Lawrence Livermore National Laboratory

Chemical Kinetic Models for Advanced Engine Combustion

William J. Pitz (PI)
Marco Mehl, Charles K. Westbrook
Lawrence Livermore National Laboratory
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Project ID # ACE013

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

Washington, DC

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LLNL-PRES-652979

Overview

Timeline

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

Budget

Project funded by DOE/VT:

- FY13: 600K
- FY14: 550K

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 for fuels are a critical part of engine simulation models

Partners

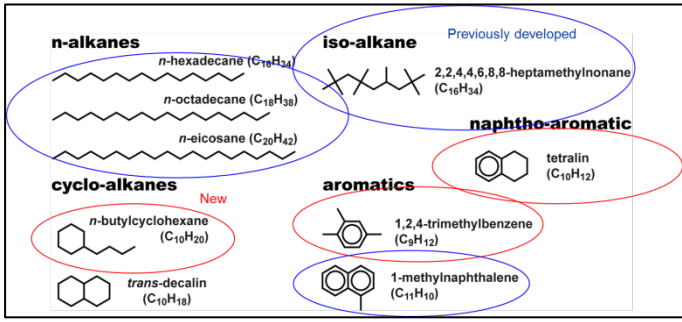
- Project Lead: LLNL – W. J. Pitz (PI)
- Part of Advanced Engine Combustion (AEC) working group:
- – 15 Industrial partners: auto, engine & energy
- – 5 National Labs & 10 Universities
- Sandia: Provides engine data for validation of detailed chemical kinetic mechanisms
- FACE Working group of the Coordinating Research Council (CRC)

Objectives and relevance to DOE objectives

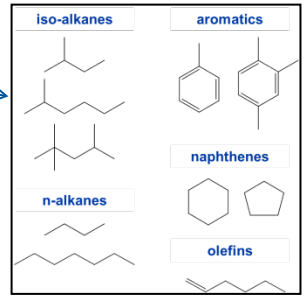
- Objectives:
  - Develop predictive chemical kinetic models for gasoline, diesel and next generation fuels so that simulations can be used to overcome technical barriers to low temperature combustion in engines and needed gains in engine efficiency and reductions in pollutant emissions

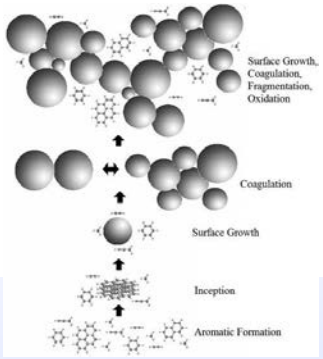
- FY14 Objectives:
  - Develop remaining kinetic models for CRC AVFL-18 nine-component diesel surrogate
  - Develop chemical kinetic models for surrogates for FACE gasoline fuels
  - Improve soot precursor models to simulate soot formation in engines

CRC AVFL-18 Diesel surrogate palette:



10-component gasoline surrogate palette:





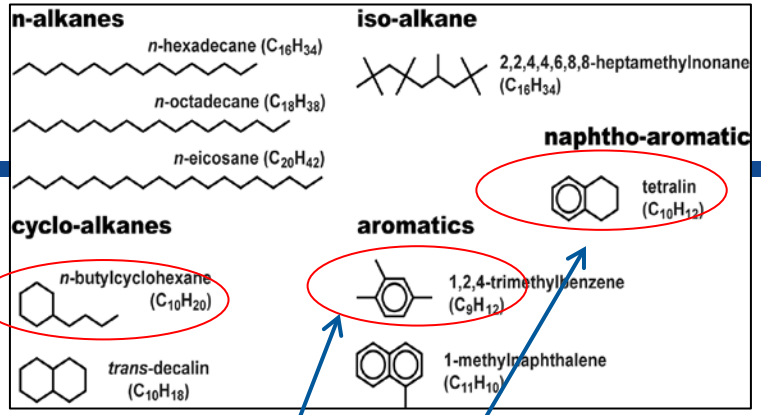
Chemical kinetic milestones

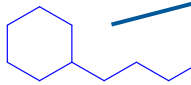
- ✓ Develop final n-butyl-cyclohexane model (December, 2013)
- ✓ Develop detailed chemical kinetic model for tri-methyl benzene (March, 2014)
- ✓ Detailed kinetic modeling of surrogates for gasoline fuels (Sept, 2014)

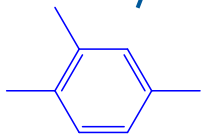
4. Develop chemical kinetic model for tetralin (June, 2014)

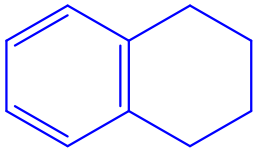
5. Develop a preliminary model for large PAH as soot precursor (Sept, 2014)

CRC AVFL-18 Diesel surrogate palette:

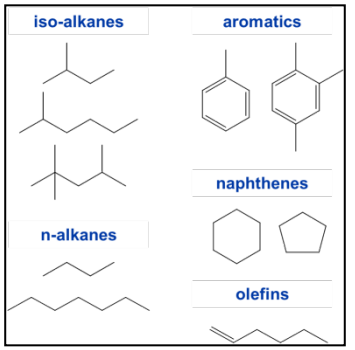


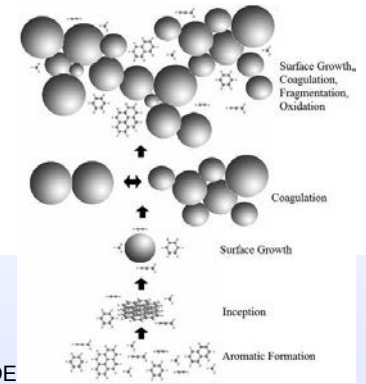






10-component gasoline surrogate palette for FACE fuels:





Approach

- Develop surrogate fuel models for gasoline, diesel, and next-generation fuels to enable the prediction of the effect of fuel properties on advanced engine combustion

- Develop chemical kinetic reaction models for each individual fuel component of importance for fuel surrogates for gasoline, diesel, and next generation fuels

- Combine mechanisms for representative fuel components to provide surrogate models for practical fuels
  - diesel fuel
  - gasoline (HCCI and/or SI engines)
  - addition of ethanol and other biofuels

- Reduce mechanisms for use in CFD and multizone HCCI engine 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

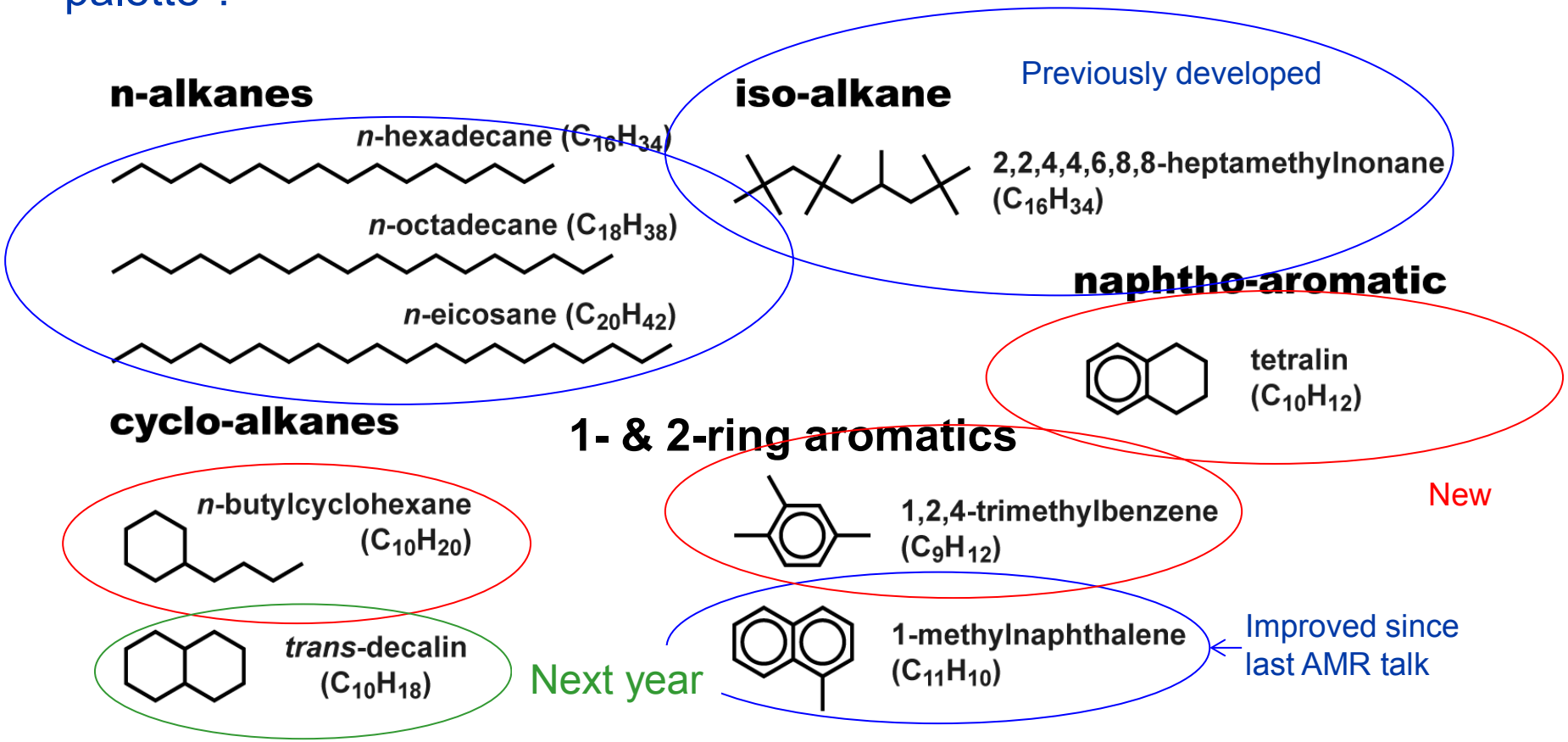
- Iteratively improve models as needed for applications
- Make models available to industry

