Lawrence Livermore National Laboratory

Chemical Kinetic Models for Advanced Engine Combustion

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Project ID # ACE013

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

Washington, DC

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

LLNL-PRES-688774

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:

- FY15: 532K
- FY16: 532K

Barriers

- Increases in engine efficiency and decreases in engine emissions are being inhibited by an inadequate ability to accurately simulate in-cylinder combustion and emission formation processes
  - Chemical kinetic models for fuels are a critical part of engine simulation models

Partners

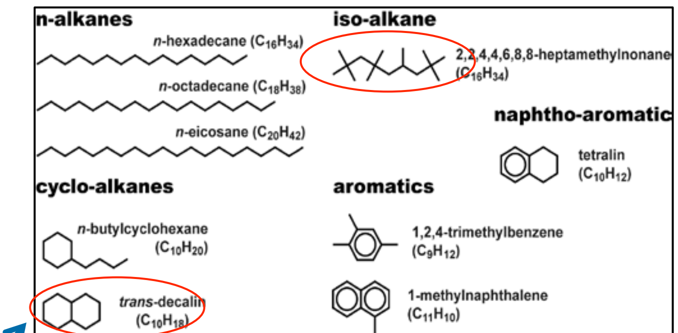
- Project Lead: LLNL – W. J. Pitz (PI)
- Part of Advanced Engine Combustion (AEC) working group:
- – 15 Industrial partners: auto, engine & energy
- – 5 National Labs & 10 Universities
- UConn: RCM data on diesel surrogate mixtures
- Sandia: Provides engine data for validation of detailed chemical kinetic mechanisms
- AVFL18a working group of the Coordinating Research Council (CRC)

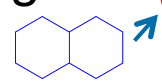
Objectives and relevance to DOE objectives

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

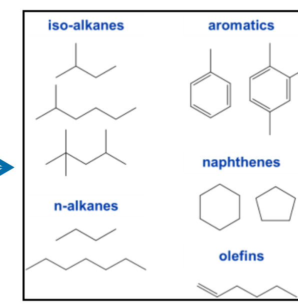
- FY16 Objectives:
  - Develop remaining kinetic model for CRC AVFL-18 nine-component diesel surrogate palette
  - Develop and improve surrogates mechanisms for high-octane gasoline fuels and gasoline fuels with ethanol
  - Improve iso-cetane mechanism using fundamentally-based rate constants

CRC AVFL-18 Diesel surrogate palette:





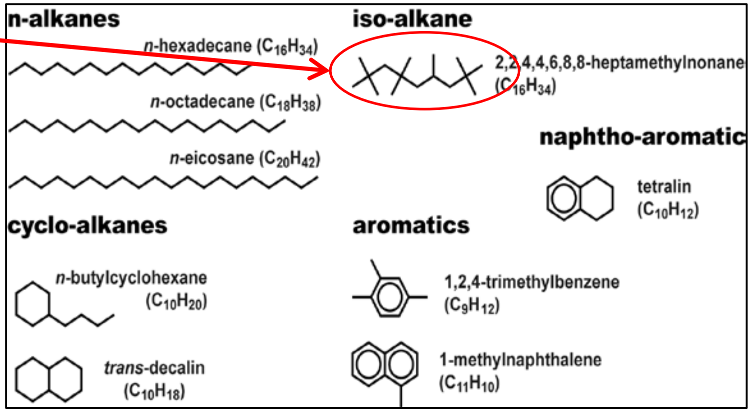
10-component gasoline surrogate palette:



Chemical kinetic milestones

- ✓ Improved mechanism for iso-cetane (December, 2015)
- ✓ Go/No-go Milestone: Pursue higher-accuracy AVFL-18a diesel surrogate palette with 4 additional components? (March, 2016)

No



CRC AVFL-18 Diesel Surrogate palette[1]

Reason: There is a need to focus on the surrogate model based on the 9-component palette which will be available for testing in FY17. This focus is expected to have a higher impact on the development of improved diesel surrogate kinetic models in the next 1-2 years than work on the higher accuracy palette.

[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).

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 surrogate fuels 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 DISI engines)
  - addition of ethanol and other biofuels

- Reduce mechanisms for use in CFD and multizone engine codes to improve the capability to simulate in-cylinder combustion and emission formation/destruction processes in engines

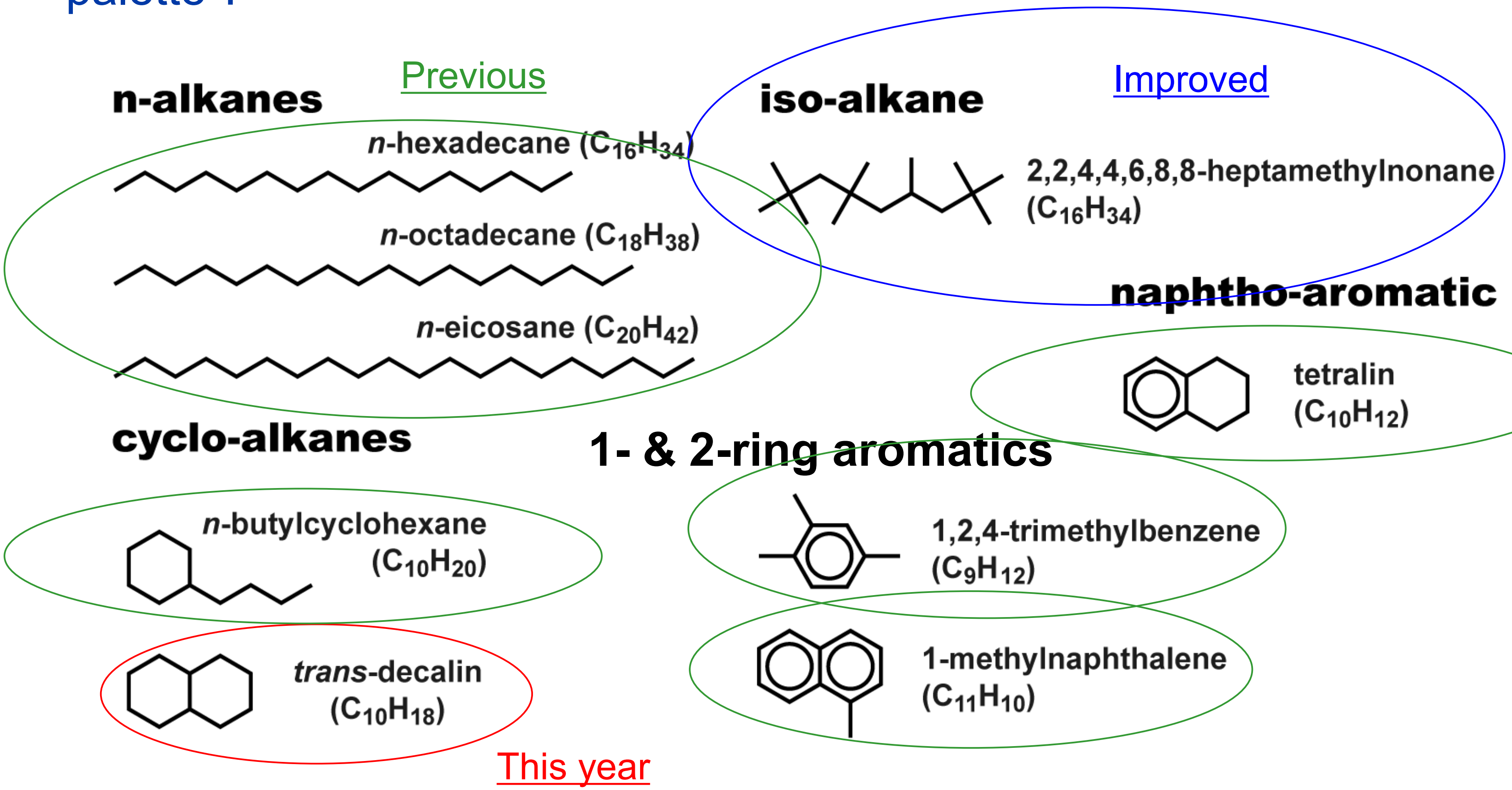
- Use the resulting models to simulate practical applications in engines, including diesel, HCCI and DISI, as needed

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

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

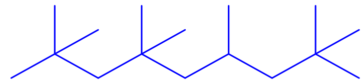
Technical Accomplishments
Diesel components selected for mechanism development in FY16

