Lawrence Livermore National Laboratory

Chemical Kinetic Models for Advanced Engine Combustion

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Lawrence Livermore National Laboratory
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Project ID # ACS013

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

Washington, DC

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Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

LLNL-PRES-750330

Overview

Timeline

- Project provides fundamental research to support DOE/ industry Advanced Engine Combustion projects
- Funded by 3-year Lab Call starting FY17

Budget

Project funded by DOE/VT:

- FY17: 532K
- FY18: 250K in FY17 funds, forward-funded

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

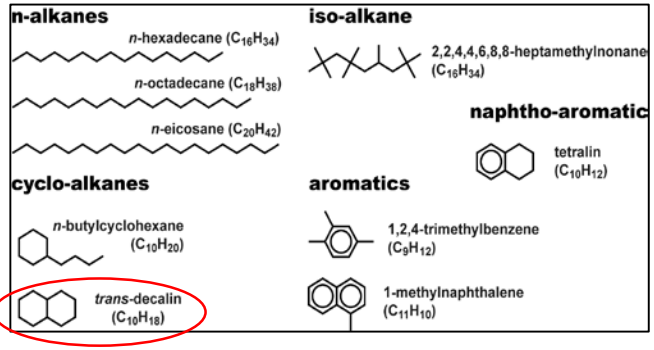
Partners

- Project Lead: LLNL – W. J. Pitz (PI)
- Part of Advanced Engine Combustion (AEC) working group:
- – 15 Industrial partners: auto, engine & energy
- – 5 National Labs & 11 Universities
- UConn: RCM data on diesel surrogate mixtures
- ANL: RCM data for mechanism validation
- AVFL-18a working group of the Coordinating Research Council (CRC)

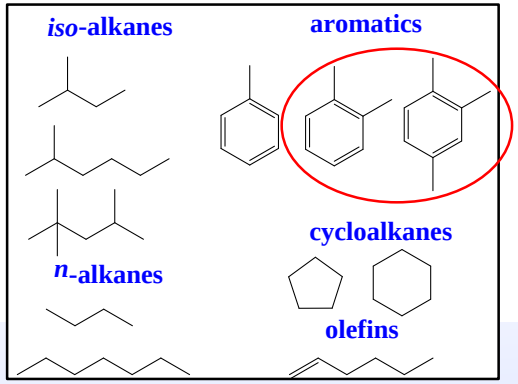
Objectives and relevance to DOE objectives

- 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

- FY18 Objectives:
  - Validate & improve diesel surrogate fuel component and mixture models using new experimental data from UCONN's RCM
  - Improve gasoline surrogate model with new data on blends of olefins and aromatics from the ANL RCM



Diesel surrogate components

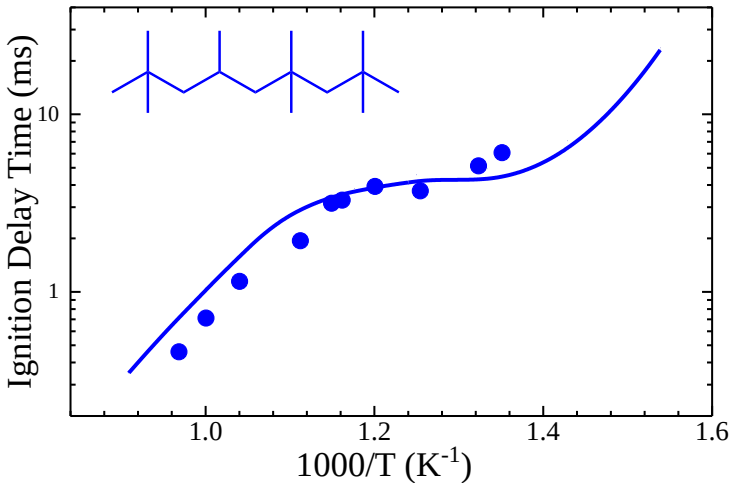


Gasoline surrogate components

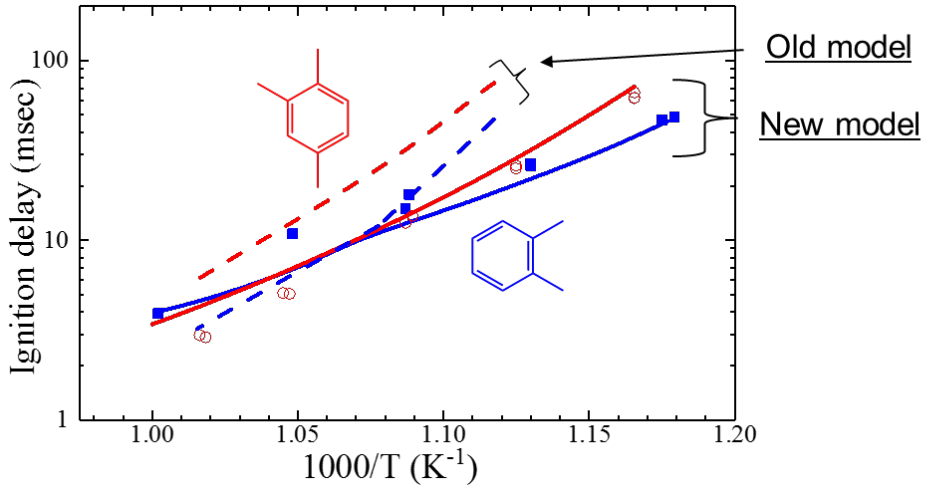
Chemical kinetic milestones

- ✓ Develop improved kinetic models for iso-cetane and 1,2,4-trimethyl benzene (June, 2018)

iso-cetane



trimethyl benzene



Approach

- Develop fuel surrogate 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 fuels
  - gasoline fuels
  - addition of ethanol and other blendstocks

