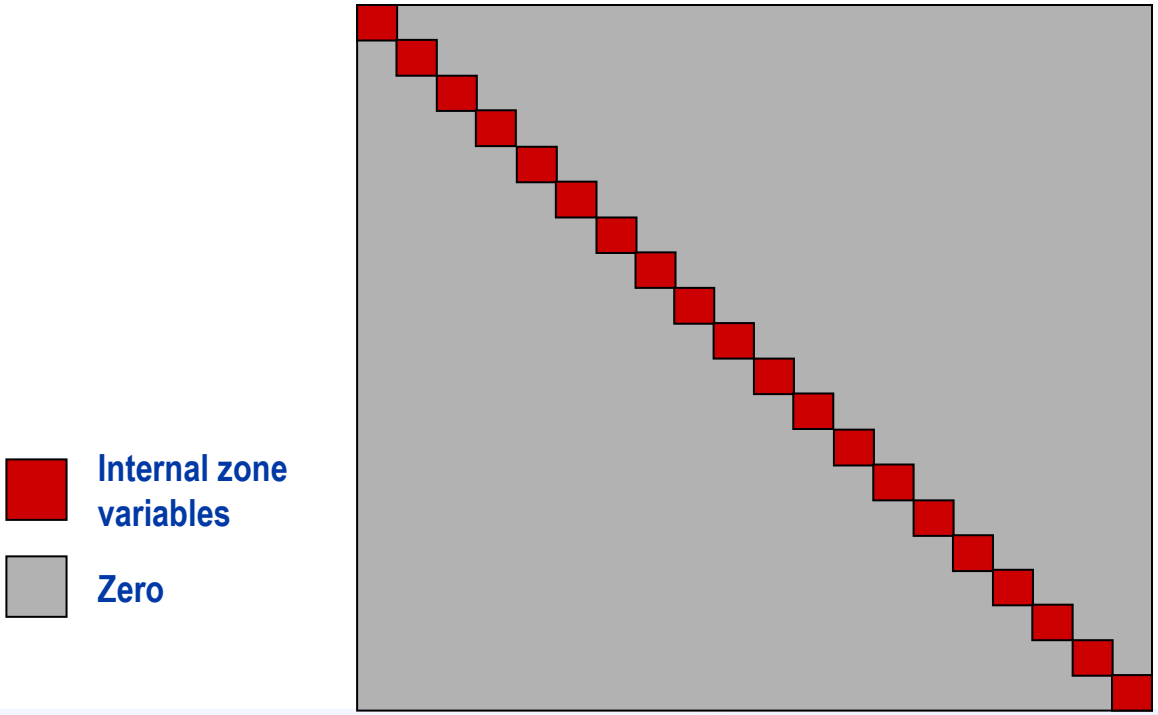


We apply LLNL's ODE integrator with an iterative matrix solver (DLSODPK)

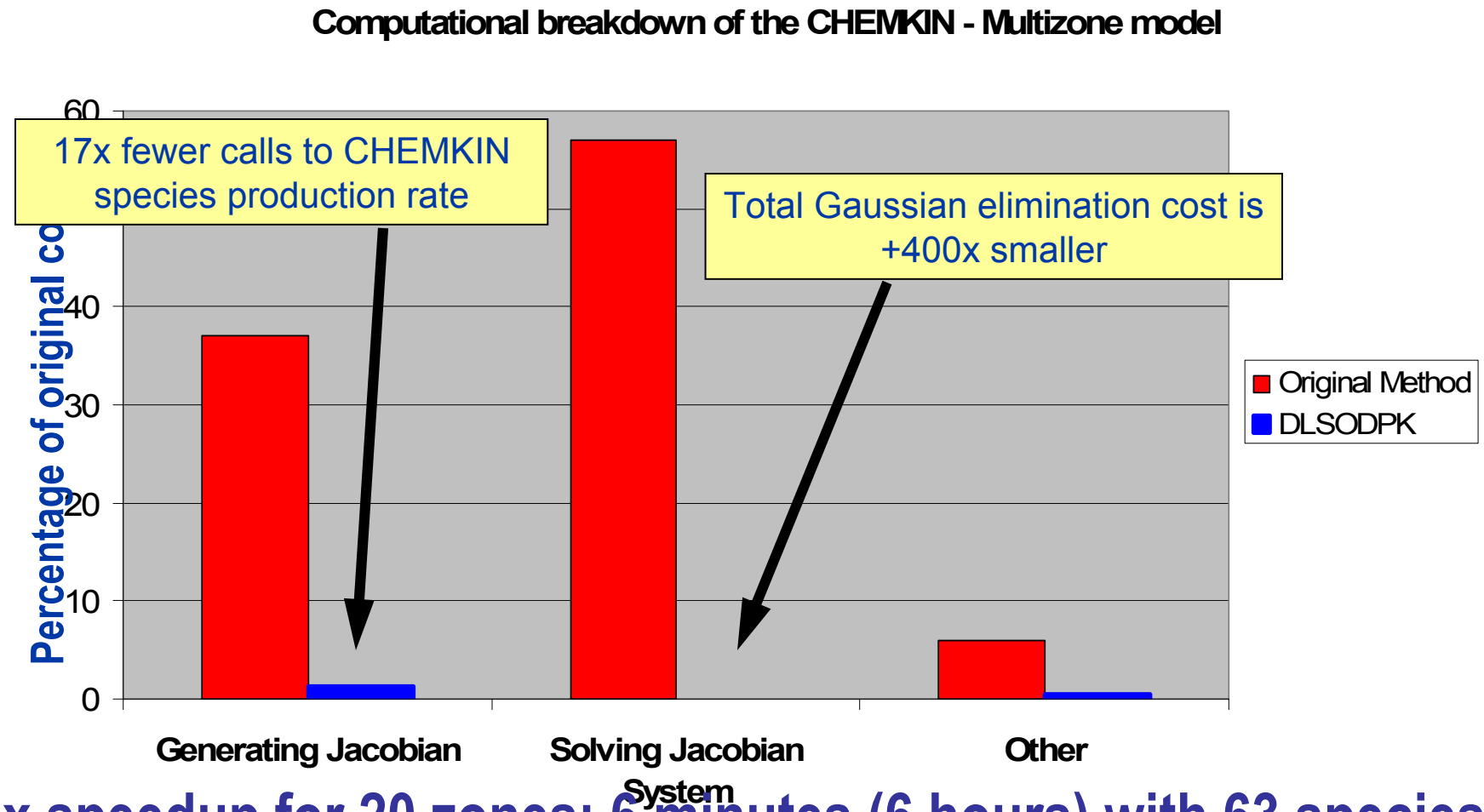
- Use LLNL's iterative solver DLSODPK along with a preconditioner matrix P

$$P^{-1}Ax = P^{-1}b$$

- Here P is the Jacobian of a simplified CHEMKIN-multizone model that yields a block diagonal matrix (neglecting interaction between zones)



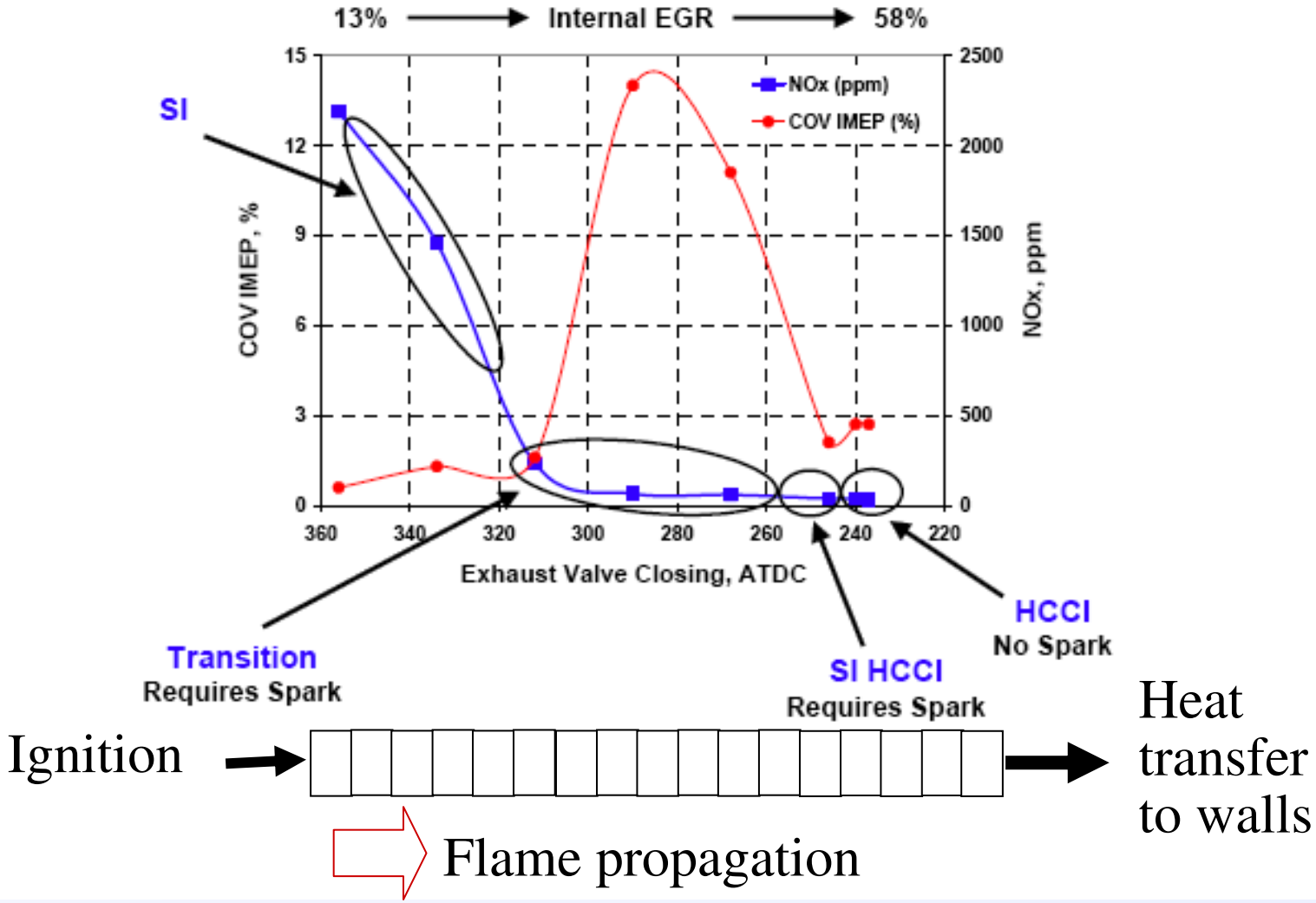
The new DLSODPK scheme accelerates computations enabling detailed multizone kinetics on desktop PCs



60x speedup for 20 zones; 6 minutes (6 hours) with 63 species

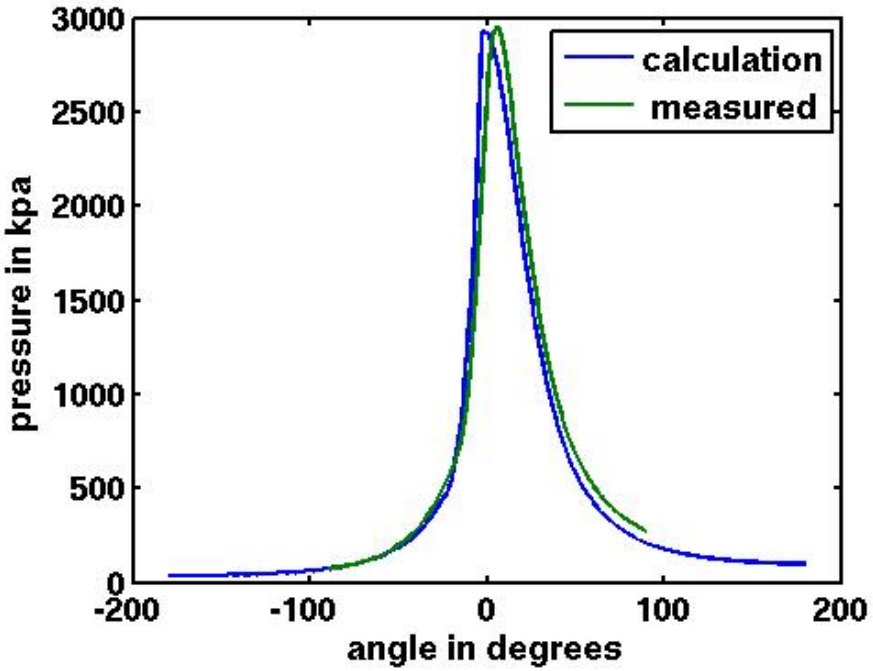
250x speedup for 40 zones; 24 minutes (100 hours) 63 species

We are analyzing ORNL results for stability and emissions during SI-HCCI transition due to increased residual gas fraction

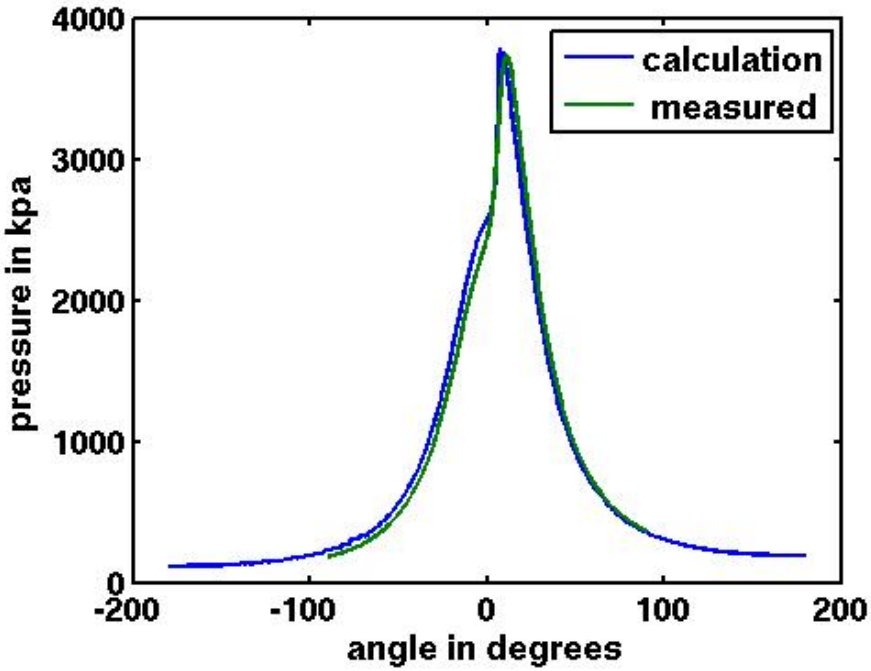


1-dimensional chemical kinetic model matches pressure traces well for motored, SI and HCCI cases

- Spark-ignited



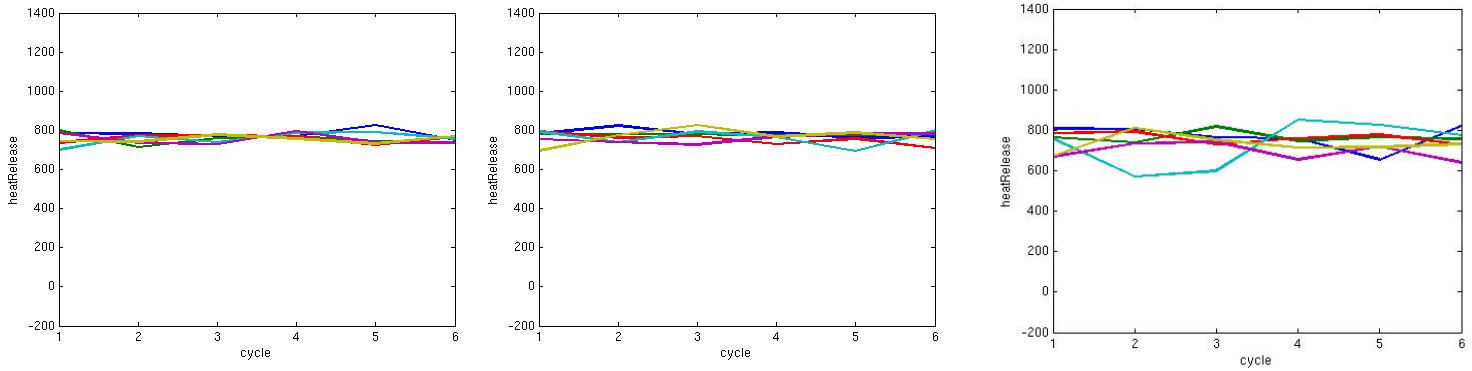
- HCCI (RGF=75%)