- Addresses barriers to increased engine efficiency and decreased emissions by allowing optimization of fuels with advanced engine combustion

Technical Accomplishments

Diesel components selected for mechanism development in FY14

Components selected from the CRC AVFL-18 Diesel Surrogate palette[1]:



[1] Coordinating Research Council (CRC) AVFL-18 Working Group. Mueller, C. J., Cannella, W. J., Bruno, T. J., Bunting, B., Dettman, H. D., Franz, J. A., Huber, M. L., Natarajan, M., Pitz, W. J., Ratcliff, M. A. and Wright, K., Energy & Fuels 26(6):3284–3303 (2012).

Fuel component and surrogate models validated by comparison to fundamental experimental data

Jet Stirred Reactors

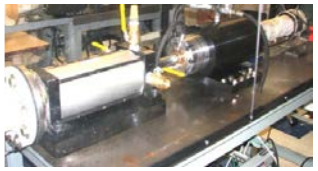
Premixed Laminar Flames


Twin premixed flames

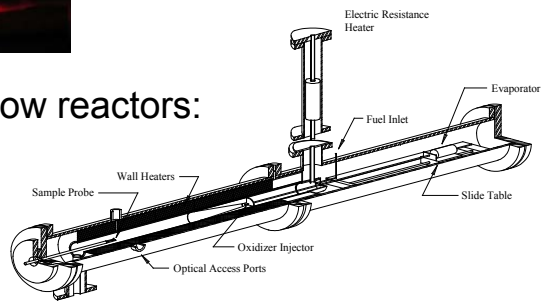
Shock tube

Non Premixed Flames

Rapid Compression Machine



High pressure flow reactors:



Engine Combustion

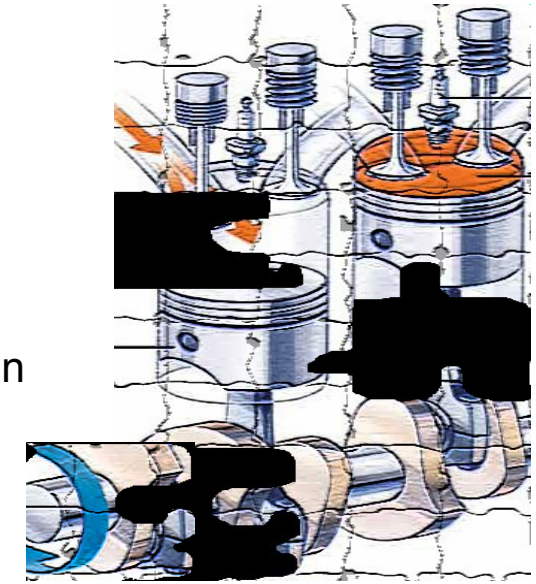
Combustion Parameters

Temperature

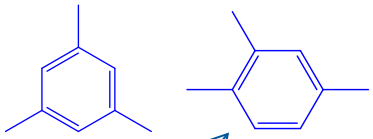
Pressure

Mixture fraction (air-fuel ratio)

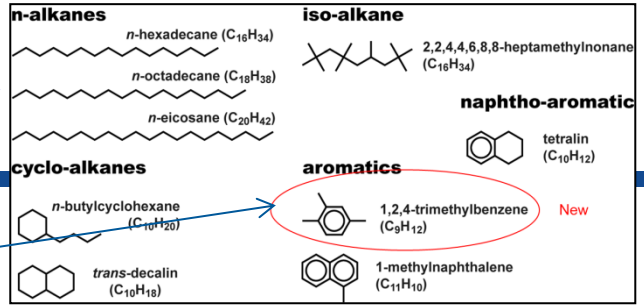
Mixing of fuel and air



Development of a mechanism for tri-methylbenzene: (2 isomers)

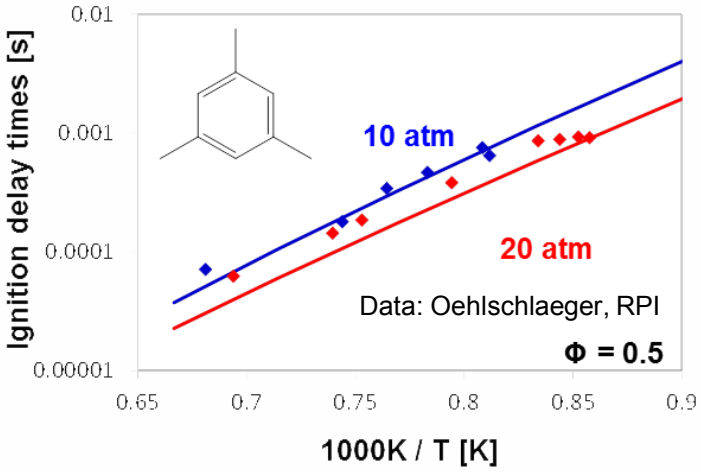


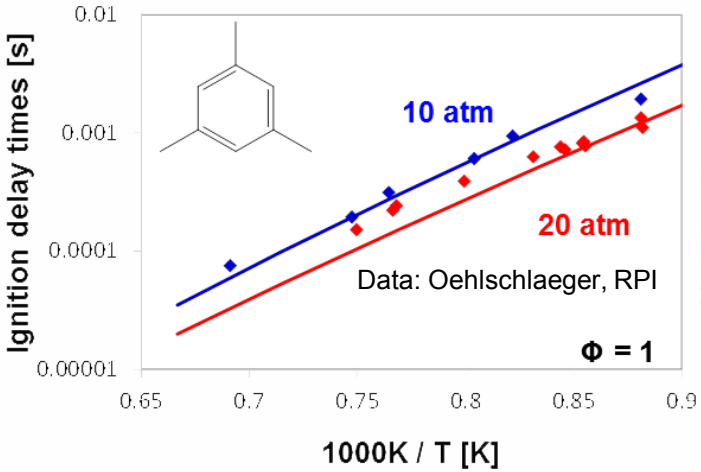
CRC AVFL-18 9-component diesel surrogate:

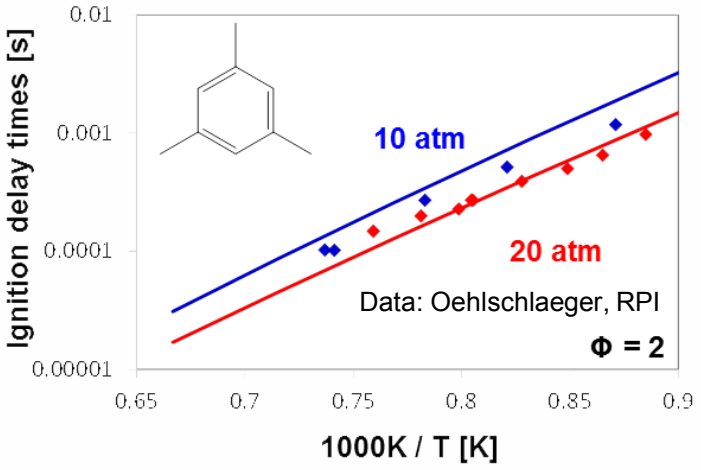


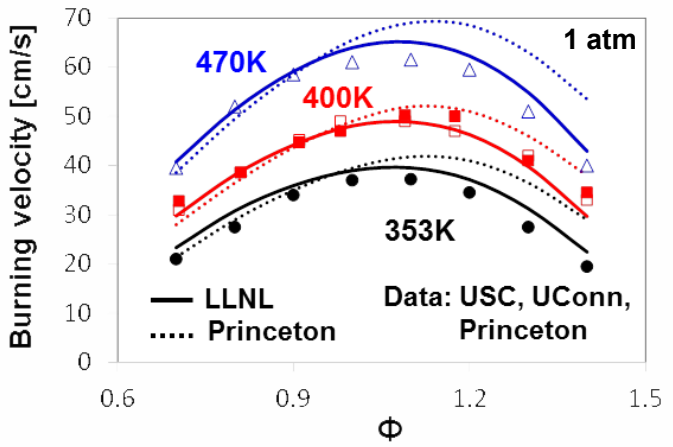
In 9-component diesel surrogate

Results for this isomer:

