Lawrence Livermore National Laboratory

Chemical Kinetic Models for Advanced Engine Combustion

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

Washington, DC

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LLNL-PRES-772592

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: 500K
- FY19: 625K

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

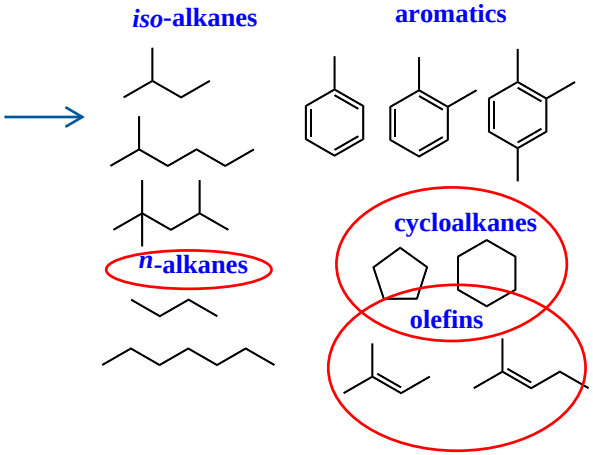
Partners

- 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

- Project 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

- FY19 Objectives:
  - Develop fuel surrogate kinetic models with more representative components for real fuels to increase accuracy of autoignition predictions and to cover a range of real fuels. Validate kinetic mechanisms over a range of temperature, pressure, and equivalence ratio relevant to engine combustion.

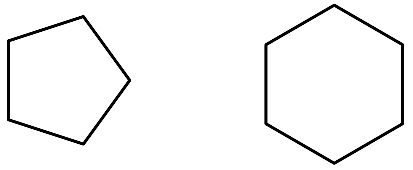


Gasoline surrogate components

Chemical kinetic milestones

- Q2: Improved cycloalkane mechanisms (for 2-3 cycloalkane mechanisms) (improved cyclopentane complete; cyclohexane delayed until Q4)

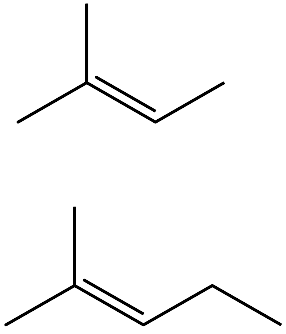
cycloalkanes



cyclopentane cyclohexane

- Q4: Improve C5-C6 iso-alkene kinetic models compared to fundamental experimental autoignition data from a rapid compression machine (RCM) on C5-C6 iso-alkenes and on a full boiling-range FACE-F gasoline. (On track)

Iso-alkenes



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

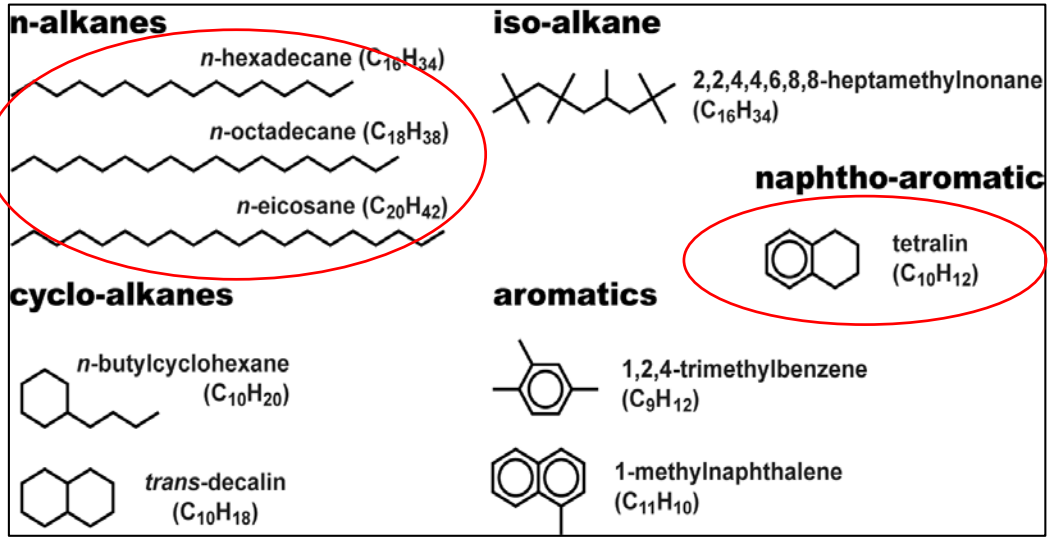
- Use the resulting models to simulate practical applications in engines, including diesel, advanced compression ignition and DISI, as needed

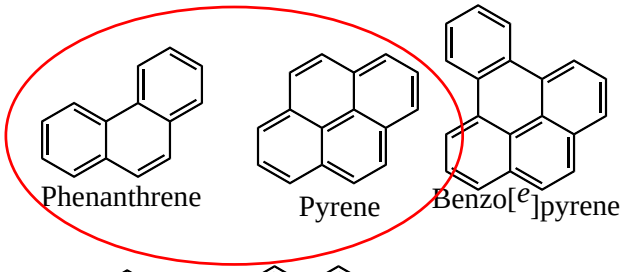
- Iteratively improve kinetic models as needed for applications
- Make kinetic models available to industry

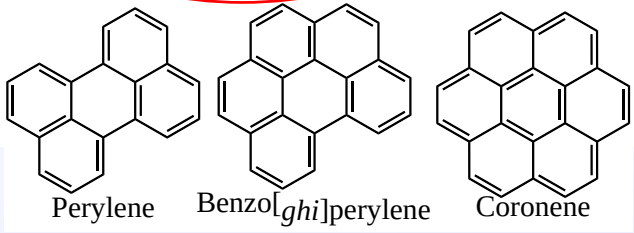
- Addresses barriers to increased engine efficiency and decreased emissions by allowing optimization of fuels with advanced engine combustion

