RCM Studies to Enable Gasoline-Relevant Low Temperature Combustion

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Project ID # ACE054
FY2015 DOE Vehicle Technologies Program Annual Merit Review
Advanced Combustion Engine R&D / Combustion Research
Wednesday, June 10, 2015
Program Managers: Gurpreet Singh, Leo Breton

Overview

Timeline

- Project started FY 2011
- Project directions and continuation are evaluated annually

Barriers

- Lack of fundamental knowledge of advanced engine combustion regimes
- Lack of modeling capability for combustion and emission control

Budget

- Project funded by DOE / VTP
  - → FY13 funding: $320 k
  - → FY14 funding: $325 k
  - → FY15 funding: $500 k

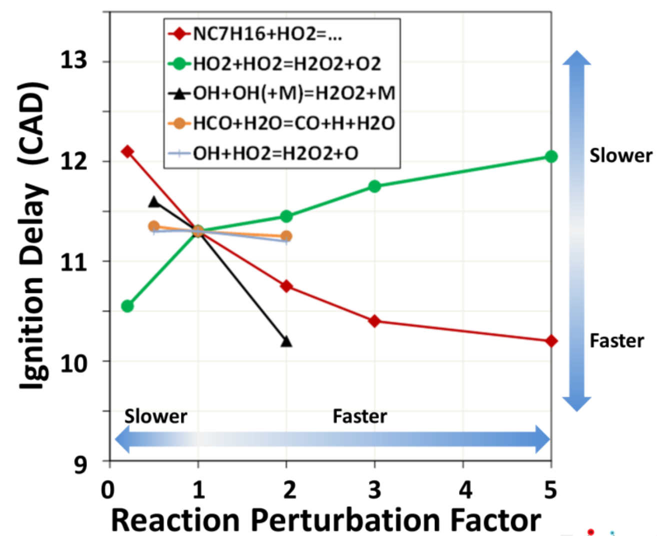
Partners

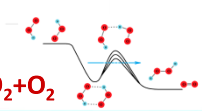
- ANL – UQ/GSA tools, chemical analysis, gasoline LTC engine
- LLNL – gasoline surrogate model, simulation tools
- KAUST, Chevron – fuels, fuel models
- Northeastern U. – mechanism diagnostics
- International RCM Workshop

Objectives and Relevance to DOE

- Acquire fundamental data, and help develop / validate / refine chemical kinetic and relevant models for transportation-relevant fuels (conventional and future gasolines, diesels and additives) at conditions representative of advanced combustion regimes, leveraging collaborations with BES-funded groups, and researchers across the broader community.

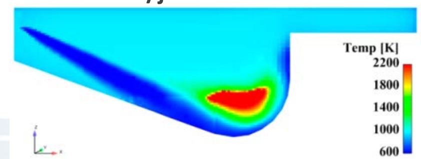
- Predictive simulations with these models, which require **low associated uncertainties**, could be utilized to overcome technical barriers to low temperature combustion (LTC), and achieve required gains in engine efficiency and pollutant reductions.

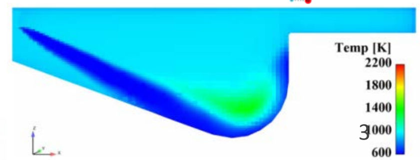




doi:10.1021/jz400874s

$HO_2+HO_2=H_2O_2+O_2$





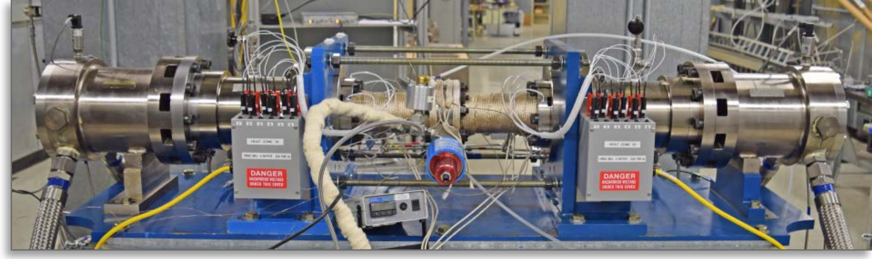
Project Milestones

FY2015 Budget – $500 K

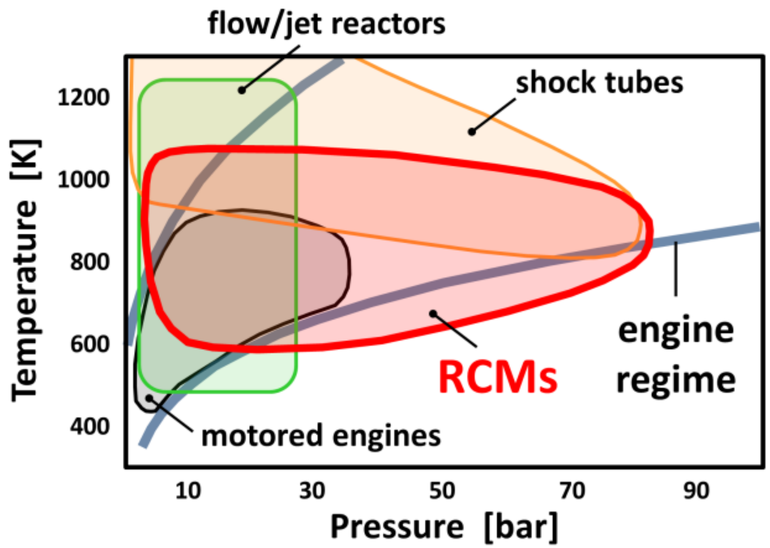
Task	Milestone	Status
1	Acquire ignition delay measurements for gasoline fuels + reactivity modifiers. [FY2014] a) 2-ethyl-hexyl nitrate (2EHN) ($C_8H_{17}NO_3$); b) di-tert-butyl-peroxide (DTBP) ($C_8H_{18}O_2$).	✓ Postponed
2	Develop, validate chemical kinetic model for gasoline fuels + reactivity modifiers. (model complete, comparisons with 2EHN) [FY2014]	✓
3	Acquire ignition measurements for gasoline surrogate components: 5-member ring naphthenes (cyclopentane, methyl cyclopentane)	MCP FY15-Q4
4	Acquire ignition measurements for blends of gasoline + ethanol: FACE-F (E0, E10, E20, E30)	✓
5	Acquire ignition measurements for multi-component surrogate blends mimicking undoped, and ethanol-blended gasoline	FY15-Q4
6	Implement UQ/GSA for LLNL gasoline surrogate model, using multiple targets (e.g., ignition delay time, heat release rate).	✓

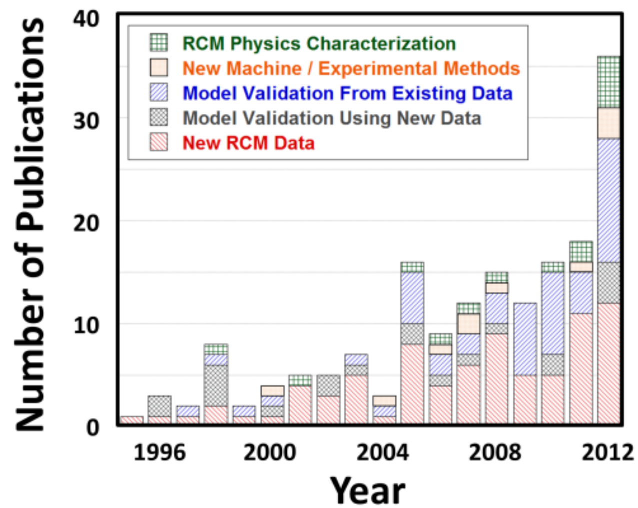
Project Approach

Rapid Compression Machine



- Utilize ANL's twin-piston RCM to acquire autoignition data

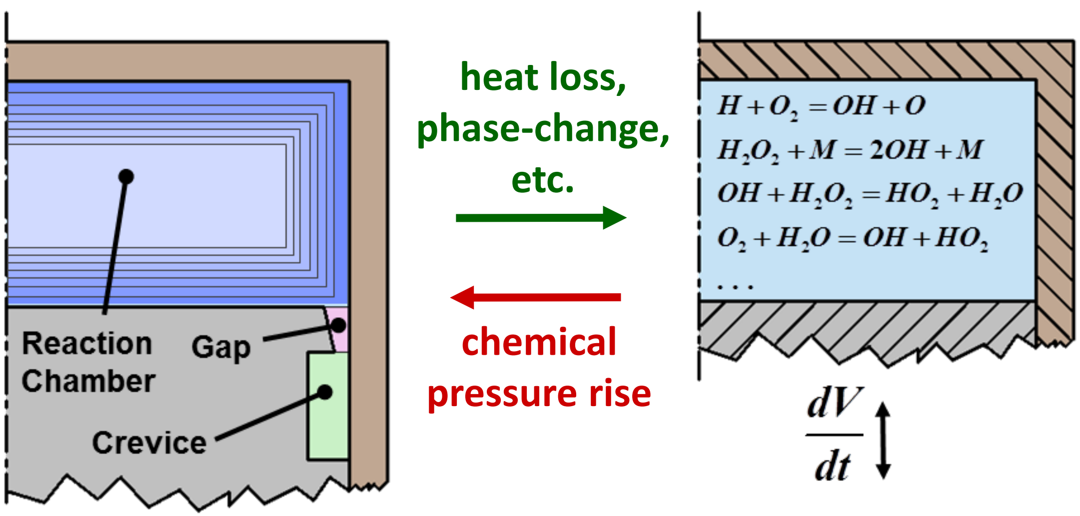




- Employ novel data analysis tools and advanced diagnostics
  - Physics-based, reduced-order system model
  - Developing new diagnostics capabilities to better probe chemistry
- Synergistically improve kinetic models using novel analysis techniques (e.g., UQ/GSA) and detailed calculations of sensitive processes (e.g., individual reaction rates)

Project Approach
RCM System Model

- **Physics-based, reduced-order model coupled with chemical kinetics software – accounting for physical-chemical interactions during experiments (e.g., LTHR + crevice flows)**
  - **Computationally-efficient approach improves simulation fidelity**
  - **Facilitates utilization of additional metrics for mechanism validation / refinement (e.g., ROHR (1st, 2nd stages))**



$$\overbrace{-\frac{V^{\gamma+1}}{\gamma}\left[\frac{\ln V}{V^{\gamma}}\frac{d\gamma}{dt}+\frac{1}{C}\frac{dP}{dt}\right]}^{\text{derive from physical model}} = \frac{dV}{dt}$$

supply to kinetics software

doi:10.1016/j.combustflame.2012.07.010

Project Approach

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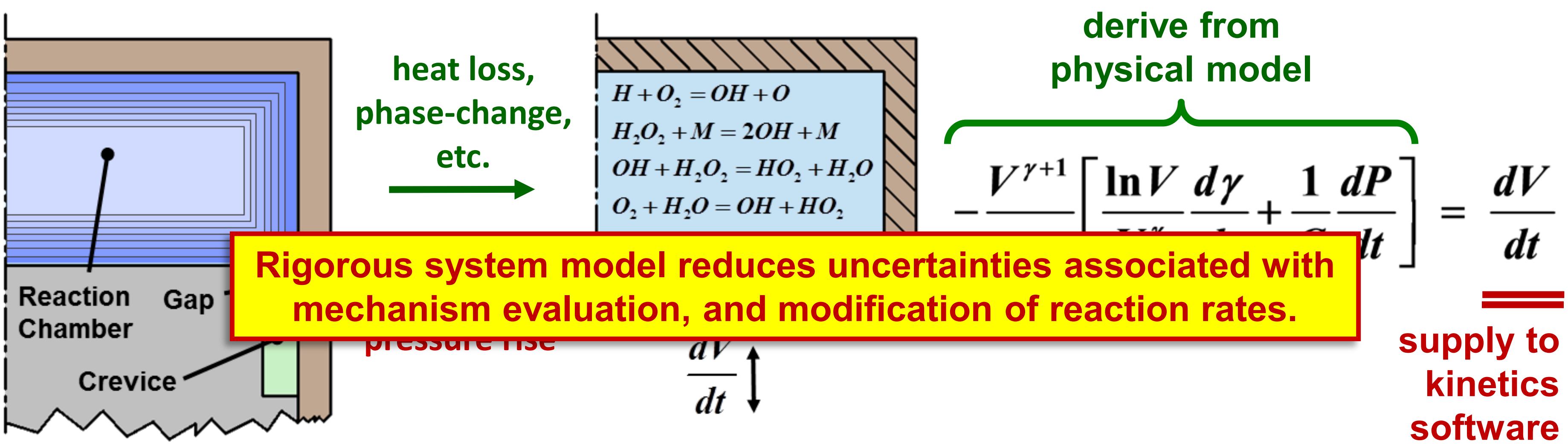