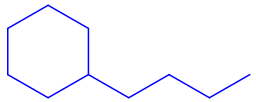




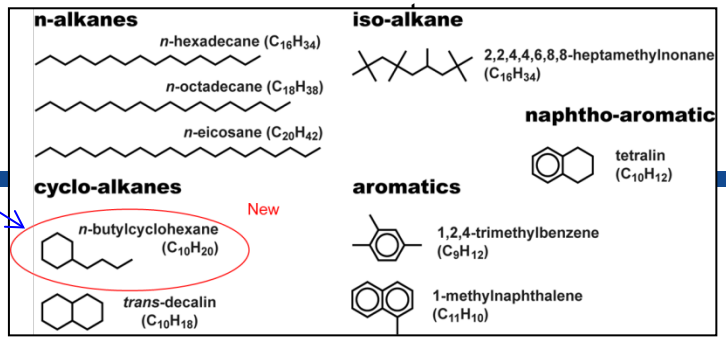




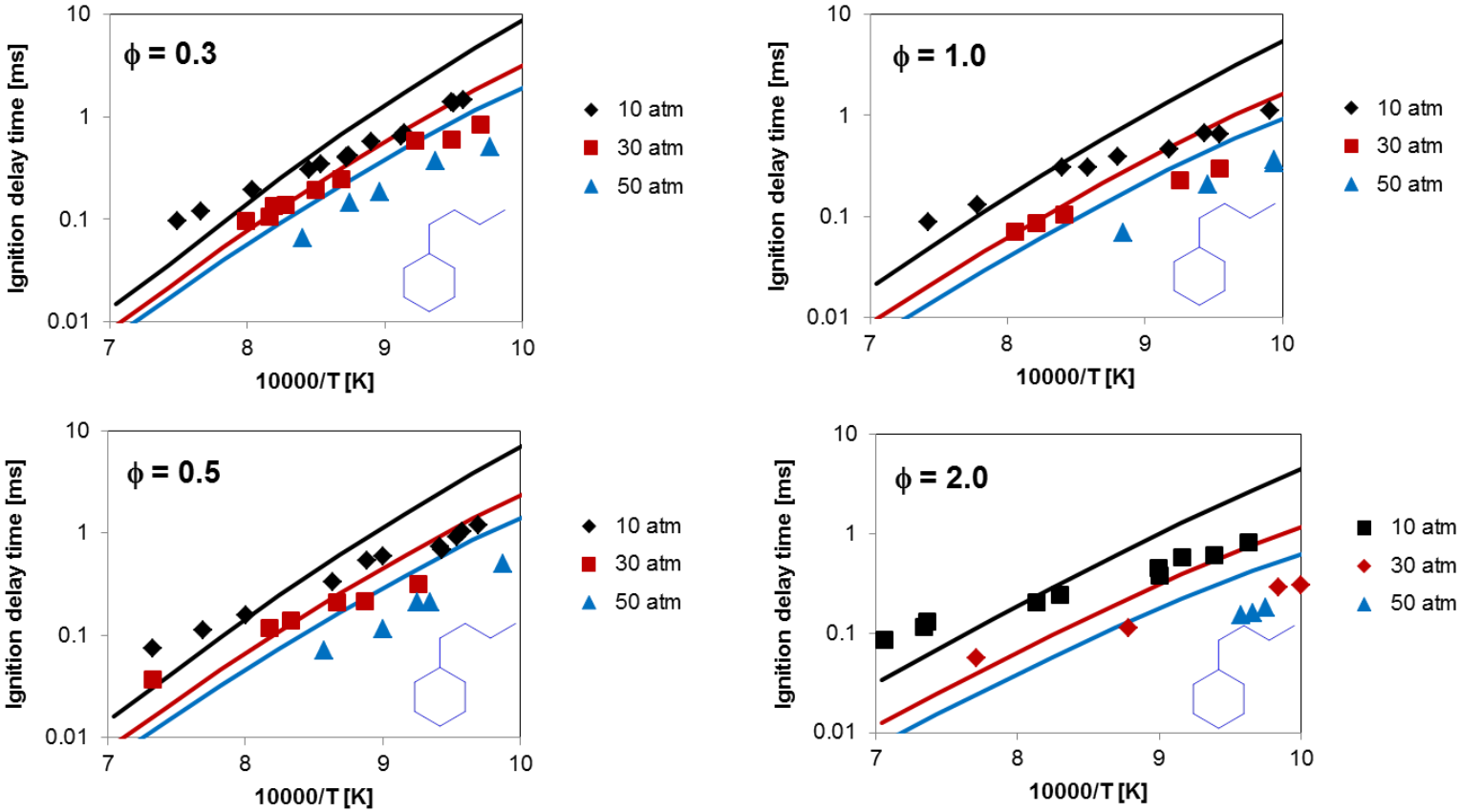
New mechanism for n-butylcyclohexane developed



CRC AVFL-18 9-component diesel



Mechanism validated against shock-tube experimental data with reasonable agreement



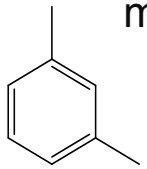
Experimental data: Conway and Curran, NUIG 2014

A two-component diesel surrogate model developed for CFD engine applications: n-dodecane and m-xylene (Collaboration with Argonne and UCONN)

- Being considered as part of Engine Combustion Network (ECN) effort:

n-dodecane

77%vol



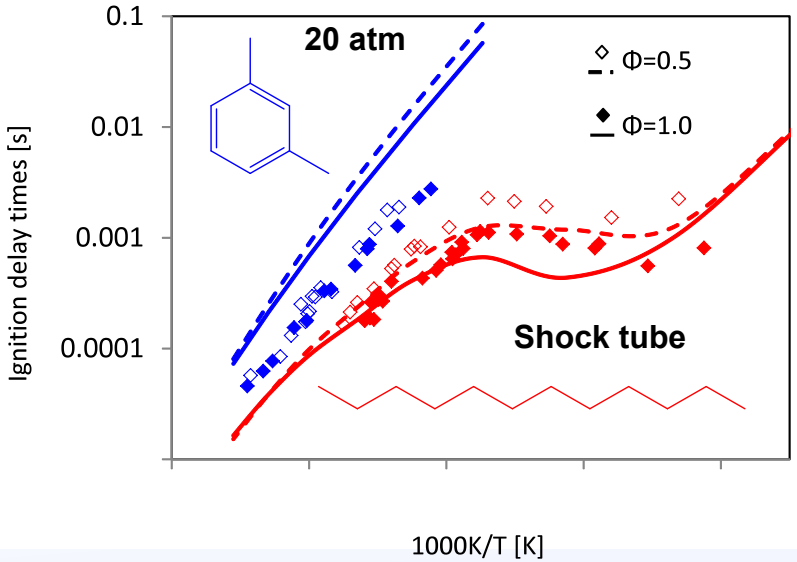
m-xylene

23%vol

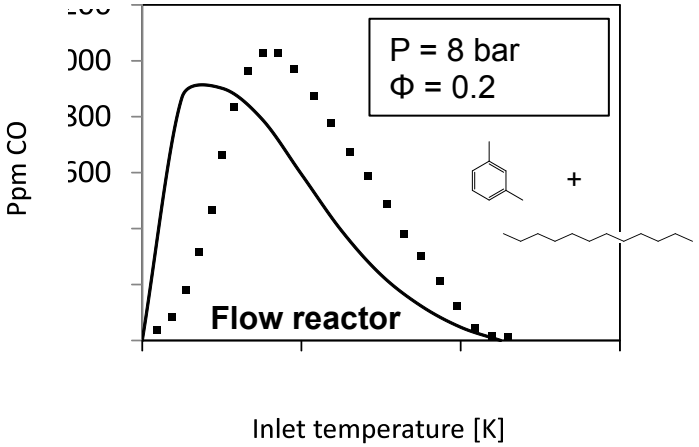
Called "SR23"

- A detailed kinetic mechanism for the surrogate was assembled which gives agreement obtained with experimental data:

Surrogate fuel components:



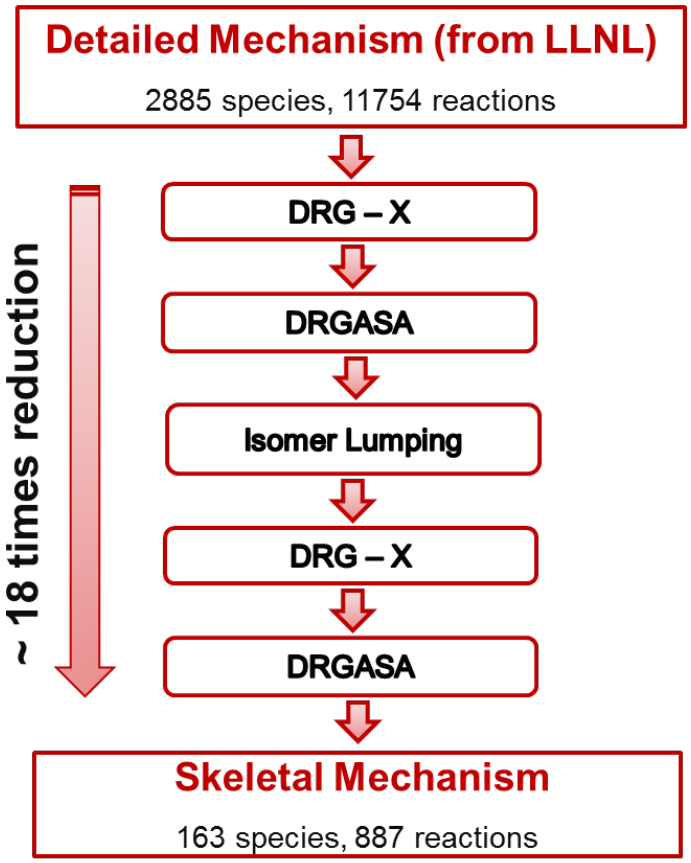
Surrogate SR23:



Experimental data: Natelson, et al., Comb. Sci. Tech, 2011

Blue symbols: Shen and Oehlschlaeger, Combustion and Flame, 2009
Red symbols: Vasu et al., Proc. Combust. Inst., 2009

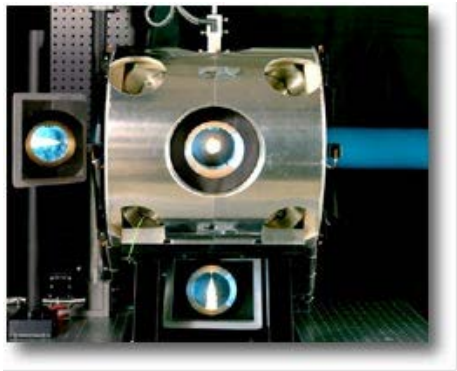
The surrogate model was reduced at UConn using X-DRG targeting ignition delay times



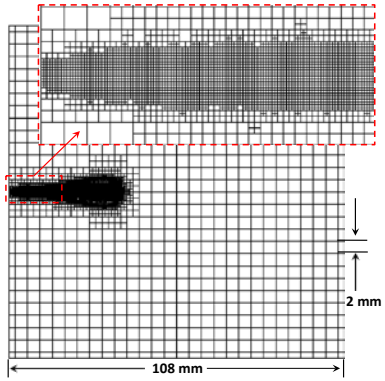
Range of operation:

- ✓ Pressure: 1-100 atm
- ✓ Equivalence ratio: 0.5-2.0
- ✓ Initial temperature: 700 – 1800 K

Applied to constant-volume chamber:



Sandia – L. Pickett

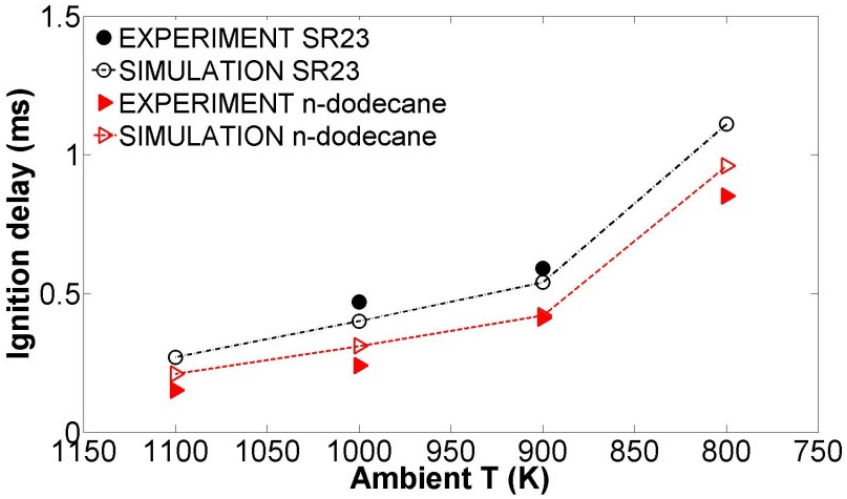


ANL – S. Som

Y. Pei, W. Liu, M. Mehl, S. Som, T. Lu, WJ, Pitz,

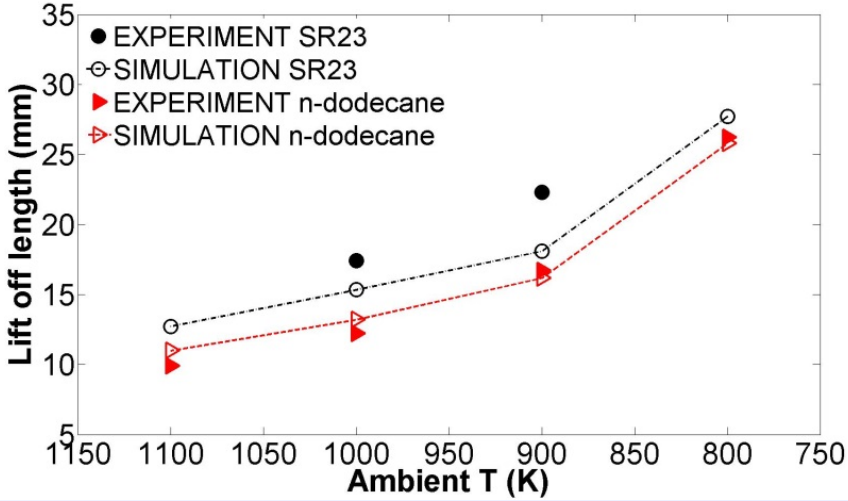
Proc. ASME Internal Combustion Engine Division, submitted, 2014

CFD Simulations under engine conditions performed at ANL to reproduce experimental data taken at Sandia



Ignition delay times are well predicted

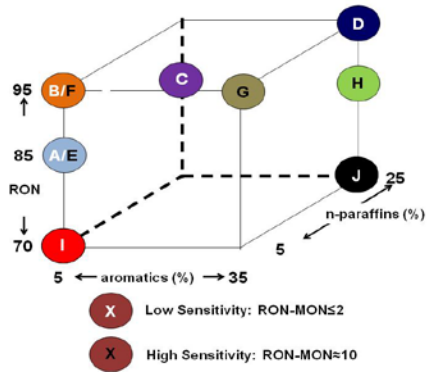
Some discrepancies in lift-off lengths currently under investigation



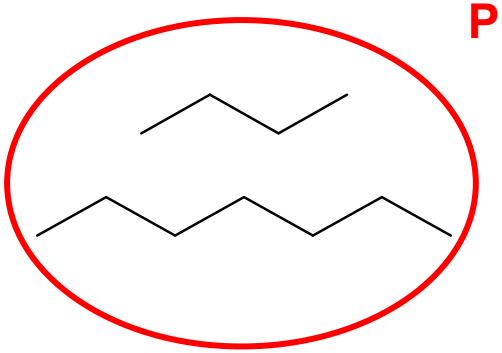
Y. Pei, W. Liu, M. Mehl, S. Som, T. Lu, WJ, Pitz,

Proc. ASME Internal Combustion Engine Division, submitted, 2014

Modeling of gasoline fuels: Developed 10-component surrogate palette to match properties of FACE gasoline fuels (Collaboration with KAUST, UConn, and RPI)