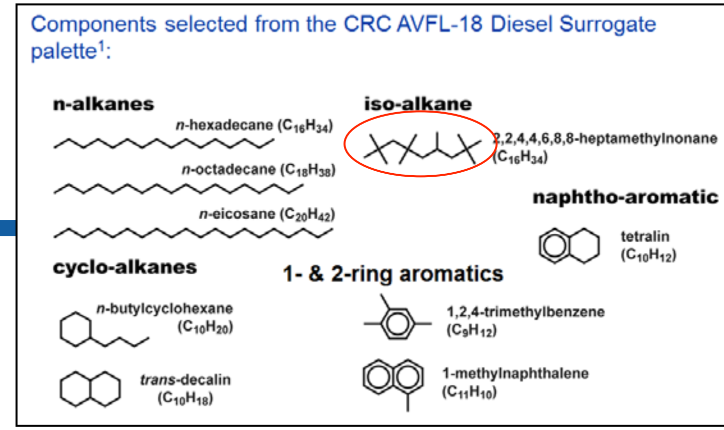
Components selected from the CRC AVFL-18 Diesel Surrogate palette[1]:



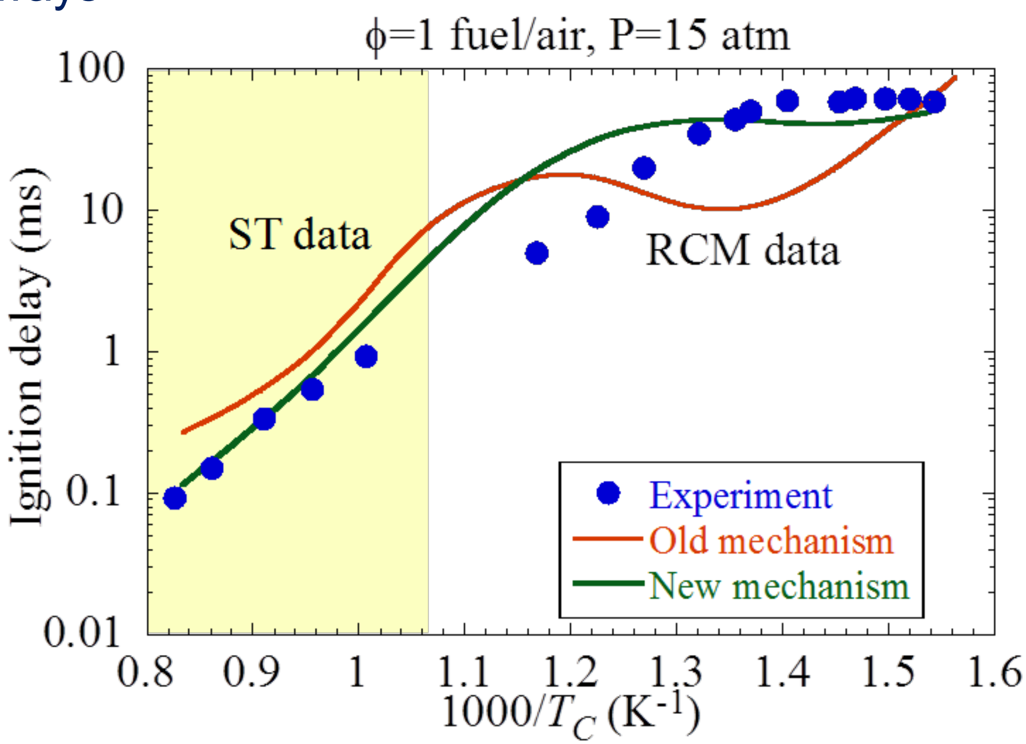
[1] Coordinating Research Council (CRC) AVFL-18 Working Group. Mueller, C. J., Cannella, W. J., Bruno, T. J., Bunting, B., Dettman, H. D., Franz, J. A., Huber, M. L., Natarajan, M., Pitz, W. J., Ratcliff, M. A. and Wright, K., Energy & Fuels 26(6):3284–3303 (2012).

Improved heptamethylnonane (HMN) kinetic model developed





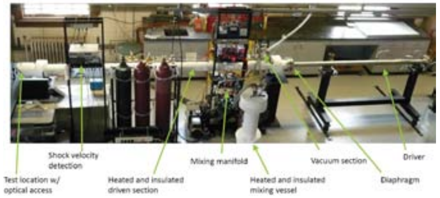
- Updated thermodynamic properties of species, reaction rates, and added additional reaction pathways



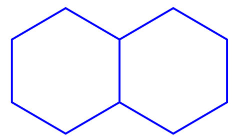
Mechanism update performed by LLNL student employee G. Kukkadapu

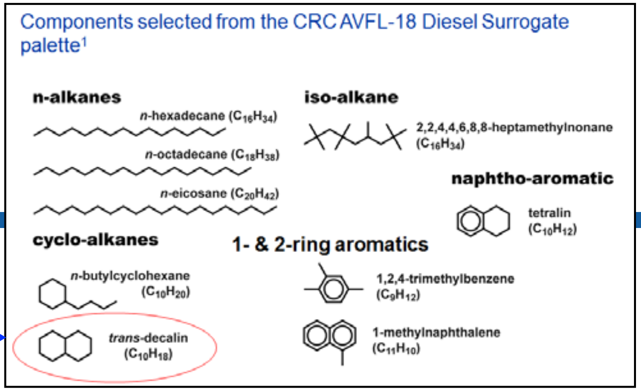
New RCM data from Kukkadapu and Sung, UCONN, 2015
Shock tube (ST) data taken from Oehlschlaeger et al., Combust. Flame, 2008.

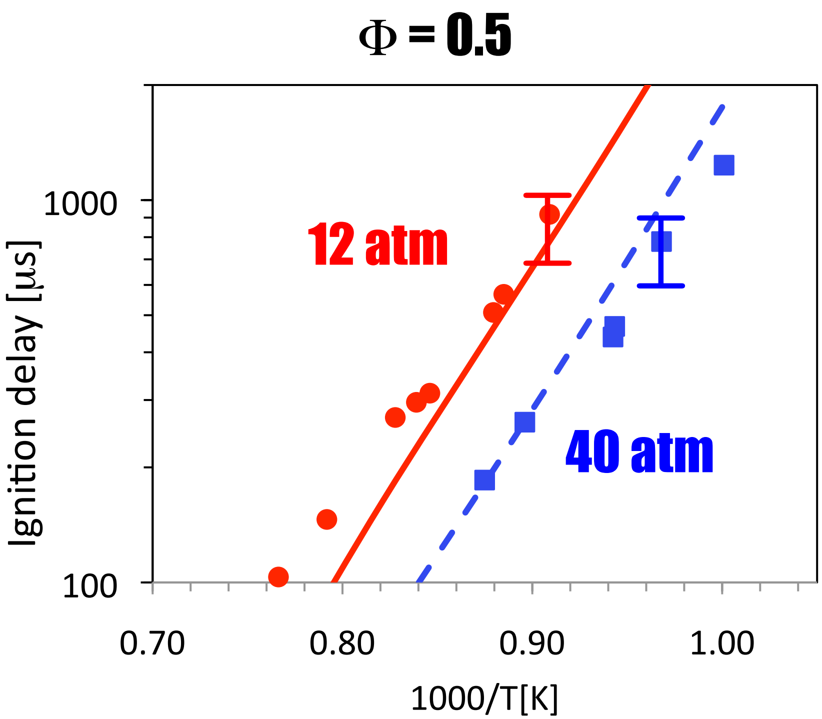
Decalin: Developed high-temperature kinetic mechanism and will finish low-temperature mechanism this year

