

08 JUNE 2016



RCM STUDIES TO ENABLE GASOLINE-RELEVANT LOW TEMPERATURE COMBUSTION



**S. SCOTT GOLDSBOROUGH (PI), ALEKSANDR FRIDLYAND, JEFFREY SANTNER,
COLIN BANYON**

Project ID # ACE054

FY2016 DOE Vehicle Technologies Program Annual Merit Review

Advanced Combustion Engine R&D / Fuel and Lubricant Technologies

Wednesday, June 8, 2016

Program Managers: Gurpreet Singh, Leo Breton

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OVERVIEW

Timeline

- Project started FY 2011
- Project directions and continuation reviewed annually, and in FY 2017 VTO Lab Call

Budget

- Project funded by DOE / VTP
 - FY 2014 funding: \$325 k
 - FY 2015 funding: \$500 k
 - FY 2016 funding: \$490 k

Barriers

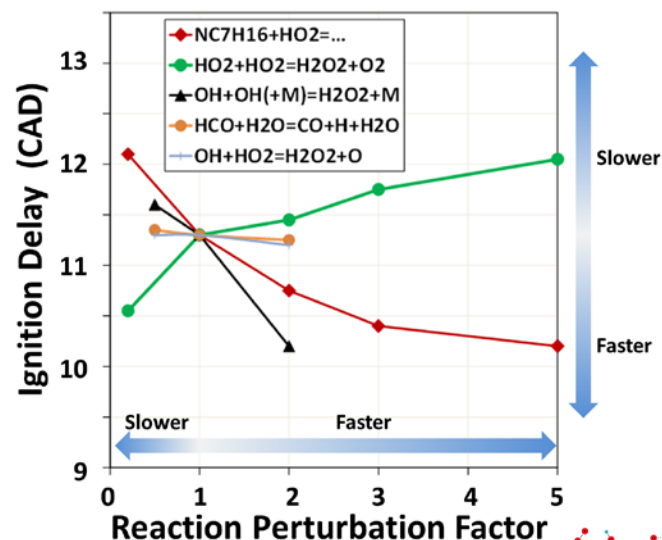
- Lack of fundamental knowledge of advanced combustion engine regimes
- Lack of modeling capability for combustion and emission control

Partners

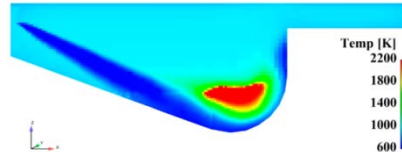
- ANL – Lead, Goldsborough (PI)
- LLNL – gasoline surrogate model, simulation tools
- KAUST, Chevron – fuels, fuel models
- UC Berkeley, SNL – HCCI engine data
- Northeastern U. – UQ/GSA mechanism diagnostics
- International RCM Workshop

OBJECTIVES AND RELEVANCE TO DOE

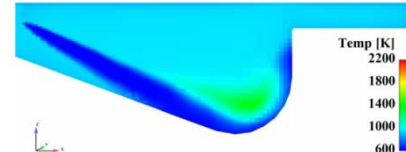
- Acquire fundamental data, and help develop / validate / refine chemical kinetic and relevant models for transportation-relevant fuels (conventional and future gasolines, diesels and additives) at conditions representative of advanced combustion regimes, leveraging collaborations with BES-funded groups,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