Technical Accomplishments

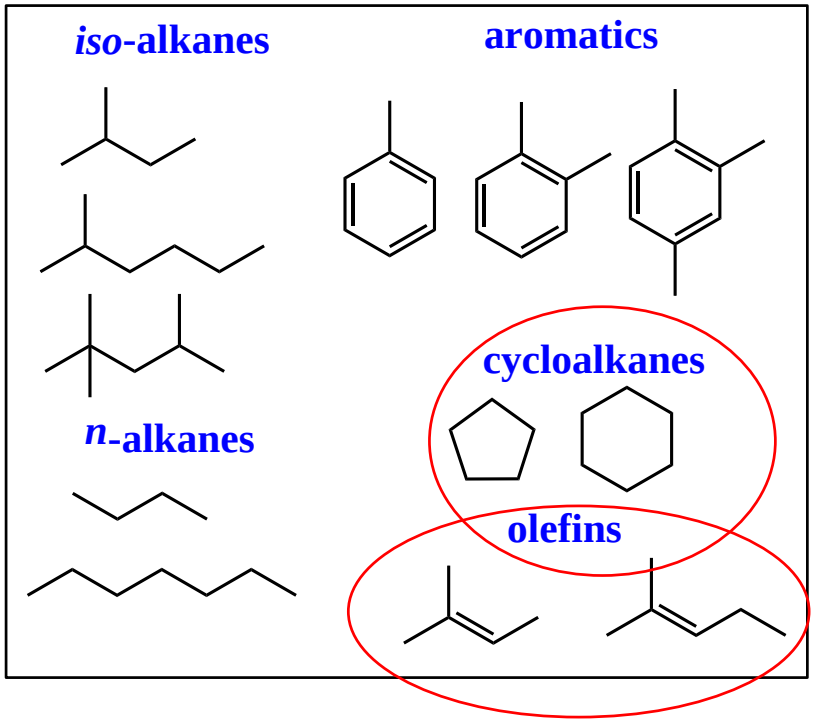
Diesel surrogate components





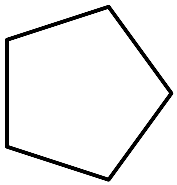


Gasoline surrogate components



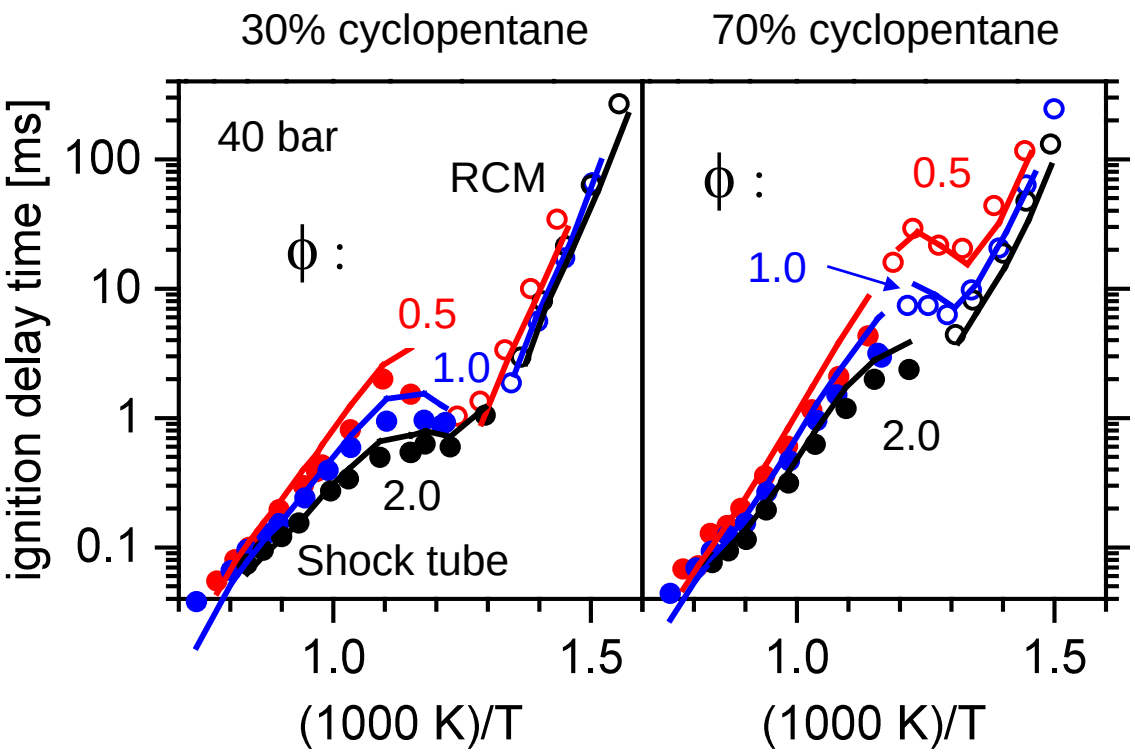
Improved polycyclic aromatic hydrocarbons (PAH) model

Improved kinetic model for cyclopentane and its blending behavior

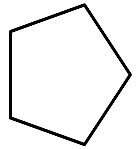


Gasoline surrogate components

Cyclopentane/DME ignition delay time comparisons:



Cyclopentane



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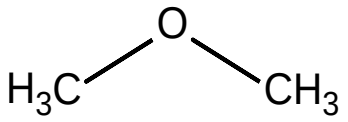
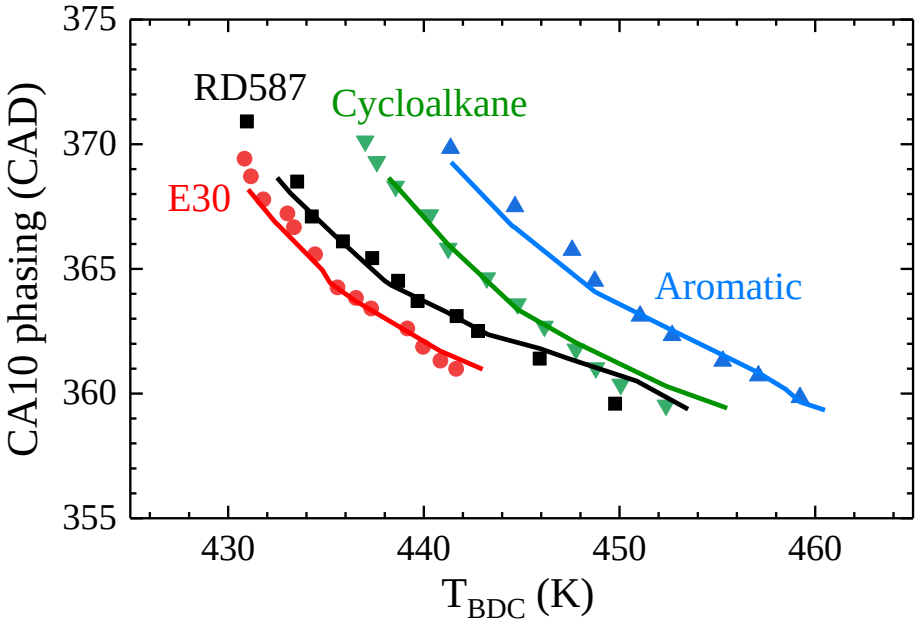


dimethylether (DME)