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

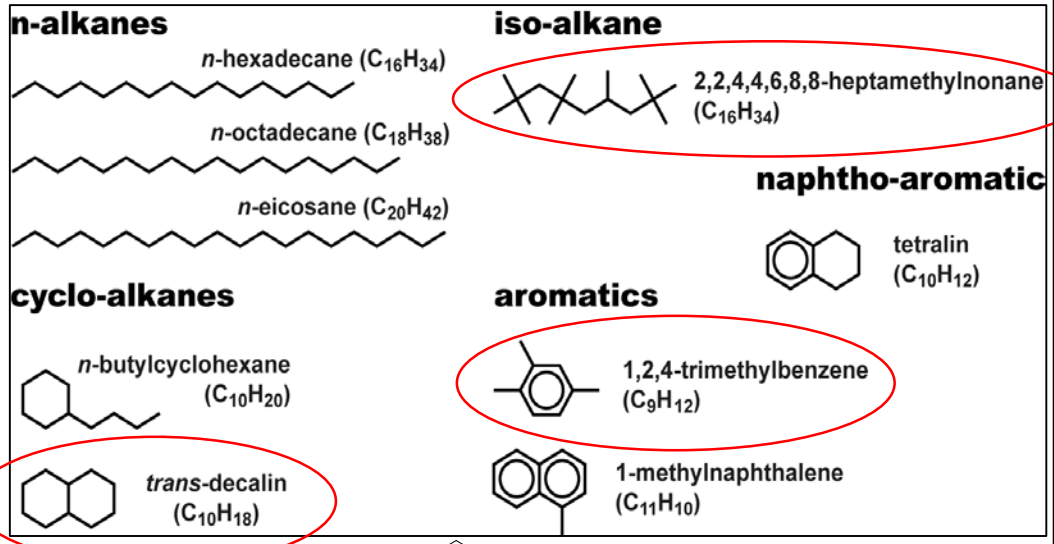
- Use the resulting models to simulate practical applications in engines, including diesel, advanced compression ignition and DISI, as needed

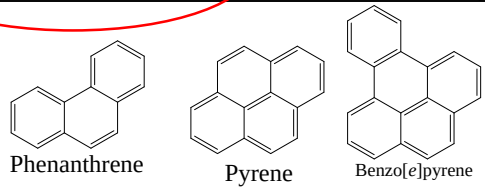
- Iteratively improve kinetic models as needed for applications
- Make kinetic models available to industry

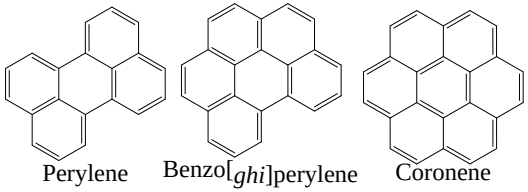
- Addresses barriers to increased engine efficiency and decreased emissions by allowing optimization of fuels with advanced engine combustion

Technical Accomplishments:

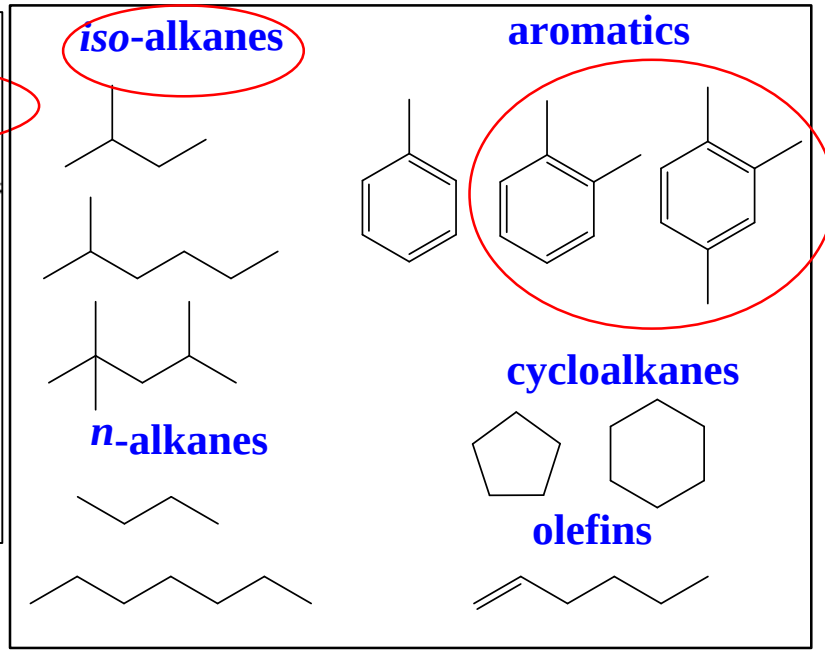
Diesel surrogate components







Gasoline surrogate components

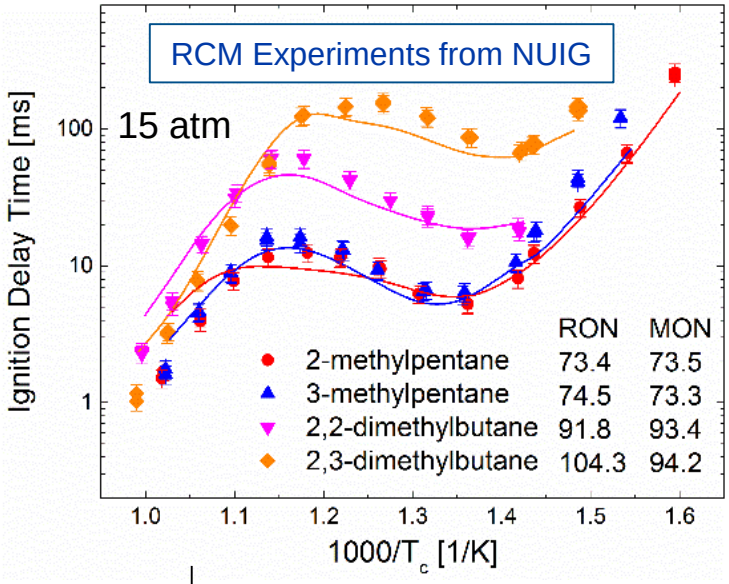


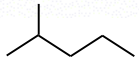
Preliminary PAH model

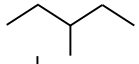
Large iso-alkane models improved by using rate rules developed for C6 isoalkanes and iso-octane

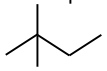
Gasoline and diesel surrogate compounds

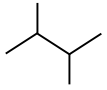
C6 iso-alkanes



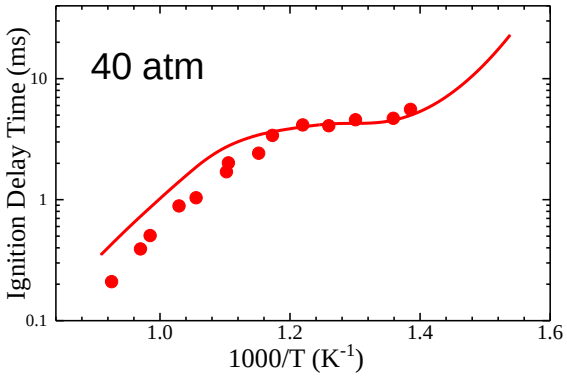

2-methylpentane


3-methylpentane

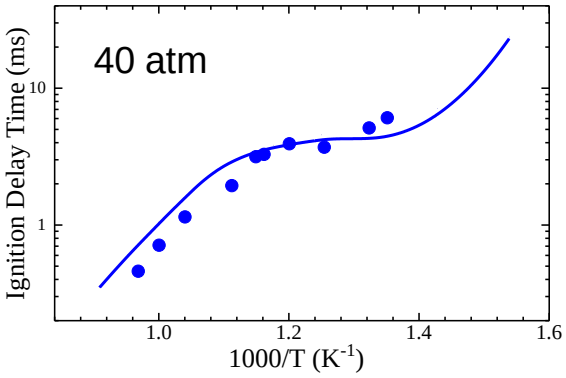

2,2-dimethylbutane


2,3-dimethylbutane

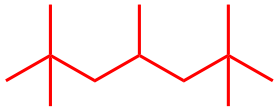
iso-dodecane

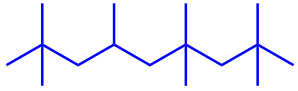


iso-cetane



Shock tube experimental data from Won et al. Comb. Flame (2016)

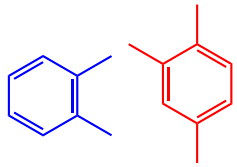




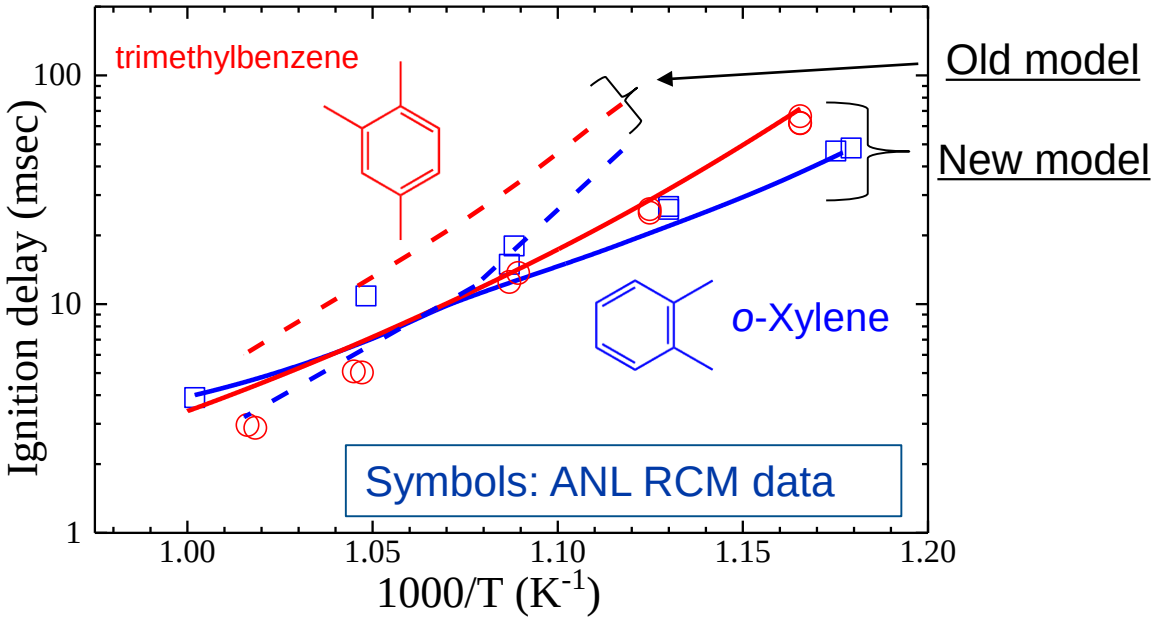
(All data are stoichiometric, fuel/air mixtures)

iso-Alkane model covering C6-C16 carbon structures developed using a consistent set of reaction rate rules