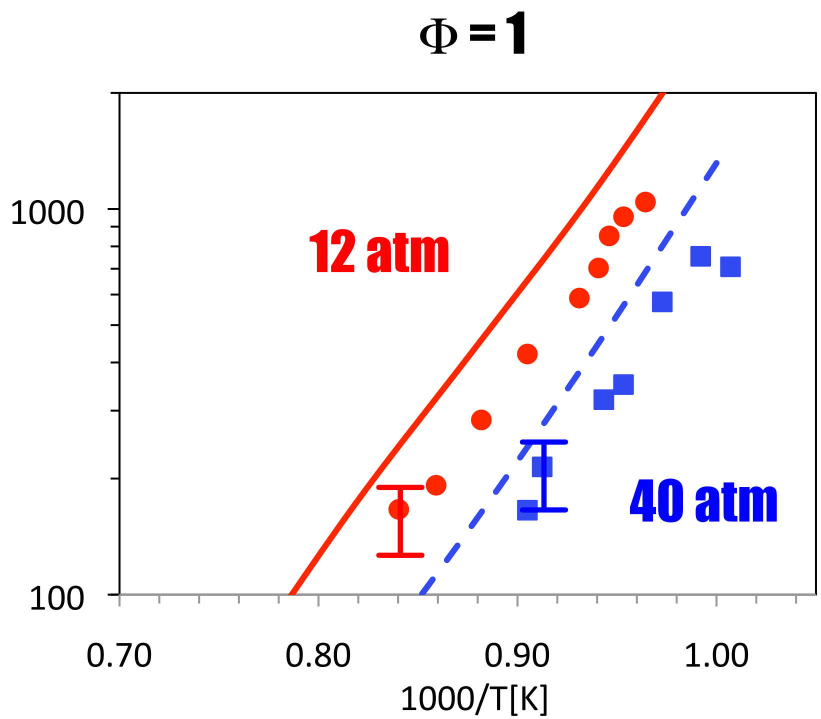


shock tube





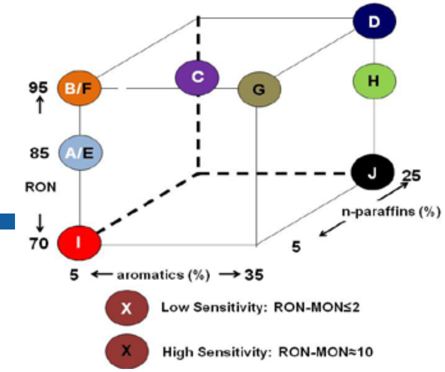




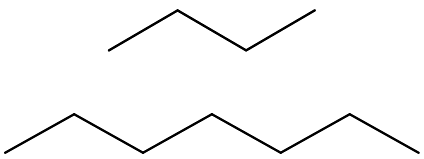
Experimental shock tube ignition data: Oehlschlaeger, Shen et al. Energy & Fuels 2009

Improving gasoline surrogate models:

Fuel component mechanisms in 10-component gasoline surrogate palette are being improved and validated

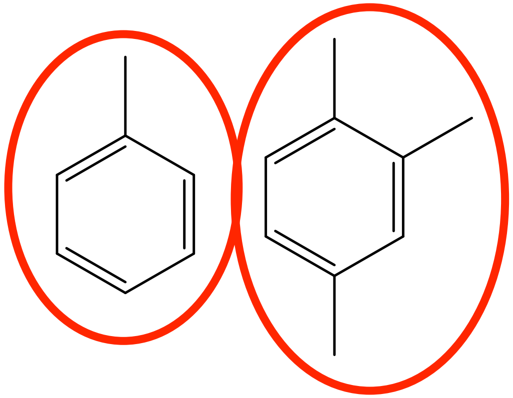


n-alkanes



Allow to match the average chain length

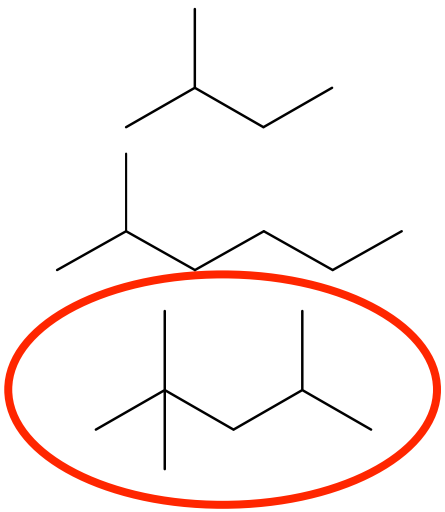
aromatics



To match the molecular weight and the degree of alkyl substitution

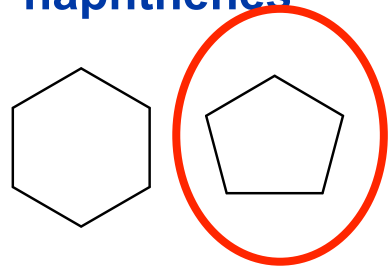
iso-alkanes

Improved



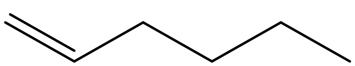
To match the average molecular weight and the degree of branching

naphthenes



Two representative species

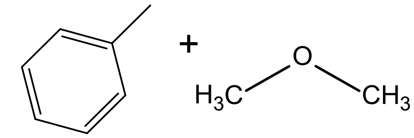
olefins



Major unsaturated linear species

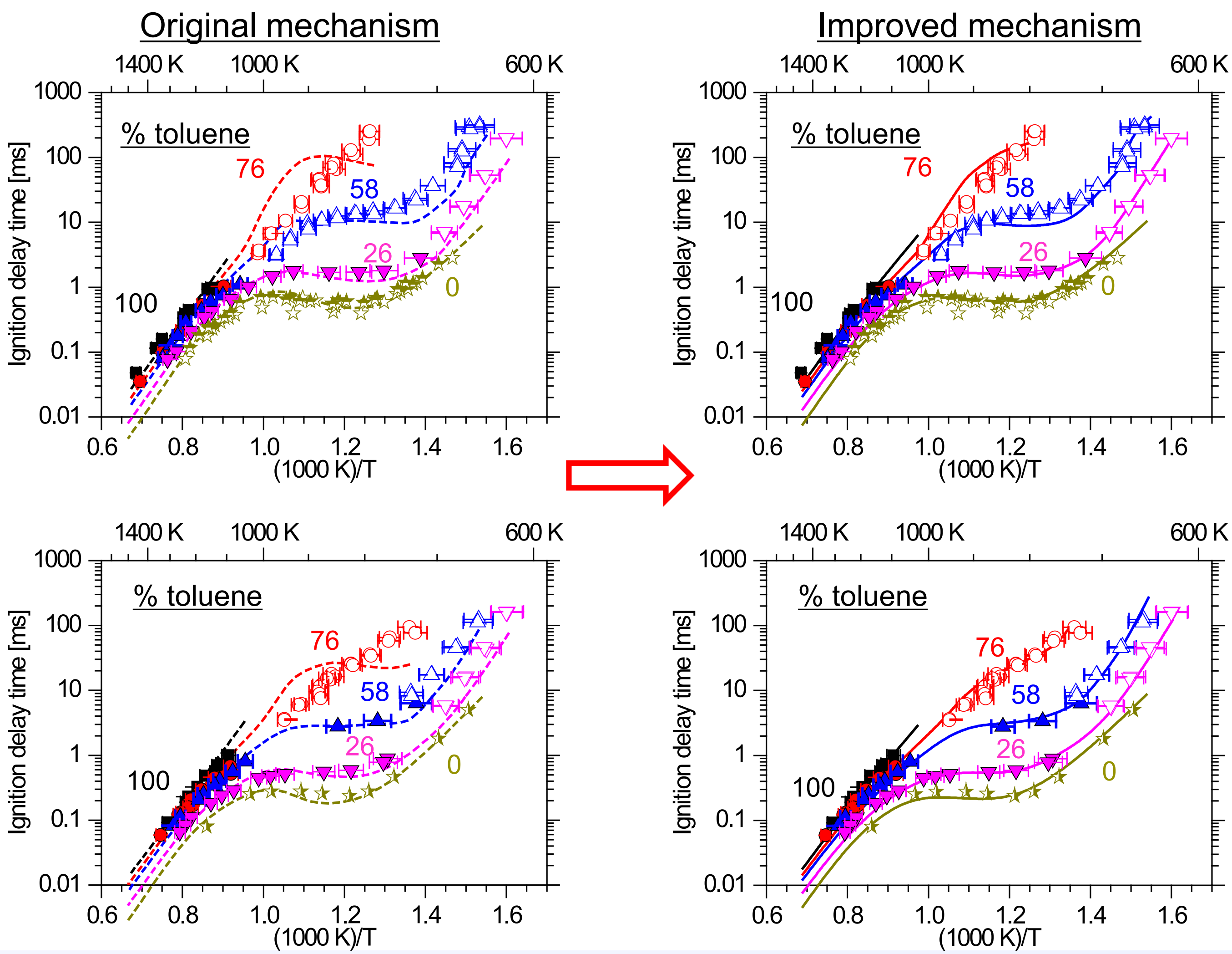
Collaborative work with NUI-Galway, KAUST, and UCONN