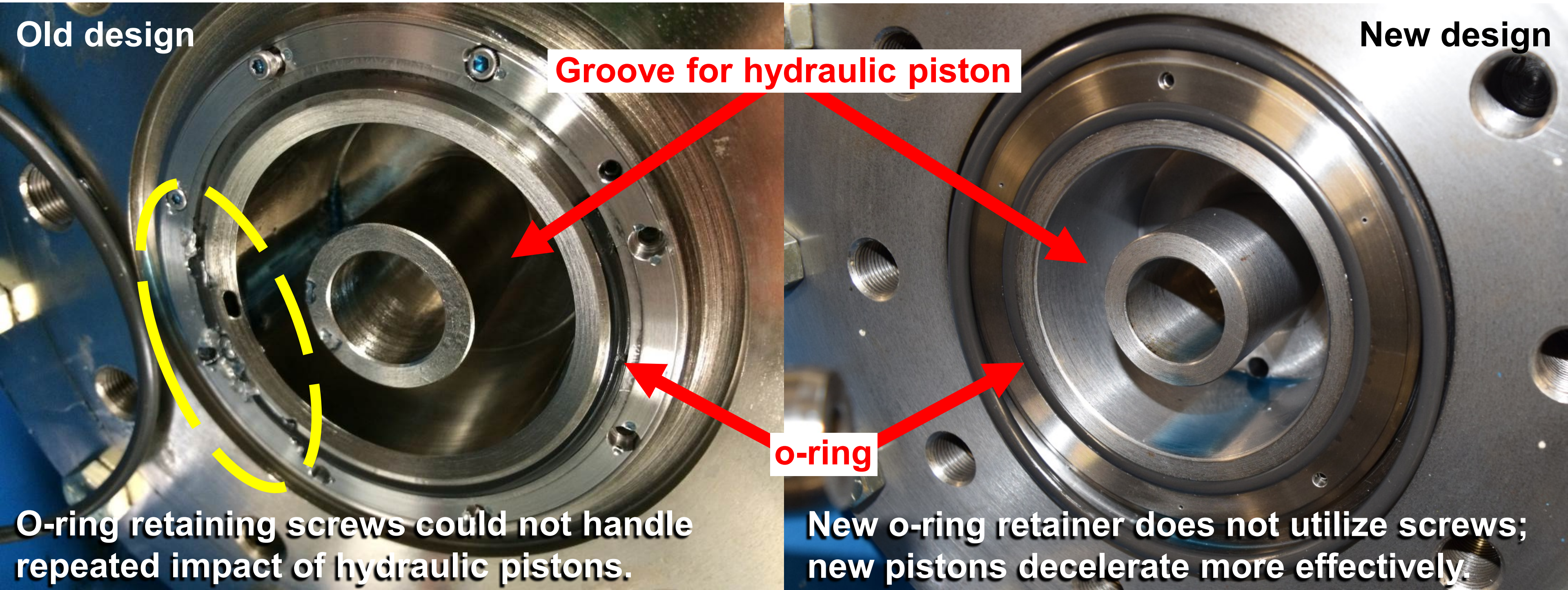
Rigorous system model reduces uncertainties associated with mechanism evaluation, and modification of reaction rates.

doi:10.1016/j.combustflame.2012.07.010

Technical Accomplishments / Progress

Modifications to twin-piston RCM in FY2014/15

- Unplanned redesign and fabrication of several components for RCM resulted in several months of downtime
  - Hydraulic chamber pistons and seals damaged during operation



Technical Accomplishments / Progress

Modifications to twin-piston RCM in FY2014/15

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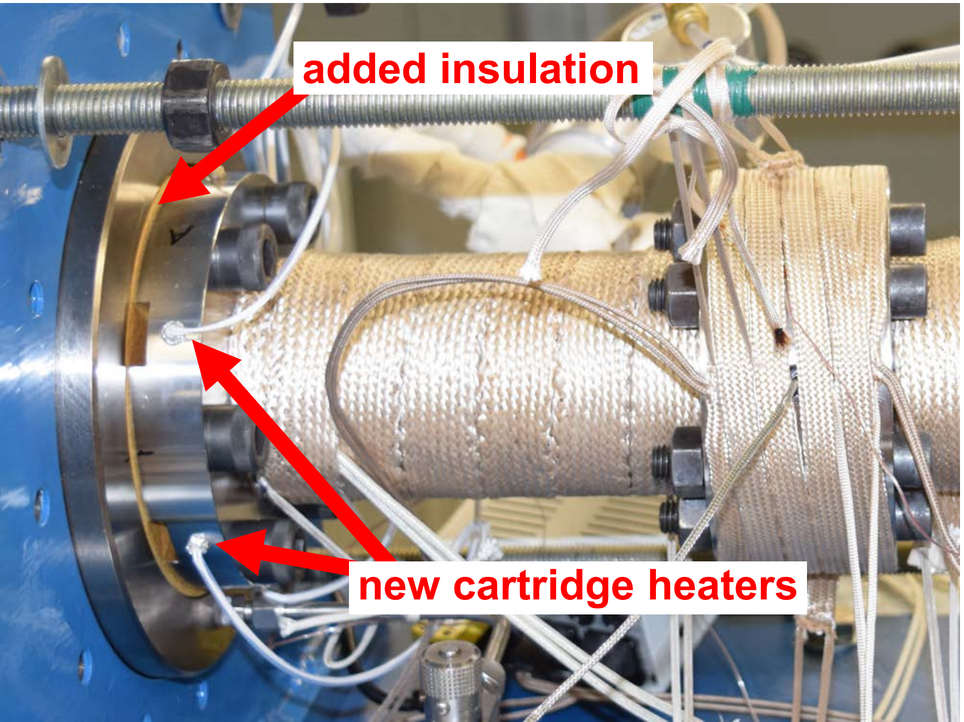
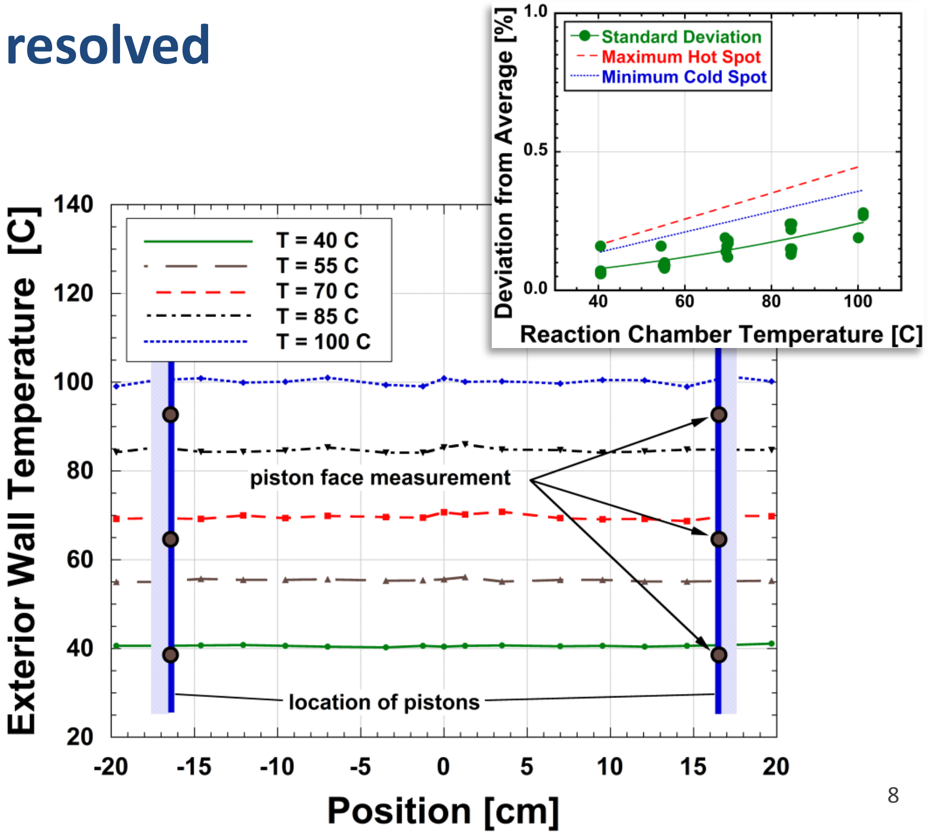
  - Hydraulic chamber pistons and seals damaged during operation
  - Reaction chamber heating system also improved for uniformity
  - Some minor issues still being resolved



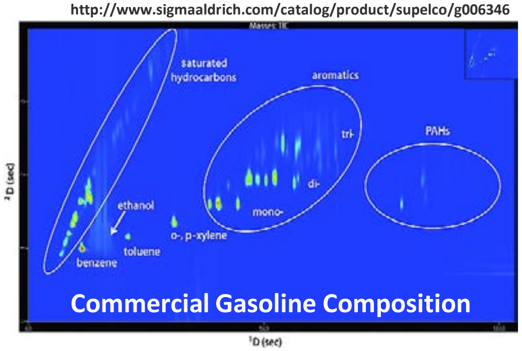


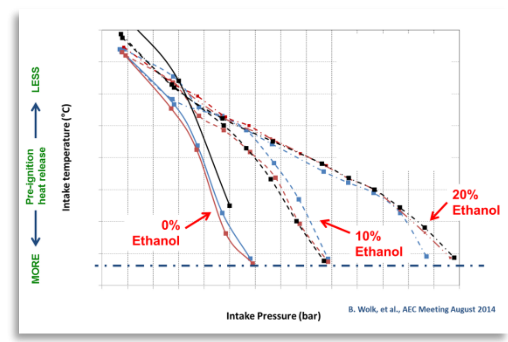
Technical Accomplishments / Progress

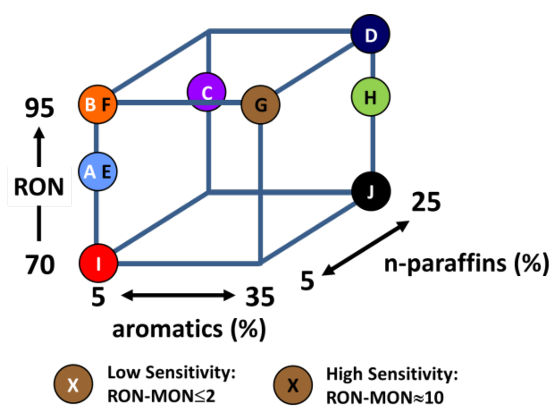
Gasoline and Surrogates

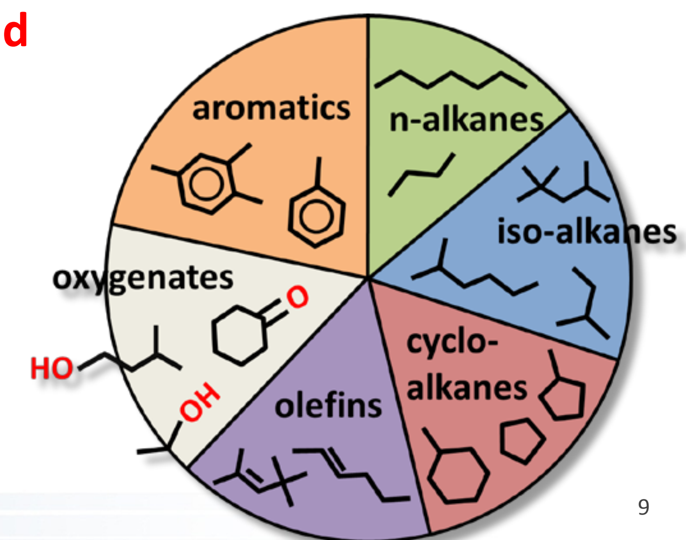
- Predictive modeling of LTC to guide design
  - Gasoline is complex, compositionally variant
    - ➜ How do various features affect LTC behavior, especially autoignition phenomena at low and intermediate temperature?
    - ➜ How can real fuels be represented by low order (4-10) component surrogates?
    - ➜ Data needed to compare ignition behavior of real fuels with surrogates.
    - ➜ Data needed for surrogate components and blends, and blends of fuels with ethanol