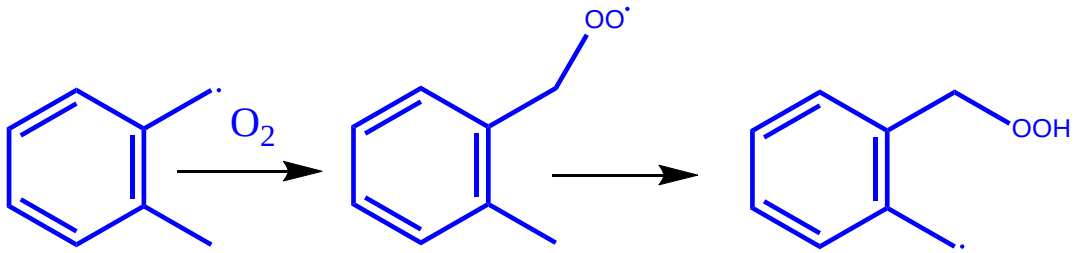
Aromatic mechanisms improved



Gasoline and diesel surrogate compounds



- *Improvement in performance of model is mainly due addition of low* temperature chemistry (RO2 chemistry) of *o*-Xylene and 1,2,4 trimethylbenzene

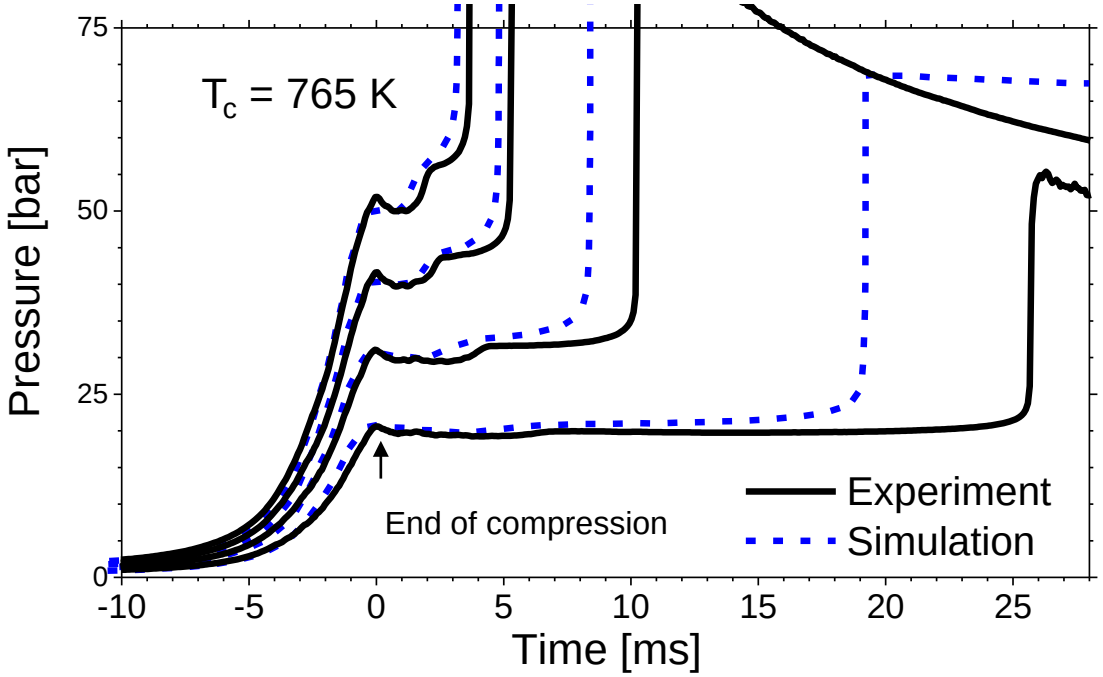


Kukkadapu, Kang, Wagnon, Zhang, Mehl, Palaciosc, Wang, Goldsborough, Westbrook and Pitz, 37th International Symposium on Combustion (2018) accepted.