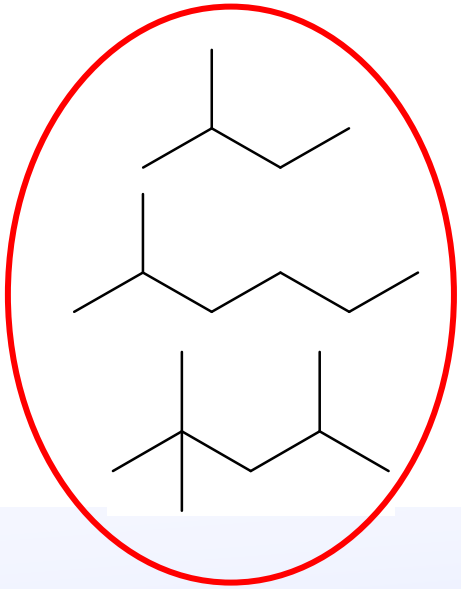
n-alkanes



Previous work

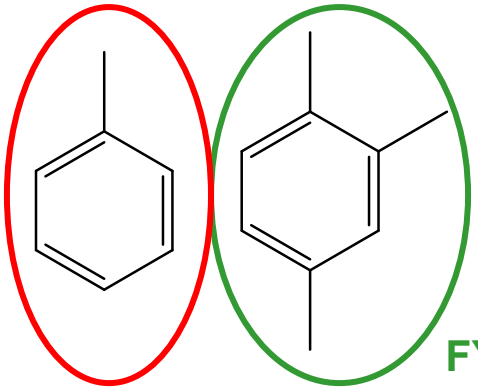
Allow to match the average chain length

iso-alkanes



To match the average molecular weight and the degree of branching

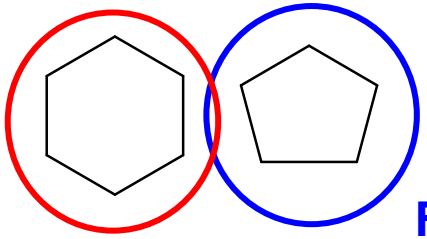
aromatics



To match the molecular weight and the degree of alkyl substitution

FY2014 (also diesel surrogate compound)

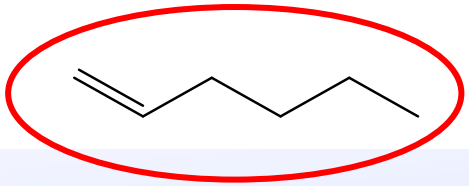
naphthenes



Two representative species

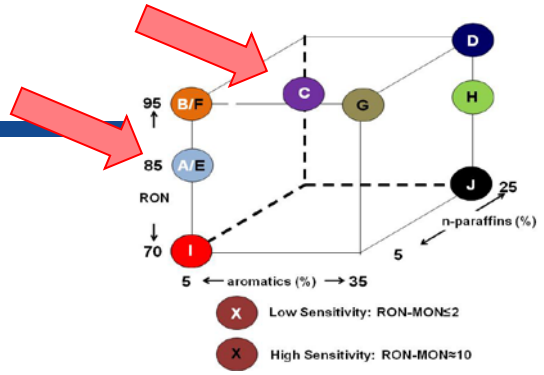
Future work

olefins



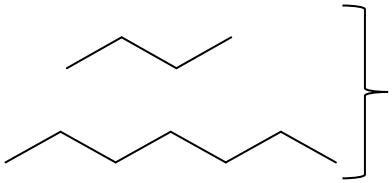
Major unsaturated linear species

Modeled FACE gasoline fuels A and C in the shock tube and RCM (Collaboration with KAUST, UConn, and RPI)

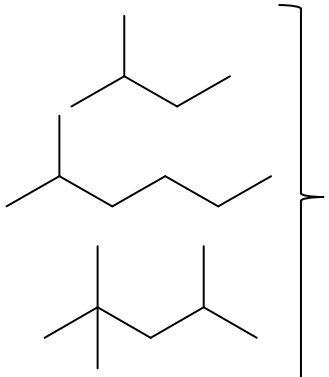


Used 6 components in palette: (based on detailed hydrocarbon analysis)

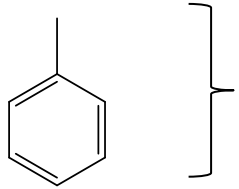
n-alkanes:



iso-alkanes:



aromatics:

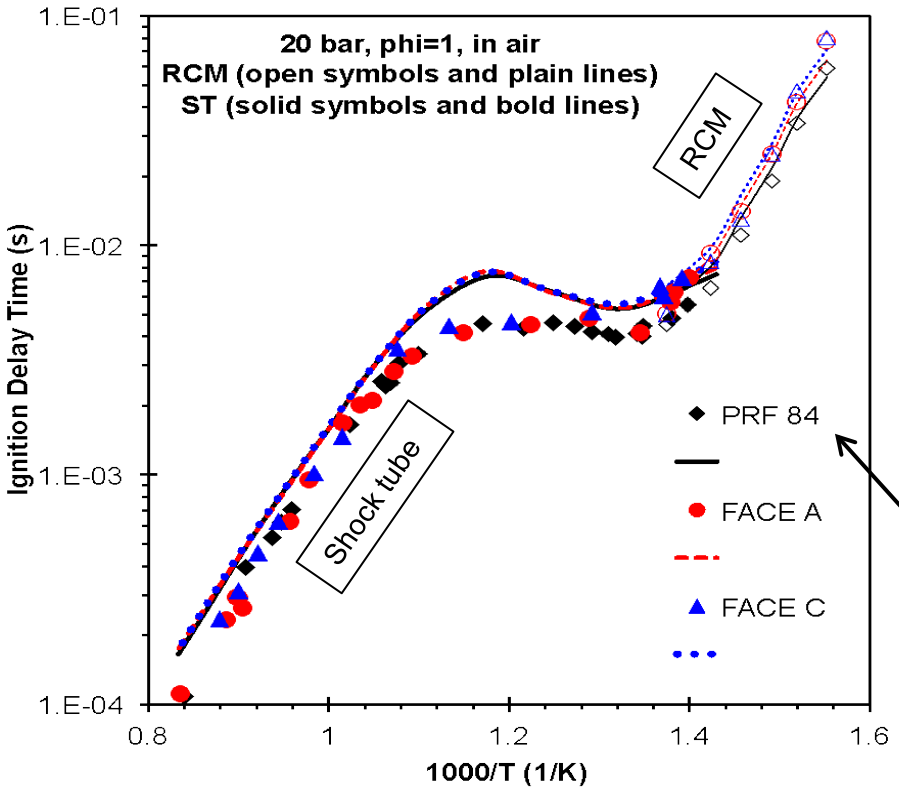


Comparison of FACE gasolines (bold) and surrogate mixtures

	FACE A	FACE A Surrogate	FACE C	FACE C Surrogate
AKI	83.5	84	84	84
Sensitivity	-0.1	0	1.1	0
H/C ratio	2.29	2.29	2.27	2.26
Avg. mol. wt.	98	100	97	98
		Hydrocarbon Type, liquid mol%		
n-alkanes	13	14	29	28
iso-alkanes	84	86	65	69
Aromatics	0.3	0	4.4	3.0
Alkenes	0.4	0	0.4	0
Cycloalkanes	2.4	0	1.5	0

Sarathy, Kukkadapu, Mehl, Wang, Javed, Park, Oehlschlaeger, Farooq, Pitz, and Sung, Proc. Combust. Institute, Submitted (accepted for presentation), 2014

Comparison of surrogate modeling simulations with shock tube data and RCM data for FACE fuel



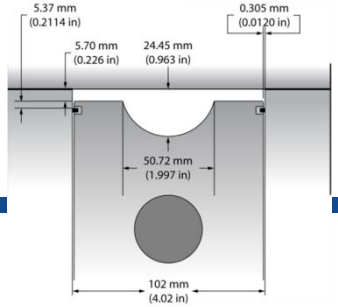
- Both model and experiment show little effect of fuel composition for these mixtures with nearly the same AKI and sensitivity
- Experiments at 10, 20 and 40 bar

PRF84 reference fuel for comparison

Shock tube experiments: Oehlschlaeger et. al., RPI
RCM experiments: Curran et al., NUIG

Sarathy, Kukkadapu, Mehl, Wang, Javed, Park, Oehlschlaeger, Farooq, Pitz, and Sung, Proc. Combust. Institute, Submitted (accepted for presentation), 2014

Modeling of Sandia HCCI engine experiments with gasoline surrogates model including ethanol



ITHR (Intermediate Temperature Heat Release) in gasoline/ethanol blends was experimentally investigated in Sandia HCCI engine (Dec and co-workers)

ITHR helps to extend the load limit for HCCI operation

Modeling:

- Single zone model
- Imposed T and P @ CA330 from engine experiments
- Adjusted EGR in simulations so that CA50 in model matched CA10 in experiments