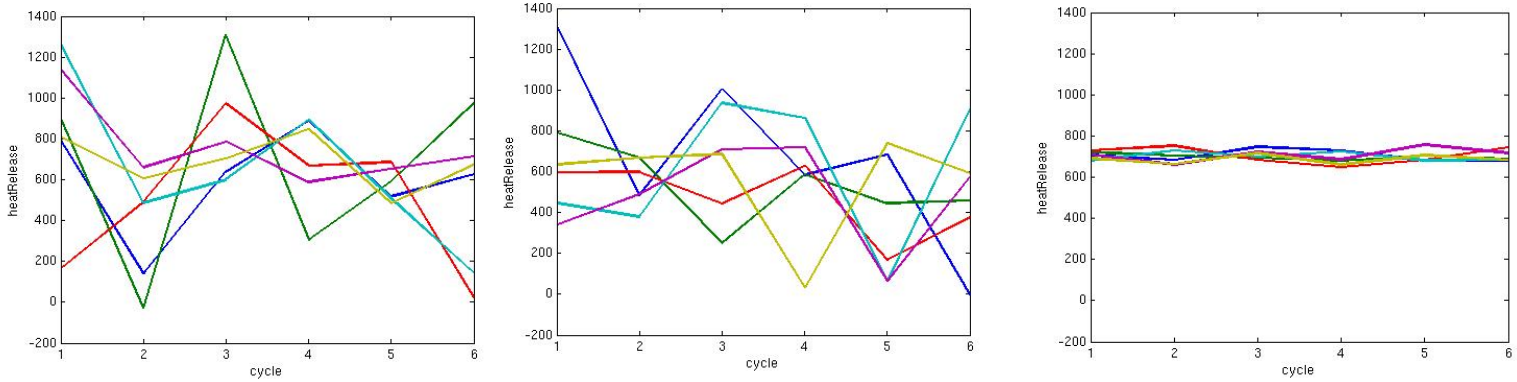
ORNL Test data for SI to HCCI transition: heat release patterns vary with residual gas fraction

Spark-ignited (RGF~10%)

Increasing RGF



Increasing RGF

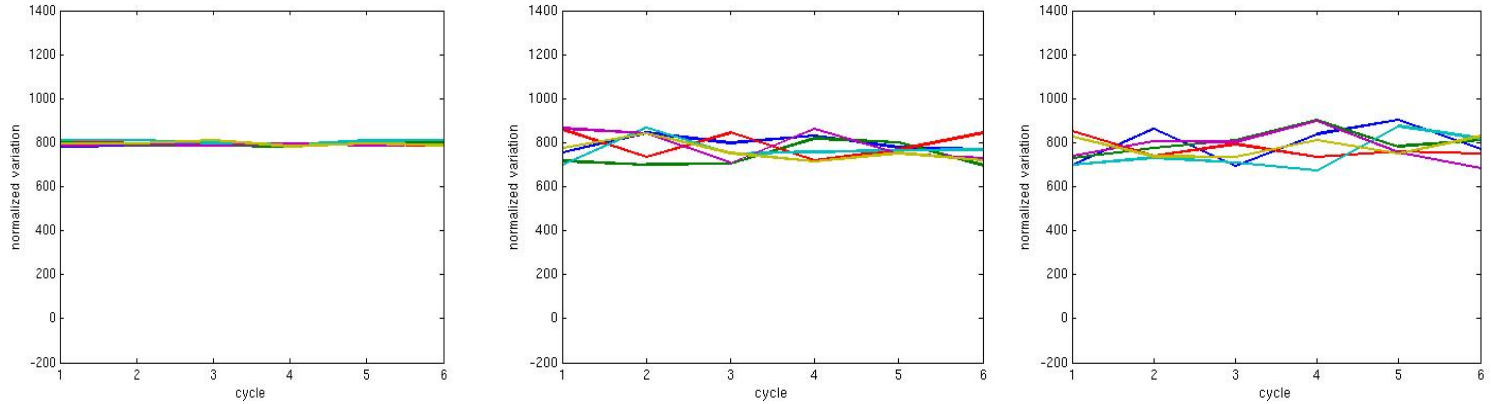


HCCI (RGF~60%)

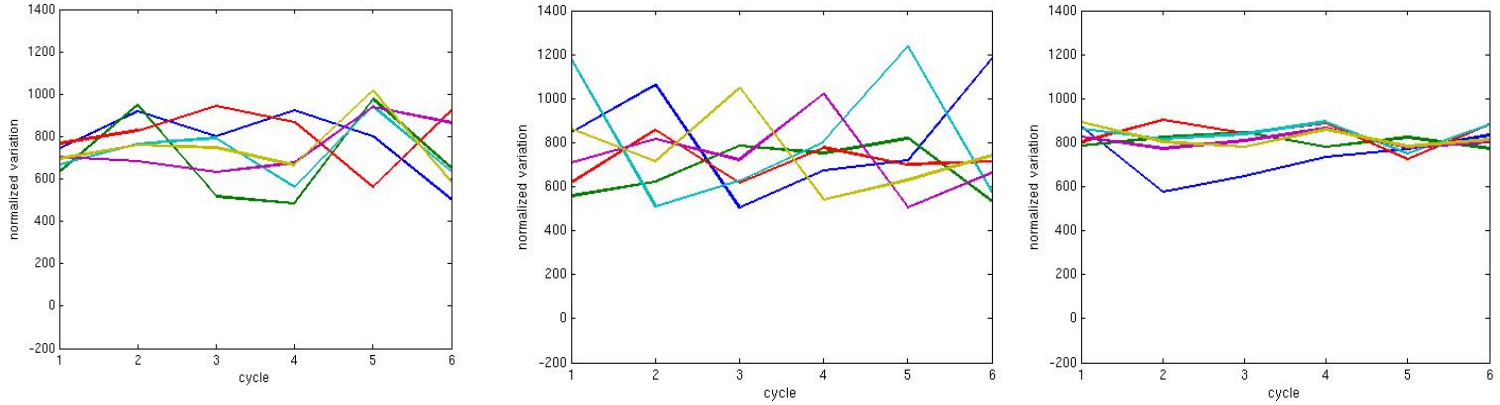
LLNL Simulation results for SI to HCCI transition: heat release patterns vary with residual gas fraction

Spark-ignited (RGF~10%)

Increasing RGF

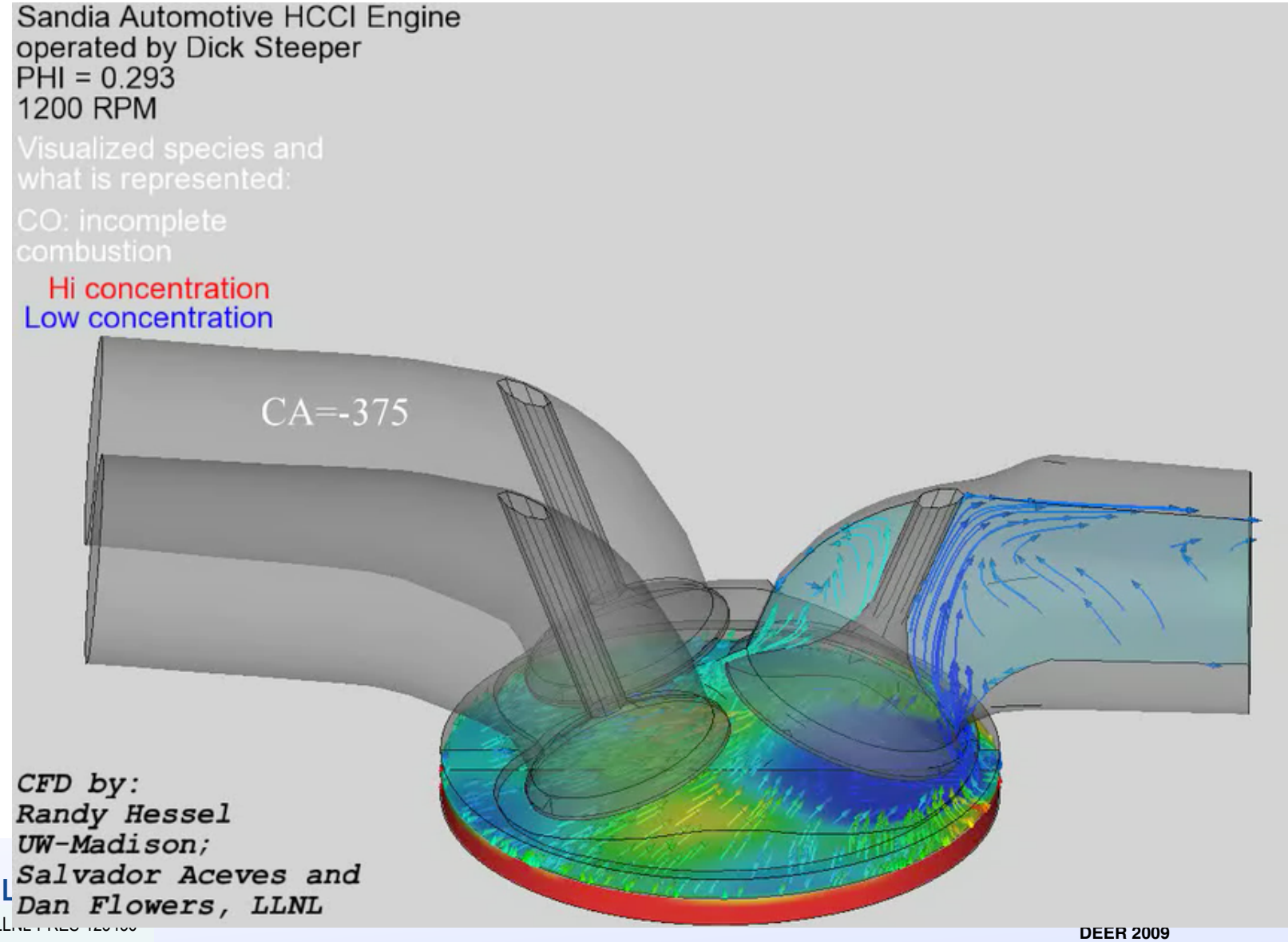


Increasing RGF

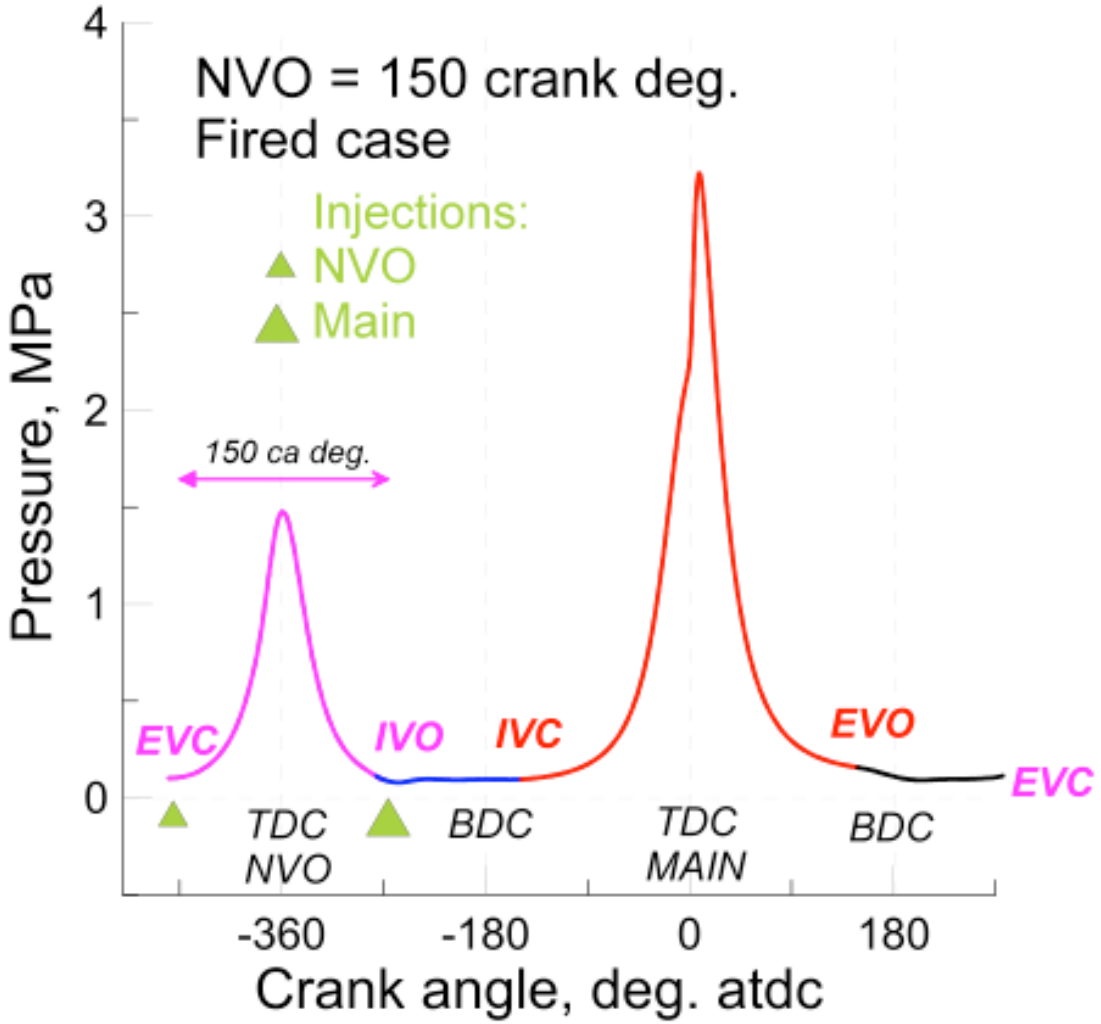


HCCI (RGF~60%)

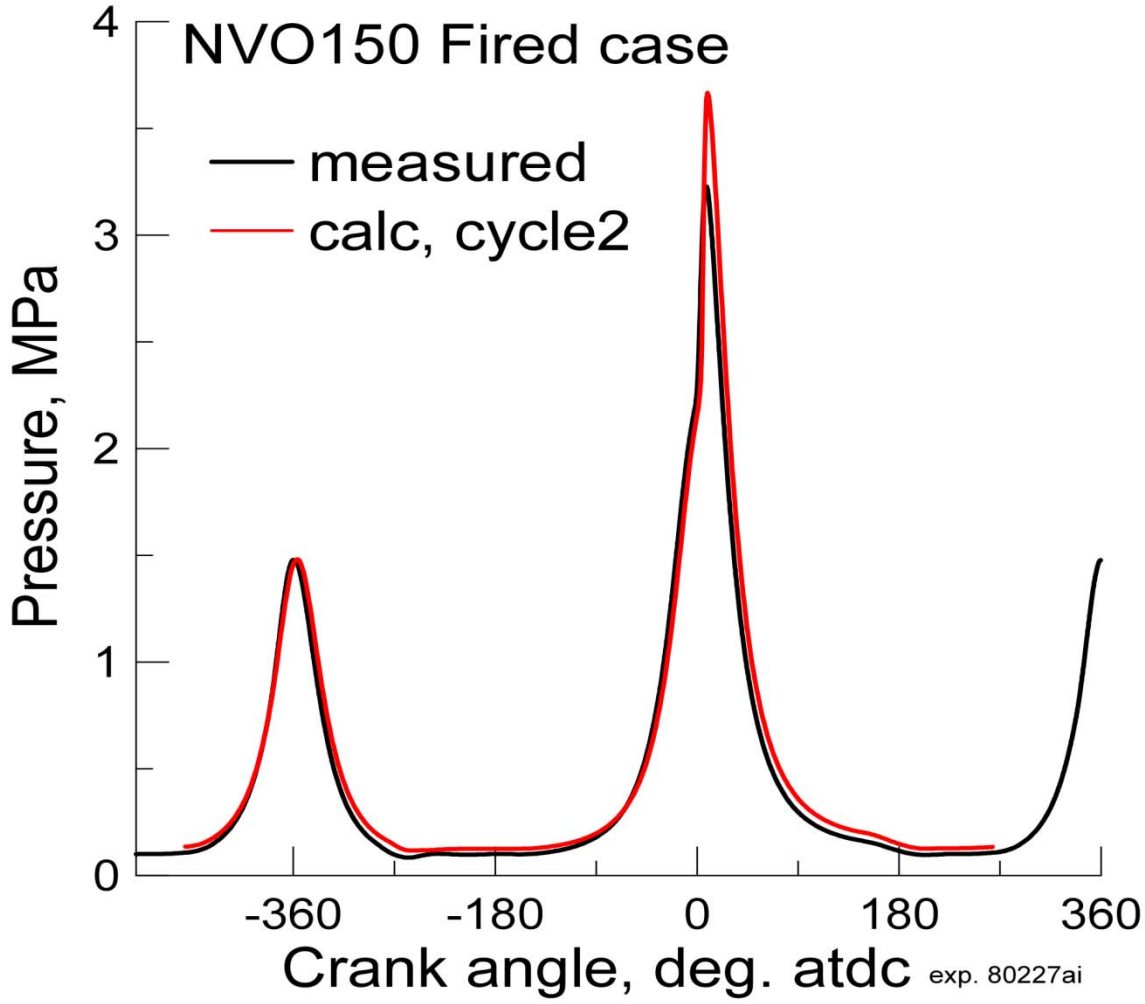
We are analyzing three consecutive cycles of the Sandia automotive PCCI engine (Steeper)