Gasoline surrogate mechanism accurately simulates E10 gasoline in Argonne RCM

Gasoline surrogate model

Simulated and experimental pressure histories of RD5-87

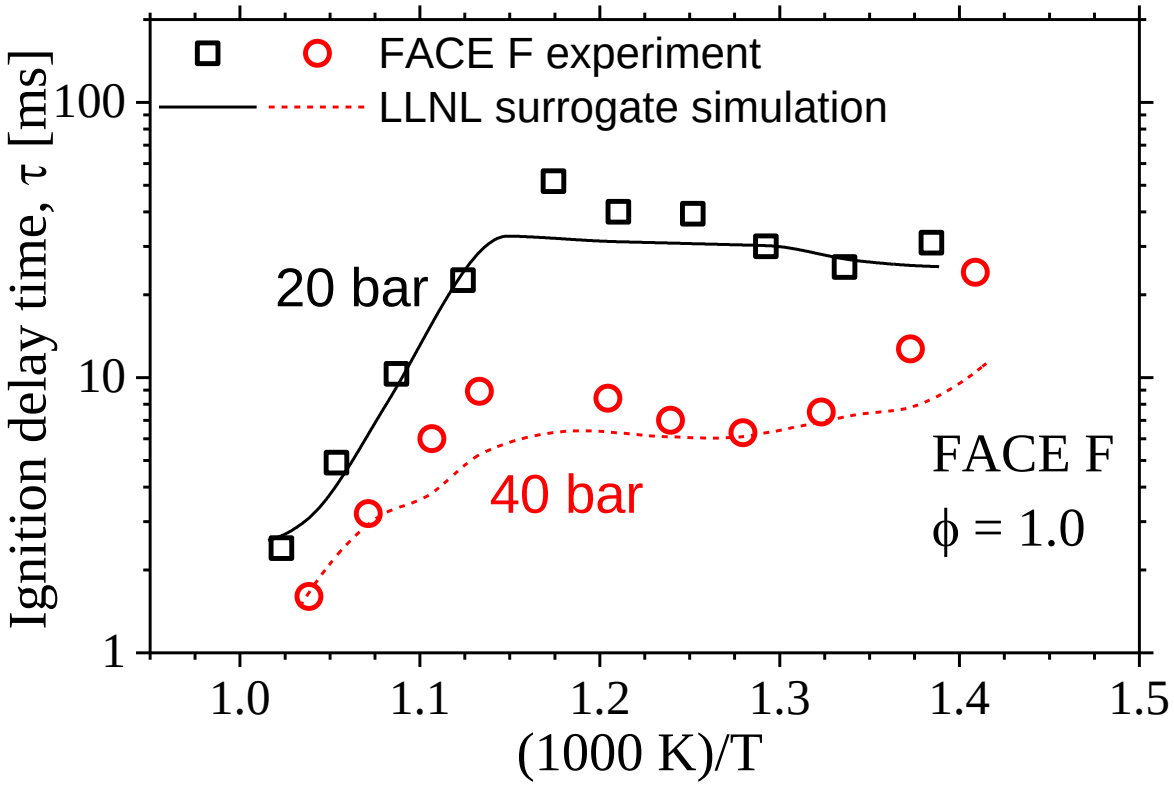


- RD5-87 is a research gasoline designed to represent an average E10, market, regular gasoline
- Experiments performed in Argonne RCM

Simulations track well the heat release rate, and thereby the pressure history in the RCM experiments from ANL (Goldsborough et al.)

Gasoline surrogate model well simulates FACE F gasoline

Gasoline surrogate model



FACE F:

- high RON (95)
- moderate OS (6)
- high iso-alkanes

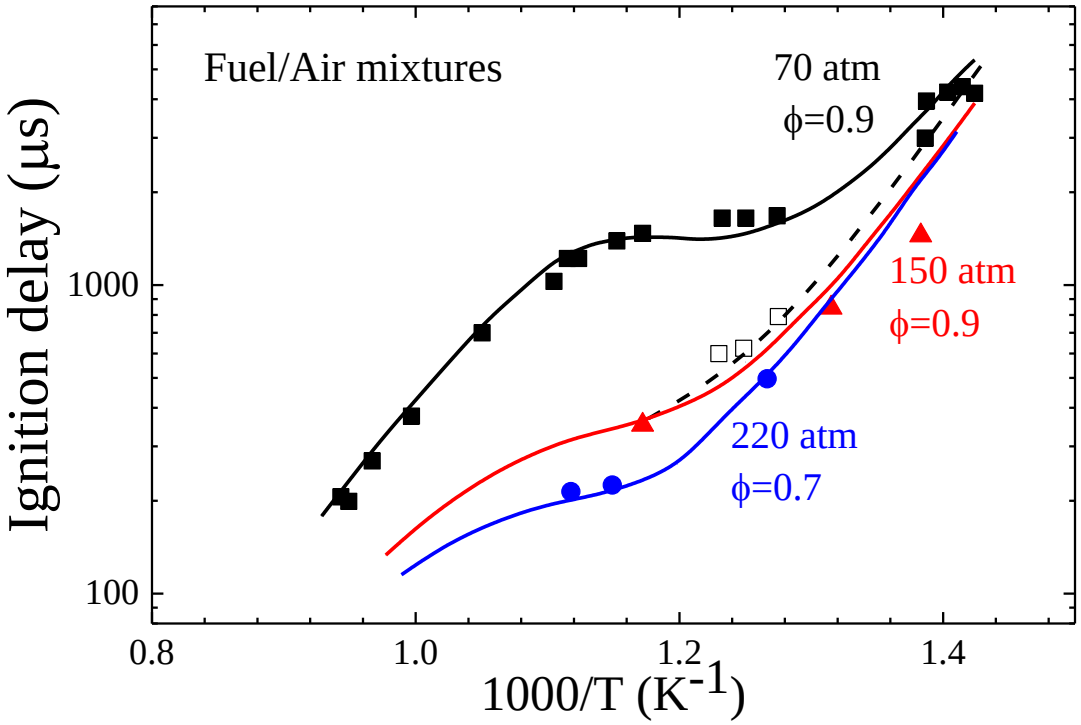
Dilute conditions studied to simulate EGR effects

FACE F gasoline measured in ANL RCM (Goldsborough et al.)

Kang, Fridlyand, Goldsborough, Wagnon, Mehl, Pitz and McNenly, 37th International Symposium on Combustion (2018), accepted.

Gasoline surrogate model well simulates ignition behavior at very high pressures (70 to 220 atm!)