The toluene mechanism was updated and its behavior in fuel blends improved



20 atm

40 atm



Collaborative project between NUIG and LLNL

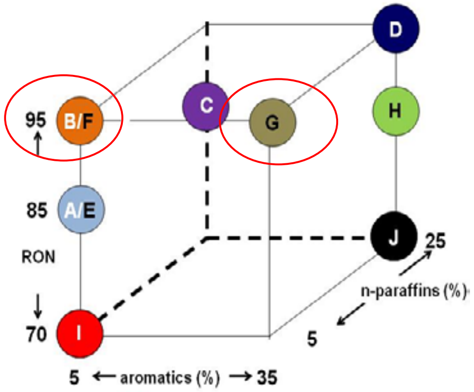
Shock tube and RCM measurements

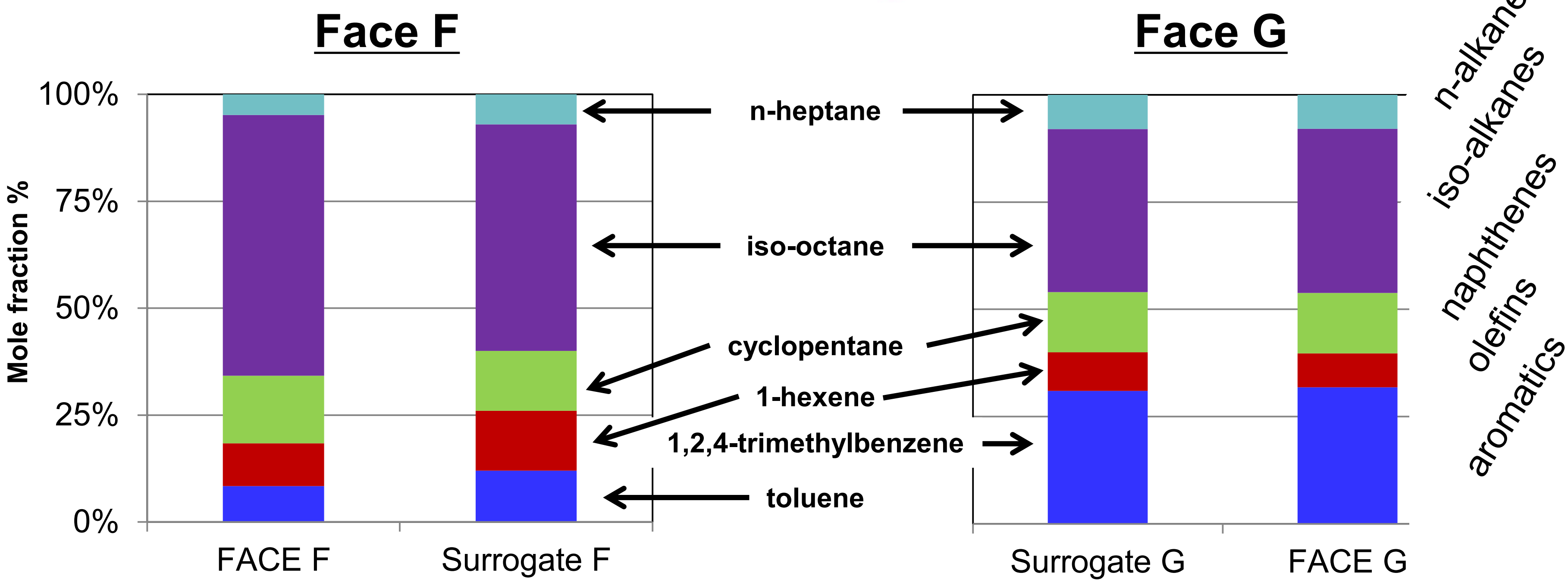
Toluene + dimethyl ether (ϕ = 1)

Zhang, Somers, Mehl, Pitz, Cracknell, and Curran, Proc. Combust. Inst. (2016), accepted.

Developed surrogates for Face F and G high-octane gasoline fuels have been formulated using LLNL correlations

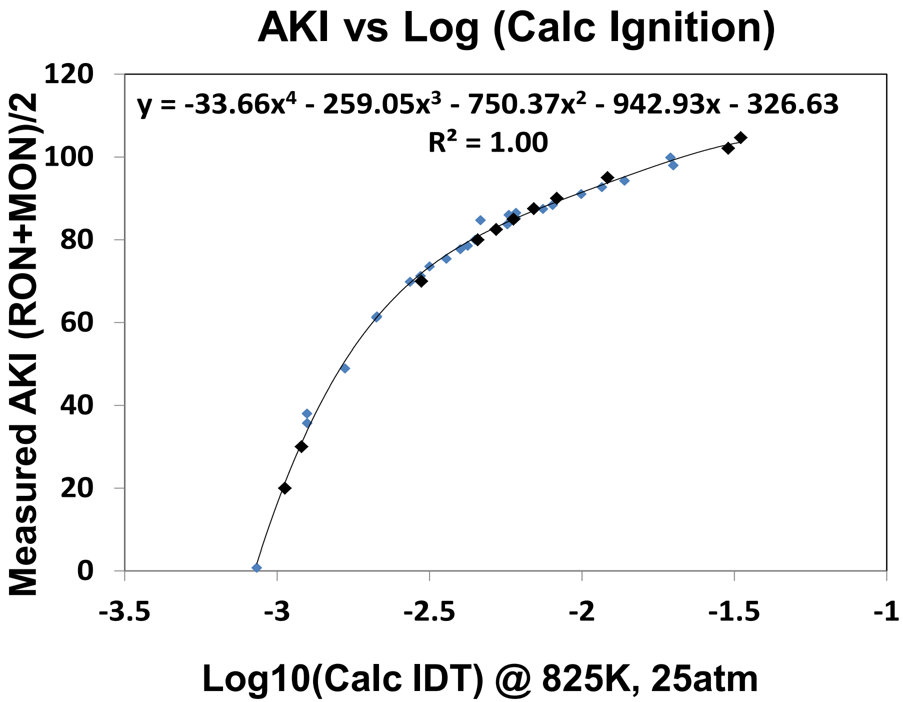
	FACE F	FACE G
RON	94.4	96.5
MON	88.8	85.4
AKI	91.6	91
Sensitivity	5.6	11.1
H/C ratio	2.1	1.8

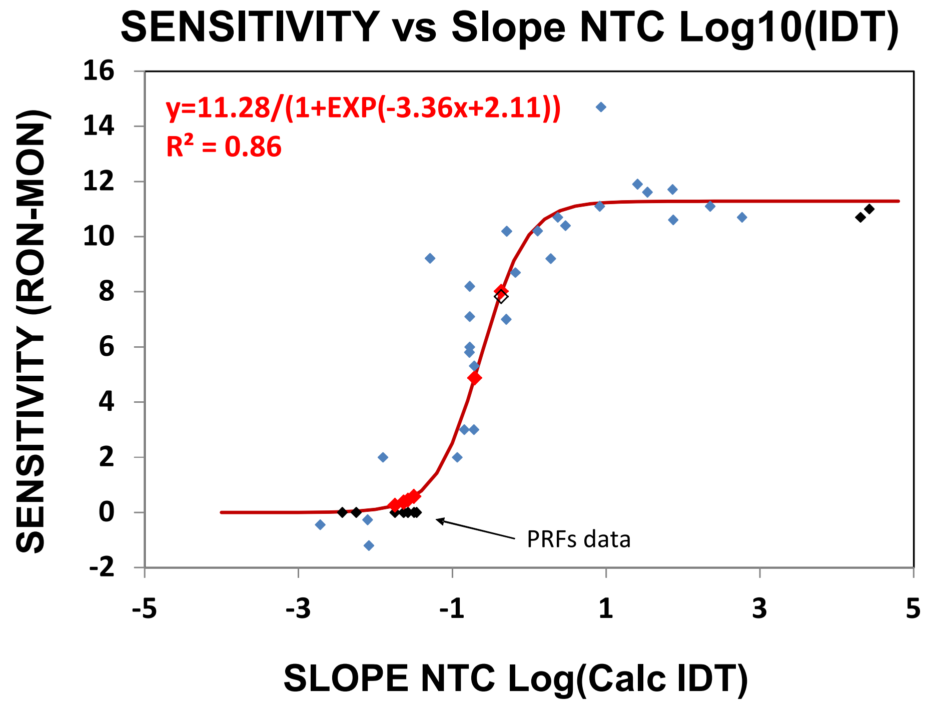




Match gasoline surrogate mixture using AKI and octane sensitivity of target gasoline fuel