$\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$



PROJECT MILESTONES

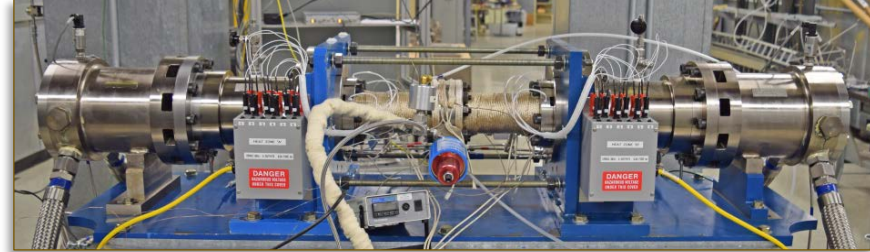
FY 2016

Task	Milestone	Status
1	Acquire ignition delay measurements for gasoline surrogate components: 5-member ring naphthenes (cyclopentane, methyl cyclopentane, ethyl cyclopentane)	
2	Acquire additional ignition measurements for full boiling-range gasoline, and blends of this with ethanol: FACE-F (E0, E10, E20, E30, E100)	
3	Acquire ignition measurements for multi-component surrogate blends to mimic 'neat', and ethanol-blended gasoline	FY16 – Q3
4	Conduct UQ/GSA simulations with improved uncertainty representations for LLNL gasoline surrogate model	
5	Conduct UQ/GSA simulations for multi-component fuel blend	FY16 – Q4

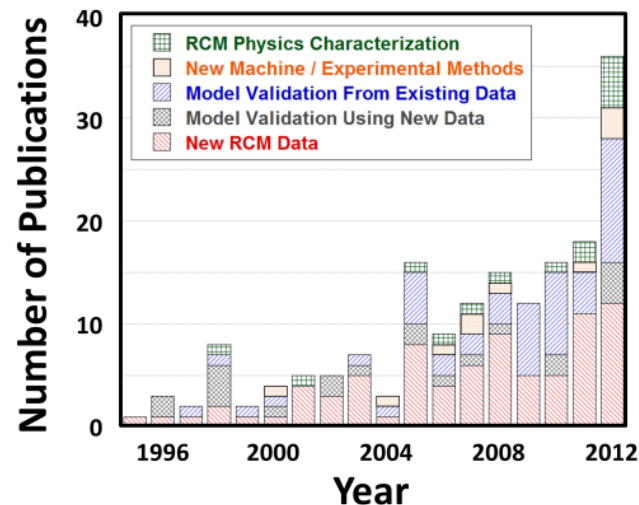
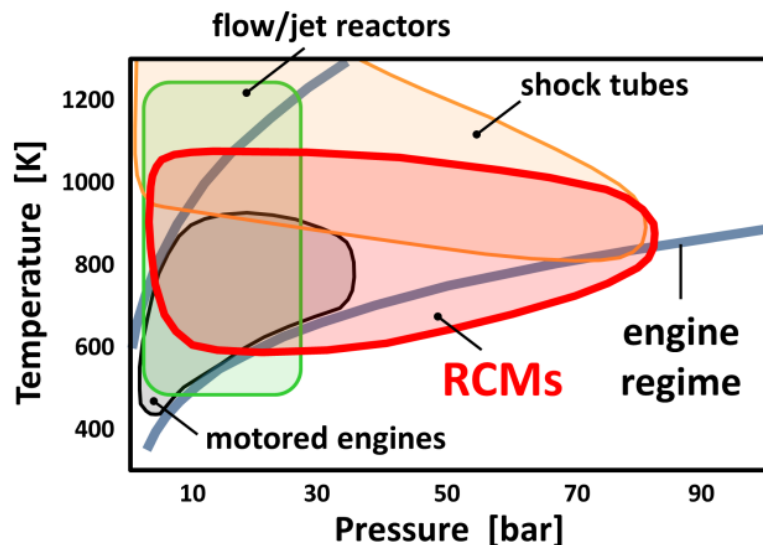
PROJECT APPROACH

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/measurements of sensitive processes (e.g., individual reaction rates)