Gasoline surrogate model



High performance gasoline fuel

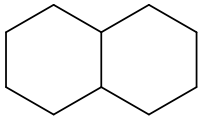
Properties	Gasoline	Surrogate
Olefins	9	14
Aromatics	2	2
n-Paraffins	3	3
iso-Paraffins	81	76
Naphthenes	5	5
RON	101	99.3
MON	94	95.2

Symbols: Experimental data from Stanford high-pressure shock tube
Curves: LLNL gasoline surrogate model

Validations give confidence in the ability to predict fuel behavior at high-pressure conditions

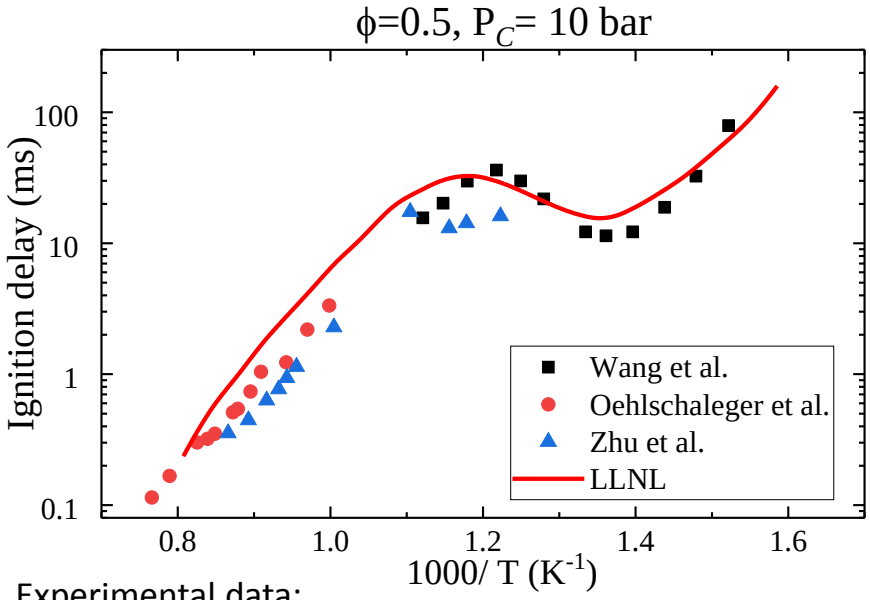
Davidson, J. K. Shao, R. Choudhary, M. Mehl, N. Obrecht and R. K. Hanson, 37th Combustion Symposium, Accepted (2018).

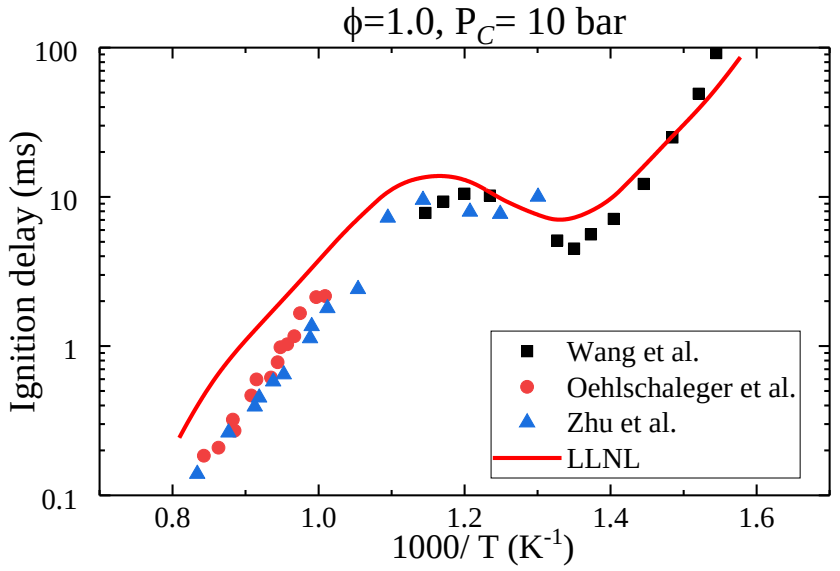
trans-Decalin kinetic model greatly improved



Diesel surrogate compounds

- For the first time, a detailed kinetic model for the low temperature chemistry of trans-decalin developed
- New experimental ignition delay data obtained from RCM experiments from Univ. of Connecticut (UCONN)





Experimental data:

RCM: Wang, Zhang, Kukkadapu, Wagnon, Mehl, Pitz and Sung, Combust. Flame, in press (2018).

Shock tube: Oehlschlaeger et al., Energy & Fuels (2009)

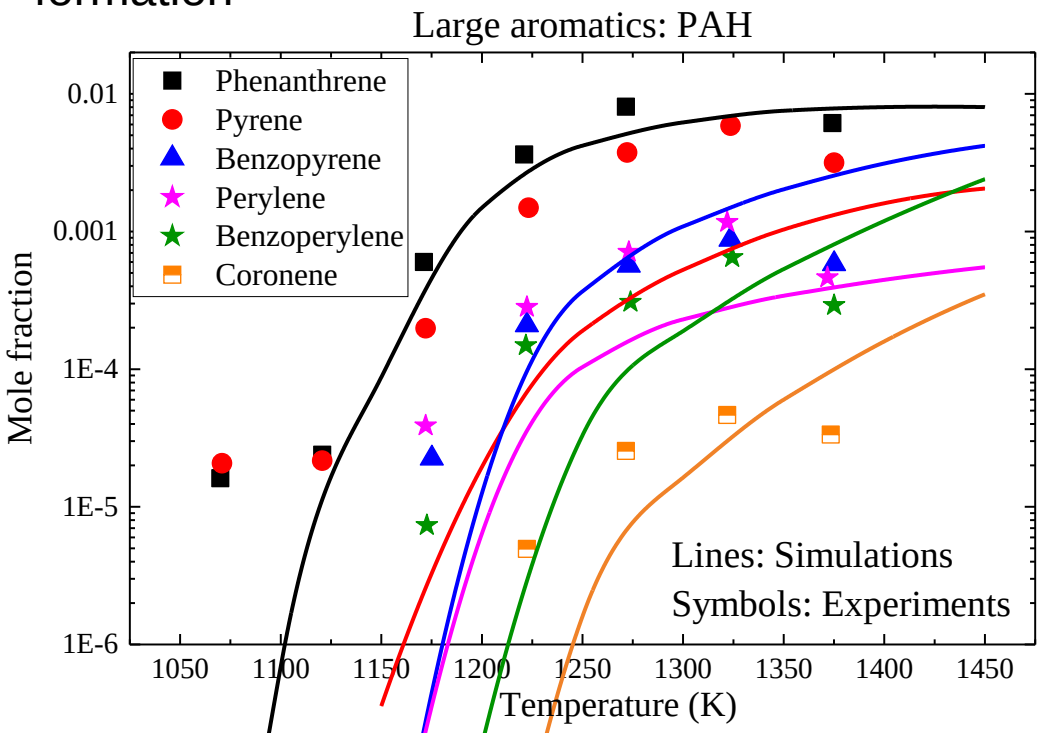
Zhu et al. , Combustion and Flame 161 (2014).