http://www.sigmaaldrich.com/catalog/product/supelco/g006346



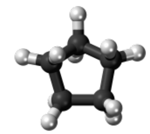


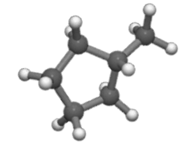


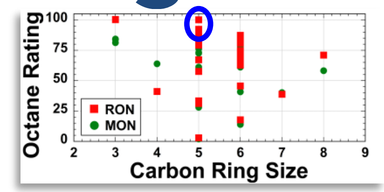


Technical Accomplishments / Progress

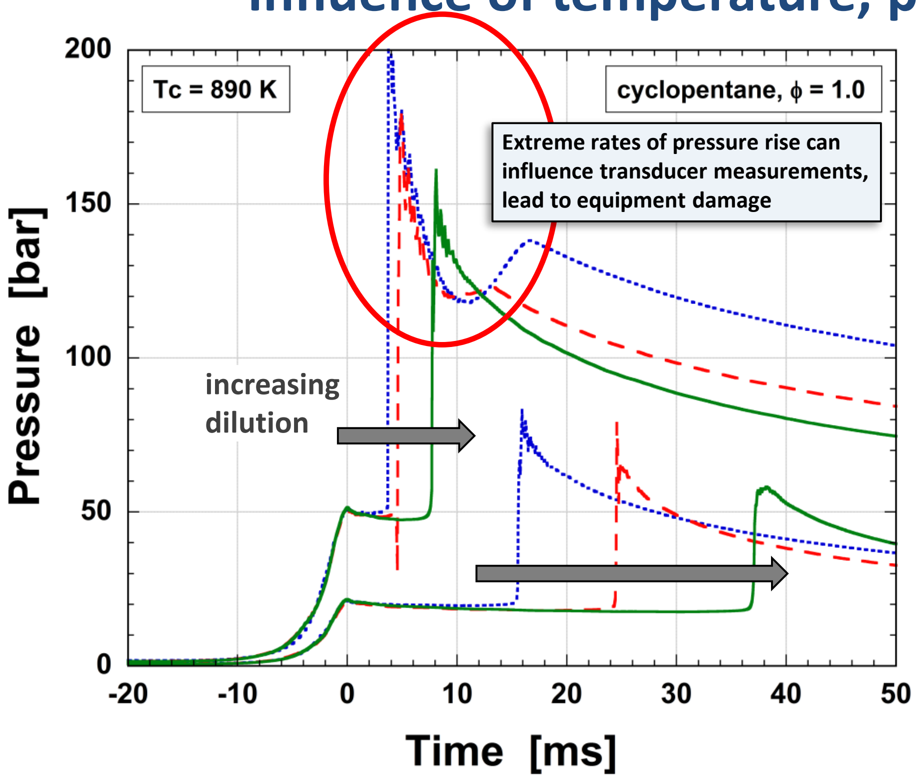
SURROGATE COMPONENTS

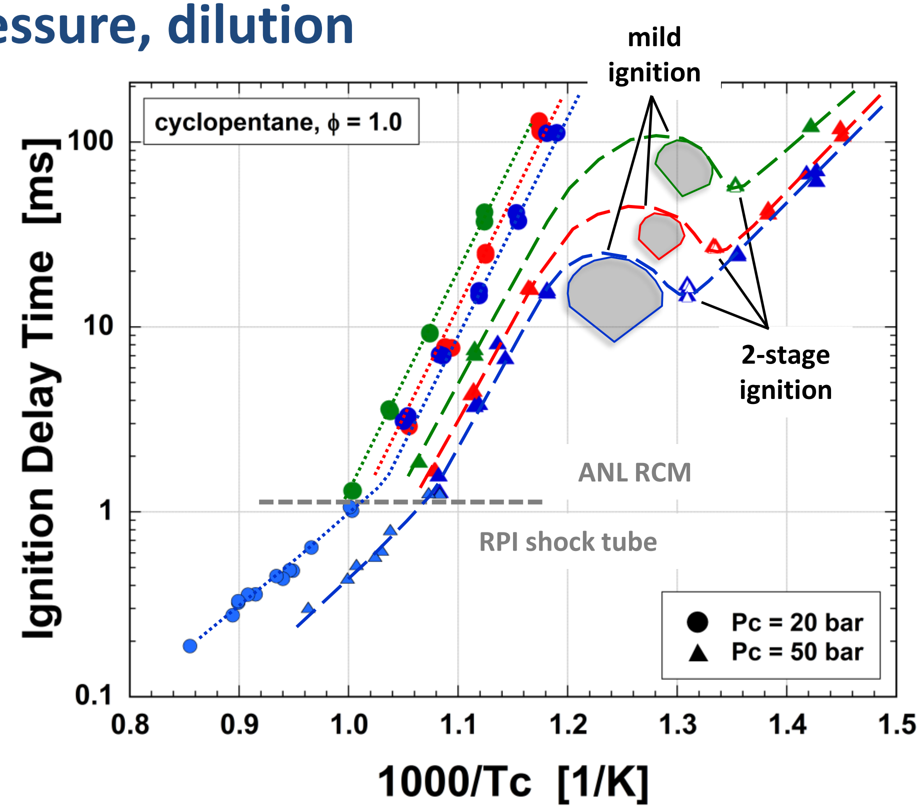






- 5-member ring naphthenes
  - Providing necessary combustion data for representative hydrocarbons at LTC conditions. FY2015 tests with CP, MCP.
  - Influence of temperature, pressure, dilution





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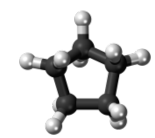

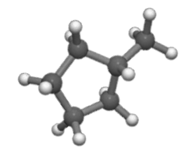

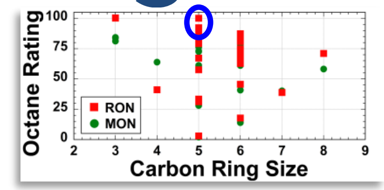

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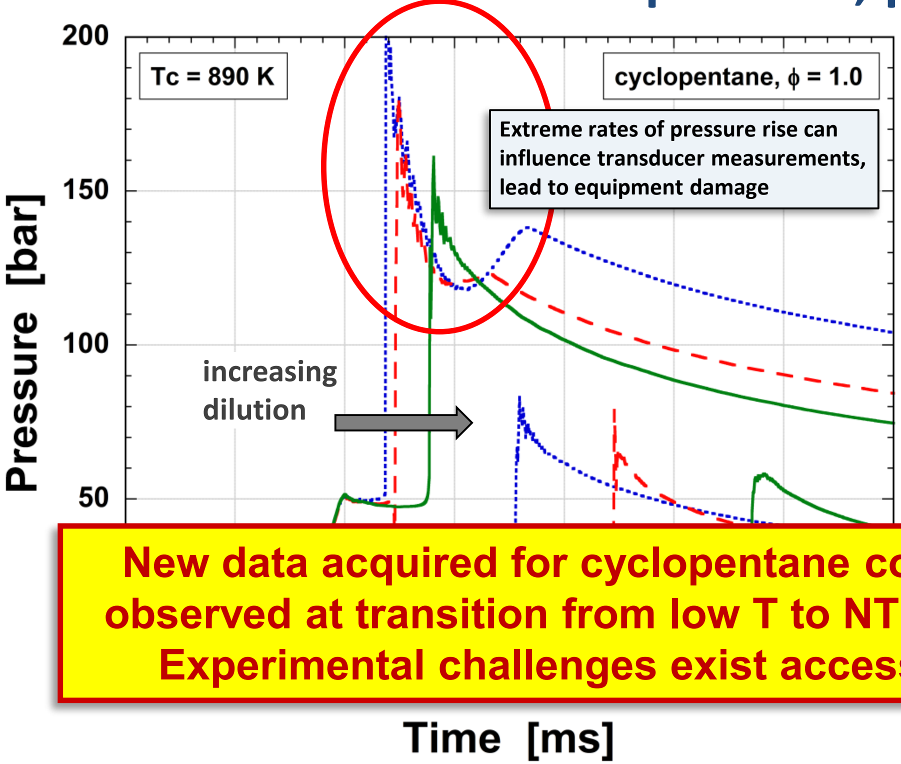
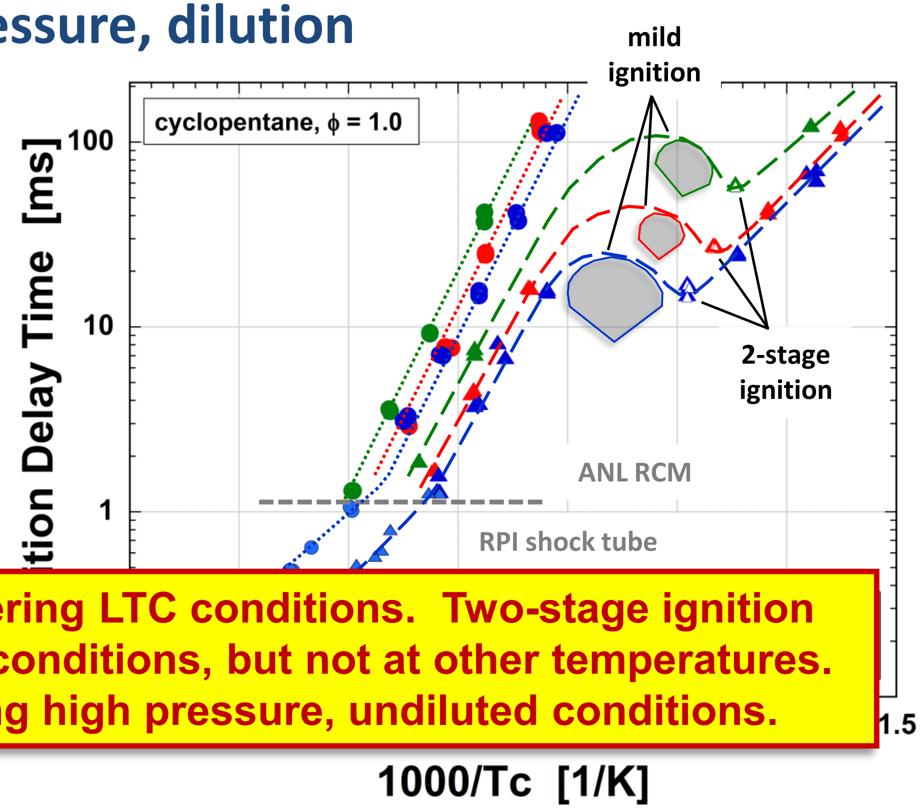


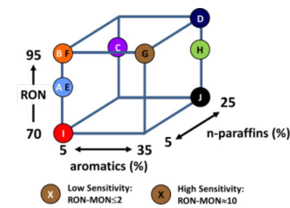


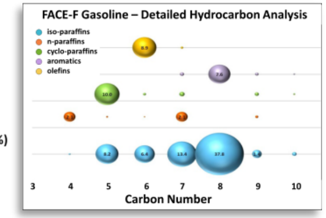
New data acquired for cyclopentane covering LTC conditions. Two-stage ignition observed at transition from low T to NTC conditions, but not at other temperatures. Experimental challenges exist accessing high pressure, undiluted conditions.