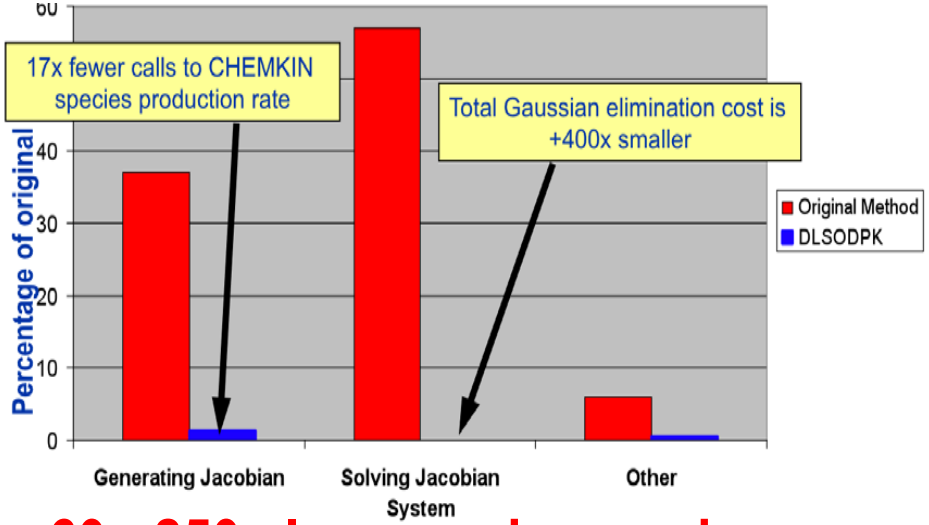
The Sandia engine runs in PCCI mode with dual injection: one injection during NVO and a main injection



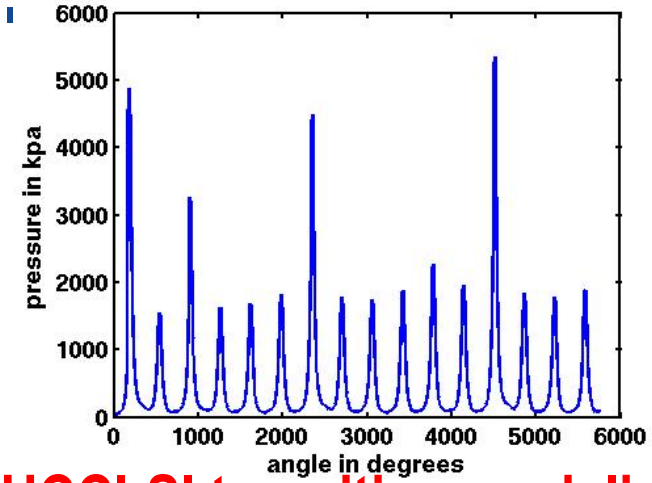
KIVA3V-MZ-MPI shows promise for accurately predicting direct injected PCCI



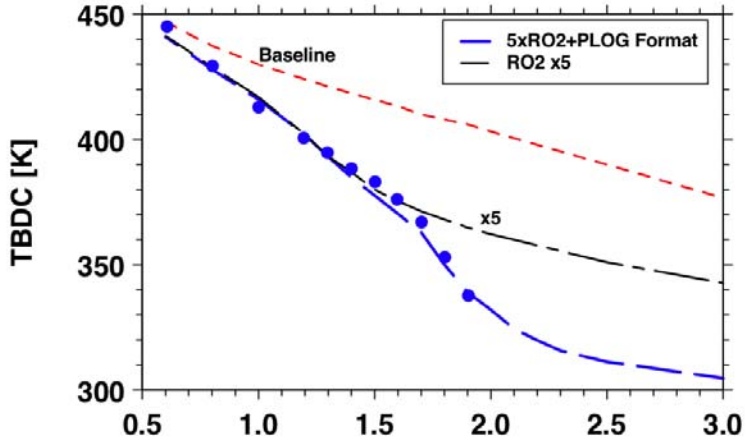
Summary: we are enhancing our analysis capabilities and improving computational performance



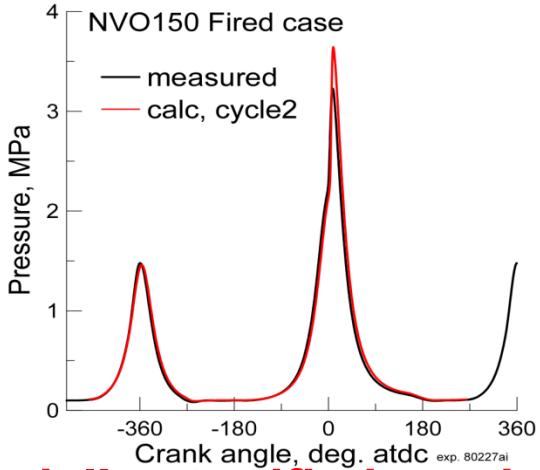
60x-250x Improved numerics



HCCI-SI transition modeling

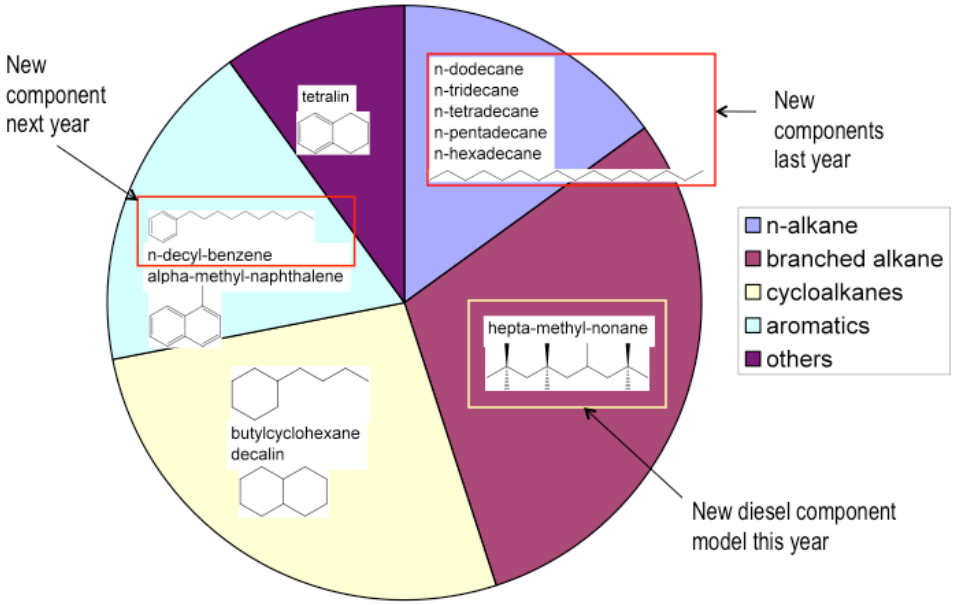


Gasoline surrogate

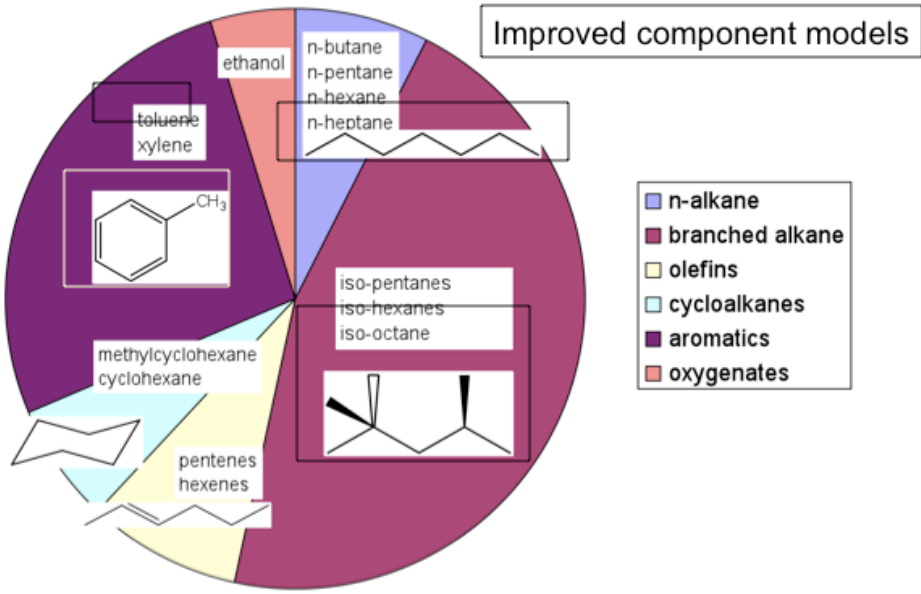


Partially stratified combustion

Summary: we are expanding the range of mechanisms available for representative fuel components



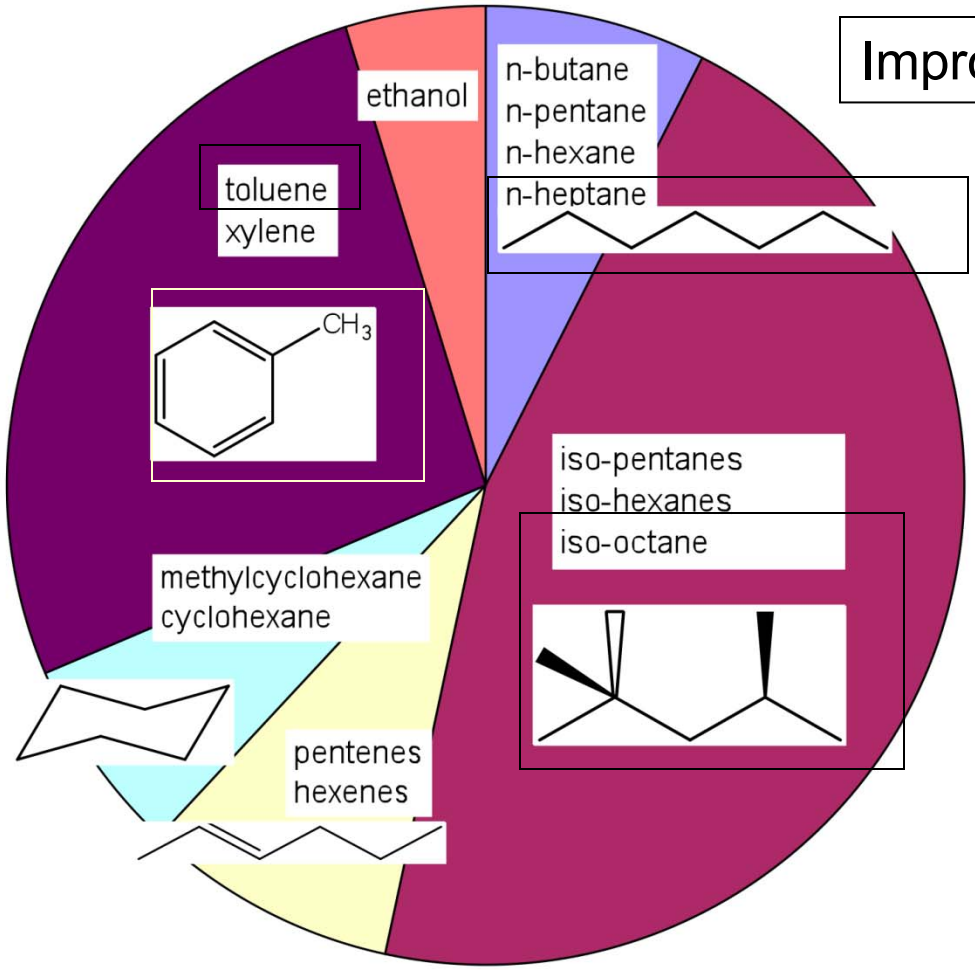
Diesel Fuel Palette



Gasoline Fuel Palette

Appendix

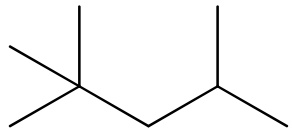
Recent improvements to fuel surrogate models: Gasoline

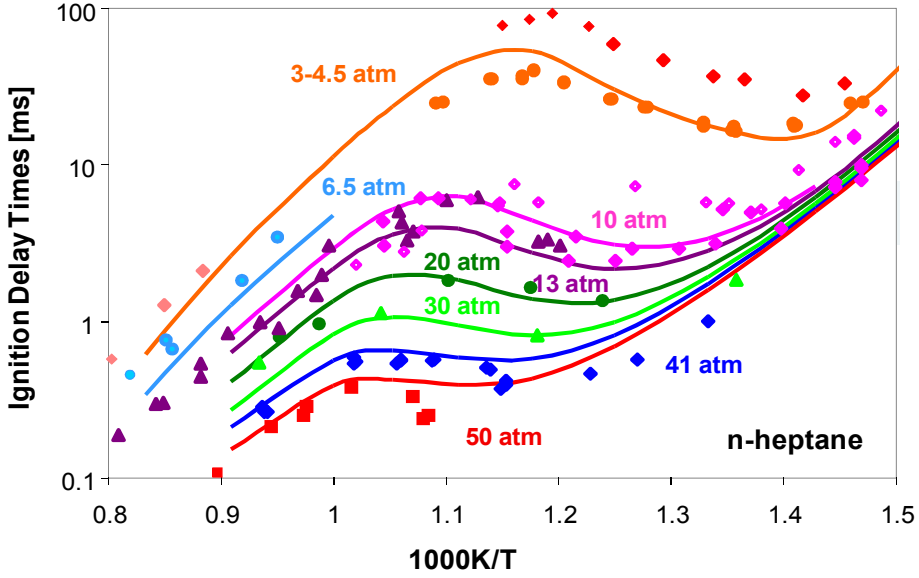


Improved component models

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

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





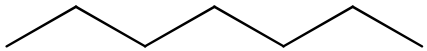
Shock tube and rapid compression machine validation of n-heptane & iso-octane mechanisms:

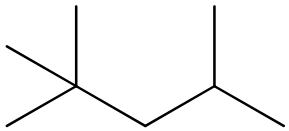
n-heptane:

P = 3 - 50 atm

T = 650K - 1200K

Φ= 1



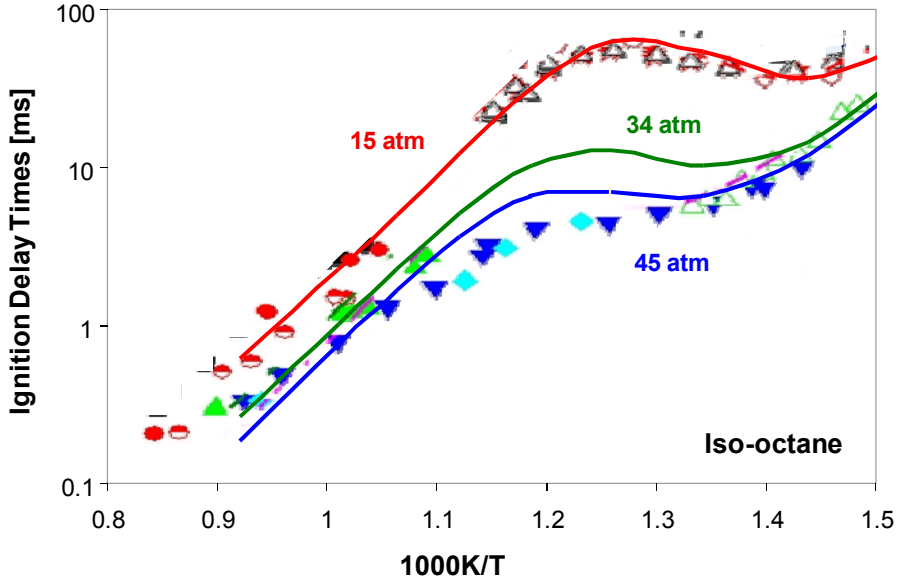


iso-octane:

P = 15 - 45 atm

T = 650K - 1150K

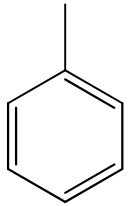
Φ= 1

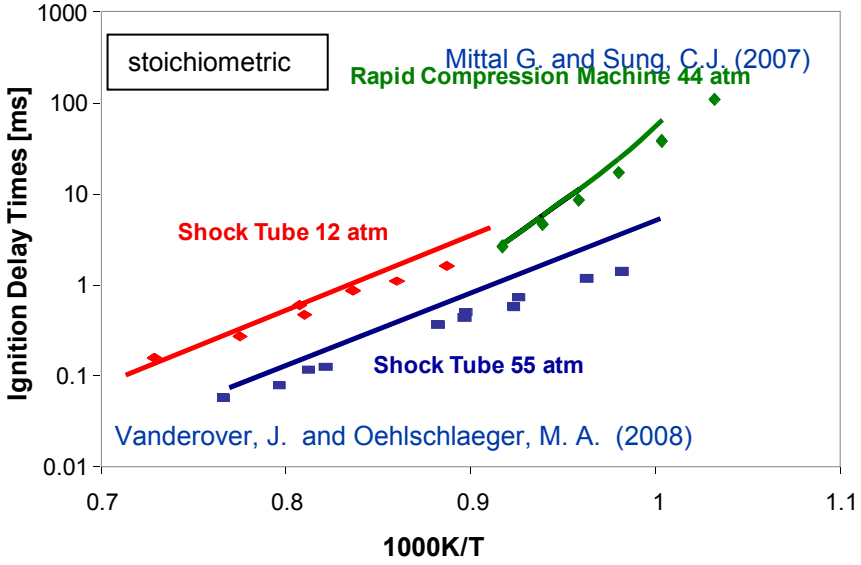


Significant improvements over the whole range of pressures

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

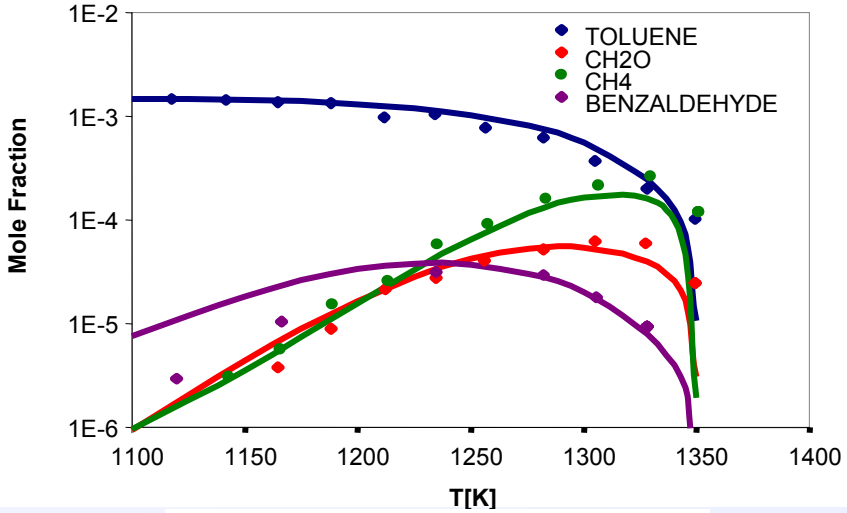




Good agreement with experimental measurements

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

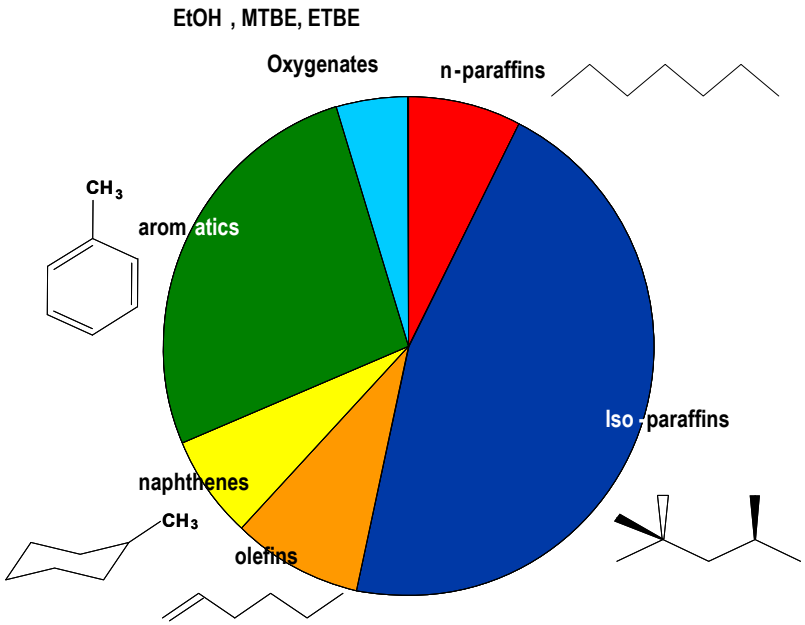
Species profiles measured in a jet stirred reactor are correctly reproduced as well
P = 1 atm
T = 0.1s

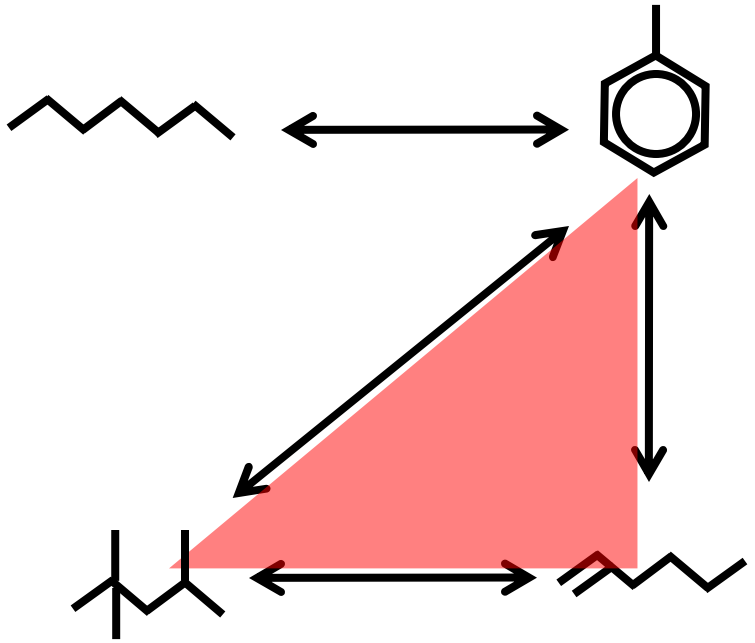


Dagaut, P., G. Pengloan, Ristori, A. (2002)

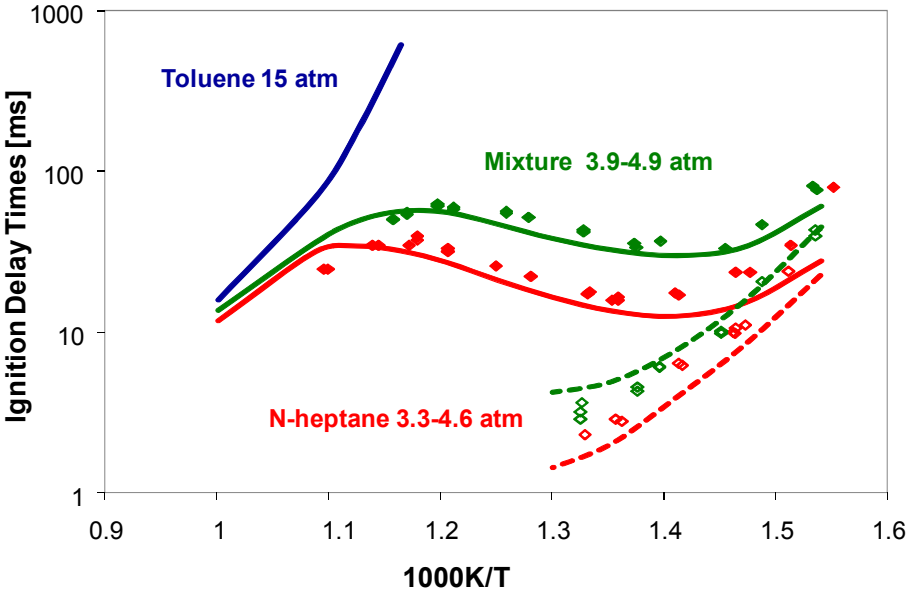
Examined binary and surrogate mixtures relevant to gasoline fuels

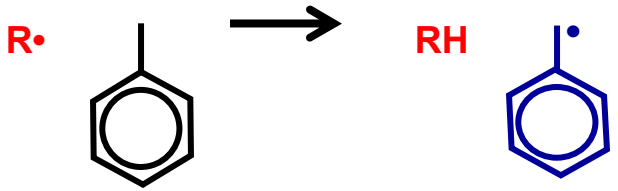
Gasoline fuel surrogate palette





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



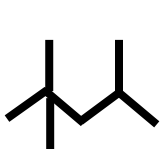


Allylic site on toluene depresses reactivity of mixture by formation of unreactive benzyl radicals

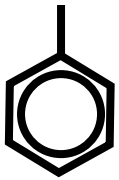
Toluene delays the low temperature heat release and high temperature ignition

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

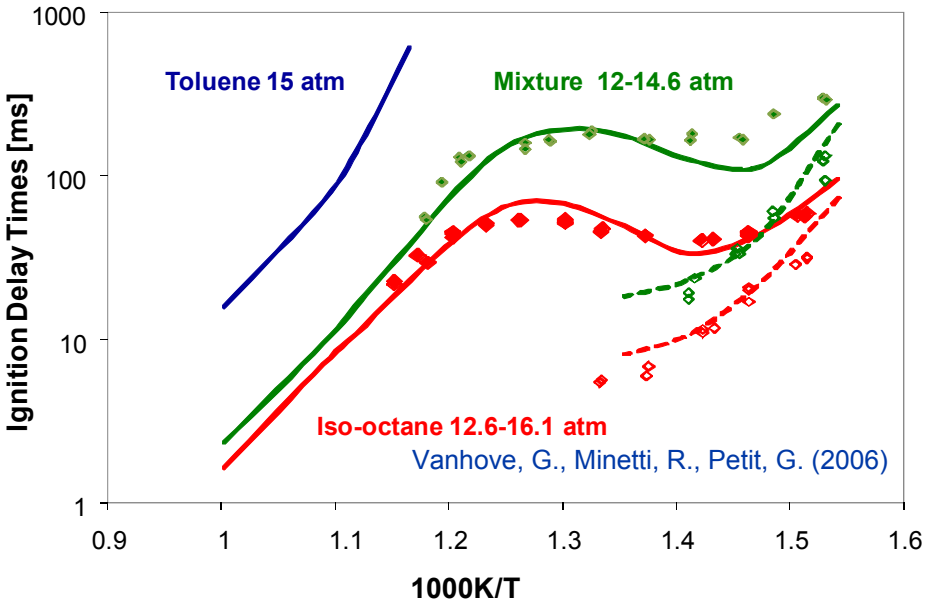
Iso-octane/toluene mixtures well simulated

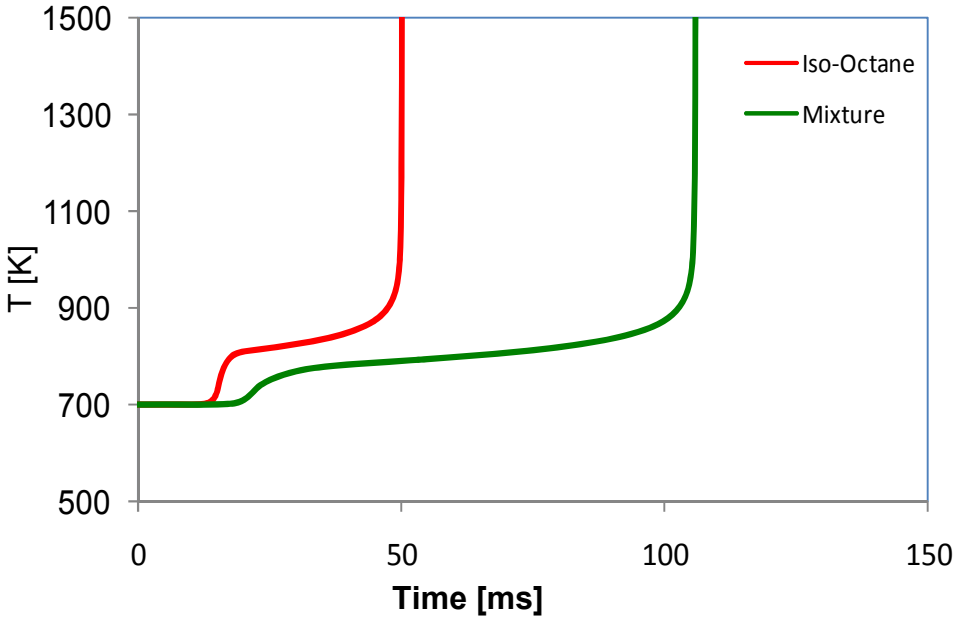


65%



35%

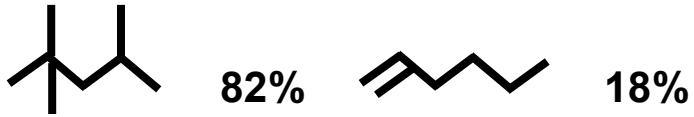


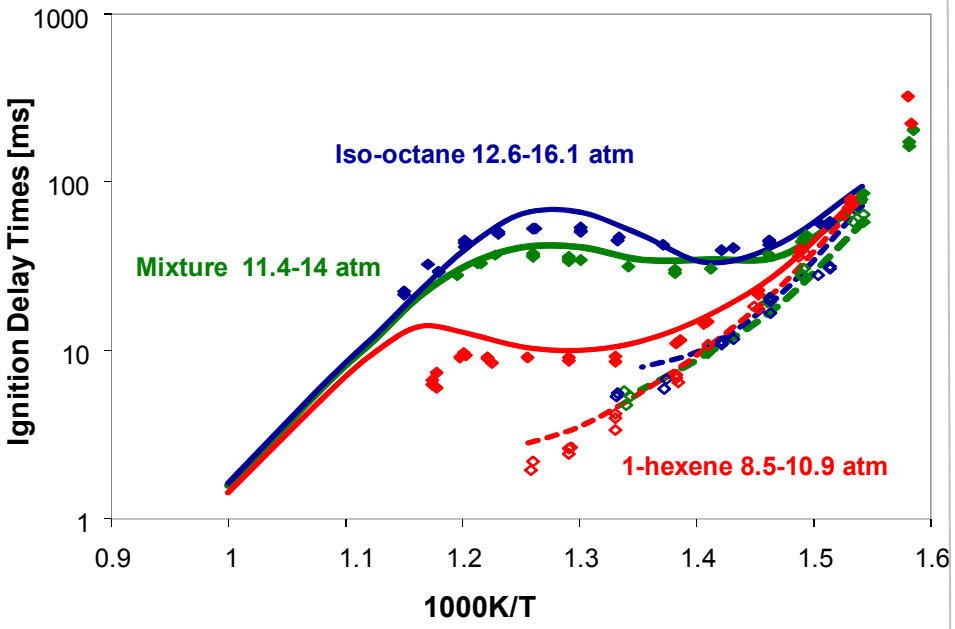


Interactions similar to those observed for n-heptane

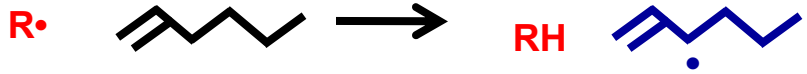
Toluene addition lowers low temperature heat release and delays high temperature ignition