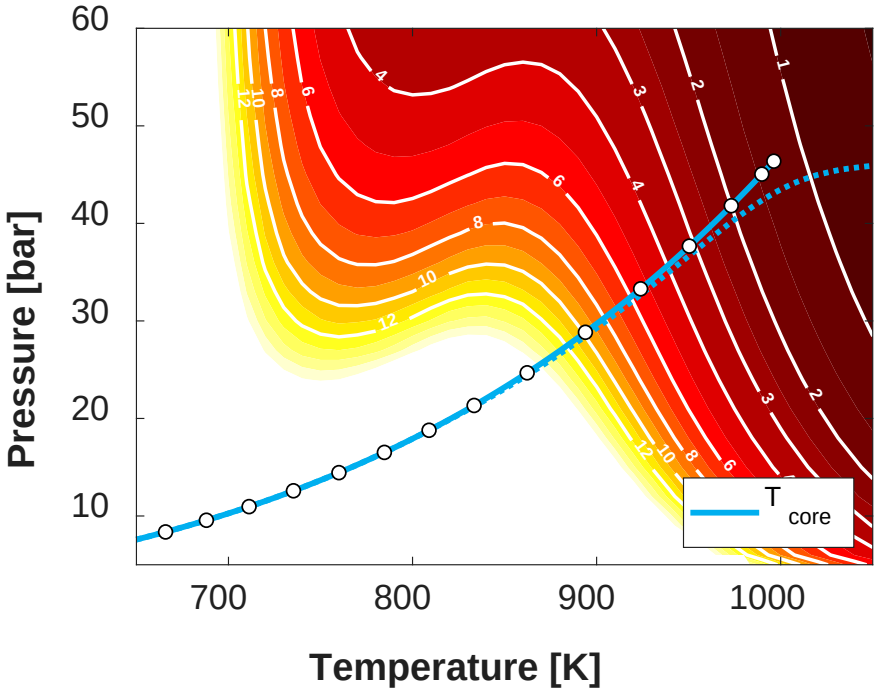
Experiments: Lokachari and Curran, Nat'l Univ. Ireland, Galway (NUIG)
Simulations: LLNL kinetic model
Wagnon et al. US National Combustion Meeting, 2019

LLNL gasoline kinetic model: validation in engine and use in engine analysis

Ignition phasing predictions compare very well with measurements in HCCI engine by Lopez-Pintor and Dec at SNL



Used in methodology to help determine feasible range of operation for mixed-mode engine operation (SNL, Sjöberg)

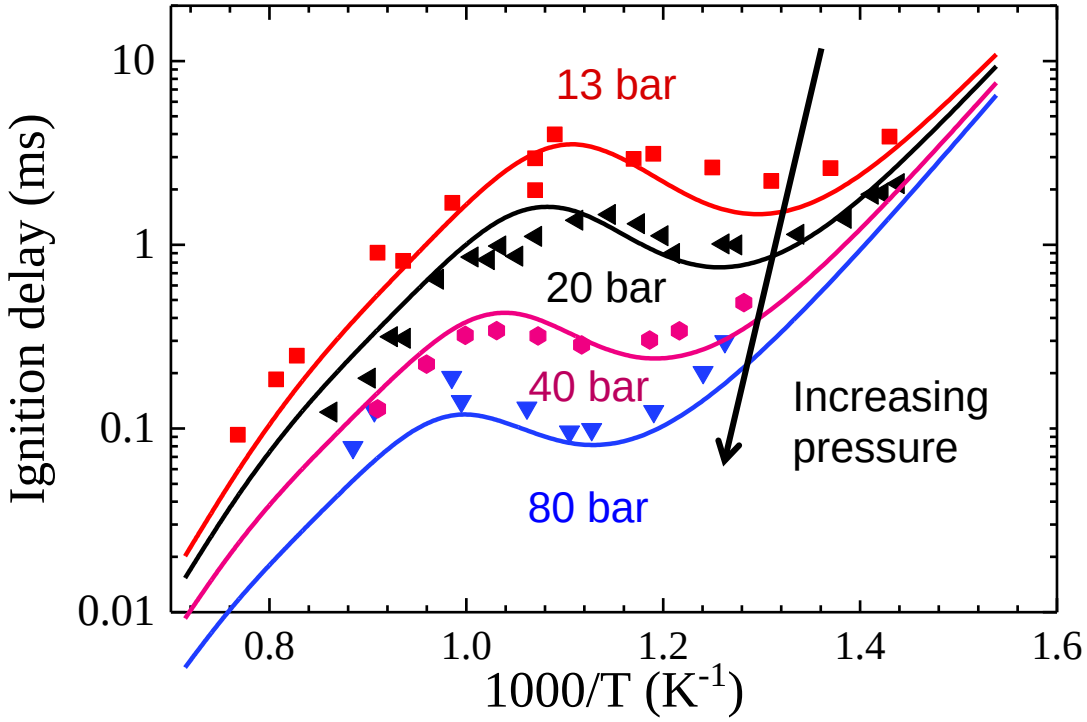


Improved kinetic model well simulates effect of pressure on ignition of n-alkanes

n-decane

Diesel surrogate components

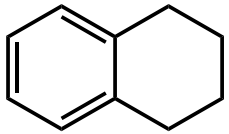
Comparison of n-decane ignition delay times in shock tube



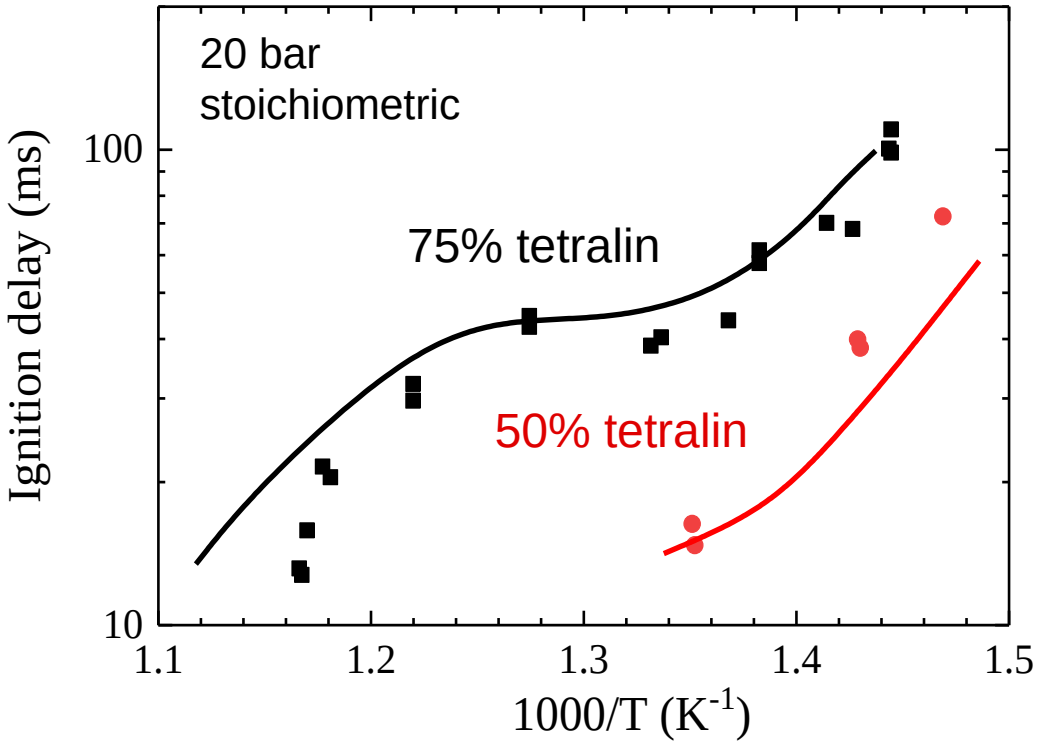
fuel/air stoichiometric mixtures

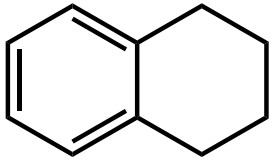
Symbols: experimental data, Pfahl et al. 1996, Tekawade et al. 2017, Zhukov et al. 2008
Curves: simulations, LLNL kinetic model