TECHNICAL ACCOMPLISHMENTS / PROGRESS

TECHNICAL ACCOMPLISHMENTS / PROGRESS

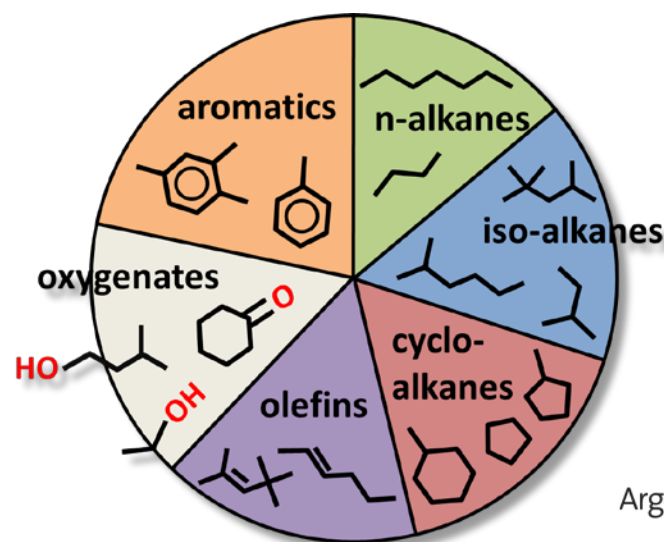
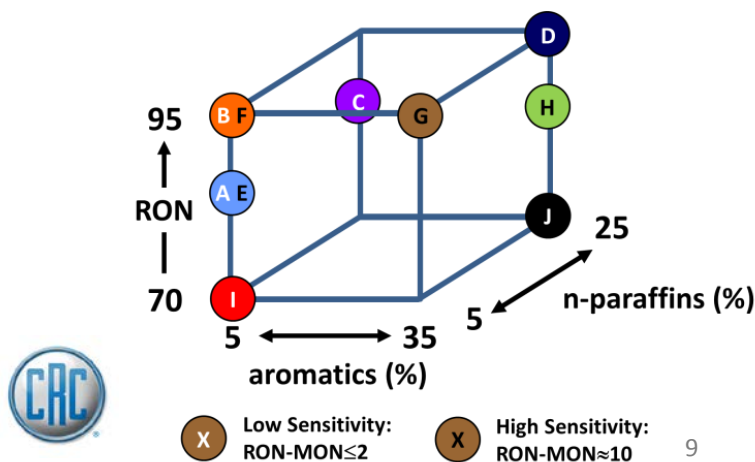
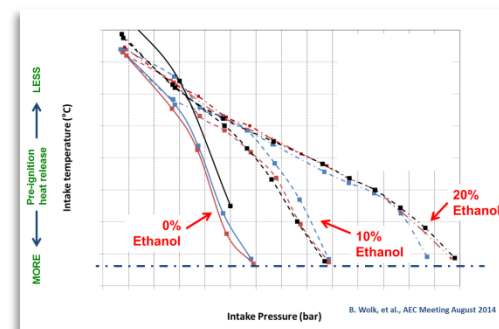
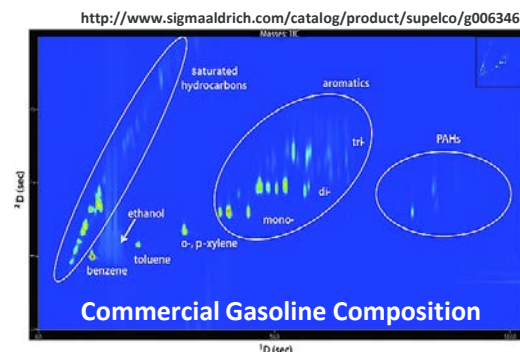
Twin-Piston Rapid Compression Machine

- Modifications and upgrades implemented since FY 2015 AMR to reduce measurement uncertainties and increase throughput
 - Redesigned heating system / control for mixture feedline from supply tank;
 - Continuous monitoring of reaction chamber temperature distribution;
 - High-resolution static pressure transducers (± 0.25 % of reading);
 - High-speed DAQ card (1 MHz, 16-bit) to improve heat release analysis during high-temperature heat release;
 - Incorporated high-precision, automated feed valve for reaction chamber ;
 - Previously limited to ~16 shots/day; up to 40 shots/day now possible, with excellent repeatability.
- Operational challenges still exist
 - Synchronous twin-piston operation difficult to achieve; typically ~2-3 ms delay. Efforts underway in FY 2016 to improve this, including integration of piston position sensor for high accuracy dynamic measurement;
 - Piston seals often subjected to repeated thermal cycling, requiring replacement after 1-2 weeks of use. Different ring-pack configurations / seal designs and materials are being investigated.