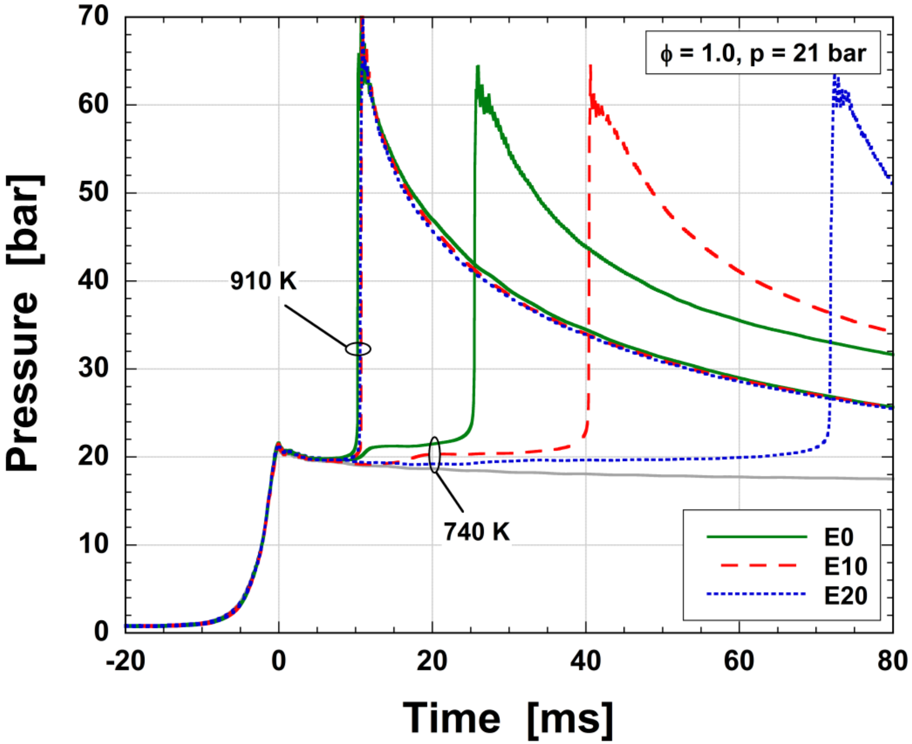
Technical Accomplishments / Progress

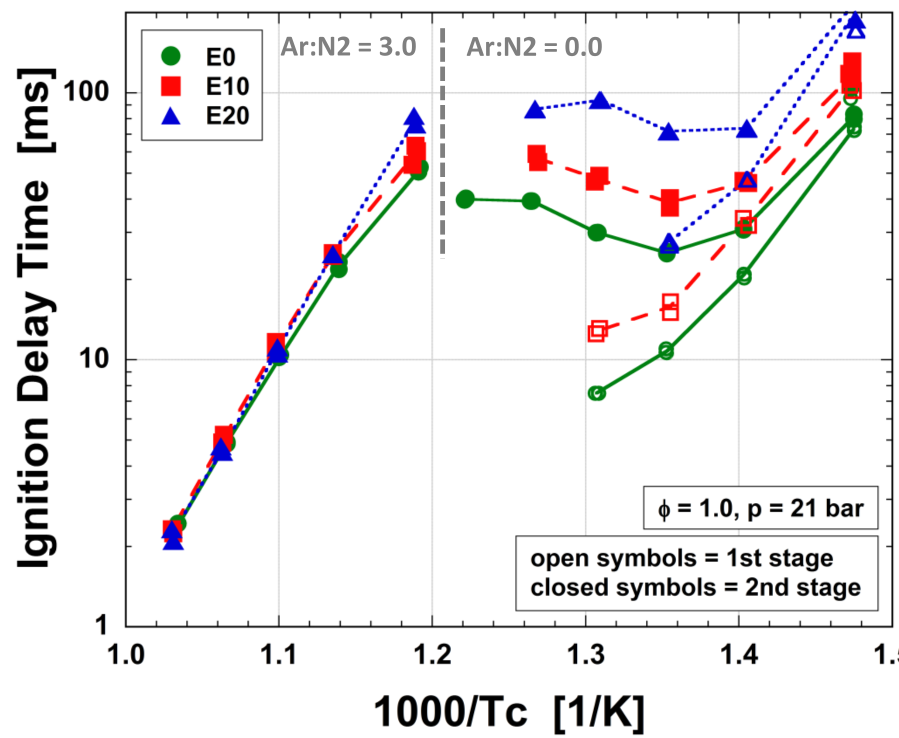
Gasoline / Ethanol Blends

- FACE-F used as representative gasoline
  - Composition, properties well-characterized
  - Investigating influence of blending levels (E0, E10, E20, E30) on ignition chemistry, suppression of reactivity









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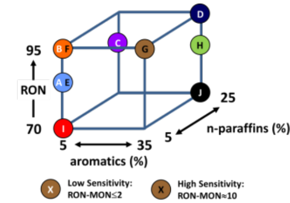

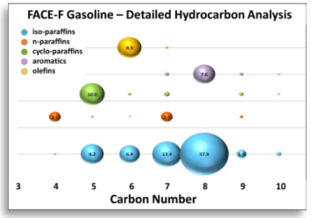

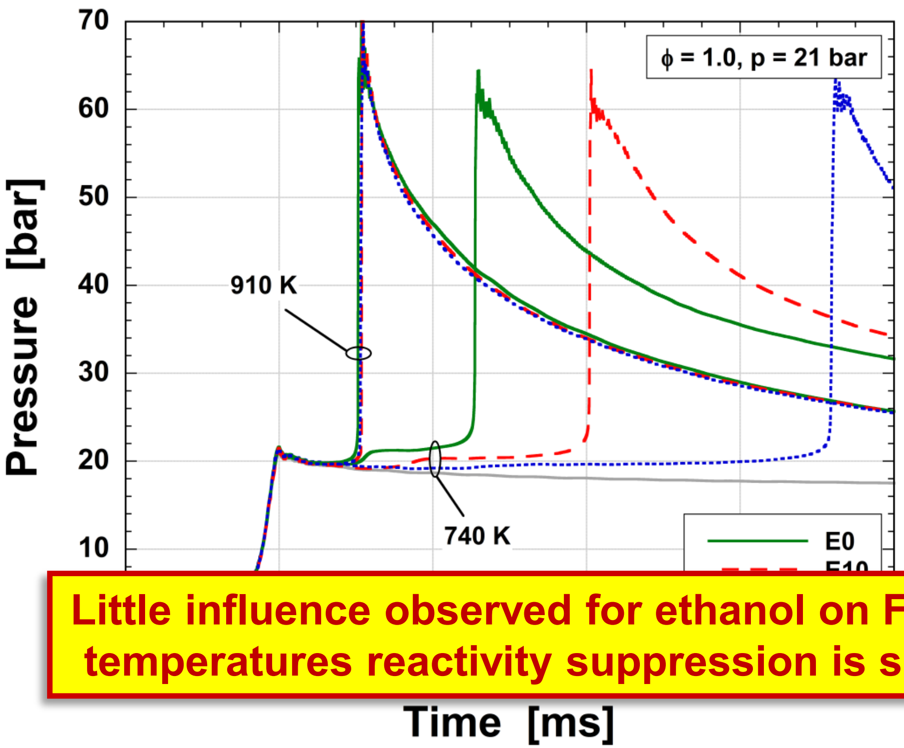

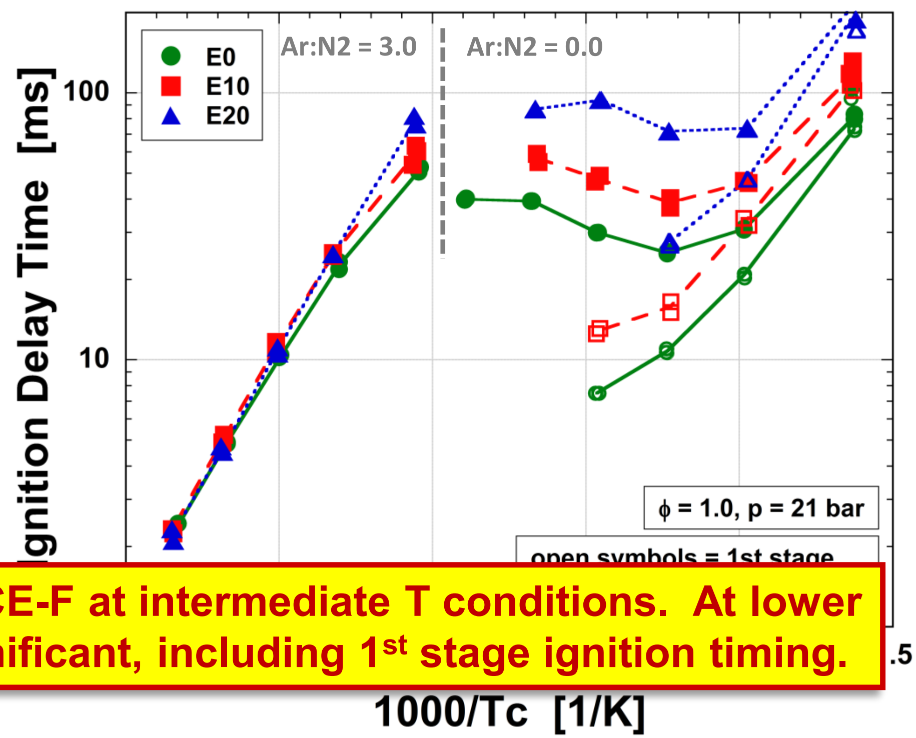

Little influence observed for ethanol on FACE-F at intermediate T conditions. At lower temperatures reactivity suppression is significant, including 1st stage ignition timing.