Improved kinetic model for tetralin and its blending behavior



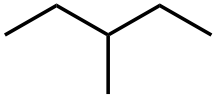
Diesel surrogate components





tetralin

+



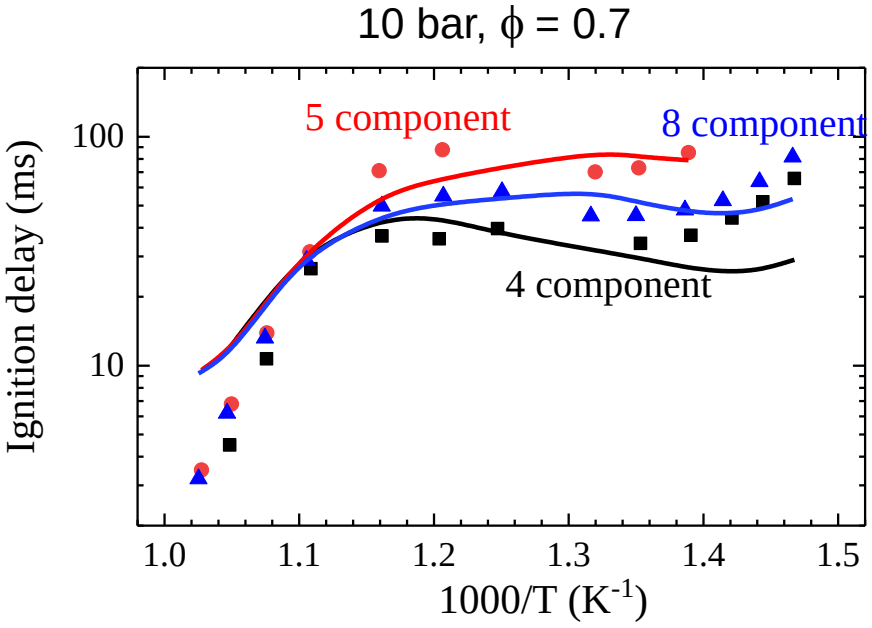
3-methyl pentane

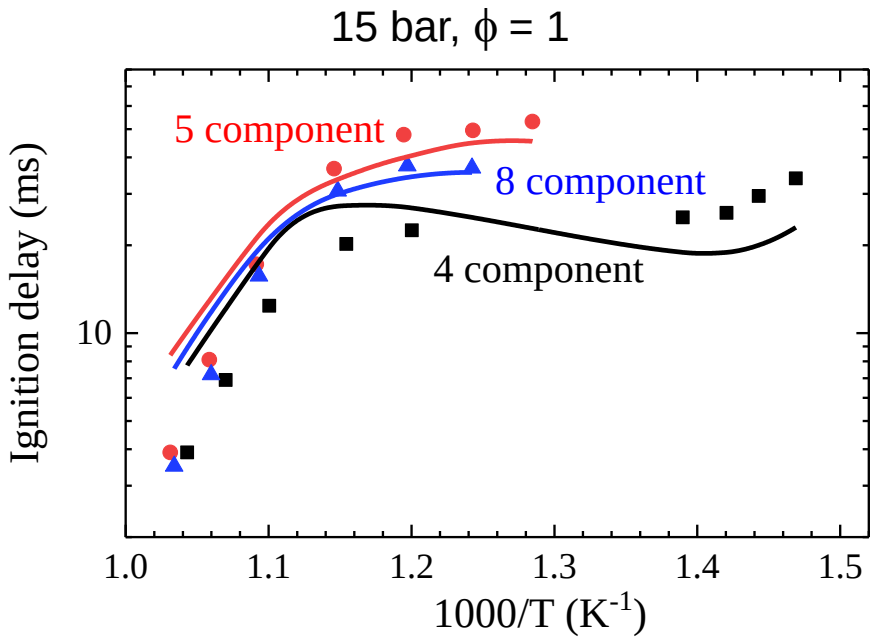
Symbols: experimental RCM data, Farooq's group, KAUST, Djebbi et al. 2019 (in preparation)
Curves: simulations, LLNL kinetic model

Improved diesel surrogate model compares well with RCM experiments

Diesel surrogates

Direct comparison of model and experiments of CRC diesel surrogates:



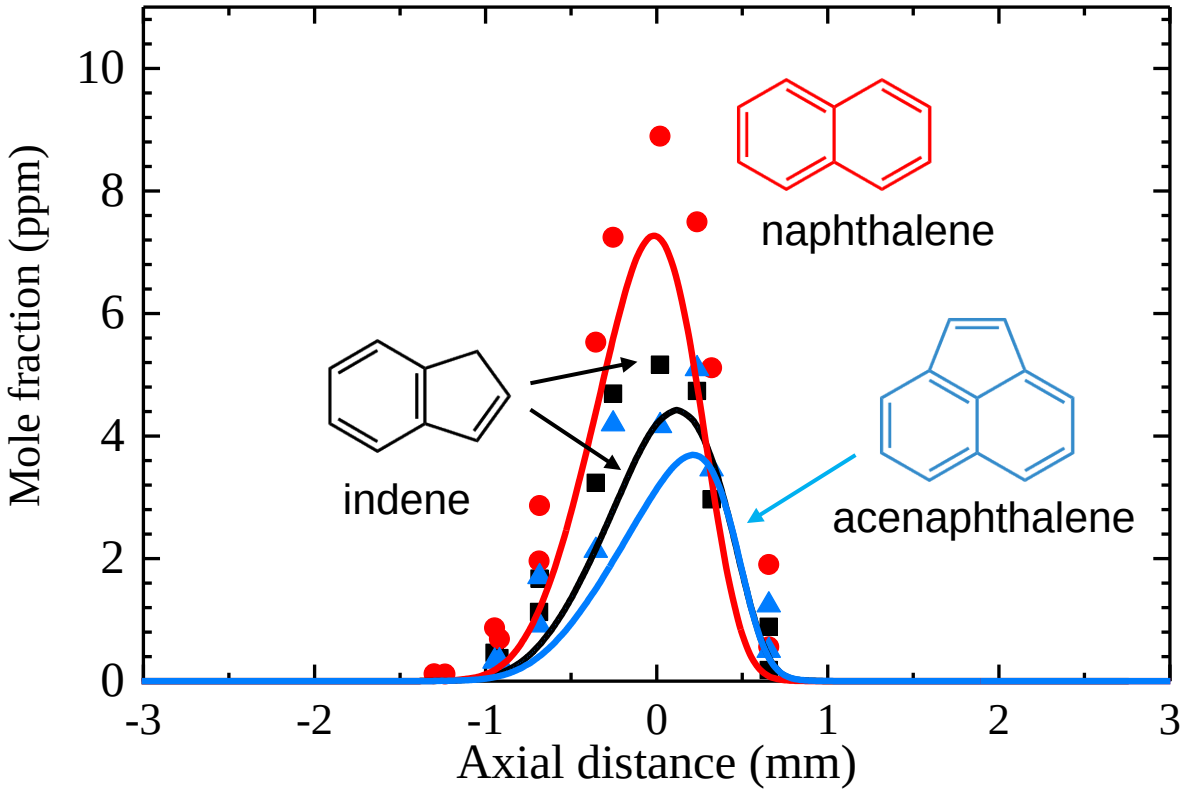


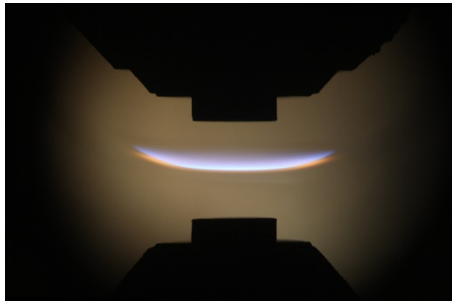
Coordinated Research Council (CRC) supported diesel surrogate RCM experiments at Univ. of Connecticut (UCONN) and provided surrogate fuels

Wang, Kukkadapu, Zhang, Wagnon, Mehl, Pitz, Westbrook and Sung, US National Combustion meeting, 2019

Improved PAH kinetic model: Predictions compare well with measurements in counterflow diffusion flame for ethylene

PAH model





Yale counterflow diffusion flame burner

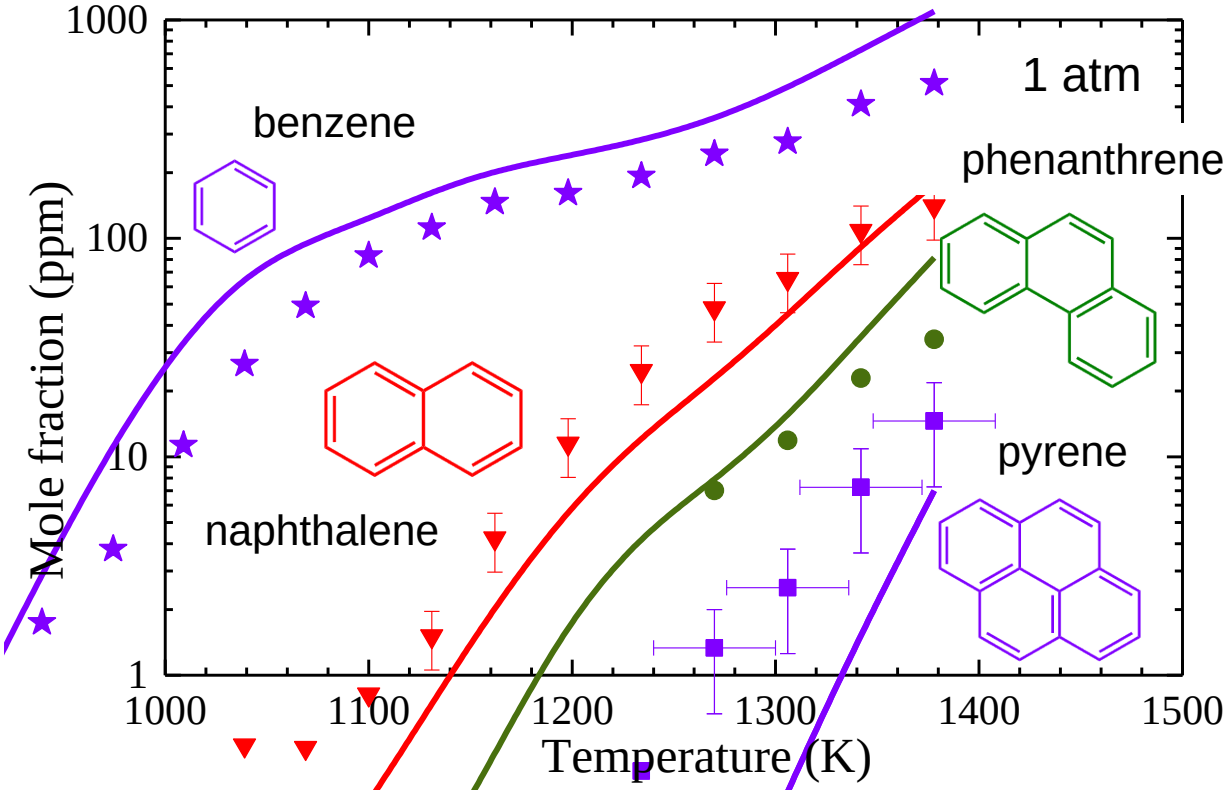
Symbols: experiments, Carbone, Gleason, Gomez, Proc. Combustion Inst., 2017
Curves: simulations, LLNL kinetic model

Improved PAH kinetic model: Predictions compare well with measurements for simple gasoline surrogate

PAH model

Pyrolysis in simple gasoline surrogate in a flow reactor

(n-heptane/iso-octane/toluene blend)