TECHNICAL ACCOMPLISHMENTS / PROGRESS

Investigating Gasoline and Surrogates

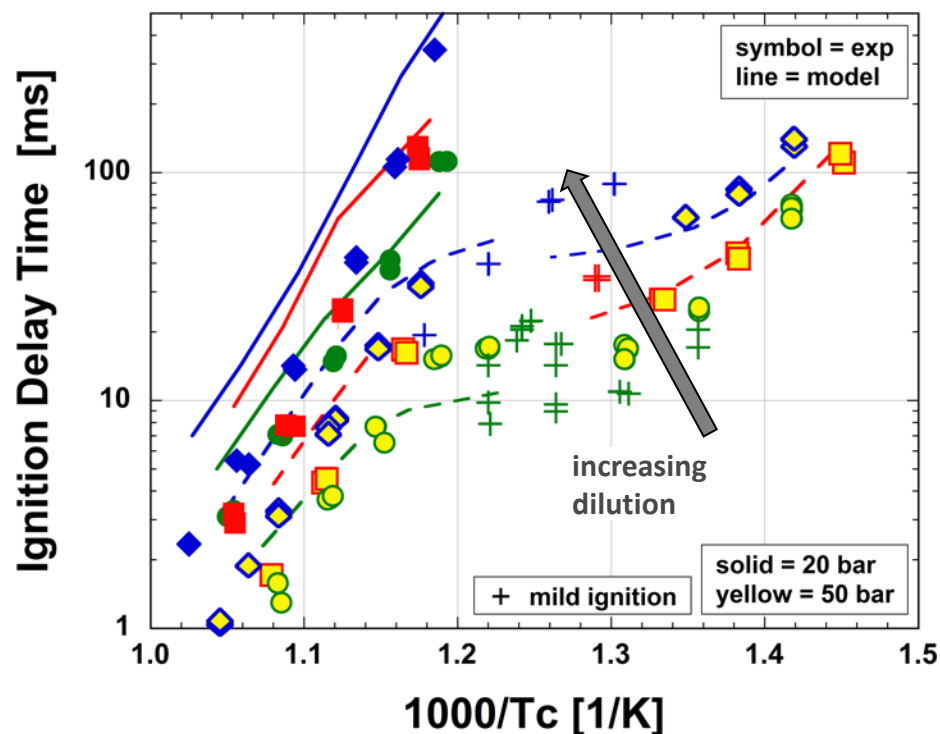
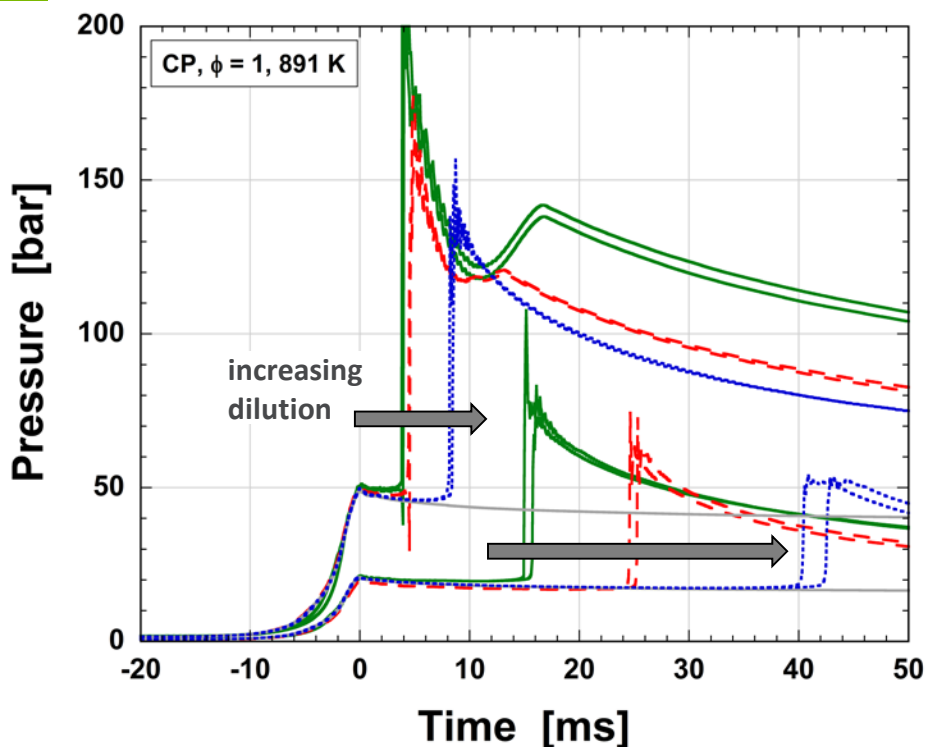
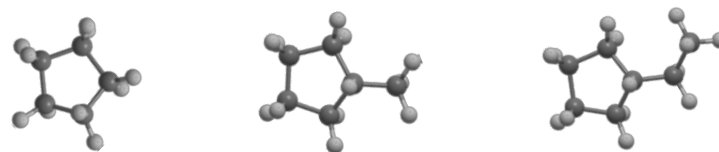
- Predictive modeling of LTC needed to guide design
 - Gasoline is complex, compositionally variant
 - How do these features affect LTC behavior, especially autoignition phenomena at low and intermediate temperatures ($T = 600\text{--}1100\text{ K}$)?
 - How can real fuels be represented by multiple-component (3-10) formulations?
 - Data are needed to compare autoignition behavior of real, full boiling range fuels with surrogates, including individual components, blends of these and mixtures with ethanol.