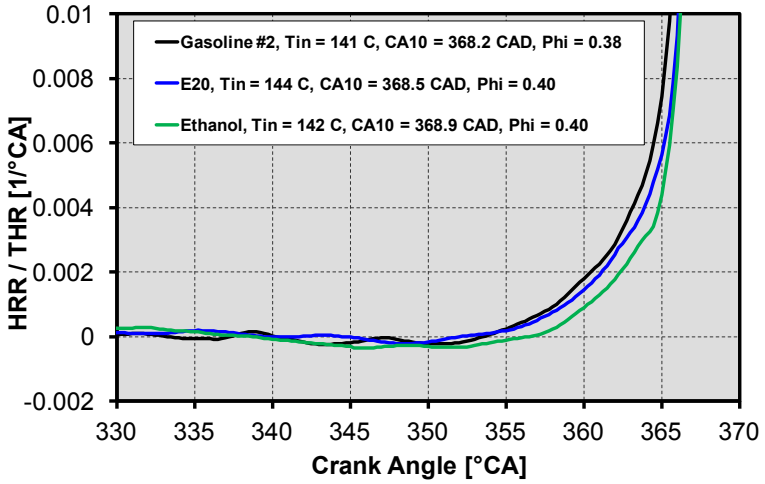
  → The EGR in the simulations matched the experimental value within few %

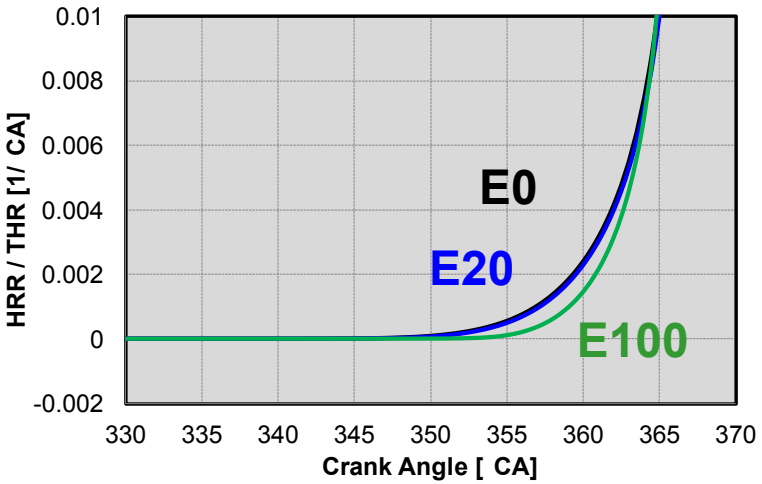
The model reproduces the trends for ITHR highlighted by the experiments with reasonable qualitative and quantitative agreement

Experiments

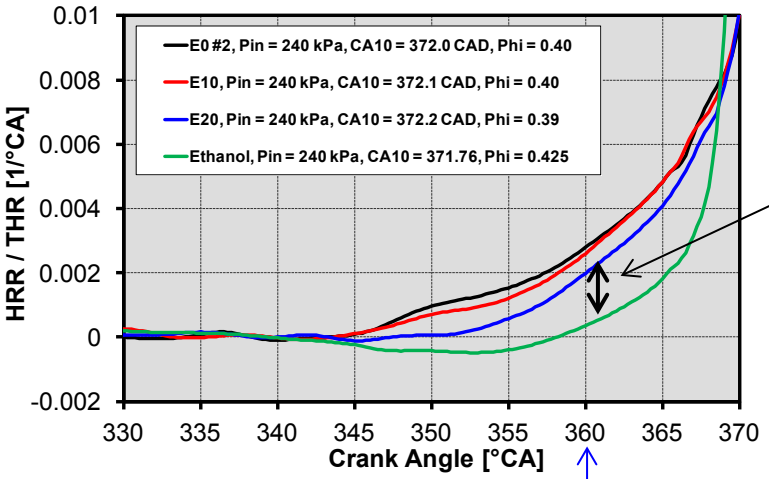
Calculations

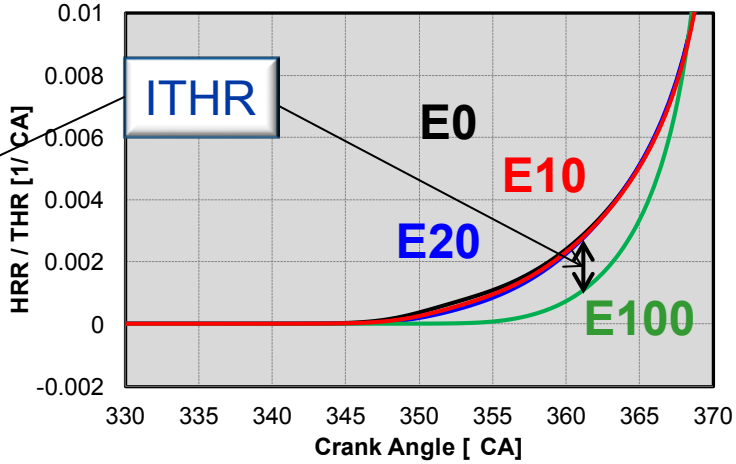
100kPa





240kPa





Mechanisms are available on LLNL website and by email

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

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Science and Technology

home > science and technology > chemistry > combustion

Print View

- Hydrogen
- Ethanol
- Butanol isomers
- Iso-pentanol
- 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
- Gasoline Surrogate
- 2-Methyl Alkanes
- Primary Reference Fuels: iso-Octane / n-Heptane Mixtures
- 2,2,4,4,6,8,8-Heptamethylnonane

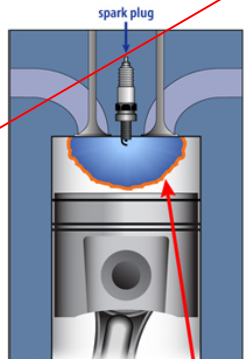
Combustion Chemistry

Go Directly to Mechanisms...

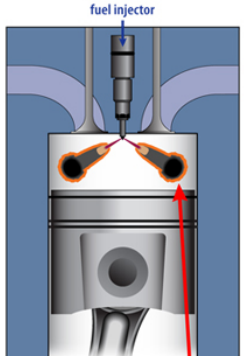
The central feature of the Combustion Chemistry project at LLNL is our development, validation, and application of detailed chemical kinetic reaction mechanisms for the combustion of hydrocarbon and other types of chemical fuels. For the past 30 years, our group has built hydrocarbon mechanisms for fuels 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.

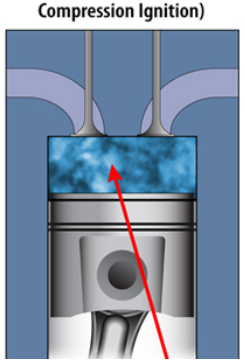
Gasoline Engine (Spark Ignition)



Diesel Engine (Compression Ignition)



HCCI Engine (Homogeneous Charge Compression Ignition)



Gasoline Surrogate

FY2013 Reviewer's comments and our response

Overall, the reviewer's comments were very positive

- One reviewer commented: "… it would have been interesting to see a more tangible link to the industry, either by demonstrated use of the presenter's work or incorporation into commercial tools."
- Response: "We get a number of requests annually from OEMs and energy companies for our mechanisms. LLNL fuel mechanisms formed much of the basis of the those mechanims provided by two of the major commercial chemical kinetic modeling and CFD tool developers which are used by industry."
- The reviewer suggested: "As for most other projects, this reviewer would like to see more work on gasoline. This reviewer asked about the long-term roadmap for the further development of gasoline surrogates, and whether the models had been fully validated over a range of equivalence ratios and EGR concentrations".
- Response: In FY 14, we have developed surrogate models for FACE gasoline fuels, which have received a lot of interest from the automotive and energy companies. We have compared the surrogate model predictions to experiments in shock tubes and RCMs at equivalence ratios of 0.5 and 1. Our base chemistry has been validated for high amounts of EGR. We have prioritized our development of models for surrogate fuel components based on the composition of gasoline FACE fuels and certification gasoline fuels being used by the DOE working group collaborators.

Collaborations

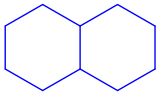
- Our major current industry collaboration is via the DOE working group on Advance Engine Combustion
  - All results presented at Advanced Engine Combustion Working group meetings (Industry, National labs, Universities)
  - Multiple exchanges of chemical kinetic models with industry
  - Collaboration on gasoline/gasoline-ethanol engine experiments with Sandia:
    - John Dec on HCCI and Magnus Sjöberg on DISI
  - Collaboration with Sibendu Som at Argonne on diesel reacting sprays
- Second interaction is collaboration with many universities
  - Prof. Sung's group, U of Conn., Dr. Sarathy, KAUST, and Prof. Dibble, UC Berkeley and Prof. Oehlschlaeger, RPI on gasoline surrogates
  - Dr. Curran at Nat'l Univ. of Ireland on gasoline and diesel fuel components in RCM and shock tube
  - Prof. Reitz, Univ. of Wisc., on development of reduced chemical kinetic models for diesel surrogate components
  - Prof. Lu, U. of Conn. on mechanism reduction
  - Prof. Pfefferle, Yale, on soot chemistry
- Participation in other working groups with industrial representation
  - CRC Fuels for Advanced Combustion Engines (FACE) Working group and CRC AVFL-18a (Surrogate fuels for kinetic modeling)
  - Engine combustion network (ECN)
- Ford: Kinetic modeling support for leaner lifted-flame combustion (LLFC)
- EFRC proposal: Fundamental Chemical Kinetic Mechanisms of Next Generation Fuels
  - 4 national labs, 3 universities