Technical Accomplishments / Progress

Gasoline / Ethanol Blends

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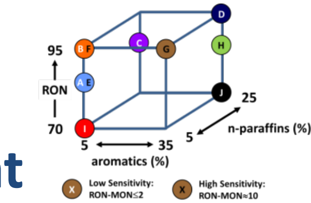
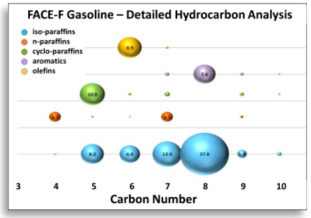
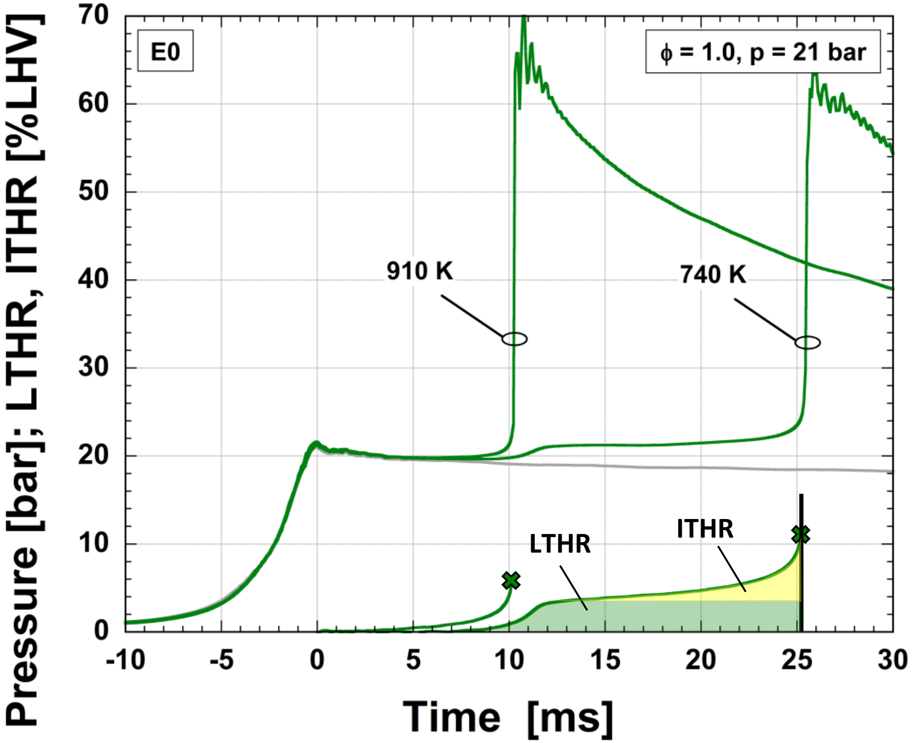
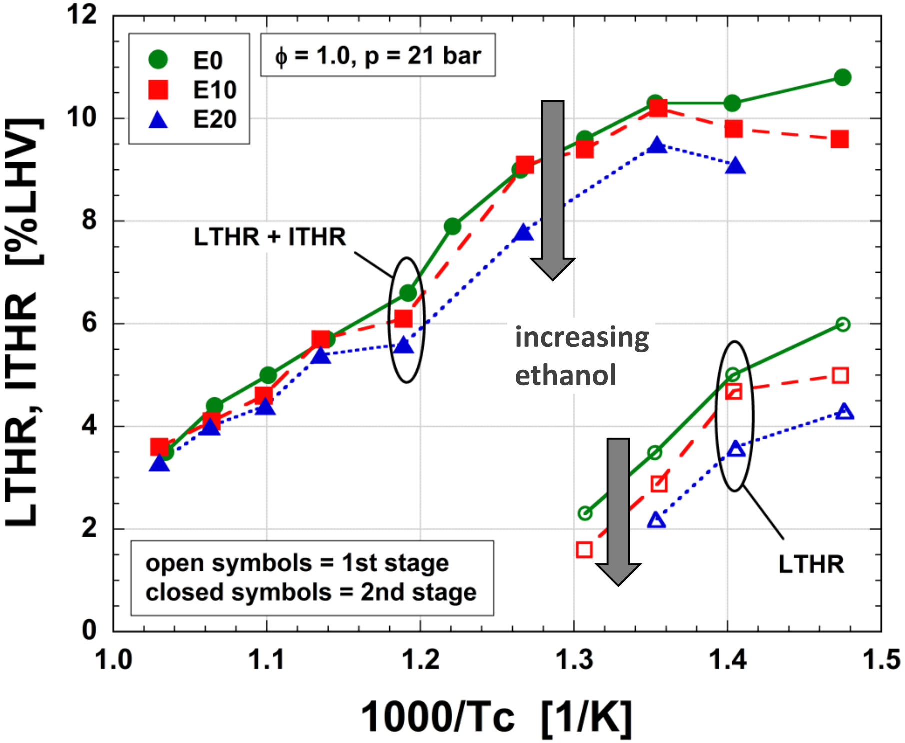
  - Characterizing influence of ethanol on heat release behavior covering LTHR and ITHR
  - Kinetic modeling of experiments in collaboration with LLNL









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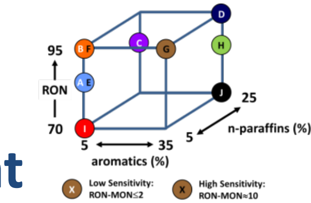
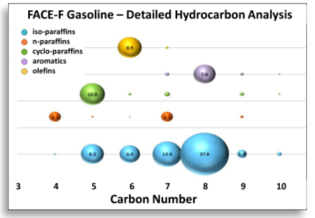
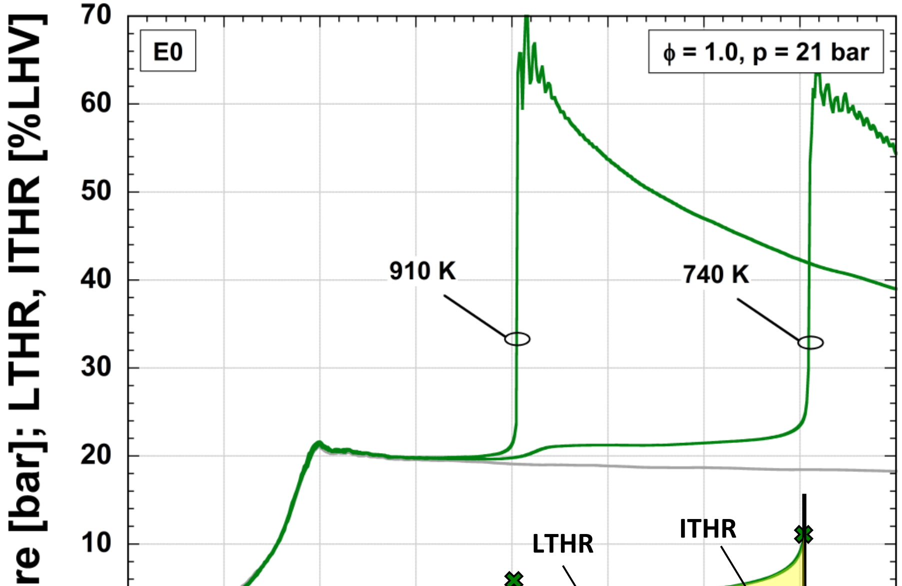
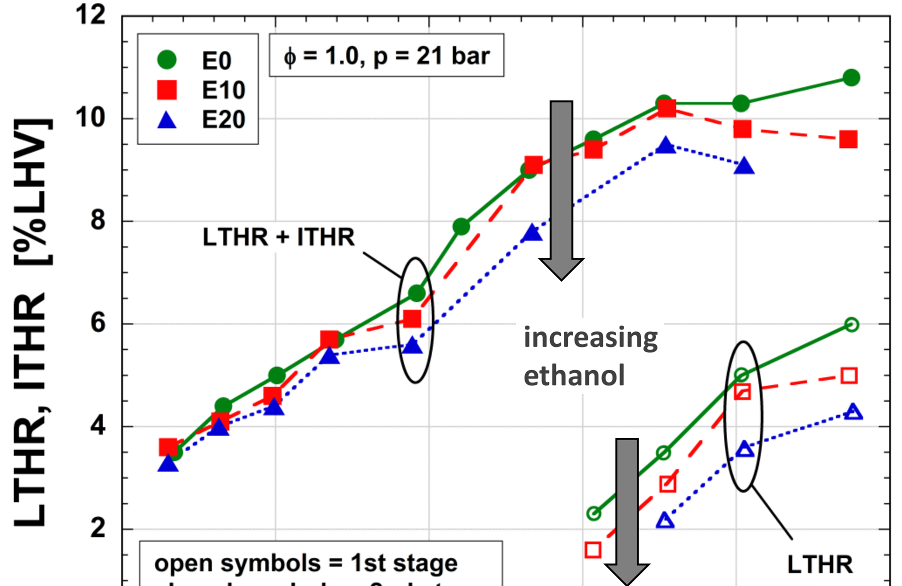






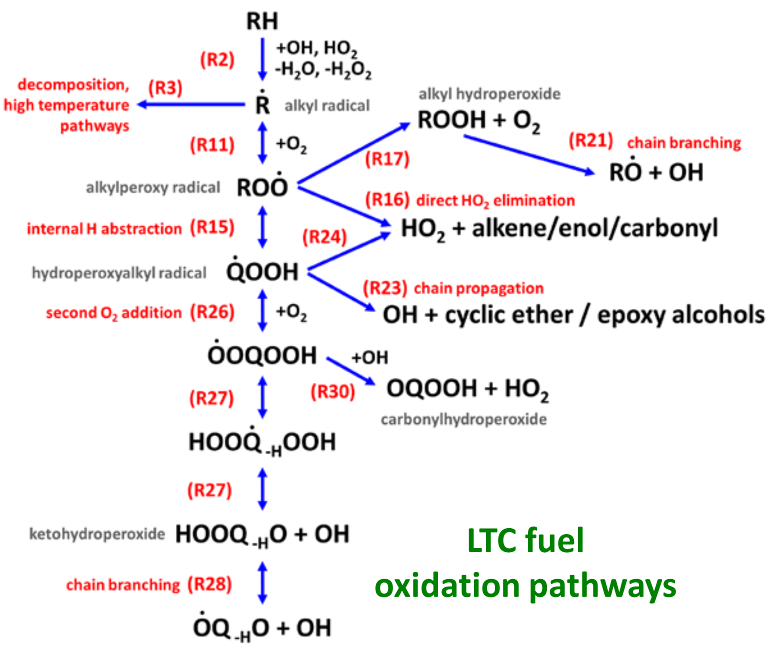


Ethanol suppresses preliminary exothermicity, but less influentially at intermediate temperatures. Reductions in LTHR greater than LHV displacement. What are chemical kinetic causes? How do these affect engine combustion?