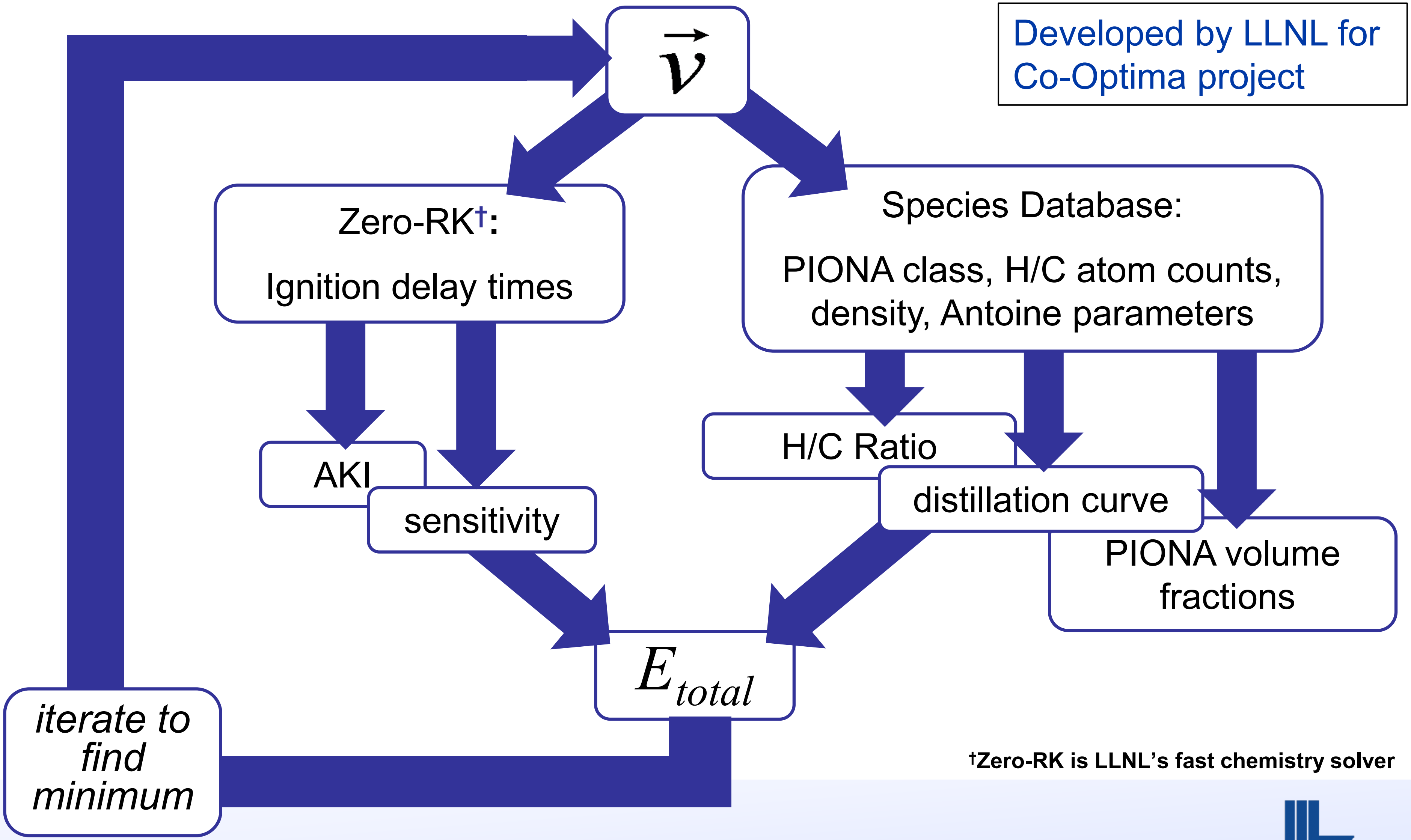
The AKI and RON of the target gasoline fuel are matched using two correlations:





New surrogate generator allows more accurate matching of surrogate mixtures to target fuels

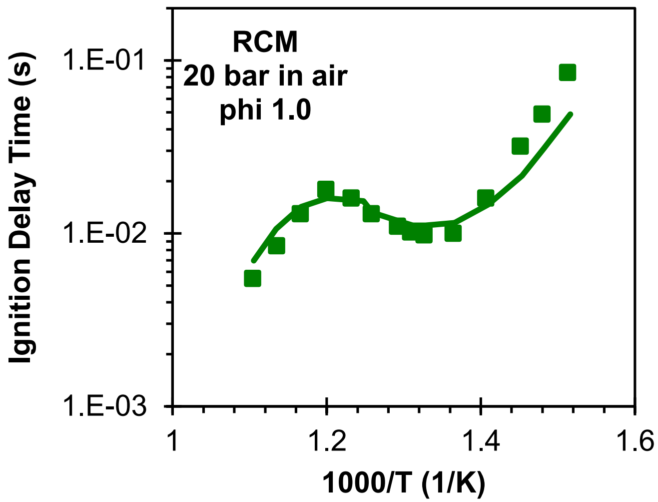
Developed by LLNL for Co-Optima project



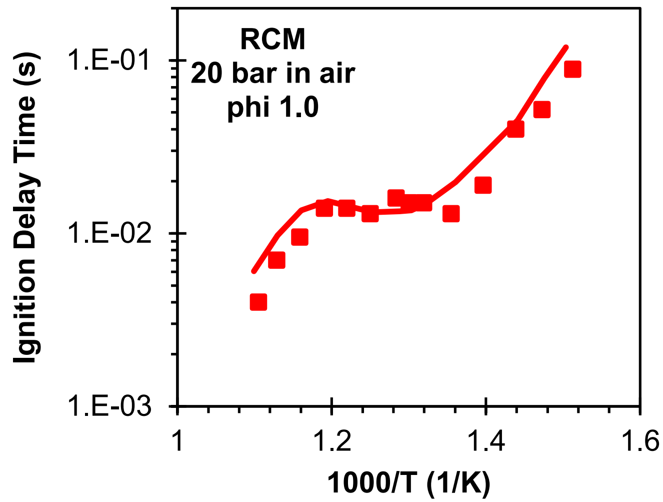
†Zero-RK is LLNL's fast chemistry solver

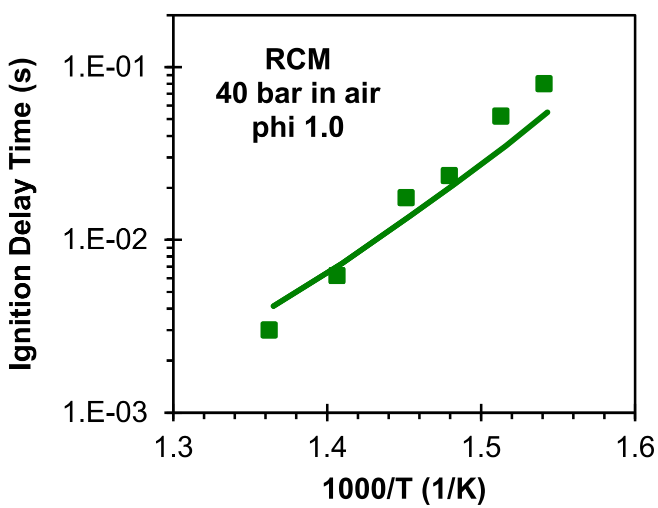
Validated and improved gasoline surrogate mechanism using UConn RCM experimental data for Face F & G