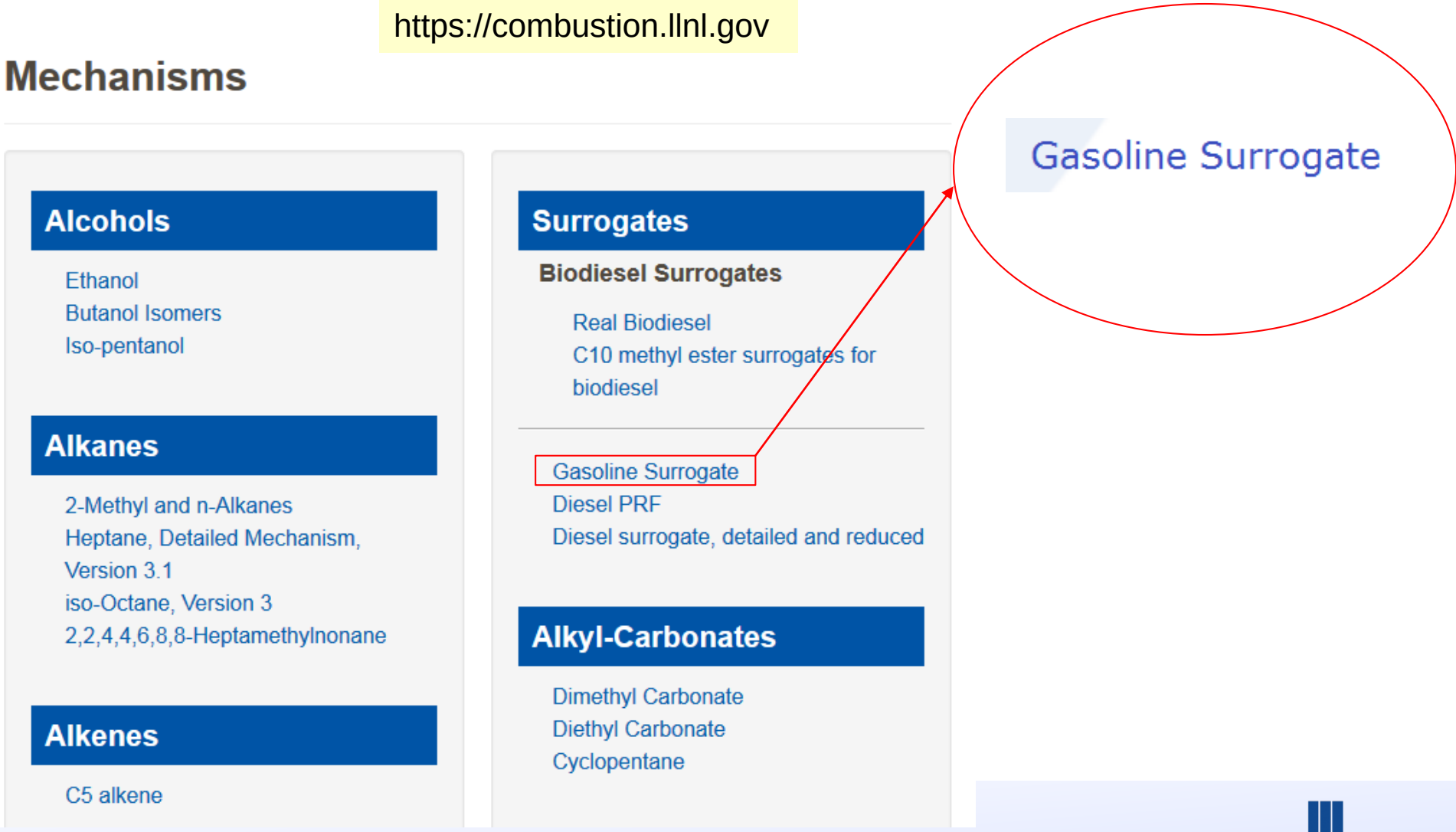


Symbols: experiments, Shao et al., Proc. Combust. Inst. (2019)

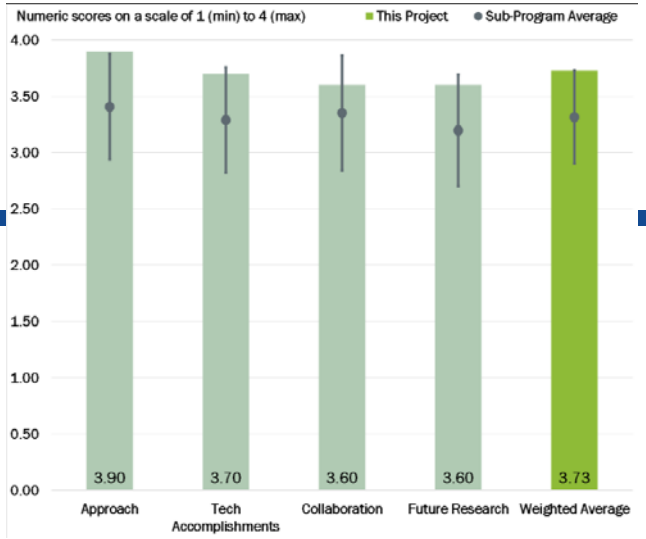
Curves: simulations, LLNL kinetic model

Mechanisms are available on LLNL website and by email

https://combustion.llnl.gov



FY2018 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: "as the number of surrogate components increases there will be point of diminishing return."
- Response: "There is a need to have enough components to cover the distillation curve because early or late vaporization of components could affect ignition delay and soot formation. We are trying to manage the size of the model by choosing fuel components with symmetrical molecular structures and avoiding inclusion of unnecessary reaction classes when possible."
- The reviewer commented: "On the log scale, the [ignition delay] difference can be as high as a factor of two. The reviewer questioned what the strategy is for closing the gap."
- Response: "We have been steadily reducing the uncertainty in predictions like ignition delay and flame speed by including rate constants fits and thermodynamic properties from fundamental quantum chemistry calculations from collaborators and from the literature."

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:
    - John Dec on HCCI and Magnus Sjöberg on SACI engines
    - Jim Szybist, boosted SI, ORNL
  - Collaboration at ANL with Scott Goldsborough on RCM experiments and Sibendu Som on gasoline and diesel CFD simulations
- Second interaction is collaboration with many universities:
  - Prof. Curran at Nat'l Univ. of Ireland on gasoline and diesel fuel components in RCM and shock tube
  - Prof. Sung's group, Univ. of Conn., and Prof. Sarathy, KAUST
- 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

- Improve accuracy of chemical kinetic mechanisms so that desired predictability needed by engine designers can be achieved
- More accurately simulate the fuel effects with changing exhaust gas recirculation (EGR), equivalence ratio, and fuel composition
- Chemical models for that accurately predict fuel blending compared to shock tube and RCM experimental data
- Predictive models for diesel surrogates, particularly new versions of diesel surrogates that can better represent diesel fuel properties
- Reduced kinetic models that work with sufficient accuracy for computational fluid dynamic (CFD) simulations of engine combustion
- Sufficient accuracy of kinetic models and other submodels needed to predict cycle-to-cycle variation in engines

Future work

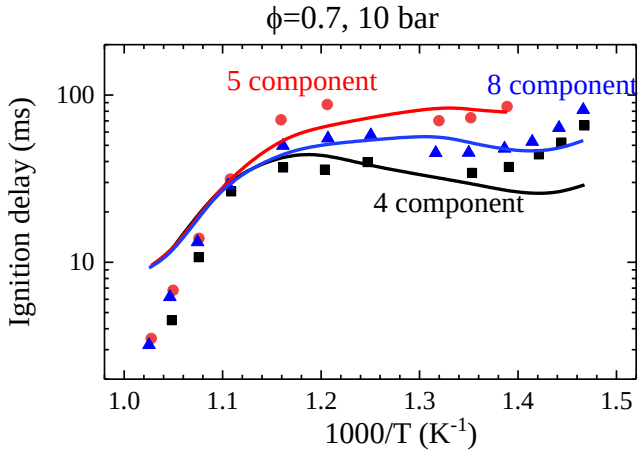
- EGR: Improve fuel surrogate kinetic models for accurate and validated predictions of autoignition with EGR over a range of temperature, pressure, and equivalence ratio relevant to engine combustion
  - Improve model behavior for flame speeds with added EGR to better simulate early flame kernel development
  - Validate kinetic models for effects of O_2, H_2O, CO_2, NO in EGR
- Interface PAH model with soot model and validate compared to soot measurements from fundamental shock-tube and flame experiments, and spray-chamber combustion experiments (e.g. spray A, G).
- Develop fuel surrogate kinetic models for new components to cover volatility and reactivity range of real gasolines and diesel.