Technical Accomplishments / Progress

UQ Gasoline Surrogate Model

- **Methodology to implement UQ/GSA using LLNL model**
  - **~10^4 correlated uncertainties. Apply based on: (a) foundational (C_0-C_4) chemistry, or (b) reaction class (where 'rate rules' are used)**
  - **Detailed accounting of 7,336 reactions necessitates automated means to identify and classify individual reactions**

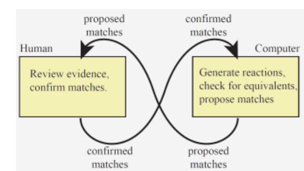


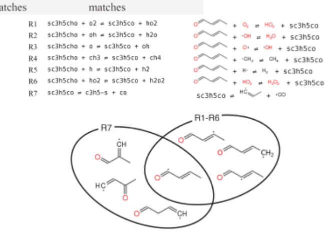
LTC fuel oxidation pathways

No.	Reaction Classes	UF
1	Unimolecular fuel decomposition.	10
2	H-atom abstraction from the fuel.	2
3	Alkyl radical decomposition.	5
4	Alkyl radical isomerization.	3
5	H-atom abstraction reactions from alkenes.	3
6	Addition of radical species O and OH to alkenes.	3
7	Reactions of alkenyl radicals with HO_2, CH_3O_2, and $C_2H_5O_2$.	3
8	Alkenyl radical decomposition.	30
9	Alkene decomposition.	30
10	Retroene decomposition reactions.	5
11	Addition of O_2 to alkyl radicals (R + O_2 = ROO).	2
12	R + ROO = RO + RO.	5
13	R + HO_2 = RO + OH.	4
14	R + ROO = RO + RO.	5
15	Alkyl peroxy radical isomerization (ROO = QOOH).	3
16	Concerted eliminations (ROO = alkene + HO_2).	10
17	ROO + HO_2 = ROOH + O_2.	5
18	ROO + H_2O_2 = ROOH + HO_2.	5
19	ROO + CH_3O_2 = RO + CH_3O + O_2.	5
20	ROO + ROO = RO + RO + O_2.	10
21	ROOH = RO + OH.	10
22	RO decomposition.	30
23	QOOH = cyclic ether + OH (cyclic ether formation).	10
24	QOOH = alkene + HO_2 (radical site beta to OOH group).	10
25	QOOH = alkene + carbonyl + OH (radical site gamma to OOH group).	30
26	Addition of O_2 to QOOH (QOOH + O_2 = OOQOOH).	4
27	Isomerization of OOQOOH and formation of carbonylhydroperoxide and OH.	5
28	Decomposition of carbonylhydroperoxide to form oxygenated radical species and OH.	30
29	Cyclic ether reactions with OH and HO_2.	30
30	Decomposition of large carbonyl species and carbonyl radicals.	30

Species ID, Reaction Classifier

A. **Identify species in existing kinetic models via comparison with reactions generated by RMG. Create 'dictionary' for model.**



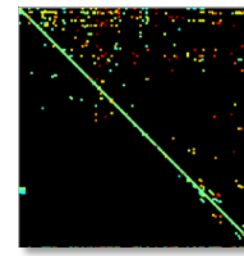


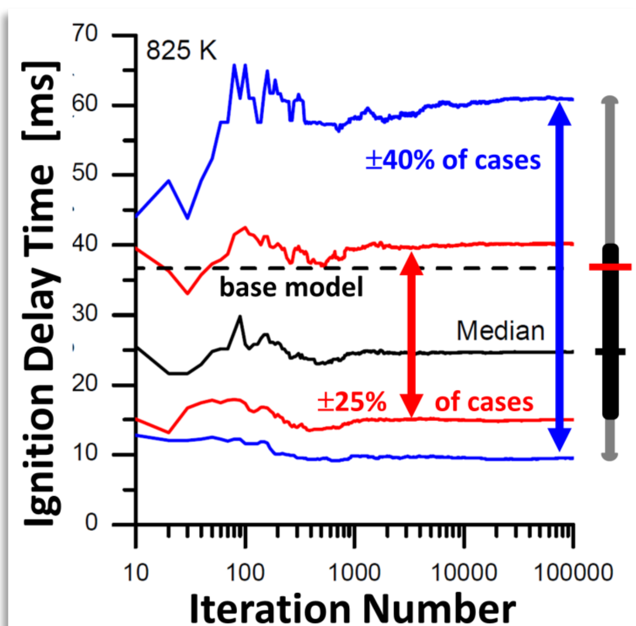
B. **Classify reactions in existing model via comparison with reactions generated by RMG using new species 'dictionary'.**

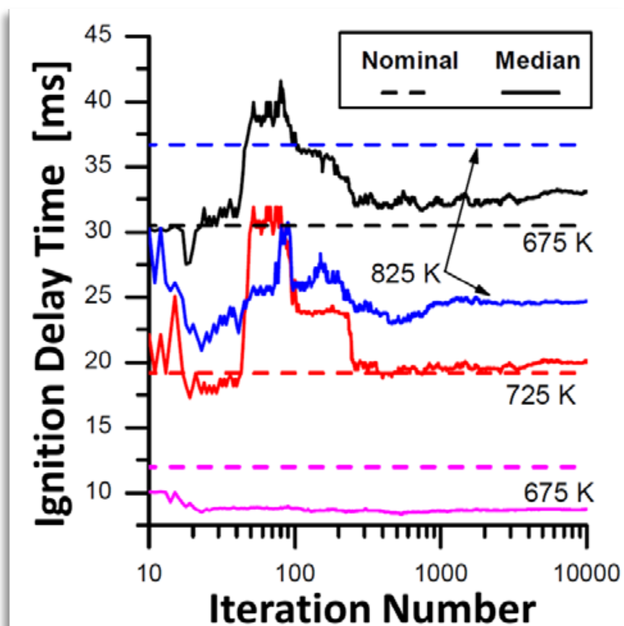
Technical Accomplishments / Progress

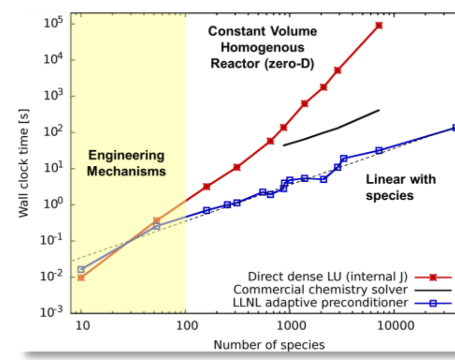
UQ Gasoline Surrogate Model

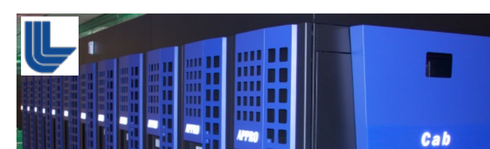
- **Methodology to implement UQ/GSA using LLNL model**
  - **Reaction rate constants simultaneously perturbed for each Monte Carlo (MC) iteration to cover a range of possible ignition histories. Many realizations required, e.g., 10^4–10^6, to achieve adequate statistical convergence.**
  - **Fast chemical kinetic solver required for MC technique**











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  - **Reaction rate constants simultaneously perturbed for each Monte Carlo (MC) iteration to cover a range of possible ignition histories. Many realizations required, e.g., 10^4–10^6, to achieve adequate statistical convergence.**
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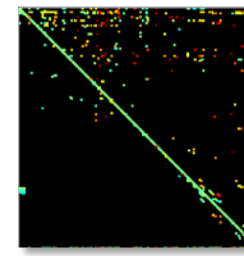
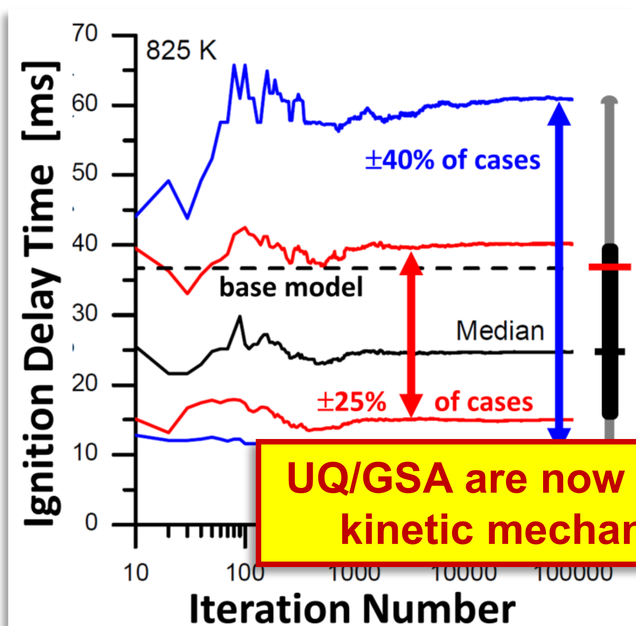
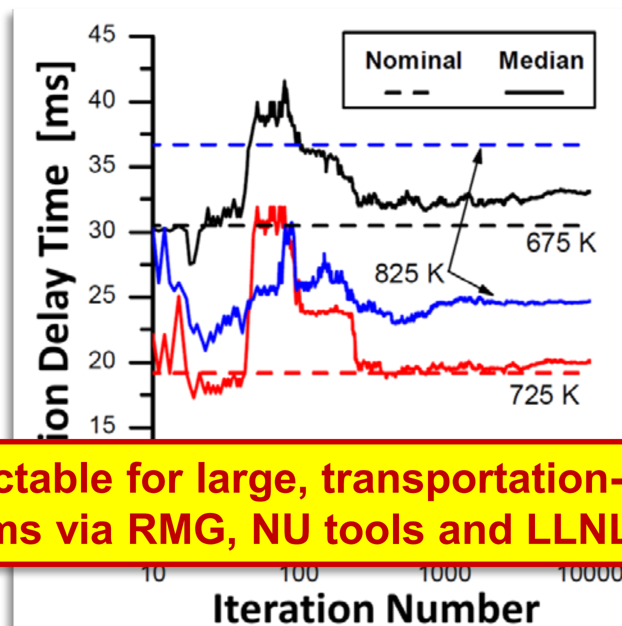
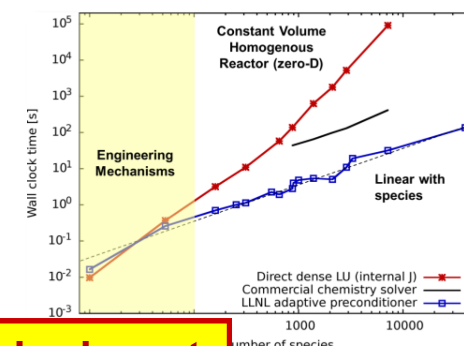
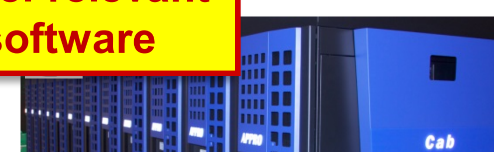