Remaining Challenges and Barriers

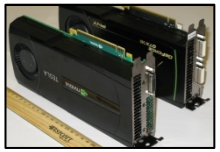
- Develop chemical kinetic mechanisms for surrogates to represent FACE gasoline and diesel fuels
- Develop predictive models for new versions of surrogates from CRC AVFL-18a that have more representative palette compounds for diesel fuels
- More accurately simulate the fuel effects with changing pressure, temperature, EGR, equivalence ratio and fuel composition

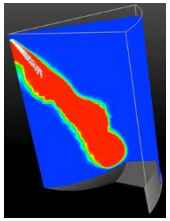
Future plans for next year: 9-comp diesel surrogate, gasoline surrogate, ECN

- Finish the 9-component surrogate mechanism for diesel
  - Develop mechanism for multi-ring cycloalkane



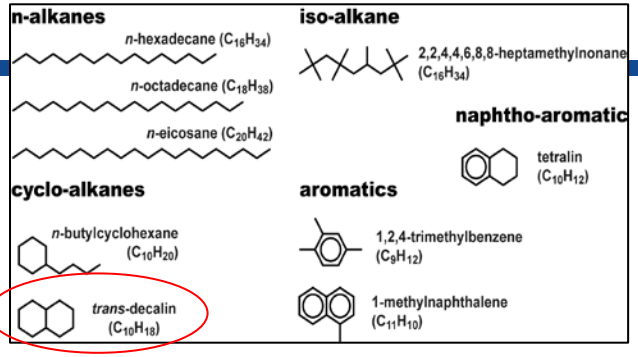
  - Provide 9-component model to LLNL fast solvers

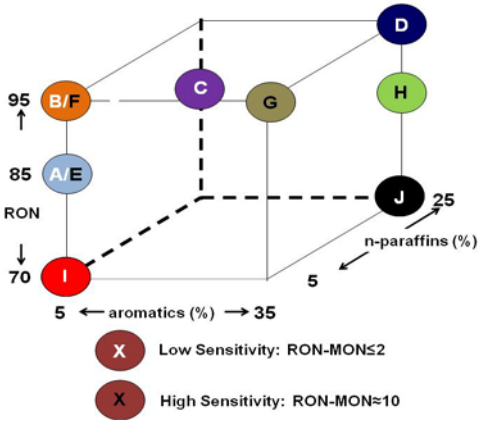




- Gasoline surrogate modeling:
  - Develop surrogates models for 3 remaining FACE gasoline fuels and new gasoline certification fuels being considered
  - Validate surrogate models using:
    - experiments to be performed by KAUST, RPI, and UC Berkeley on FACE fuels
    - Sandia HCCI experiments on gasoline certification fuels (Dec and co-workers)
  - Extend gasoline mixture correlations to include E10
- Model engine combustion with reduced models for diesel surrogate fuels for the Engine Combustion Network

CRC AVFL-18 Diesel surrogate palette:

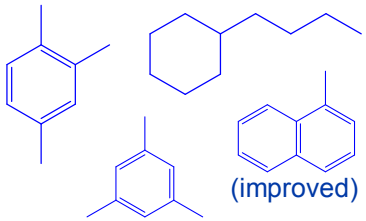




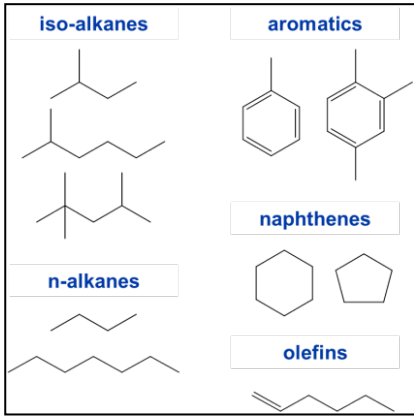
Detailed chemical kinetic modeling summary

Developing fuel surrogate models for gasoline and diesel fuels to enable accurate advanced engine combustion simulations with fuel effects

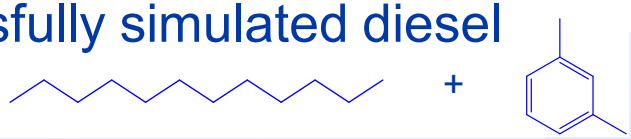
1. Developed detailed chemical kinetic models for aromatics and a cycloalkane for 9-component CRC AVFL-18 diesel surrogate



2. Developed surrogate kinetics models for gasoline/gasoline-ethanol blends
   a) Developed 10 component palette for FACE gasoline fuels
      - Validated surrogate model for FACE fuels A & C under shock tube and RCM conditions
   b) Simulated ITHR in a Sandia HCCI engine for gasoline/gasoline-ethanol fuels

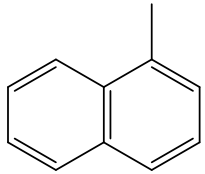


3. Developed an improved 2-component surrogate mechanism for diesel that successfully simulated diesel reacting sprays

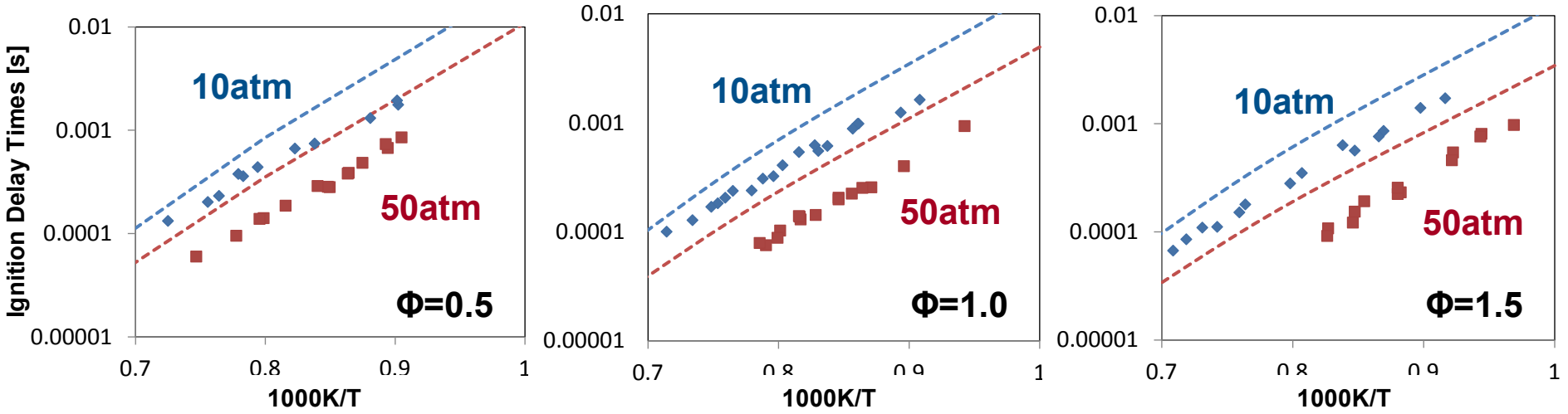


Technical Back-Up Slides

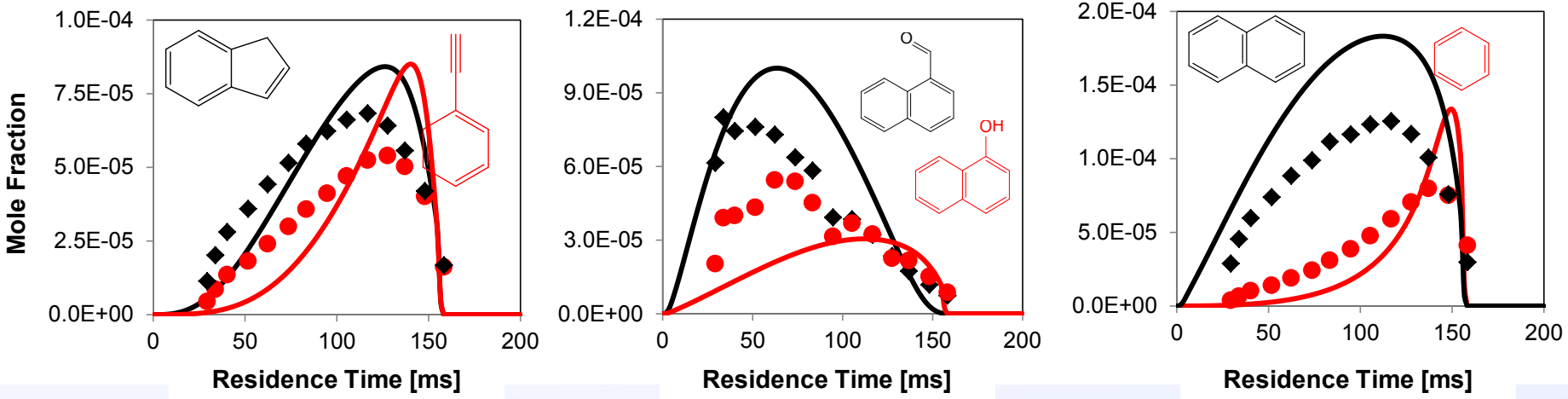
Surrogate component α-methyl naphthalene updated: Initial results were showing significant discrepancies with Ignition delay time data