Iso-octane/1-hexene mixtures well simulated



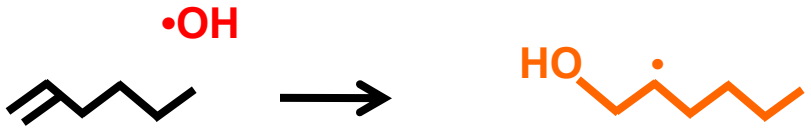


Experimental data: Vanhove, G., Minetti, R., Petit, G. (2006)



Allylic site on 1-hexene depresses reactivity of mixture

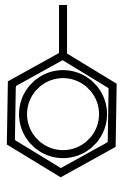
Some low temperature reactivity from 1-hexene



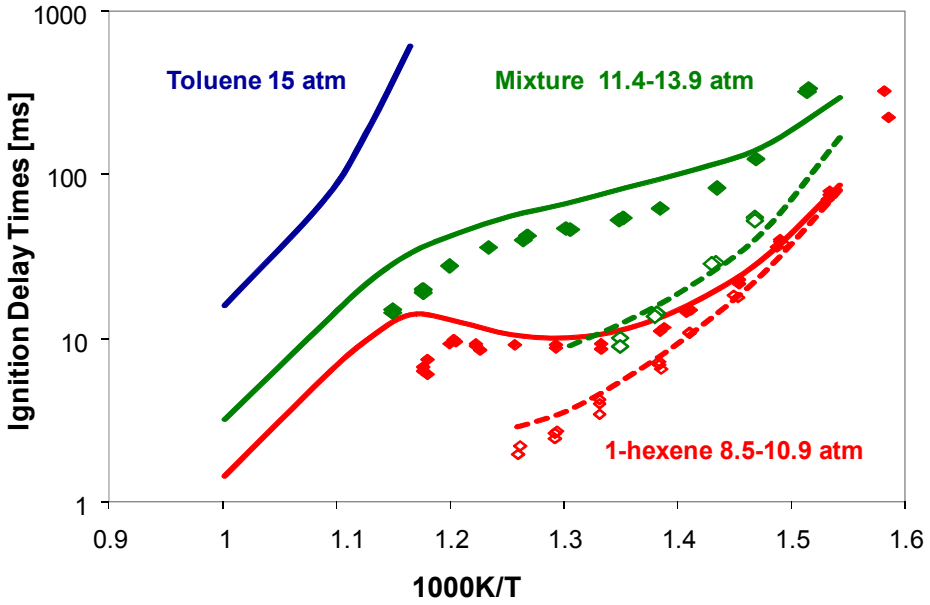
Radical Scavenging from the double bond

Reasonable agreement for toluene/1-hexene mixtures

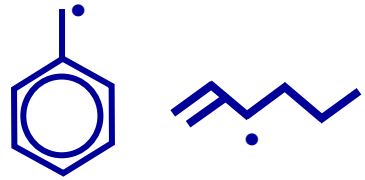
30%



70%



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

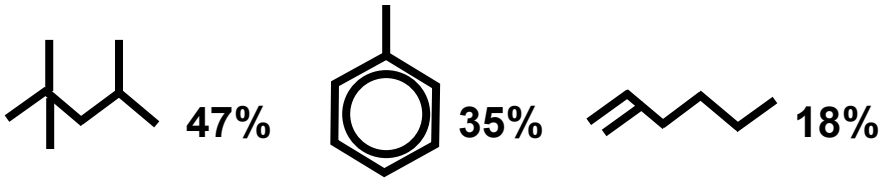


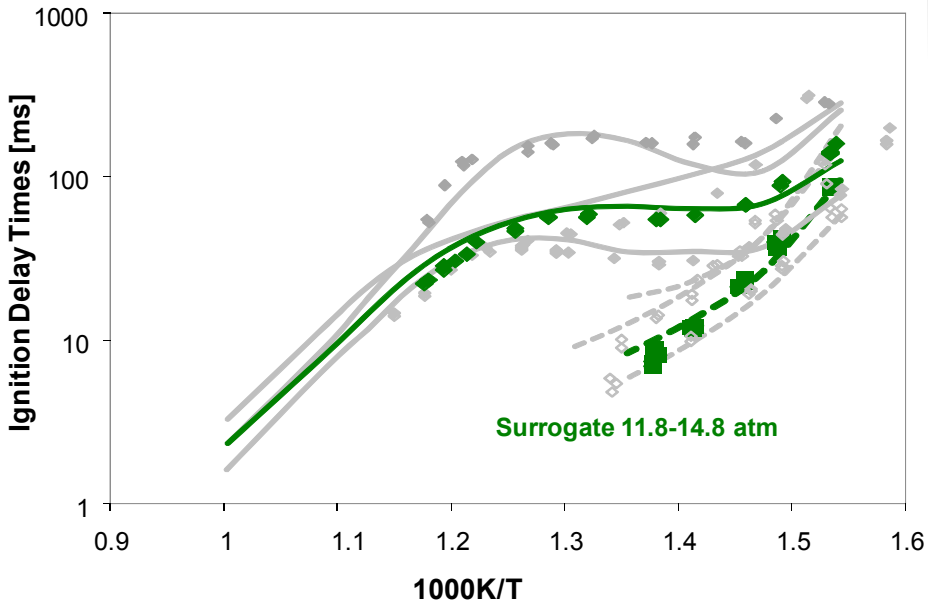
Formation of allylic radicals suppresses reactivity

Ketohydroperoxides + OH

Some low temperature reactivity from 1-hexene

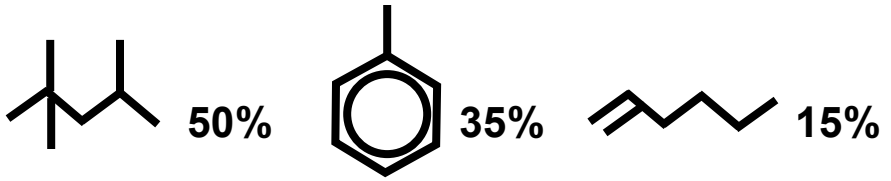
Gasoline surrogate well simulated

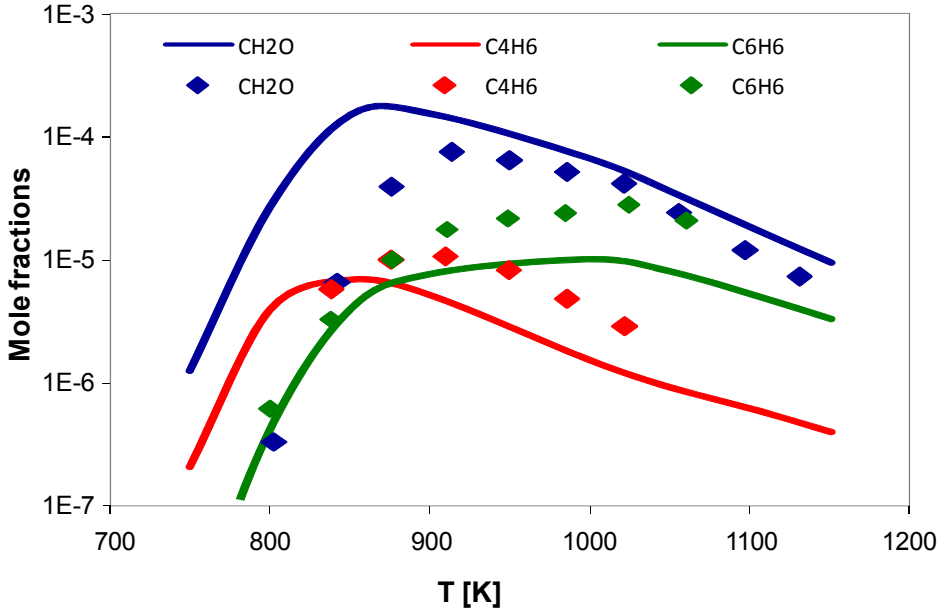




Rapid compression machine validation

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



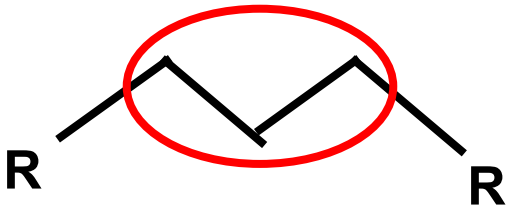


Jet stirred reactor validation: 10 atm, τ = 0.5 s

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

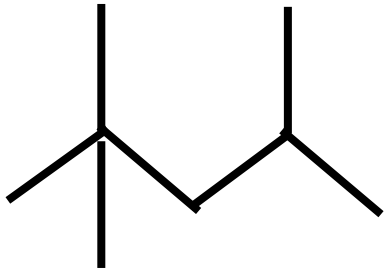
Key component interactions identified

n-alkane



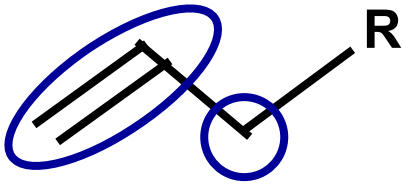
Long unsaturated chain promotes low temperature reactivity

Iso-alkane



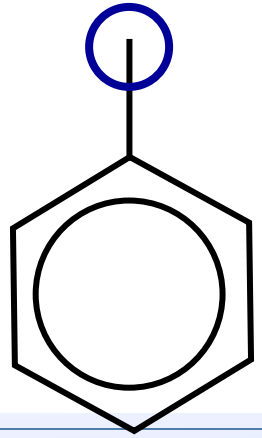
Primary sites reduce reactivity – substitutions on the chain interfere with isomerizations

n-alkene



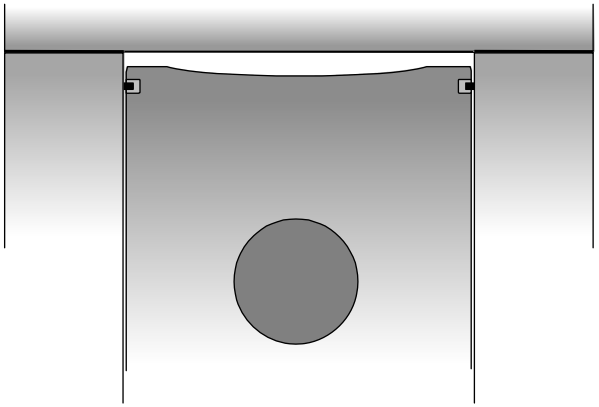
Double bonds act as radical scavenger – allylic sites depress reactivity

toluene

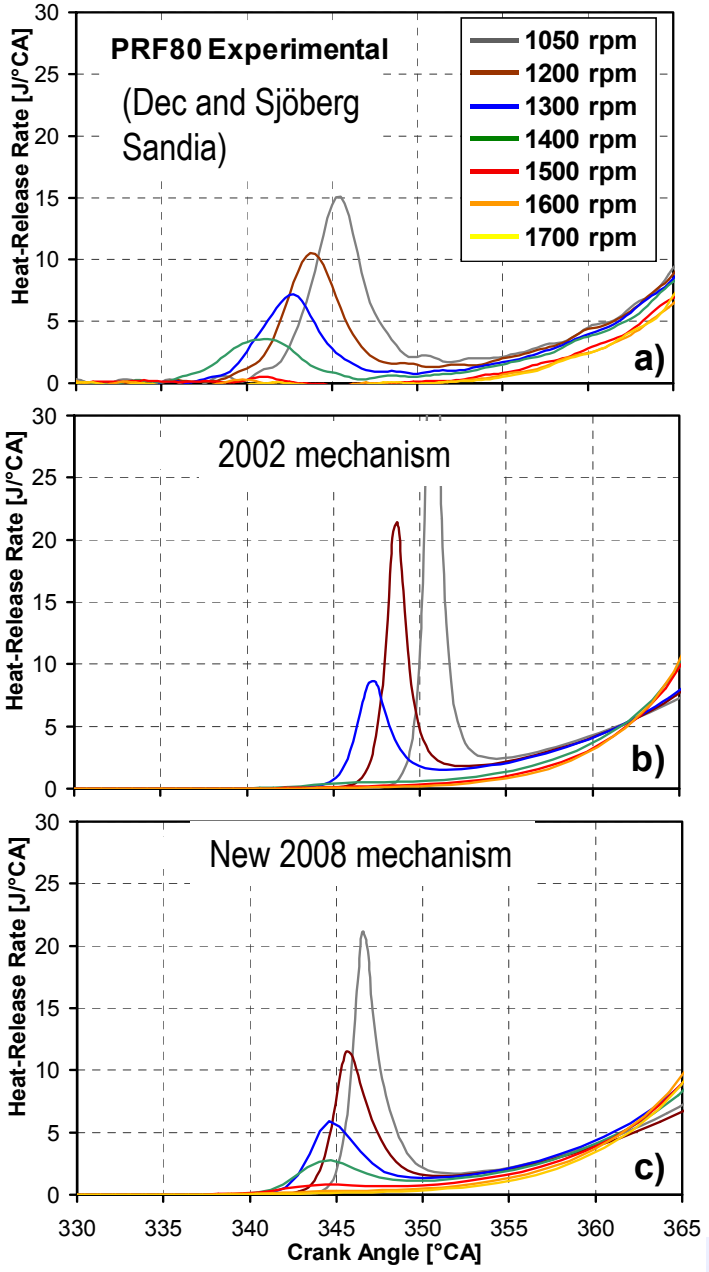


Abstraction on the benzylic site generates stable radicals – suppresses reactivity

HCCI engine results:

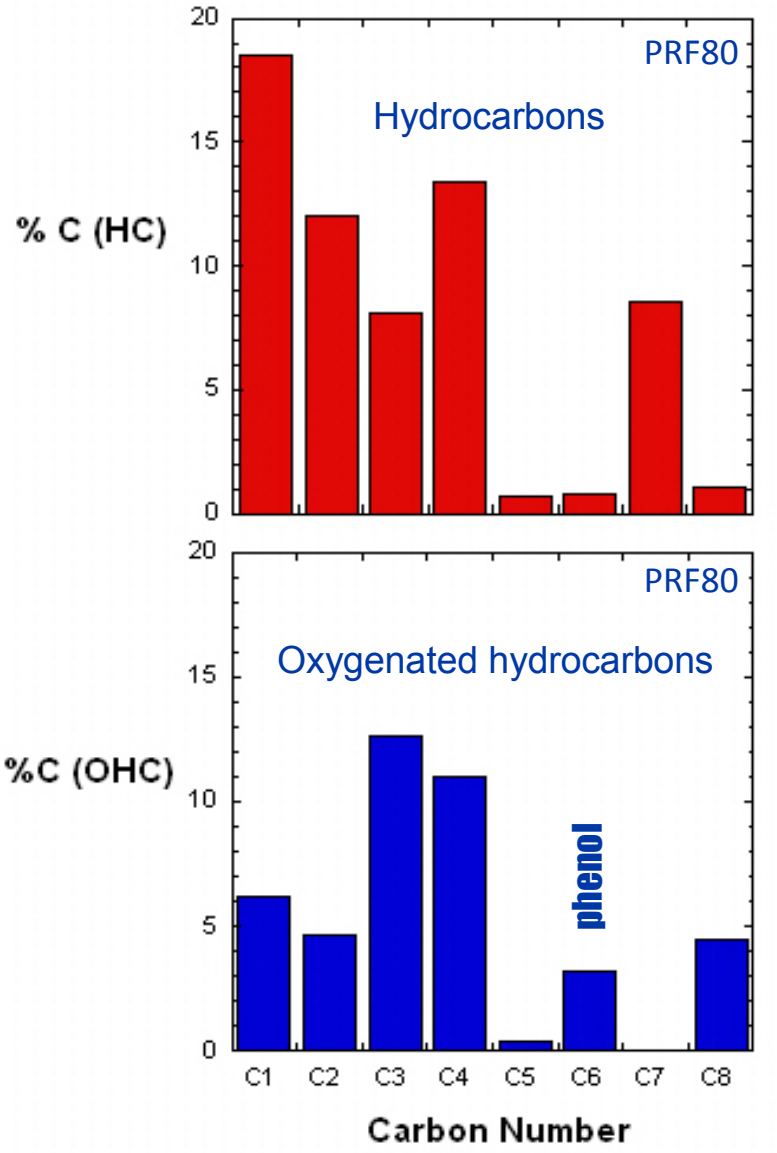


Better simulation of heat release rate

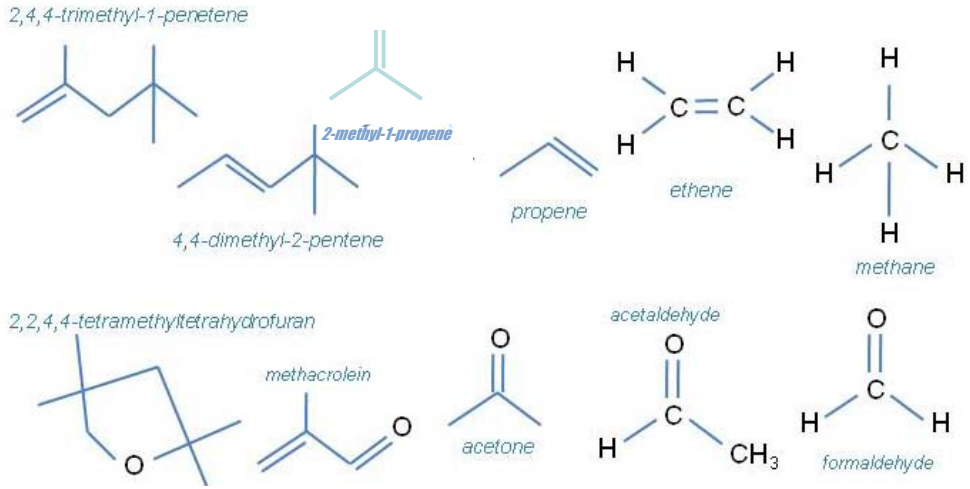


PRF80 fueling

PRF80 Initial Species Results



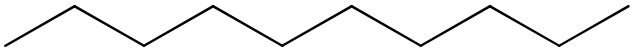
- Greater than 50 identifiable species in the exhaust
- Similarity to results from iso-octane and Chevron-Phillips Reference Gasoline
  - Many species in common, but relative amount varies
- Larger distribution of oxygenated species in near-misfire exhaust conditions



Major exhaust species besides unburned fuel

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

n-decane

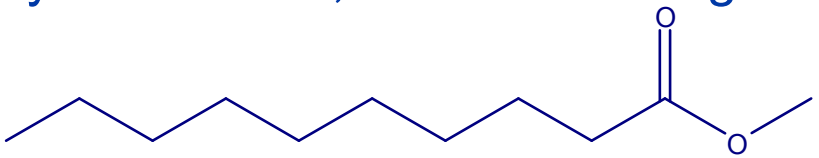


940 species
3887 reactions

⇒

211 species
794 reactions

Methyl-decanoate, biodiesel surrogate

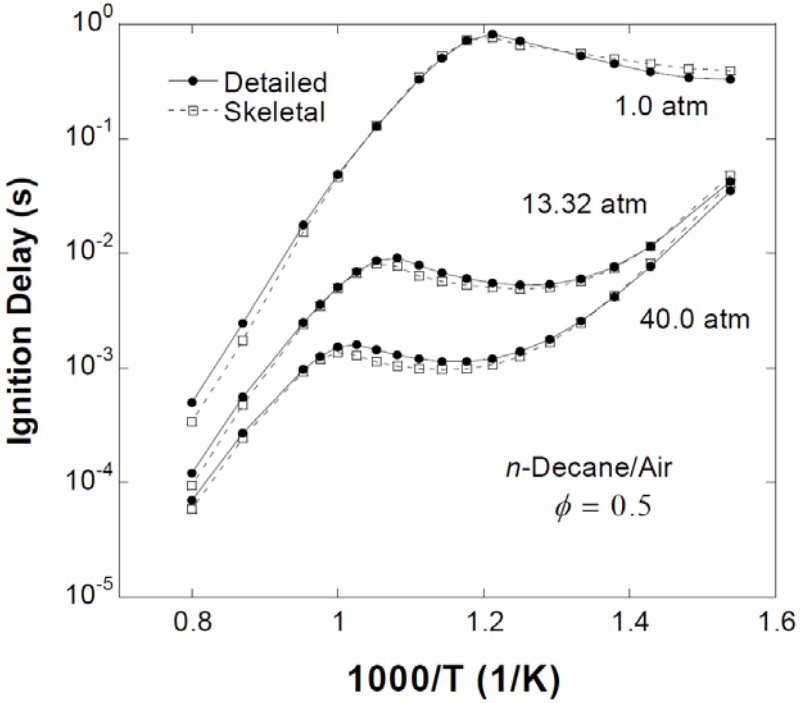


3036 species
8555 reactions

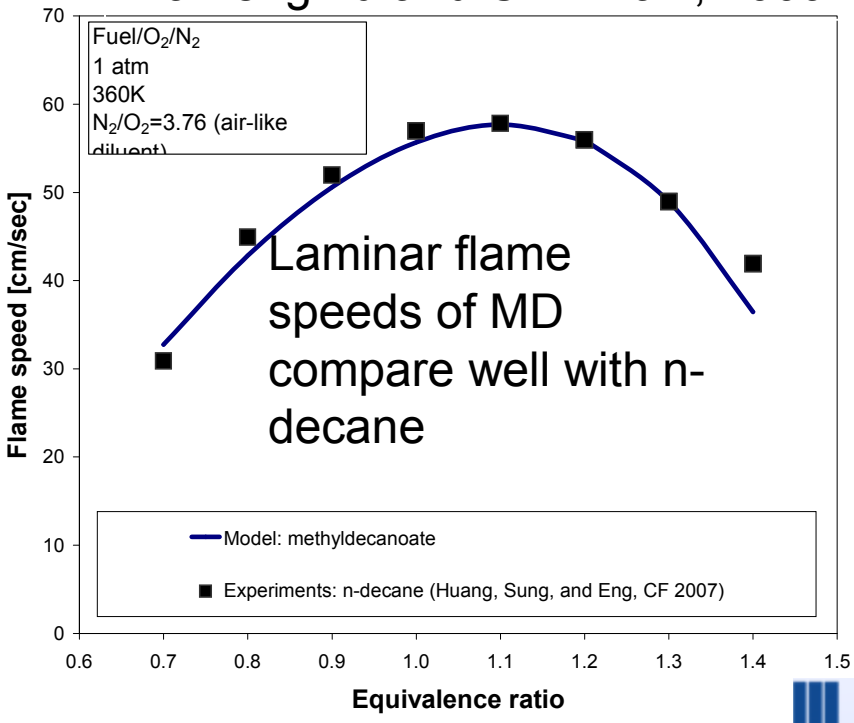
⇒

125 species
712 reactions

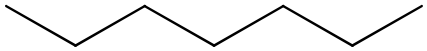
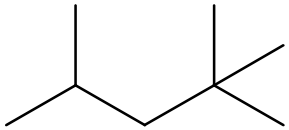
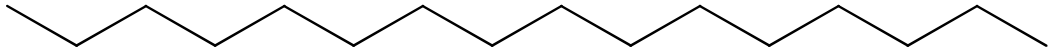
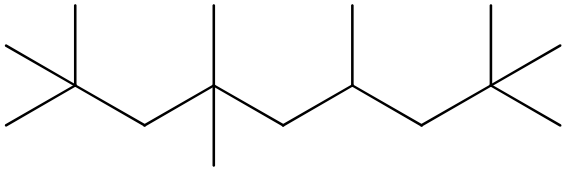
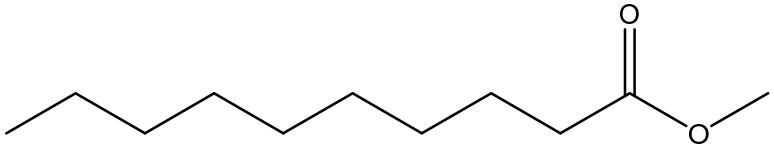
Niemeyer, Raju and Sung, *2009*



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

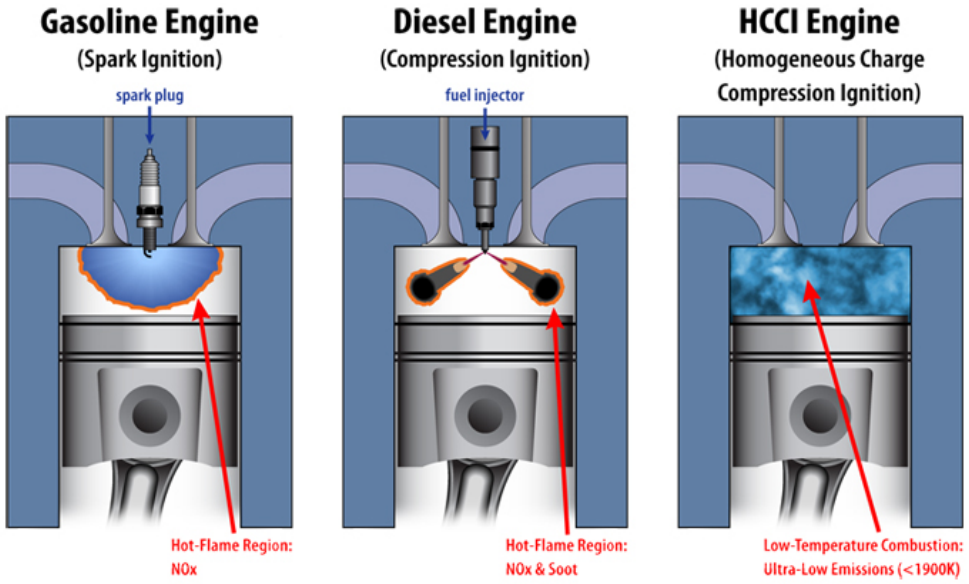
Combustion Chemistry

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.

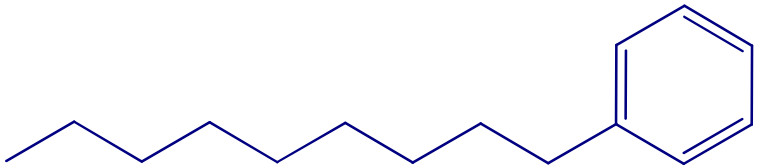
C8-C16 n-Alkanes



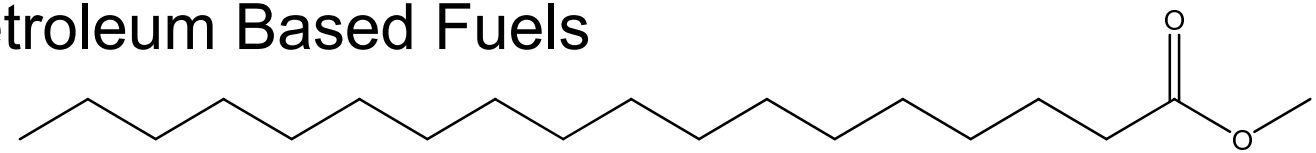
Future activities

Develop detailed chemical kinetic models for:

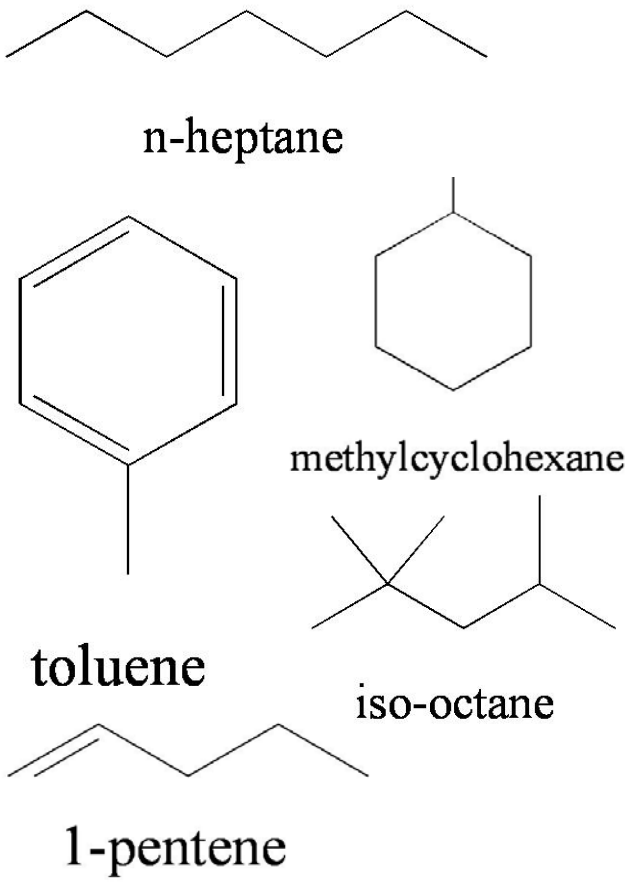
- large alkyl benzene, important component for diesel fuel



- 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

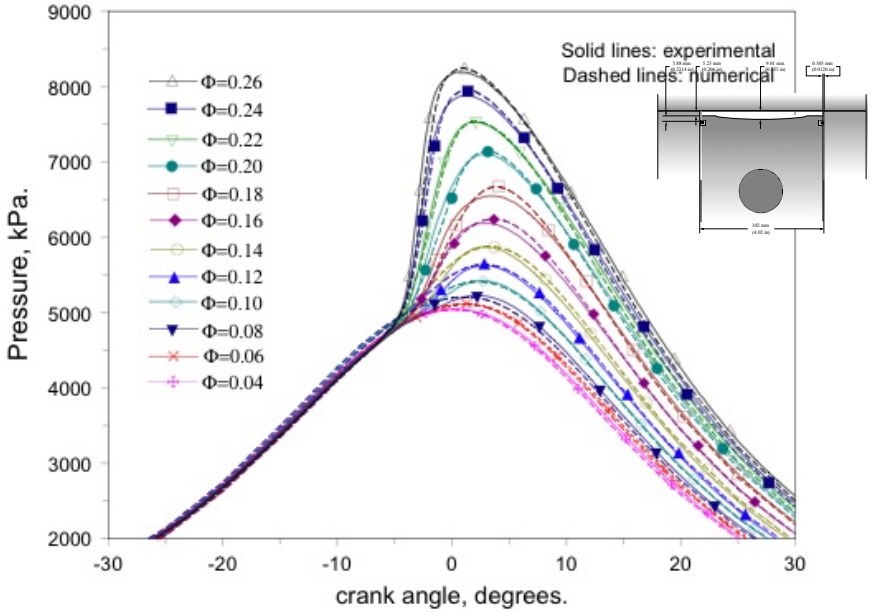


HCCI is a promising engine operating regime, and is also an excellent platform for developing & testing high fidelity chemical kinetic models