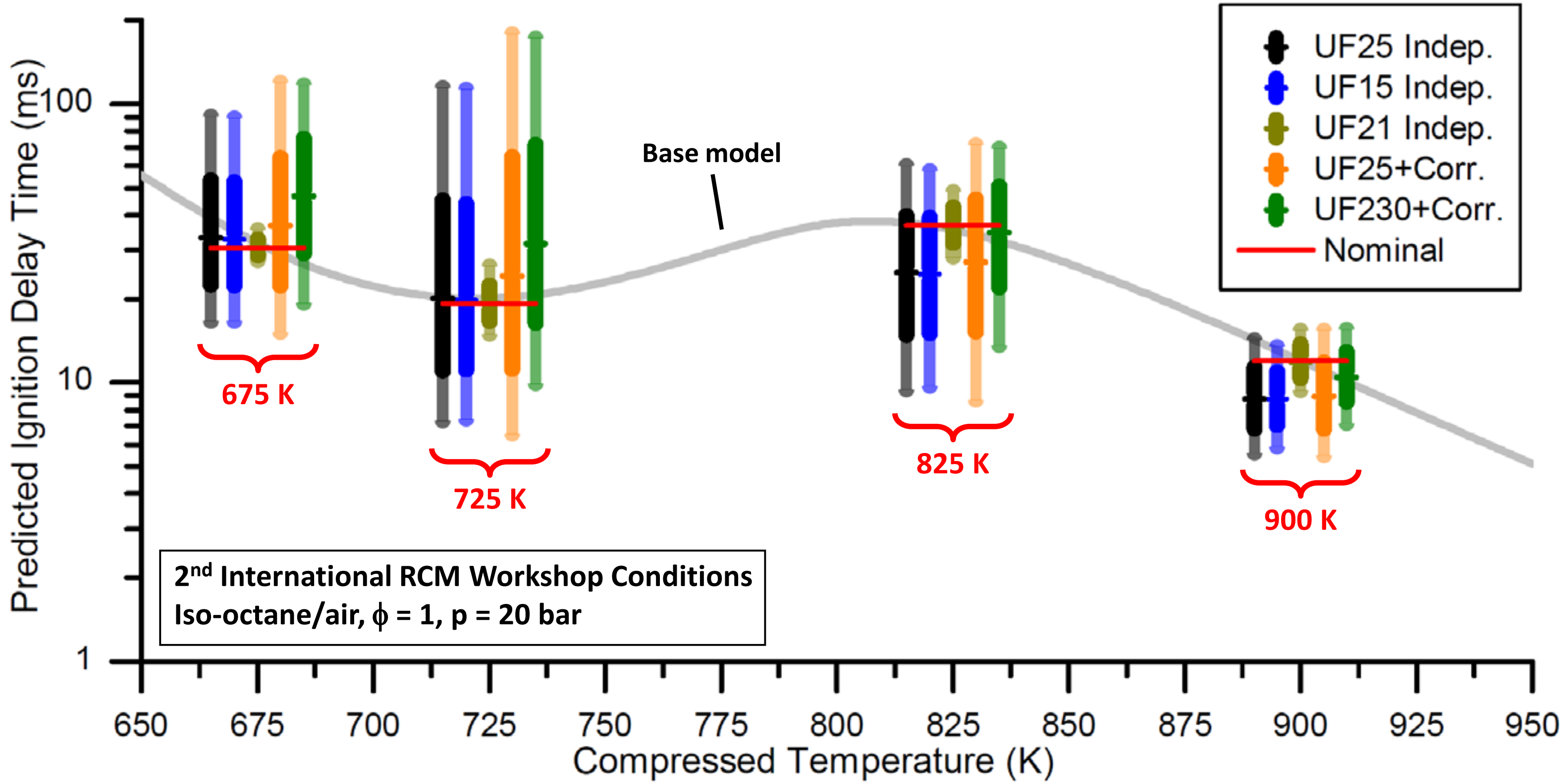


UQ/GSA are now tractable for large, transportation-fuel relevant kinetic mechanisms via RMG, NU tools and LLNL software

Technical Accomplishments / Progress

UQ Gasoline Surrogate Model

- Constant volume simulations
  - Quantifying how model uncertainties affect ignition predictions for a range of conditions using different assessments of uncertainty



Technical Accomplishments / Progress

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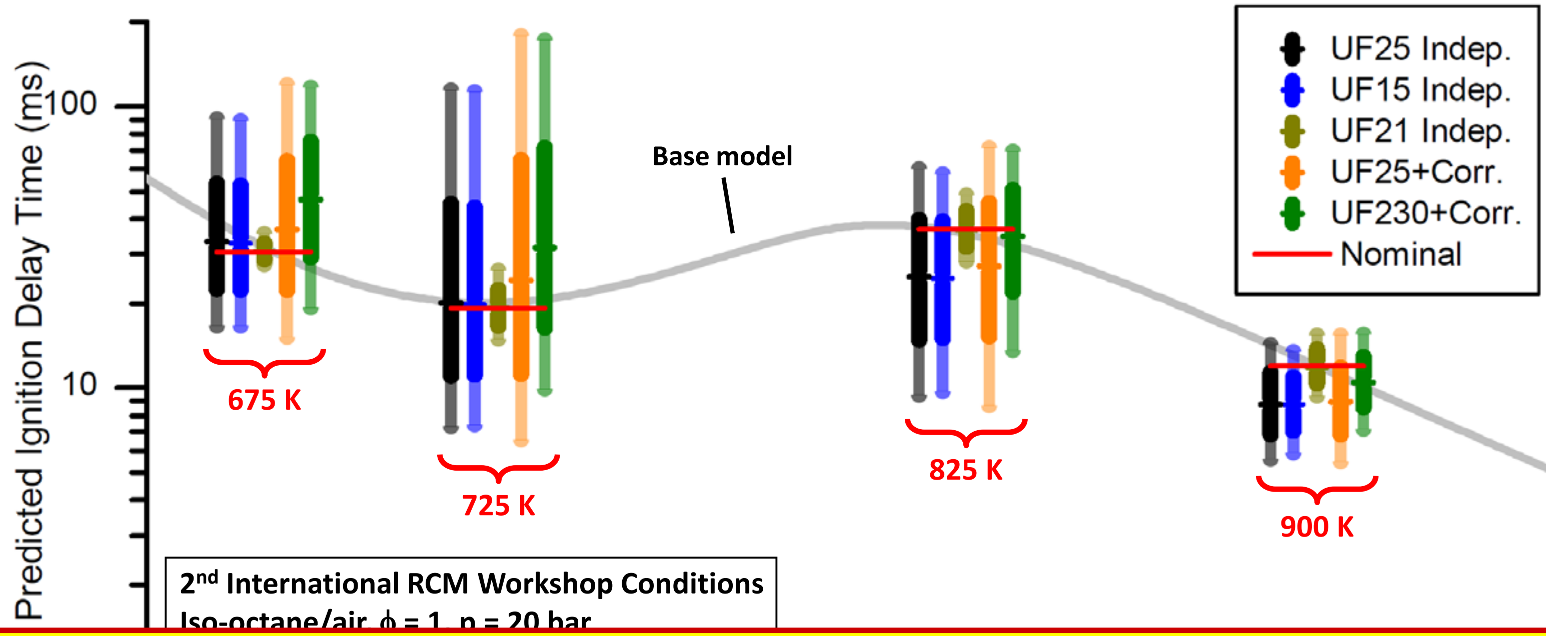
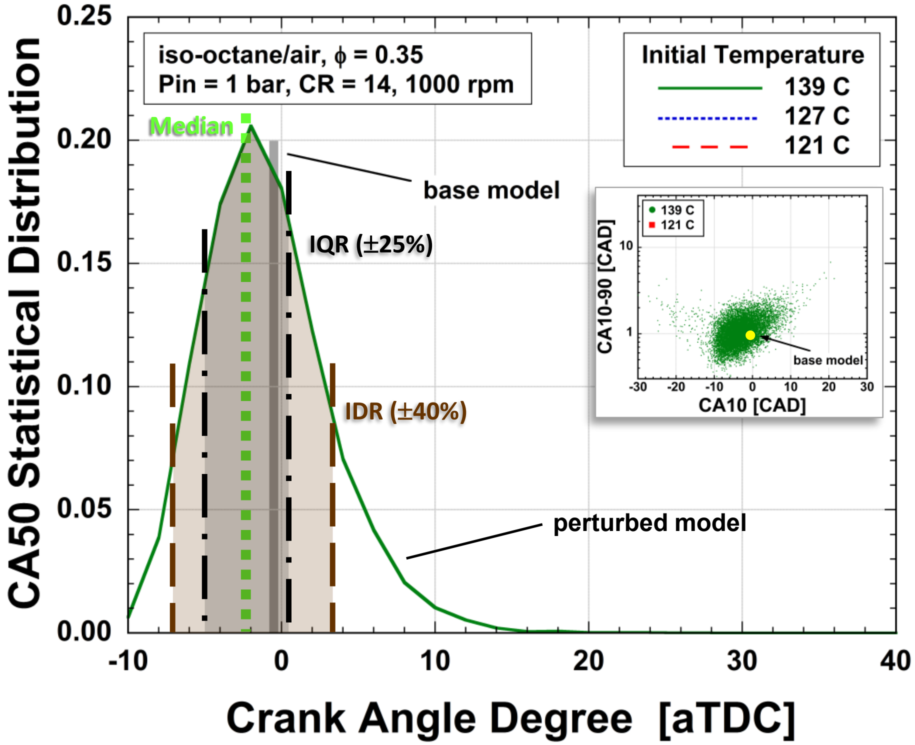


Uncertainties in chemical kinetic model (mostly fuel related here) lead to wide range of predicted ignition times. Greater differences in NTC and lower temperatures. Accounting for correlated uncertainties necessary to understand and improve confidence bands.

Technical Accomplishments / Progress

UQ Gasoline Surrogate Model

- HCCI single-zone simulations
  - Quantifying influence of model uncertainties on ignition timing and heat release profiles during IC engine-type operation



Technical Accomplishments / Progress

UQ Gasoline Surrogate Model

- HCCI single-zone simulations
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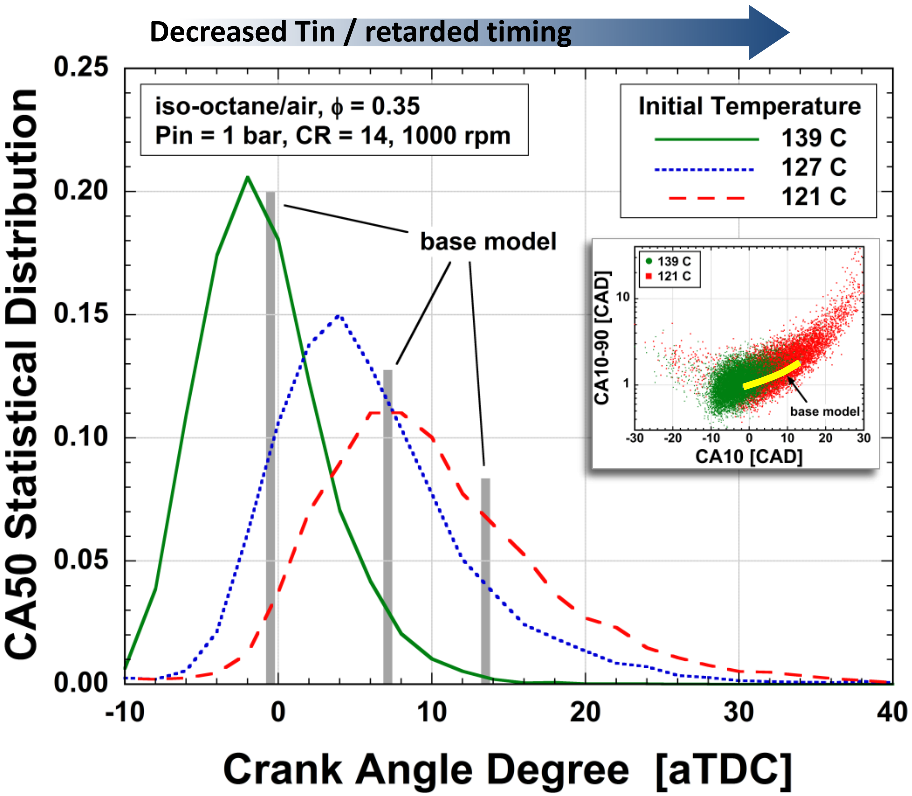
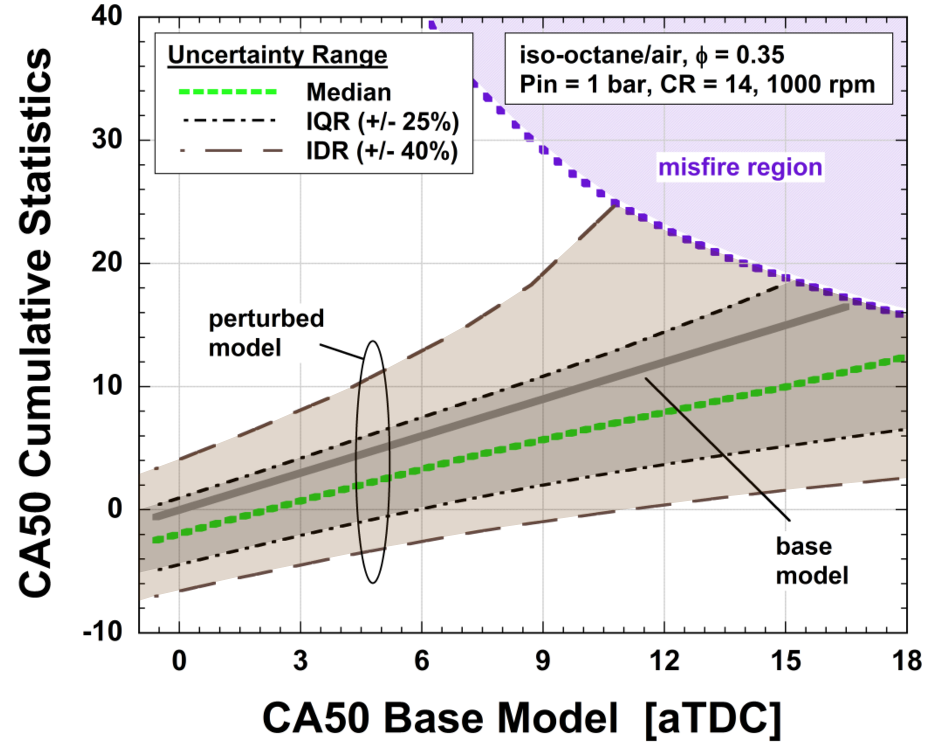
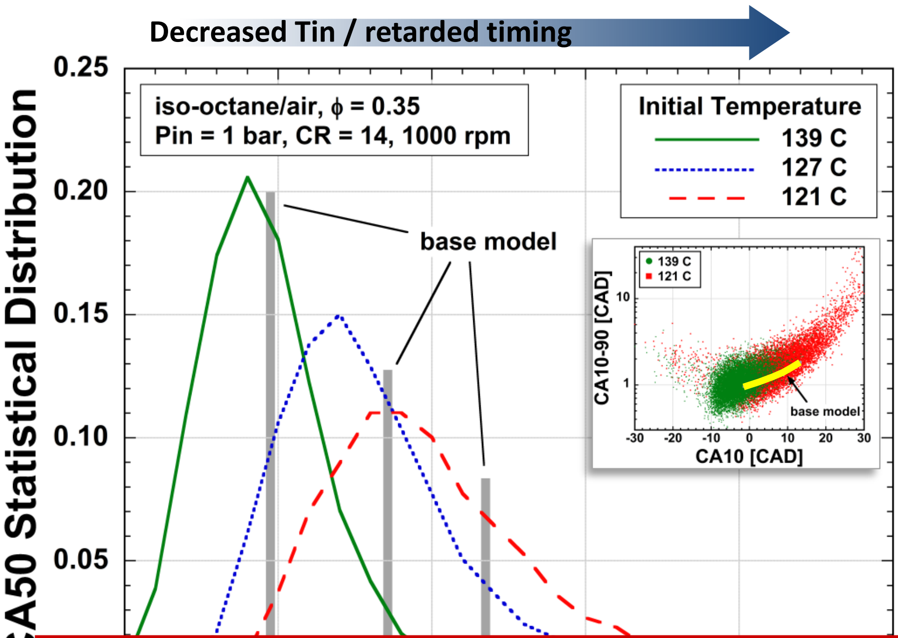