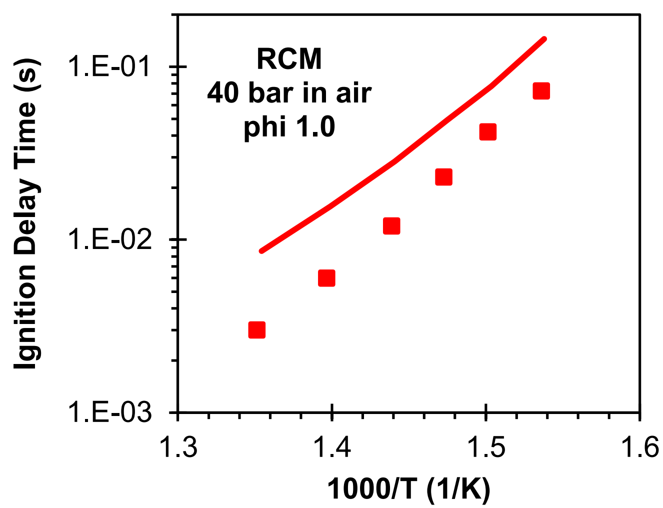
Face F



Face G





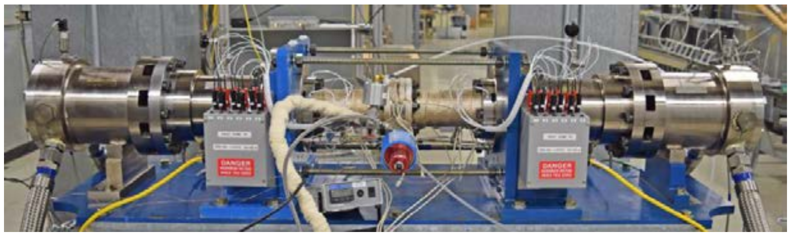


UConn RCM

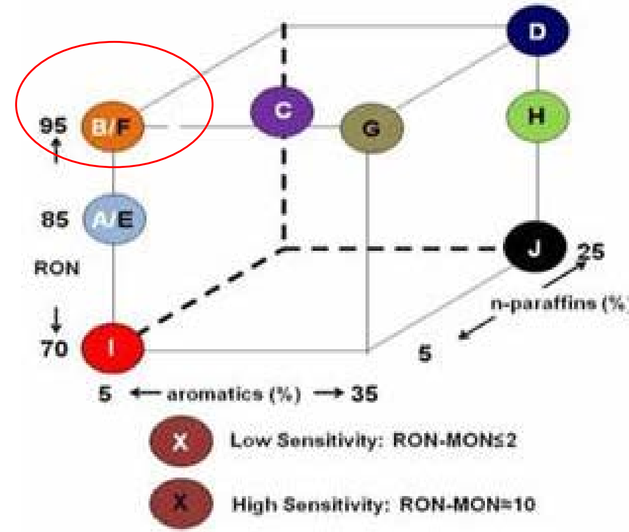
[1]Collaboration with UConn, KAUST, and RPI

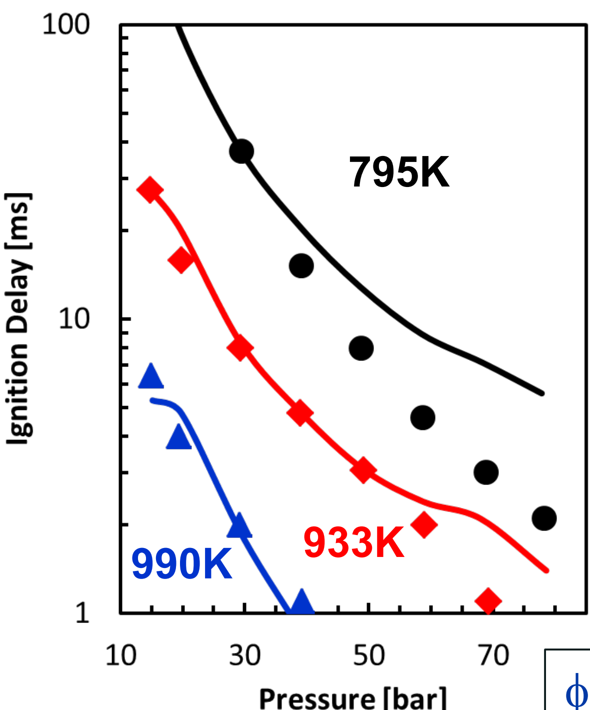
[1]Sarathy, Kukkadapu, Mehl, Javed, Ahmed, Naser, Tekawade, Kosiba, Abbad, Singh, Park, et al., Combust. Flame (2016).

Surrogate model for Face F compared to ANL RCM measurements over a wide range of temperature and pressure

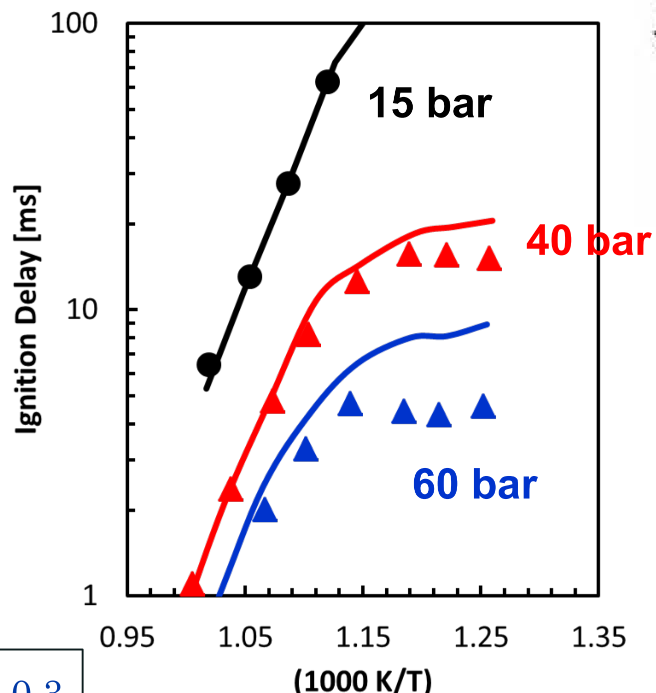


ANL RCM





$\phi = 0.3$



Model includes simulation of full compression stroke and heat transfer from ANL RCM

Mechanisms are available on LLNL website and by email

https://combustion.llnl.gov

Mechanisms

Alcohols

Ethanol
Butanol Isomers
Iso-pentanol

Alkanes

2-Methyl and n-Alkanes
Heptane, Detailed Mechanism, Version 3.1
iso-Octane, Version 3
2,2,4,4,6,8,8-Heptamethylnonane

Alkenes

C5 alkene

Surrogates

Biodiesel Surrogates

Real Biodiesel
C10 methyl ester surrogates for biodiesel

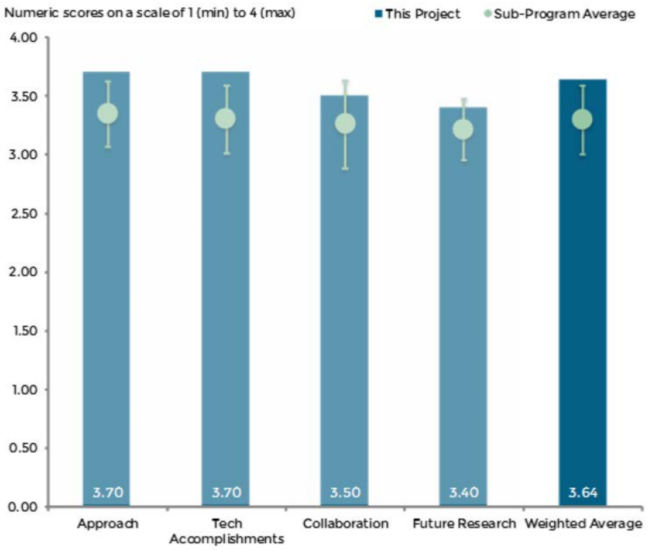
Gasoline Surrogate
Diesel PRF
Diesel surrogate, detailed and reduced

Alkyl-Carbonates

Dimethyl Carbonate
Diethyl Carbonate
Cyclopentane

Gasoline Surrogate

FY2015 Reviewer's comments and our responses



Chemical Kinetic Models for Advanced Engine Combustion: Bill Pitz (Lawrence Livermore National Laboratory) - ace013

Presenter

Bill Pitz, Lawrence Livermore National Laboratory.

Overall, the reviewer's comments were very positive

- The reviewer commented: "The reviewer observed that the approach for development of kinetic combustion models for key components present in gasoline, diesel and biofuels; combining them to form surrogate fuel mixtures; and development of reduced mechanisms and validation against experimental data from shock tube, rapid compression machines and jet-stirred reactors is extremely valuable"
- The reviewer commented: "There is also a need to bridge the gap between the chemists and the engine researchers though interactions and workshops."
- Response: "We are working with engine researchers in industry. We appreciate your suggestion and will look for further opportunities to interact with engine researchers."