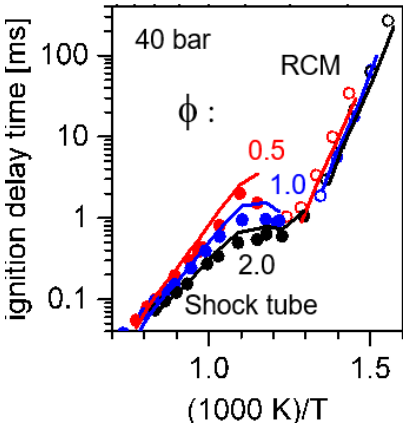
(Any proposed future work is subject to change based on funding levels)

Detailed chemical kinetic modeling summary

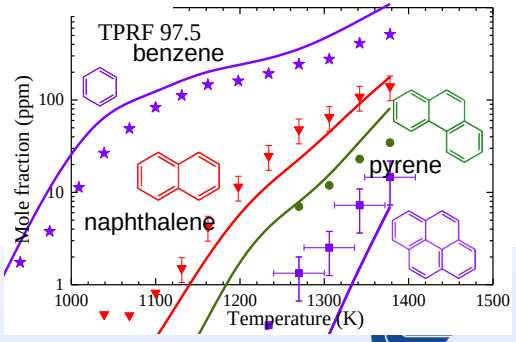
Developing fuel surrogate models for gasoline and diesel fuels to enable accurate advanced engine combustion simulations with fuel effects

- Improved component submodels
  - cyclopentane blending
  - C8 to C20 n-alkanes
  - tetralin
- Improved & validated diesel surrogate kinetic model