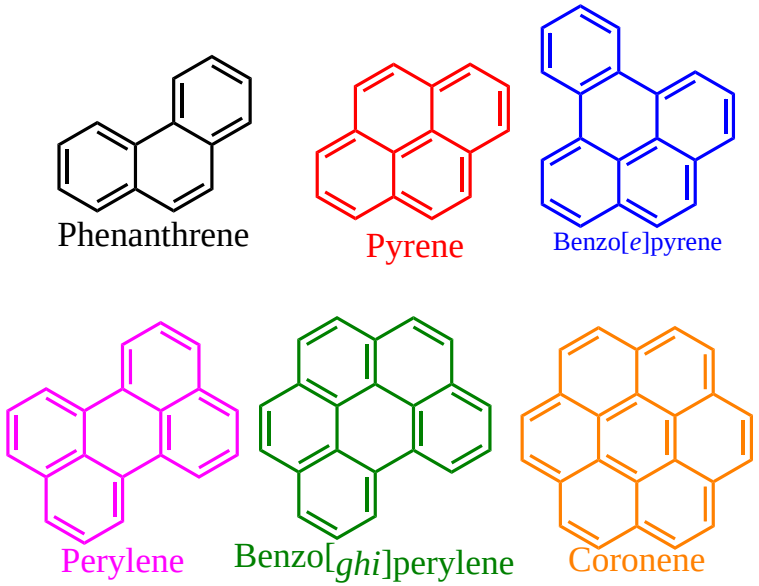
← Experimental data and kinetic model published

Preliminary PAH mechanism developed

Soot model

Includes most up-to-date reaction paths and rate constants for 3 to 7 ring PAHs formation





PAH profiles during propene pyrolysis in a flow reactor at pressure of 8 kPa and residence time of 1 sec

Experimental data was taken from Norinaga et al., IJCK, vol. 40 (2008), Pages: 199-208

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

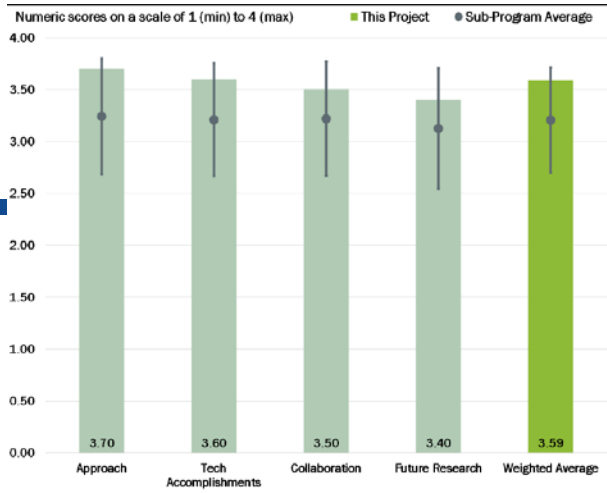
Gasoline Surrogate
Diesel PRF
Diesel surrogate, detailed and reduced

Alkyl-Carbonates

Dimethyl Carbonate
Diethyl Carbonate
Cyclopentane

Gasoline Surrogate

FY2017 Reviewer's comments and our responses



Overall, the reviewer's comments were very positive

- The reviewer commented: "The reviewer ... would like to see accelerated progress on gasoline components and the accuracy of gasoline components, especially considering dilute, boosted stoichiometric operation. Near-term LD engines will be boosted running stoichiometric with high rates of EGR."
- Response: "The gasoline surrogate mechanism successfully simulated experiments in the Magnus Sjoberg's DISI engine at Sandia where NOx in the residual gases plays an important role in autoignition in the end gas. Experiments are planned in the ANL RCM to explore EGR effects and facilitate kinetic mechanism validation."