testing

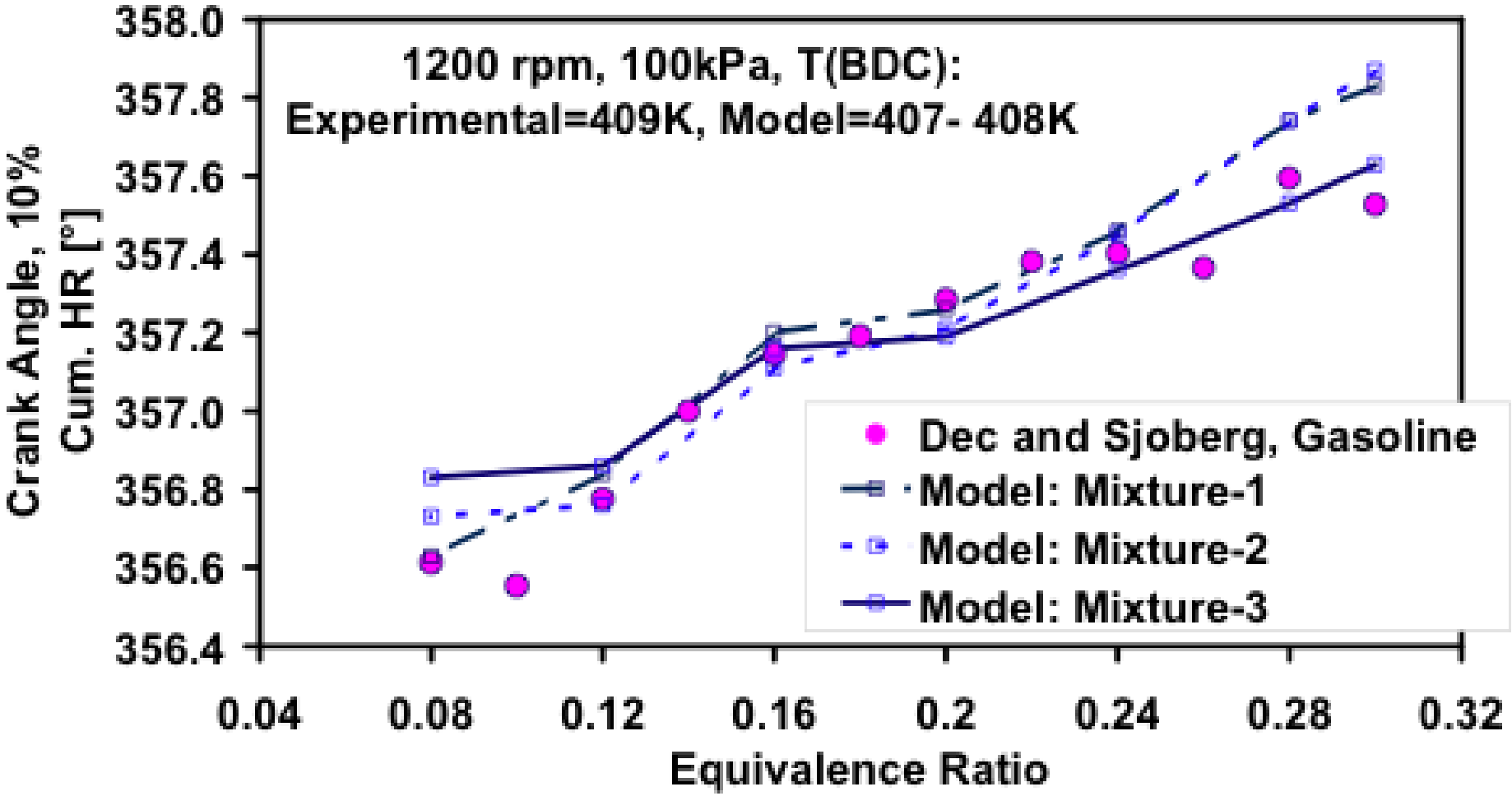
tuning



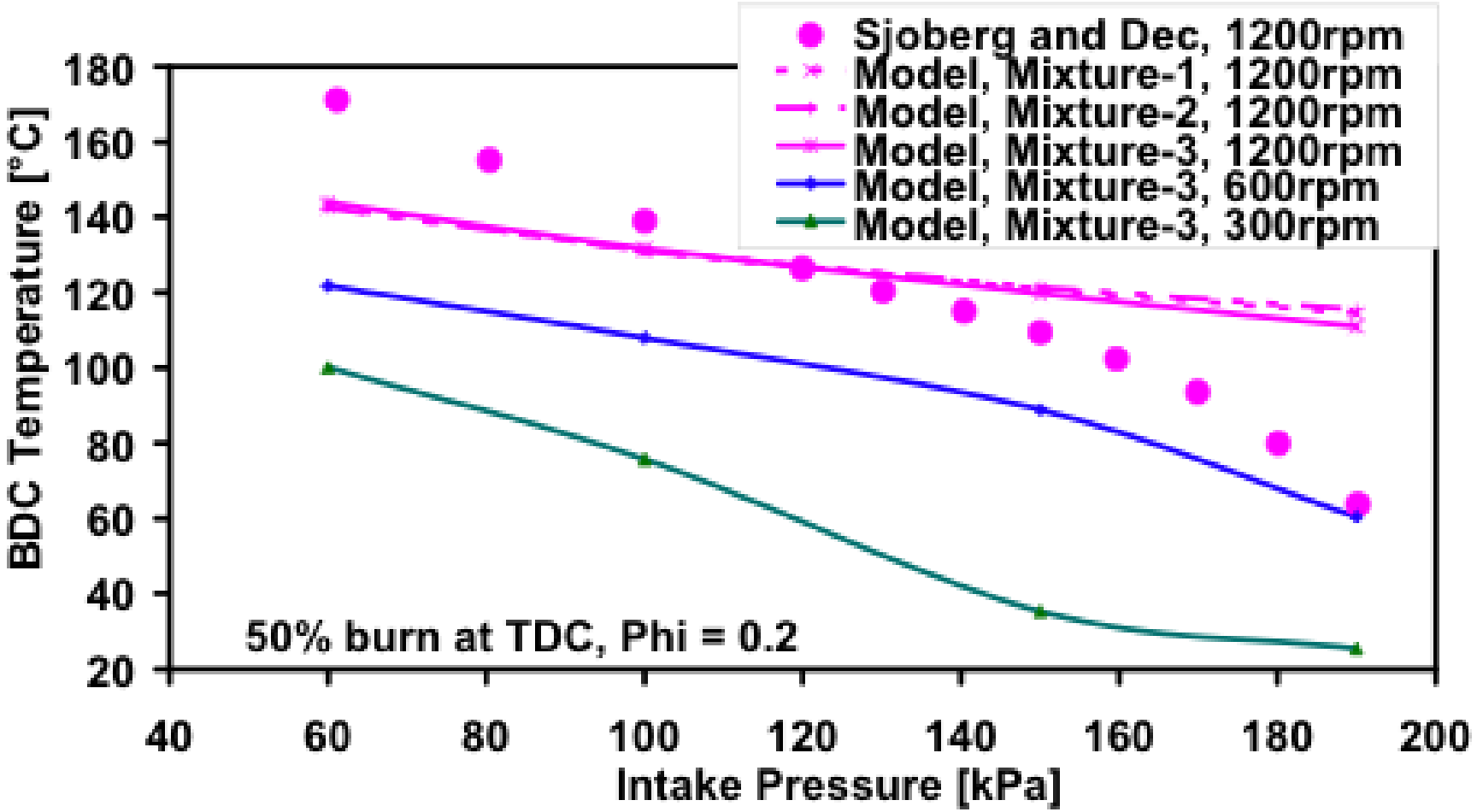
Detailed kinetics of gasoline surrogates

High fidelity engine models

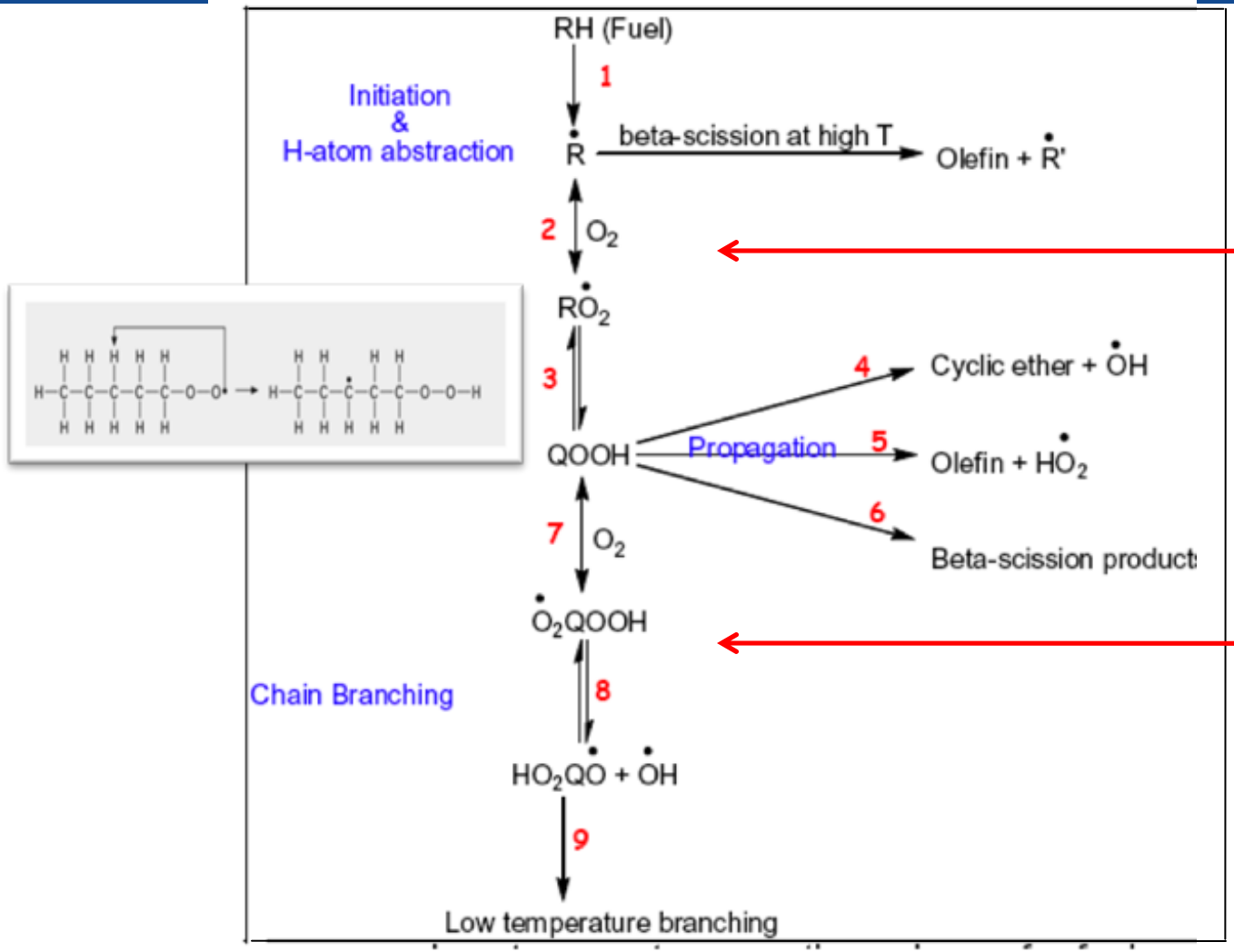
Gasoline surrogate model accurately predicts ignition time as a function of equivalence ratio



But it does not properly replicate ignition time as a function of intake pressure



Analysis of pressure sensitivity of low temperature reaction steps may offer guidance toward improving quality of agreement



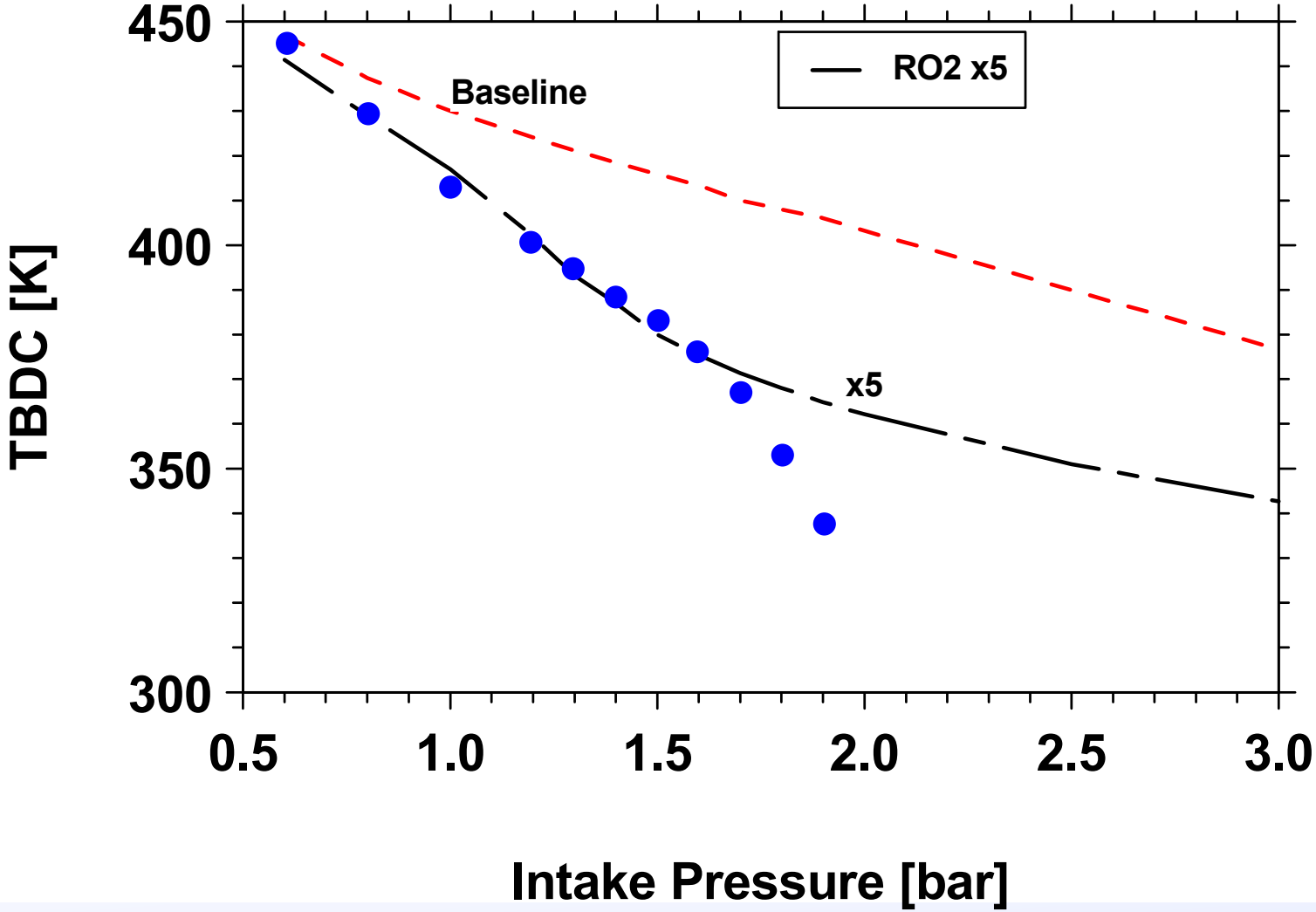
Radical recombination

$R + O_2 \rightarrow RO_2$

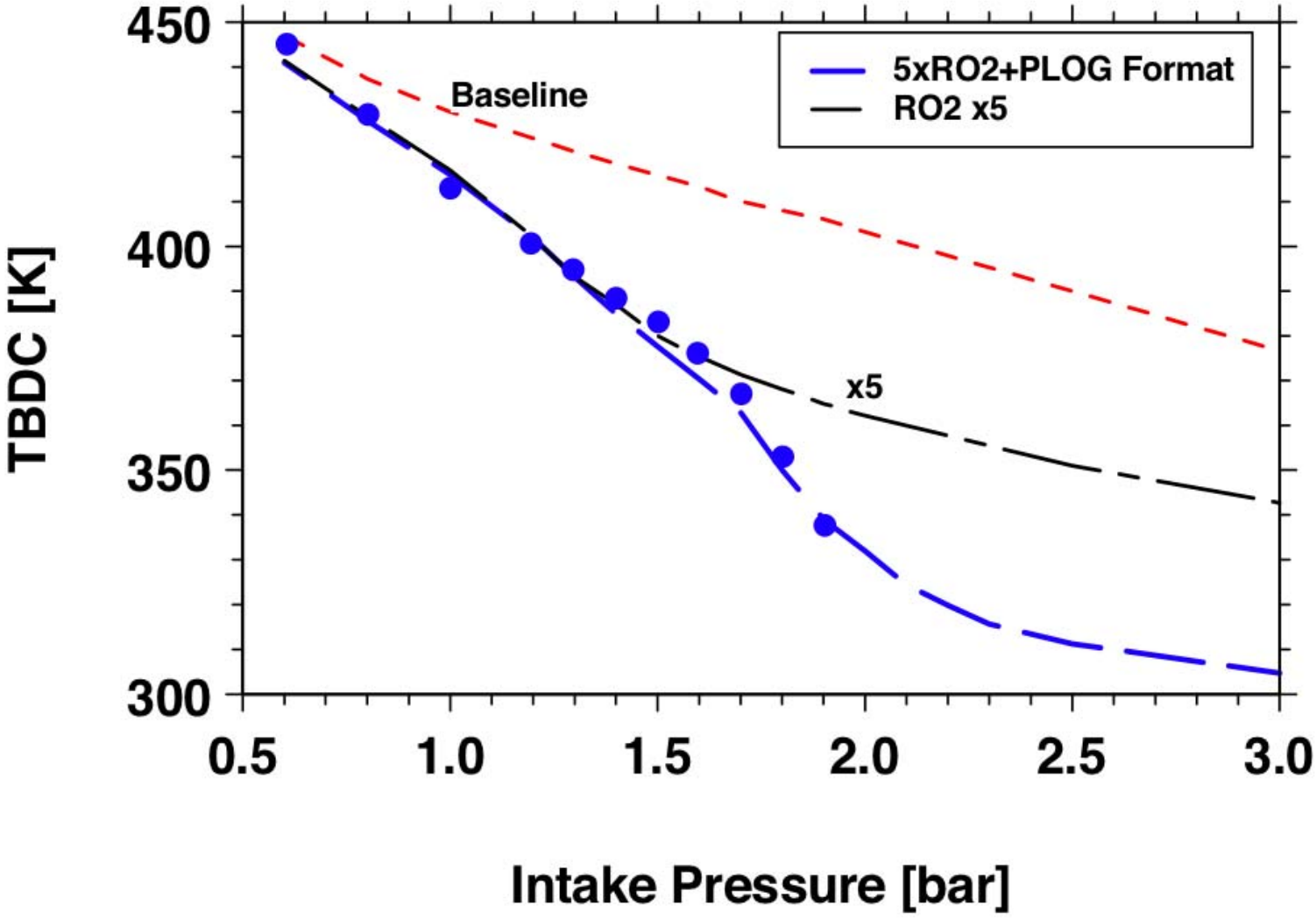
Chain branching

$O_2QOOH \rightarrow HO_2QO + OH$

Increasing the reactivity of the radical recombination reaction $R + O_2 \rightarrow RO_2$ matches experimental results up to ~1.7 bar intake