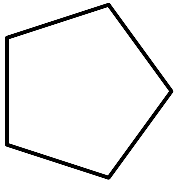


- Improved PAH submodel for soot modeling applications

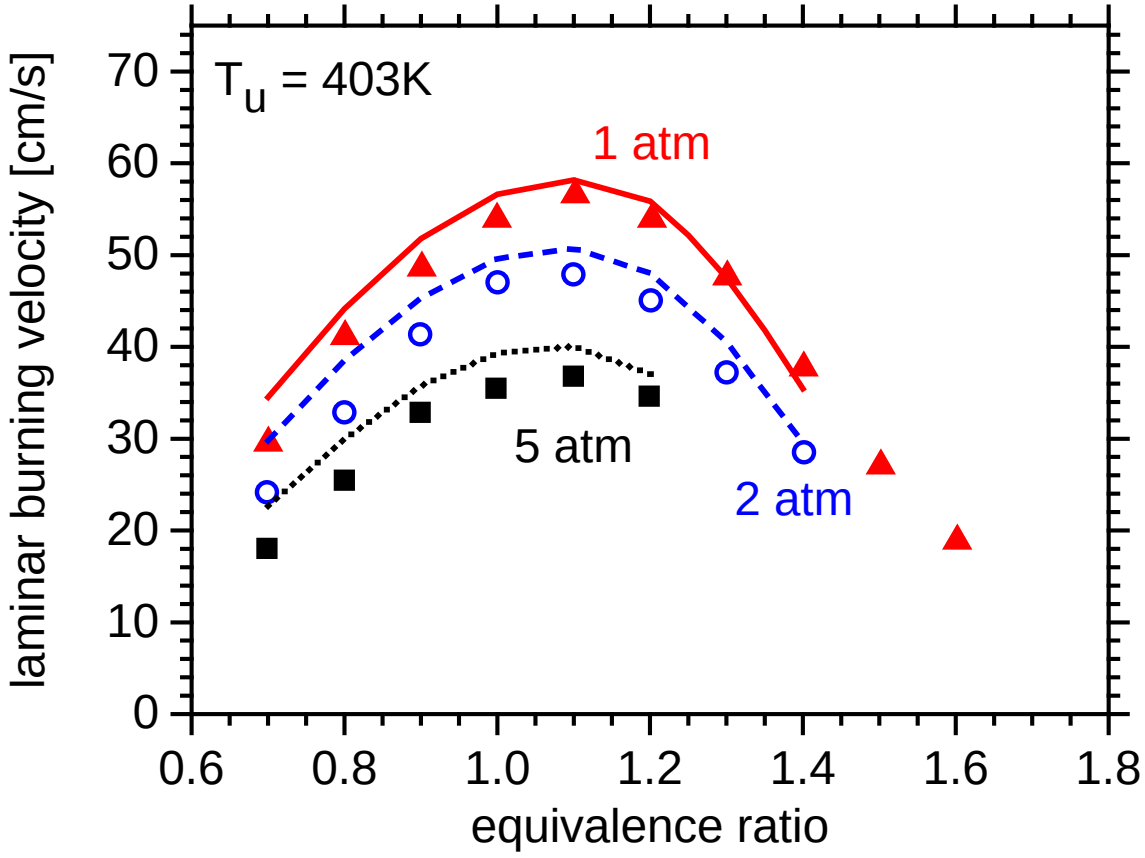


Technical Back-Up Slides

Improved kinetic model for cyclopentane flame speeds



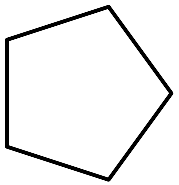
Gasoline surrogate components



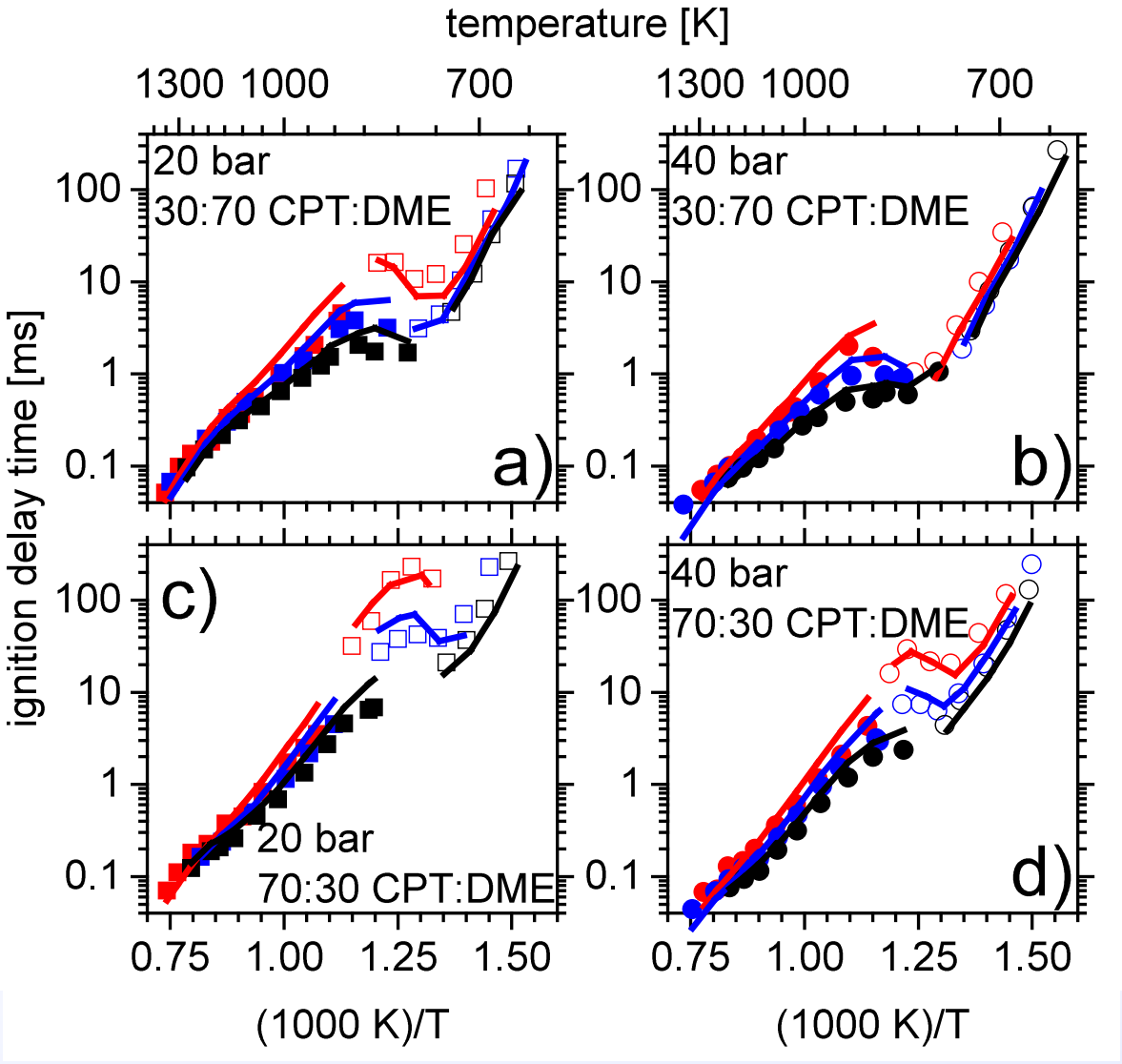
Symbols: experimental data, Zhao et al., Fuel (2018)
Curves: simulations, LLNL kinetic model

Important to predict flame speeds to simulate multimode engines

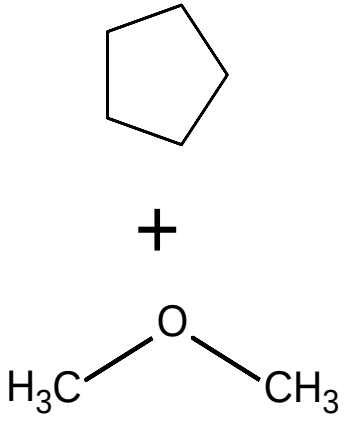
Improved kinetic model for cyclopentane model & its blending behavior



Gasoline surrogate components



Cyclopentane (CPT)



dimethylether (DME)

CRC diesel surrogate fuel compositions

	V0a (4-comp.)		V0b (5-comp.)		V1 (8-comp.)		V2 (9-comp.)	
Palette Compound Abbrev.	mol %	wt %	mol %	wt %	mol %	wt %	mol %	wt %
NHXD	27.8	32.2	0	0	2.7	3.2	0	0
NOD	0	0	23.5	32.1	20.2	27.3	10.8	15.2
NEI	0	0	0	0	0	0	0.8	1.2
HMN	36.3	42.0	27.0	32.8	29.2	35.1	0	0
2MHPD	0	0	0	0	0	0	7.3	10.2
NBCX	0	0	0	0	5.1	3.8	19.1	14.8
TIPCX	0	0	0	0	0	0	11.0	12.8
TDEC	14.8	10.5	0	0	5.5	4.0	0	0
PHP	0	0	0	0	0	0	6.0	6.4
TMB	0	0	12.5	8.1	7.5	4.8	0	0
TIPB	0	0	0	0	0	0	14.7	16.6
TET	0	0	20.9	14.8	15.4	10.8	16.4	12.0
1MN	21.1	15.3	16.1	12.3	14.4	10.9	13.9	10.9

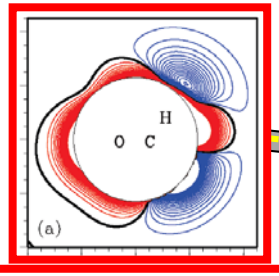
C. J. Mueller, W. J. Cannella, J. T. Bays, T. J. Bruno, K. DeFabio, H. D. Dettman, R. M. Gieleciak, M. L. Huber, C.-B. Kweon, S. S. McConnell, W. J. Pitz, and M. A. Ratcliff, "Diesel Surrogate Fuels for Engine Testing and Chemical-Kinetic Modeling: Compositions and Properties," *Energy and Fuels* 30 (2), 1445-1461 (February 2016).

1,2,4 TMB: 1,2,4-Trimethylbenzene NBCX: *n*-Butylcyclohexane TDEC: *trans*-Decalin

TET: Tetralin 1-MN: 1-Methylnapthalene NHXD: *n*-Hexadecane NEI: *n*-Eicosane

HMN: *iso*-Cetane (2,2,4,4,6,8,8-Heptamethylnonane) NOD: *n*-Octadecane

Chemical kinetic model development for practical fuels:

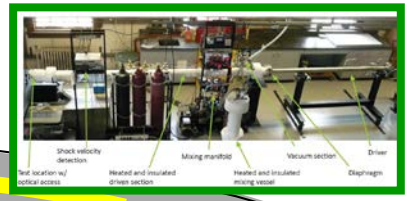


Ab initio calculations

Accurate reaction rates

Species thermodynamic properties

Reaction paths



Reaction rate rules

Detailed Chemical Kinetic Models

Fundamental Experiments

ANL, NUIG, UCONN, KAUST, UCF

Application to engines

Model Reduction

Validation against fundamental combustion data

Fast Solvers

LLNL - Numerics

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

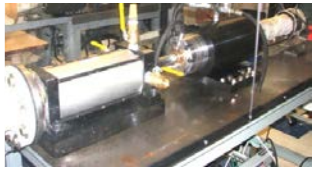
Jet Stirred Reactors

Premixed Laminar Flames

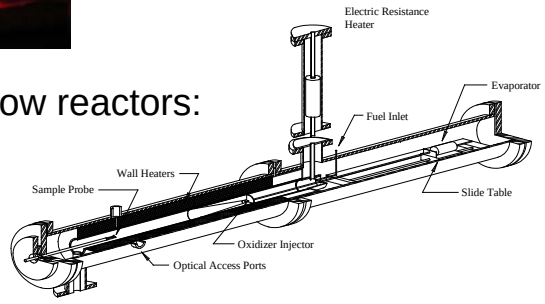
Shock tube

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