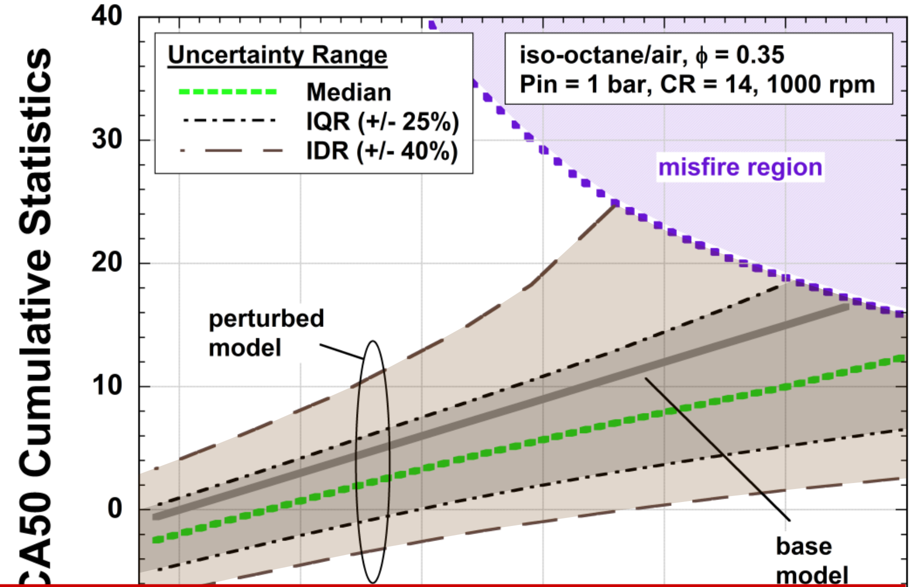


Technical Accomplishments / Progress

UQ Gasoline Surrogate Model

- HCCI single-zone simulations
  - **Quantifying influence of model uncertainties on ignition timing and heat release profiles during IC engine-type operation**



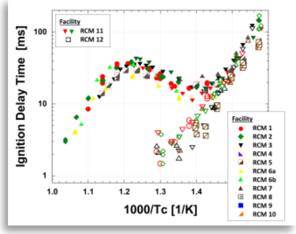


Uncertainties in chemical kinetic model lead to a range of possible ignition, heat release profiles, especially as CA50 is retarded (e.g., for HRR, noise control). Greater spread expected for 'NTC fuels', e.g., lower AKI gasoline, or boosted operation.

Collaborations

COMMUNITY-WIDE ACTIVITIES

- **ANL-led, International RCM Workshop:** patterned after ECN to better understand LTC phenomena using RCMs, esp. auto-ignition chemistry, turbulence-chemistry interactions, etc.
  - Participation includes experimentalists, modelers, theoreticians
  - Establishing consensus for 'Best Practices'
    - → approaches for reporting / analyzing / comparing data
    - → approaches for simulating the experiments
    - → uncertainty quantification for experiments and modeling
  - 14 RCM laboratories contributed to first standardized tests using iso-octane; 3rd Workshop to be held in August 2016



http://www.transportation.anl.gov/rcmworkshop/

Collaborations

ONGOING INTERACTIONS

- **DOE Working Groups on HCCI and diesel engines:** results presented at AEC MOU, ACEC Tech Team meeting, etc.
- **CRC FACE Working Group:** participate in meetings, test fuels
- **ANL:** global sensitivity analysis, mechanism refinement, gasoline LTC engine, new additives
- **LLNL:** fuel mechanism development / validation, gasoline surrogates, ToolKit development / testing
- **KAUST / Chevron:** fuel supply, model development
- **Northeastern U.:** mechanism diagnostics
- **Other organizations:** NUI Galway (kinetic models), Vrije Universiteit Brussel (reduced-order physical models), U. Michigan / U. Connecticut / UL1ST / U. Cambridge (review paper)

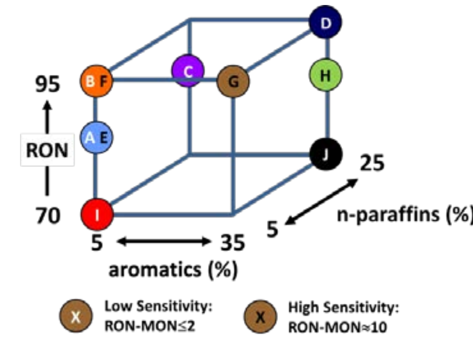
Remaining Challenges

- Improvements to gasoline surrogate model requires deeper understanding of mechanism behavior, uncertainties associated with low temperature chemistry pathways of base model
- Understanding and representing the autoignition characteristics and sensitization of full boiling-range gasoline via low order (4-10 component) surrogate blends requires improved capabilities to formulate surrogates, wider palette of surrogate components
- Ignition delay time, and preliminary heat release are integrated metrics for ignition chemistry, constraints exist with their utility; additional diagnostics could improve development / validation efforts

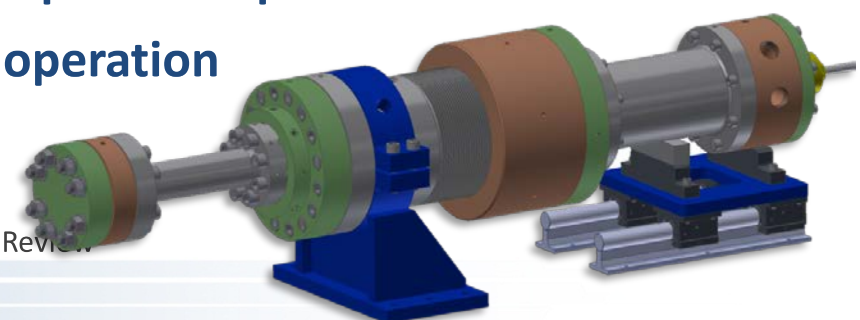
Future Work

FY2015 / FY2016

- **Utilize integrated RCM system / engine model w/ model probing tools (GSA) to improve capabilities of gasoline surrogate model**
  - **Quantify influences of NTC fuels, boosted operation**
  - **Focus on influential reactions, refine uncertainty estimates**
- **Conduct additional RCM experiments and modeling with gasoline, gasoline surrogates**
  - **Naphthenes (KAUST), multi-component blends**
  - **FACE gasoline, ethanol/gasoline blends (LLNL)**
  - **New research grade gasoline (RD587) (LLNL, SNL)**



- **Demonstrate new single-piston RCM (funded via ANL LDRD)**
  - **Funds in FY14/15 reallocated to repair twin-piston machine**
  - **New capabilities / flexibilities in operation when device is commissioned**



Response to Reviewer's Comments

- The RCM is basic research tool for validating and developing mechanisms for engine modeling, and unique approach has helped reduce uncertainties in measurements and interpretation of data. FACE fuels and standard fuels should have higher priority than fuel additives. Progress should be demonstrated in FY15 on UQ/GSA techniques for improving kinetic models and illustrate how differences between measurements and model can be resolved.
  - FY2015 activities include acquiring data for 5-member ring cycloalkanes, as well as gasoline/ethanol blends, specifically targeting FACE-F since this is a relevant, well-characterized full boiling range gasoline. Ignition delay measurements are conducted along with novel heat release analysis to understand influences of LTHR/ITHR, and provide metrics for mechanism development and validation. Challenges in applying UQ/GSA techniques to the LLNL gasoline surrogate model have been addressed in collaboration with Northeastern University and LLNL, and further analysis will be focused on recent measurements.

- The project demonstrates good coordination with DOE labs and universities and the International RCM Workshop is a great idea to establish standardized tests and 'Best Practices.' It would be nice to see even more collaboration with complementary devices like shock tubes , flow reactors, etc. for a coordinated suite of measurements, and greater interactions with industry.
  - The 2nd Workshop was held in August 2014, with additional participation by labs that use shock tubes and flow reactors, as well as fuel and engine companies. The 3rd Workshop will be held in August 2016 with coordinated follow-on work.

Summary

- **Objective**
  - Acquire data, validate/improve models for transportation-relevant fuels at advanced engine conditions
- **Approach**
  - Utilize ANL's RCM and novel data analysis tools, leverage expertise of BES-funded researchers to synergistically improve predictive models
- **Technical Accomplishments**
  - Acquired datasets to understand autoignition behavior of cyclopentane, and FACE-F gasoline blended with ethanol
  - Developed methodology, and conducted first UQ/GSA with LLNL detailed gasoline surrogate model
- **Collaborations**
  - National labs, universities and industry; International RCM Workshop
- **Future Work**
  - Additional testing with gasoline surrogates and surrogate blends, further ethanol blended gasolines
  - Refinements/extensions of UQ/GSA, cover additional conditions/fuels