We obtain improved agreement by reducing activation energy of chain branching reactions as a function of pressure



Recent Publications

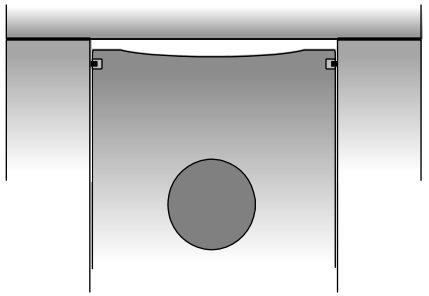
- M. A. Oehlschlaeger, J. Steinberg, C. K. Westbrook and W. J. Pitz, "The Autoignition of iso-Cetane: Shock Tube Experiments and Kinetic Modeling," Combustion and Flame, submitted (2009).
- Westbrook, C. K., Pitz, W. J., Herbinet, O., Curran, H. J. and Silke, E. J., "A Detailed Chemical Kinetic Reaction Mechanism for n-Alkane Hydrocarbons from n-Octane to n-Hexadecane," Combustion and Flame 156 (1) (2009) 181-199.
- Mehl, M., Vanhove, G., Pitz, W. J. and Ranzi, E., "Oxidation and Combustion of the n-Hexene Isomers: A Wide Range Kinetic Modeling Study," Combustion and Flame 155 (2008) 756–772.
- Herbinet, O., Pitz, W. J. and Westbrook, C. K., "Detailed Chemical Kinetic Oxidation Mechanism for a Biodiesel Surrogate," Combustion and Flame 154 (2008) 507-528. (2nd most downloaded paper in Combustion and Flame from July to September 2008).
- W. J. Pitz, C. K. Westbrook, O. Herbinet and E. J. Silke, "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, 2008.
- C. K. Westbrook, W. J. Pitz, H.-H. Carstensen and A. M. Dean, "Development of Detailed Kinetic Models for Fischer-Tropsch Fuels," 237th ACS National Meeting & Exposition, Salt Lake City, Utah, 2009.
- Dec, J.E., M.L. Davisson, M. Sjöberg, R. Leif, W. Hwang, 2008, Detailed HCCI exhaust speciation and the sources of hydrocarbon and oxygenated hydrocarbon emissions, SAE Congress Paper Number 2008-01-0053.
- Seshadri, K., Lu, T., Herbinet, O., Humer, S., Niemann, U., Pitz, W. J. and Law, C. K., "Ignition of Methyl Decanoate in Laminar Nonpremixed Flows," Proceedings of the Combustion Institute 32 (2009) 1067-1074.
- Sakai, Y., Miyoshi, A., Koshi, M. and Pitz, W. J., "A Kinetic Modeling Study on the Oxidation of Primary Reference Fuel-Toluene Mixtures Including Cross Reactions between Aromatics and Aliphatics," Proceedings of the Combustion Institute, 32 (2009) 411-418.
- Westbrook, C. K., Pitz, W. J., Curran, H. J. and Mehl, M., “The Role of Comprehensive Detailed Chemical Kinetic Reaction Mechanisms in Combustion Research” in:M. Dente, (Eds), Chemical Engineering Greetings to Prof. Eliseo Ranzi on Occasion of His 65th Birthday, AIDIC (Italian Association of Chemical Engineering) with the cultural partnership of Reed Business Information, 2008.
- Westbrook, C. K., Pitz, W. J., Westmoreland, P. R., Dryer, F. L., Chaos, M., Osswald, P., Kohse-Hoinghaus, K., Cool, T. A., Wang, J., Yang, B., Hansen, N. and Kasper, T., "A Detailed Chemical Kinetic Reaction Mechanism for Oxidation of Four Small Alkyl Esters in Laminar Premixed Flames," Proceedings of the Combustion Institute, 32 (2009) 221-228.
- C. K. Westbrook, W. J. Pitz, M. Mehl and H. J. Curran, "Detailed chemical kinetic models for large n-alkanes and iso-alkanes found in conventional and F-T diesel fuels," U.S. National Combustion Meeting, Ann Arbor, MI, 2009.
- M. Mehl, H. J. Curran, W. J. Pitz and C. K. Westbrook, "Detailed Kinetic Modeling of Gasoline Surrogate Mixtures," U.S. National Combustion Meeting, Ann Arbor, MI, 2009.

Recent Publications

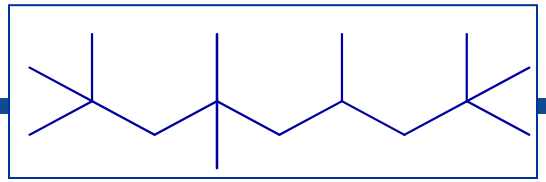
1. **Pathline Analysis of Full-cycle Four-stroke HCCI Engine Combustion Using CFD and Multi-Zone Modeling,** Randy P. Hessel, David E. Foster, Richard R. Steeper, Salvador M. Aceves, Daniel L. Flowers, SAE Paper 2008-01-0048.
2. **Modeling Iso-octane HCCI using CFD with Multi-Zone Detailed Chemistry; Comparison to Detailed Speciation Data over a Range of Lean Equivalence Ratios,** Randy P. Hessel, David E. Foster, Salvador M. Aceves, M. Lee Davisson, Francisco Espinosa-Loza, Daniel L. Flowers, William J. Pitz, John E. Dec, Magnus Sjöberg, Aristotelis Babajimopoulos, SAE Paper 2008-01-0047.
3. **Liquid penetration Length in Direct Diesel Fuel Injection,** S. Martínez-Martínez, F.A. Sánchez-Cruz, J.M. Riesco-Ávila, A. Gallegos-Muñoz and S.M. Aceves, Applied Thermal Engineering, Vol. 28, pp. 1756-1762, 2008.
4. **HCCI Engine Combustion Timing Control: Optimizing Gains and Fuel Consumption Via Extremum Seeking,** N.J. Killingsworth, S.M. Aceves, D.L. Flowers, F. Espinosa-Loza, and M. Krstic, Accepted for publication, IEEE Transactions On Control Systems Technology, 2009.
5. **Demonstrating Optimum HCCI Combustion with Advanced Control Technology**, Daniel Flowers, Nick Killingsworth, Francisco Espinoza-Loza, Joel Martinez-Frias, Salvador Aceves, Miroslav Krstic, Robert Dibble, SAE Paper 2009-01-1885, 2009.

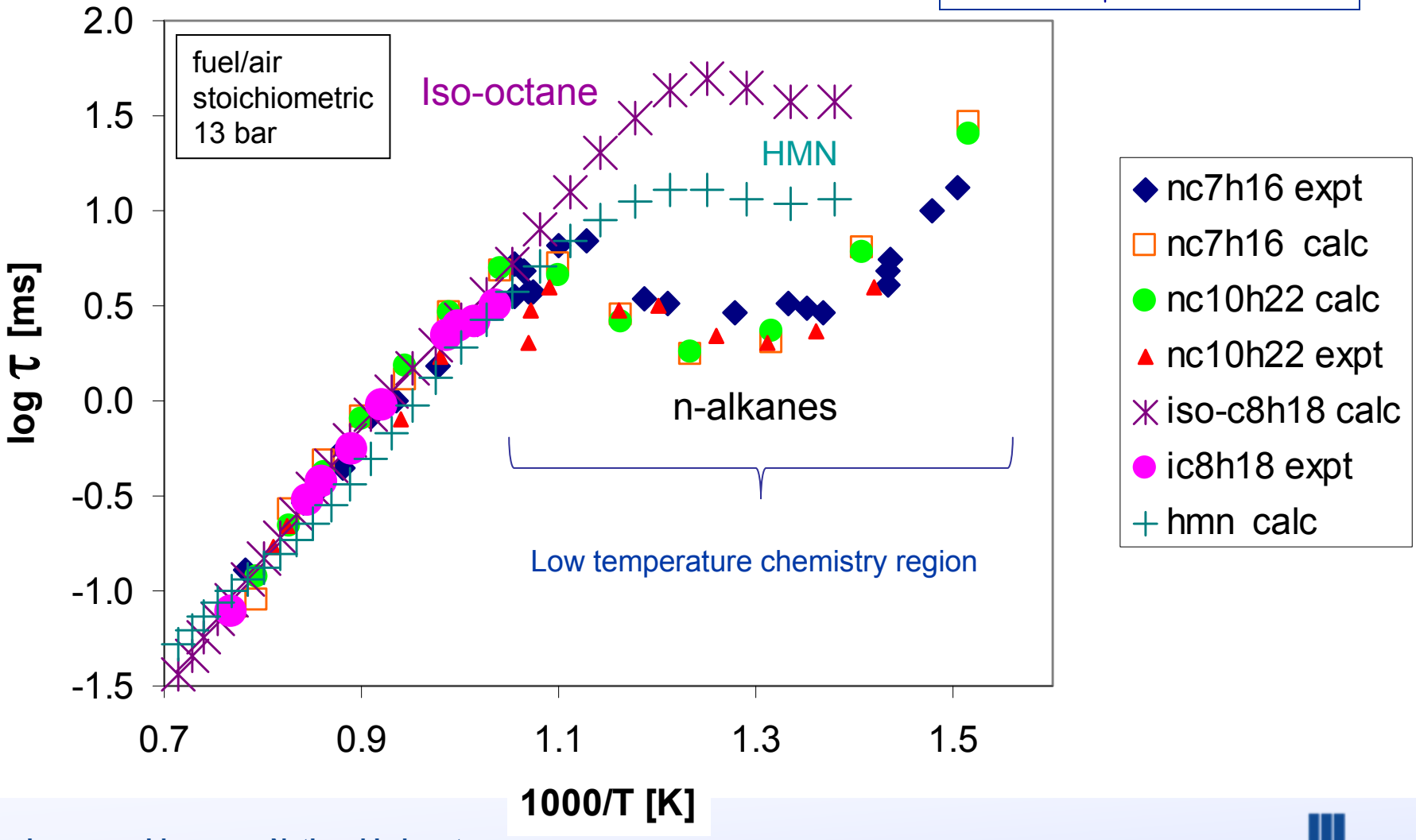
We have obtained engine speciation data for validation of HCCI KIVA multizone model with detailed chemical kinetics

- 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

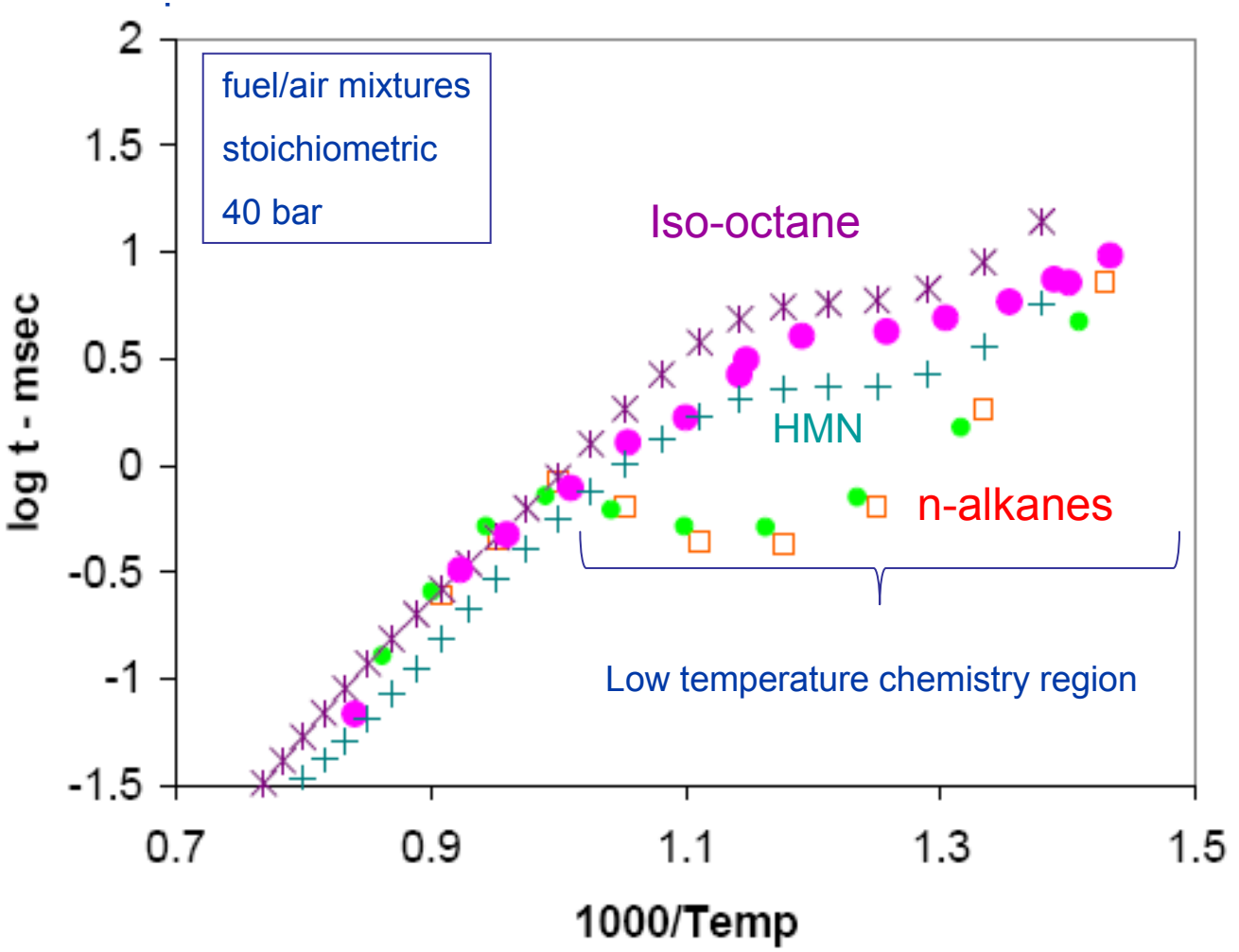


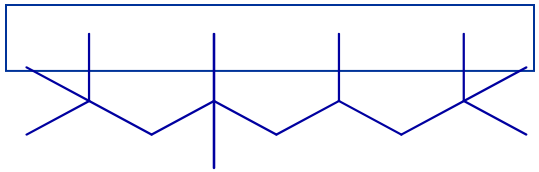
Reactivity for HMN is between those of iso-octane and large n-alkanes





Similar behavior seen at 40 bar





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iso-c8h18 calc
ic8h18 expt
hmn calc