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

Presenter
Bill Pitz, Lawrence Livermore National Laboratory

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 engine experiments with Sandia:
    - John Dec on HCCI and Magnus Sjöberg on DISI
  - Collaboration at ANL with Scott Goldsborough on RCM experiments and Sibendu Som on diesel reacting sprays
- Second interaction is collaboration with many universities:
  - Prof. Sung's group, U of Conn., and Dr. Sarathy, KAUST
  - Dr. Curran at Nat'l Univ. of Ireland on gasoline and diesel fuel components in RCM and shock tube
- Participation in other working groups with industrial representation
  - CRC Fuels for Advanced Combustion Engines (FACE) Working group and CRC AVFL-18a (Improved diesel surrogate fuels for engine testing and kinetic modeling)

Remaining Challenges and Barriers

- Develop chemical kinetic mechanisms for surrogates for diesel and gasoline fuels that are predictive at high pressures and with EGR 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 that can better represent diesel fuel properties
- 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 work

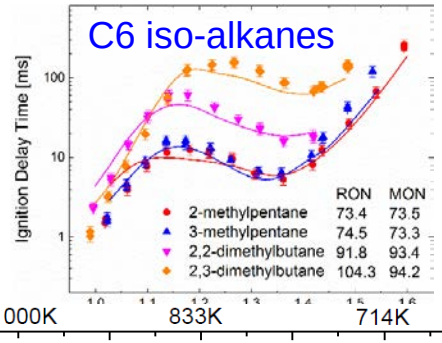
- Develop new, validated mechanisms for C5 & C6 branched olefins that better represent olefins found in gasoline using ANL RCM data
- Validate and improve gasoline surrogate component and mixture models over a wide range of pressures, temperatures, and EGR using new experimental data from ANL RCM
- Validate and improve our new chemical kinetic model for diesel surrogate components and mixtures with new experimental data from UCONN rapid compression machine
- Develop PAH/soot kinetic model and incorporate it into the diesel surrogate mechanism so that soot emissions can predicted
- Work with CFD modelers to provide reduced versions of gasoline and diesel surrogates to simulate engine combustion

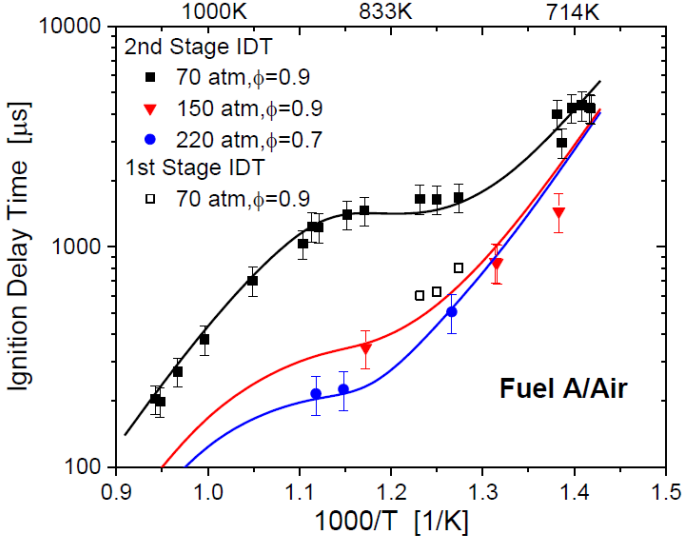
(Any proposed future work is subject to change based on funding levels)

Detailed chemical kinetic modeling summary

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

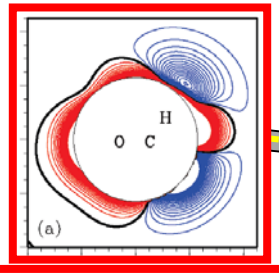
- Improved component submodels
  - iso-alkanes (C6, C12, C16)
  - Aromatics (xylene, tri-methylbenzene)
  - Decalin
- New gasoline surrogate model accurately simulates real gasoline fuels in RCM and shock tube over a wide pressure range
- Developed preliminary PAH submodel for soot modeling applications





Technical Back-Up Slides

Chemical kinetic model development for practical fuels:



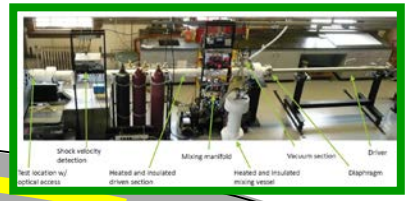
Ab initio calculations

Accurate reaction rates

Species thermodynamic properties

Reaction paths

Reaction rate rules



Detailed Chemical Kinetic Models

Fundamental Experiments

NUIG, UCONN, KAUST, USC, CNRS, RPI

Model Reduction

Validation against fundamental combustion data

Fast Solvers

Application to engines

LLNL - Numerics

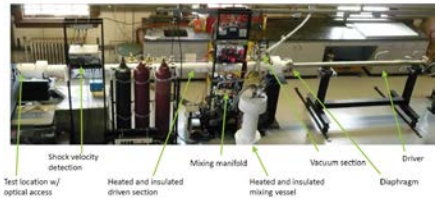
Fuel component and surrogate models validated and improved by comparison to fundamental experimental data

Jet Stirred Reactors

Premixed Laminar Flames

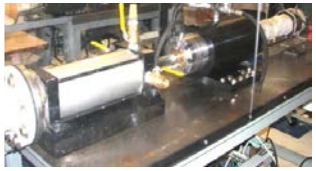
Twin premixed flames

Shock tube

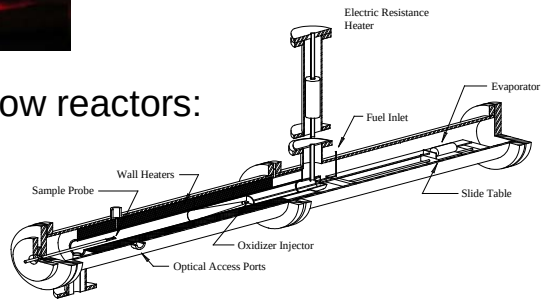


Non Premixed Flames

Rapid Compression Machine



High pressure flow reactors:



Engine Combustion

<u>Combustion Parameters</u>

Temperature

Pressure

Mixture fraction (air-fuel ratio)

Mixing of fuel and air