Collaborations

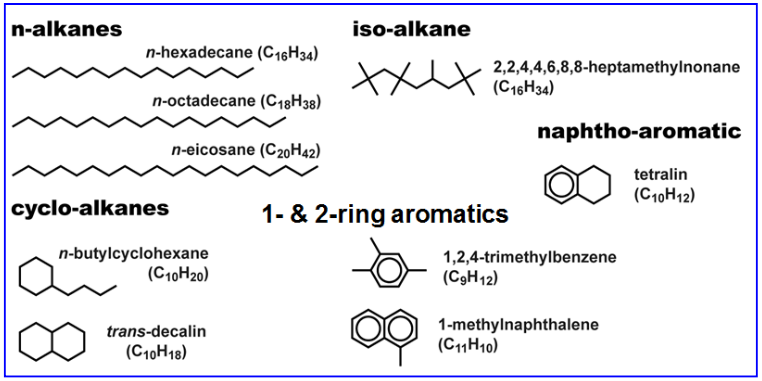
- Our major current industry collaboration is via the DOE working group on Advanced Engine Combustion
  - All results presented at Advanced Engine Combustion Working group meetings (Industry, National labs, Universities)
  - Multiple exchanges of chemical kinetic models with industry
  - Collaboration on gasoline/gasoline-ethanol engine experiments with Sandia:
    - John Dec on HCCI and Magnus Sjöberg on DISI
  - Collaboration at Argonne with Sibendu Som on diesel reacting sprays and Scott Goldsborough on RCM experiments
- Second interaction is collaboration with many universities
  - Prof. Sung's group, U of Conn., Dr. Sarathy, KAUST, and Prof. Chen, UC Berkeley
  - 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 reduced kinetic models
  - 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)
- Ford: Kinetic modeling support for leaner lifted-flame combustion (LLFC)

Remaining Challenges and Barriers

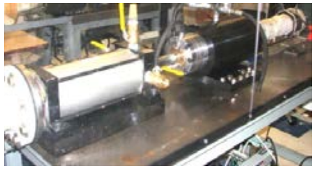
- Develop chemical kinetic mechanisms for surrogates for diesel and gasoline fuels that are predictive at high pressures found in advanced engine combustion regimes
- Improve accuracy of chemical kinetic mechanisms so that desired predictability needed by engine designers can be achieved
- Develop predictive models for diesel surrogates, particularly new versions of diesel surrogates from CRC AVFL-18a that have more representative palette compounds
- More accurately simulate the fuel effects with changing EGR, equivalence ratio and fuel composition
- Validate chemical models for blends using shock tube and RCM experimental data

Future plans for next year

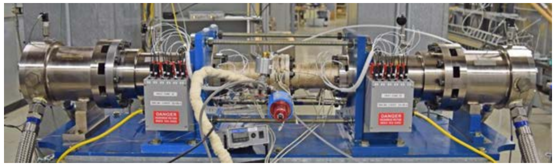
CRC AVFL-18 Diesel surrogate palette[1]:



- Validate and improve diesel surrogate models using new RCM data from UConn:
  - CRC AVFL-18a diesel surrogate mixtures: V0a (4-component), V0b (5-component), and V1 (8-component)
  - California diesel certification target fuel
- Improve n-alkanes models of large n-alkanes using n-dodecane data from UConn
- Develop of a soot model based on the sectional method



- Gasoline surrogate modeling:
  - Use new RCM facility at ANL to improve our gasoline surrogate model at high pressures
  - Improve gasoline surrogate component models using new NUIG shock tube and RCM data on heptane isomers

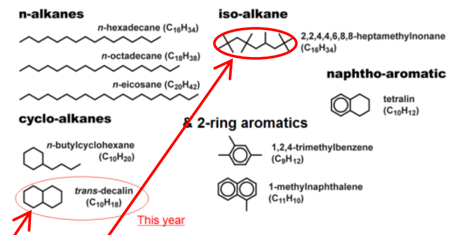


[1]Coordinating Research Council (CRC) AVFL-18 Working Group. Mueller, C. J., Cannella, W. J., Bruno, T. J., Bunting, B., Dettman, H. D., Franz, J. A., Huber, M. L., Natarajan, M., Pitz, W. J., Ratcliff, M. A. and Wright, K., Energy & Fuels 26(6):3284–3303 (2012).

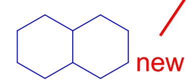
Detailed chemical kinetic modeling summary

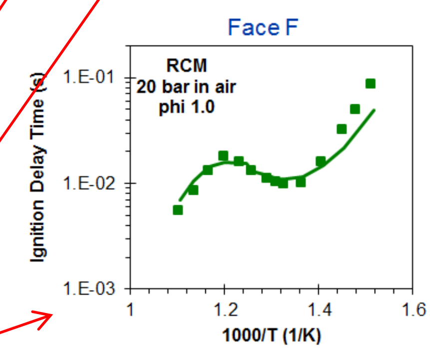
Developing fuel surrogate models for gasoline and diesel fuels to enable accurate advanced engine combustion simulations with fuel effects

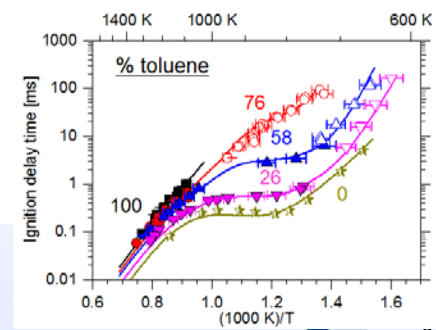
1. Developed/refined detailed chemical kinetic models for components in 9-component CRC AVFL-18 diesel surrogate palette
    1. Assembling the low-temperature mechanism for decalin this year
    2. Improved behavior of iso-cetane mechanism, a diesel surrogate fuel compound
    3. Improved gasoline surrogate models for Face F &G with newly available RCM data
    4. Improved the behavior of the toluene model in mixtures



CRC AVFL-18 9-component diesel surrogate

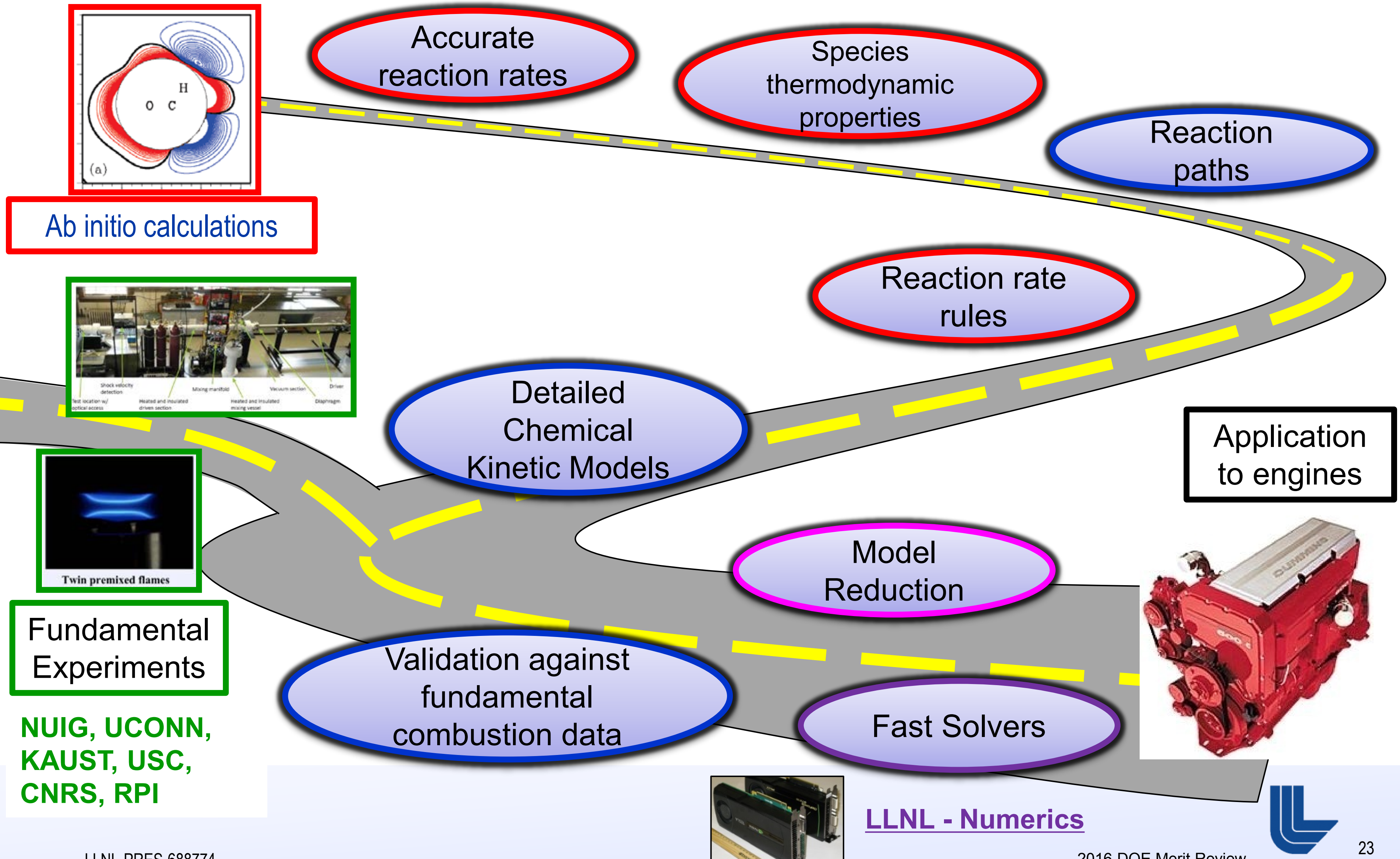






Technical Back-Up Slides

Chemical kinetic model development for practical fuels:



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

Jet Stirred Reactors

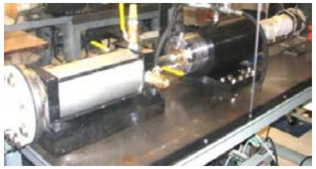
Premixed Laminar Flames

Twin premixed flames

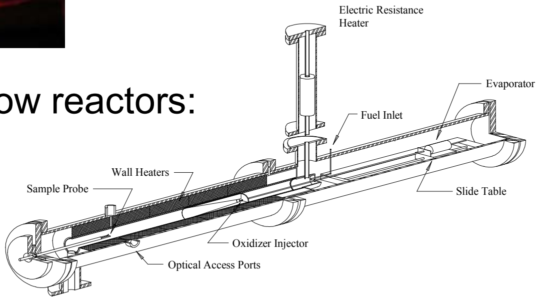
Shock tube

Non Premixed Flames

Rapid Compression Machine



High pressure flow reactors:



Engine Combustion

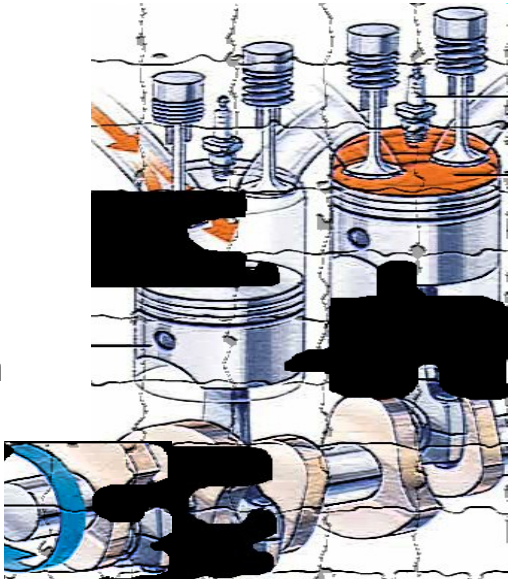
Combustion Parameters

Temperature

Pressure

Mixture fraction (air-fuel ratio)

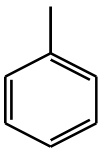
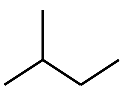
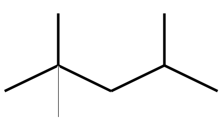
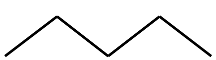
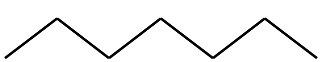
Mixing of fuel and air



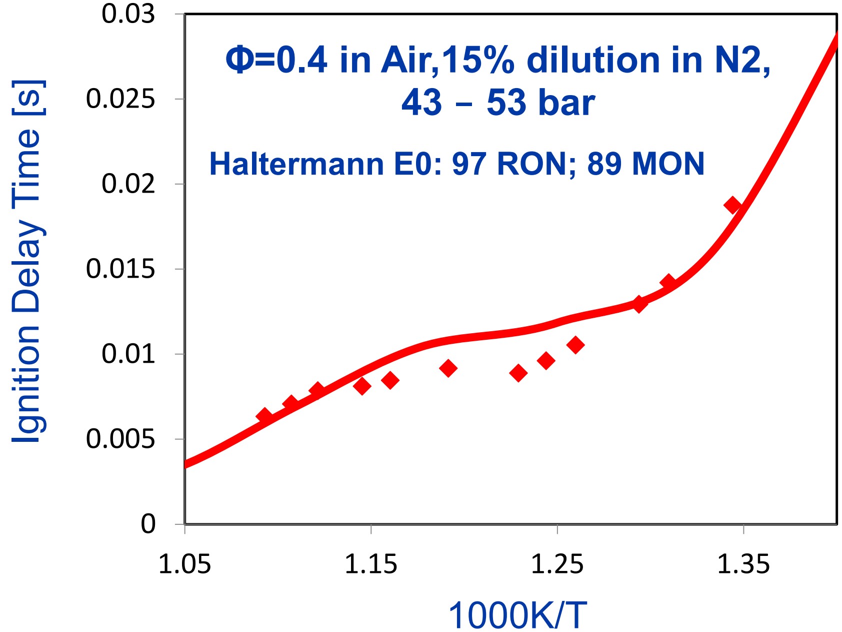
Gasoline-surrogate model developed for high-octane certification gasoline used in recent engine experiments at Sandia

Fuel used by Dec et al. in partial fuel stratification CI experiments and Sjöberg et al. in DISI experiments

Haltermann E0: 97 RON; 89 MON

5-components	Surrogate Molar Composition
	**37%**
	**27%**
	**27%**
	**5%**
	**4%**

Simulations using LLNL kinetic gasoline surrogate mechanism



RCM experiments from Sang and Cheng at MIT

Surrogate mechanism has been recently reduced to about 250 species by Wolk and Chen at UC Berkeley

CRC AVFL-18a Diesel surrogate palette[1]

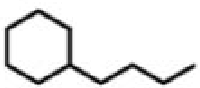
normal alkanes

n-hexadecane ($C_{16}H_{34}$), NHXD {V0a,V1}

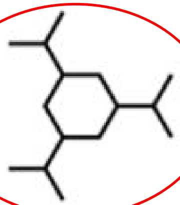
n-octadecane ($C_{18}H_{38}$), NOD {V0b,V1,V2}

n-eicosane ($C_{20}H_{42}$), NEI {V2}

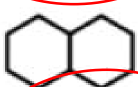
cycloalkanes (a.k.a. naphthenes)



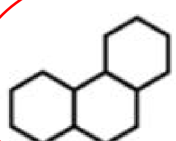
n-butylcyclohexane ($C_{10}H_{20}$), NBCX {V1,V2}



1,3,5-triisopropylcyclohexane ($C_{15}H_{30}$), TIPCX {V2}

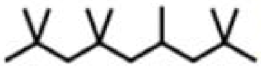


trans-decalin ($C_{10}H_{18}$), TDEC {V0a,V1}



perhydrophenanthrene ($C_{14}H_{24}$), PHP {V2}

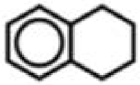
branched alkanes



2,2,4,4,6,8,8-heptamethylnonane ($C_{16}H_{34}$), HMN {V0a,V0b,V1}

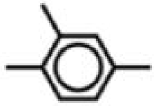
2-methylheptadecane ($C_{18}H_{38}$), 2MHPD {V2}

naphthoaromatic

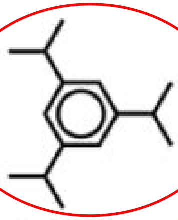


tetralin ($C_{10}H_{12}$), TET {V0b,V1,V2}

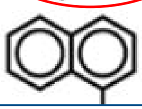
aromatics



1,2,4-trimethylbenzene (C_9H_{12}), TMB {V0b,V1}



1,3,5-triisopropylbenzene ($C_{15}H_{24}$), TIPB {V2}



1-methylnaphthalene ($C_{11}H_{10}$), 1MN {V0a,V0b,V1,V2}

[1]Coordinating Research Council (CRC) AVFL-18a Working Group. C. J. Mueller, W. J. Cannella, J. T. Bays, T. J. Bruno, K. DeFabio, H. D. Dettman, R. M. Gieleciak, M. L. Huber, C.-B. Kweon, S. S. McConnell, W. J. Pitz and M. A. Ratcliff, "Diesel Surrogate Fuels for Engine Testing and Chemical-Kinetic Modeling: Compositions and Properties," Energy & Fuels 30 (2) (2016) 1445-1461.