Old results

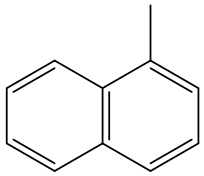


Wang et. al., 2010: Shock Tube in Air

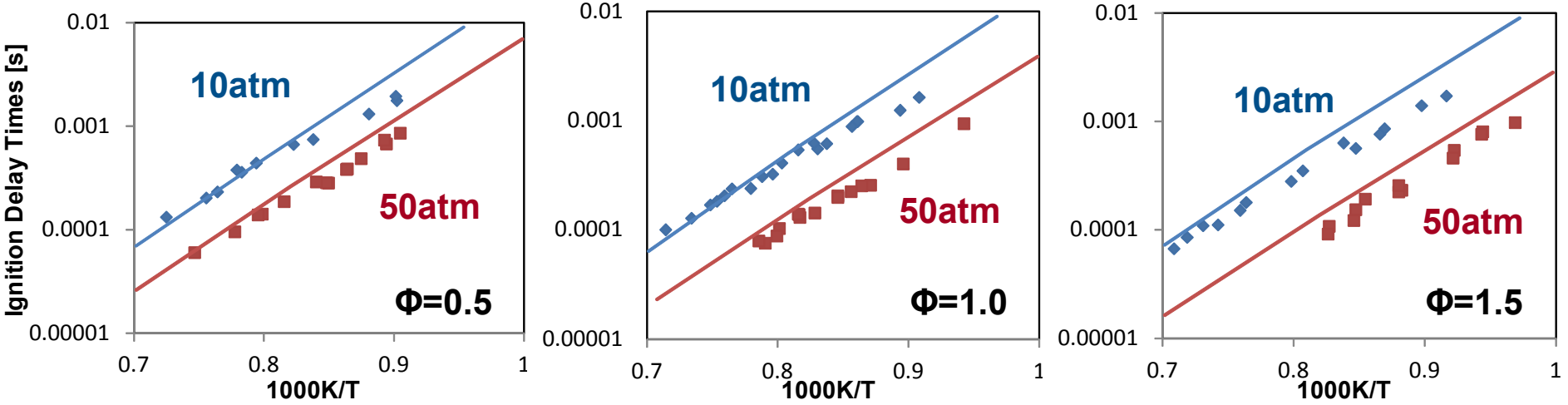


Shaddix et al., 1997: Flow Reactor - Φ=0.5, 1 atm, T=1070K

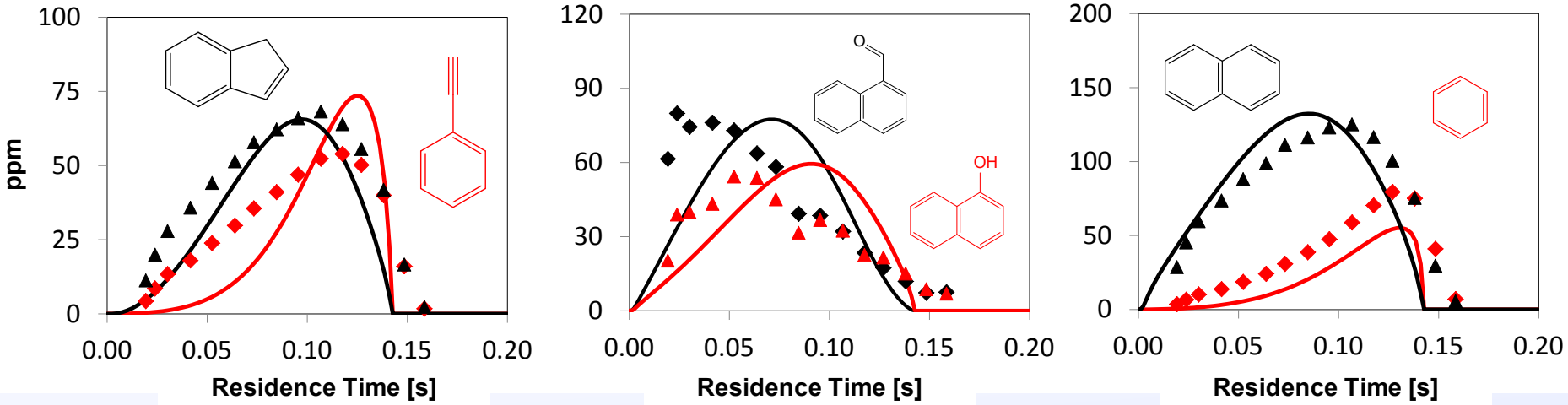
Revision of the mechanism lead to improved agreement with the data



New results



Wang et. al., 2010: Shock Tube in Air



Shaddix et al., 1997: Flow Reactor - Φ=0.5, 1 atm, T=1070K

Detailed hydrocarbon analysis of FACE A and C

FACE C has more n-alkanes and aromatics than FACE A

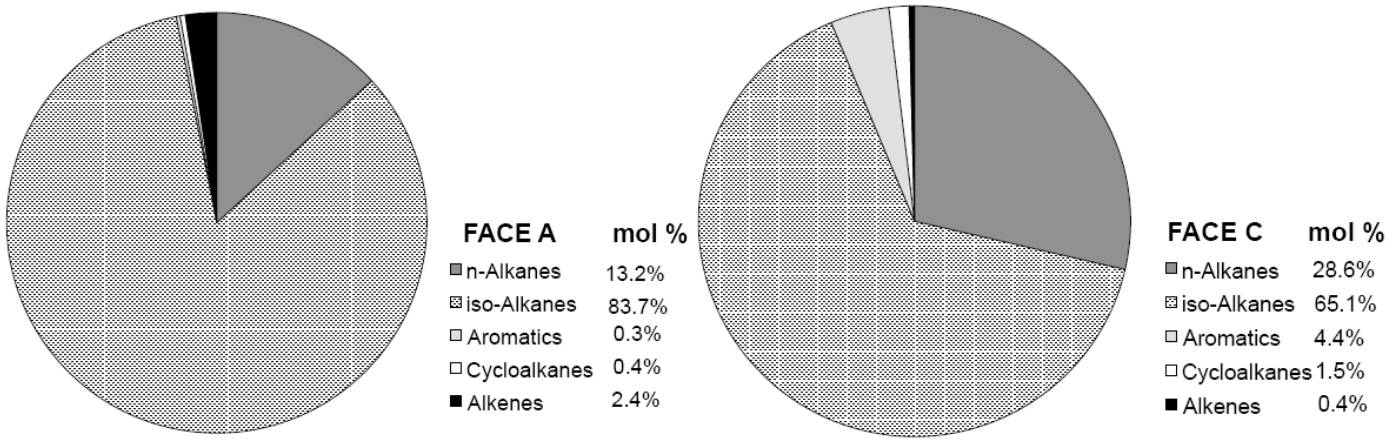
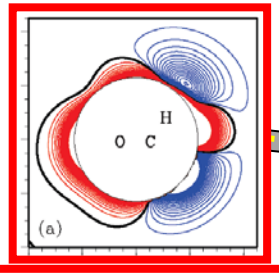


Figure S1 - PIONA analysis of FACE A (left) and FACE C (right) gasoline test fuels utilizing detailed hydrocarbon analysis (DHA)

Sarathy, Kukkadap, Mehl, Wang, Javed, Park, Oehlschlaeger, Farooq, Pitz, and Sung, Proc. Combust. Institute, Submitted (accepted for presentation) ,2014

Chemical kinetic model development for practical fuels:



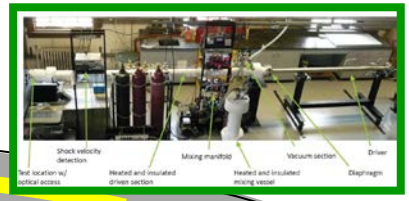
Ab initio calculations

Accurate reaction rates

Species thermodynamic properties

Reaction paths

Reaction rate rules



Detailed Chemical Kinetic Models

Fundamental Experiments

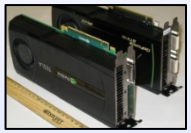
NUIG, UCONN, KAUST, USC, CNRS, RPI

Application to engines

Model Reduction

Validation against fundamental combustion data

Fast Solvers



LLNL - Numerics