TECHNICAL ACCOMPLISHMENTS / PROGRESS

Task 1 – Surrogate Components

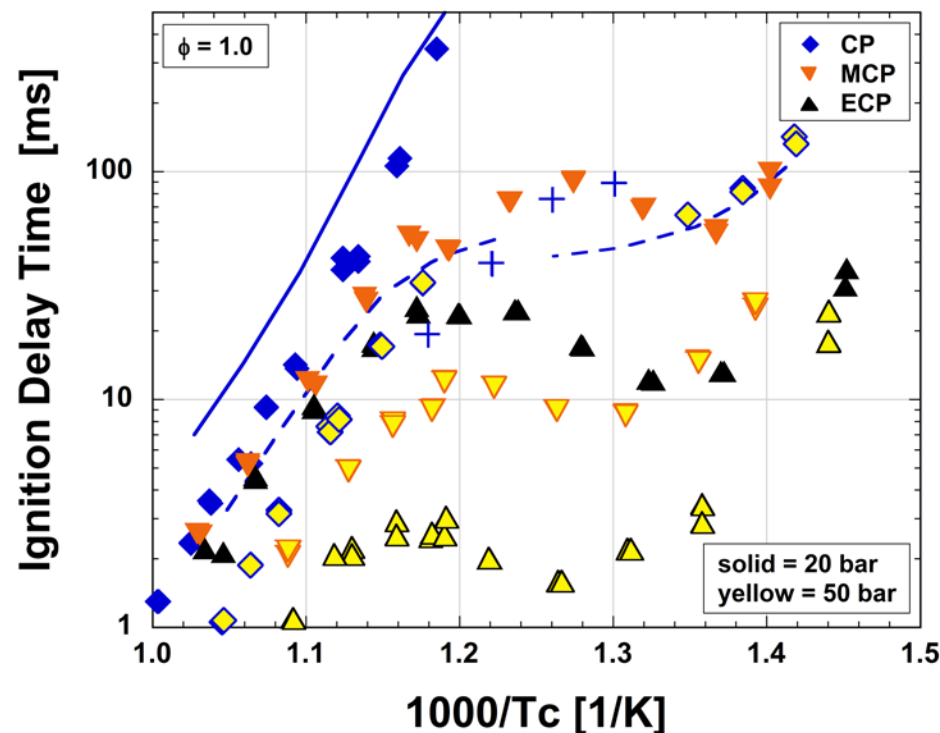
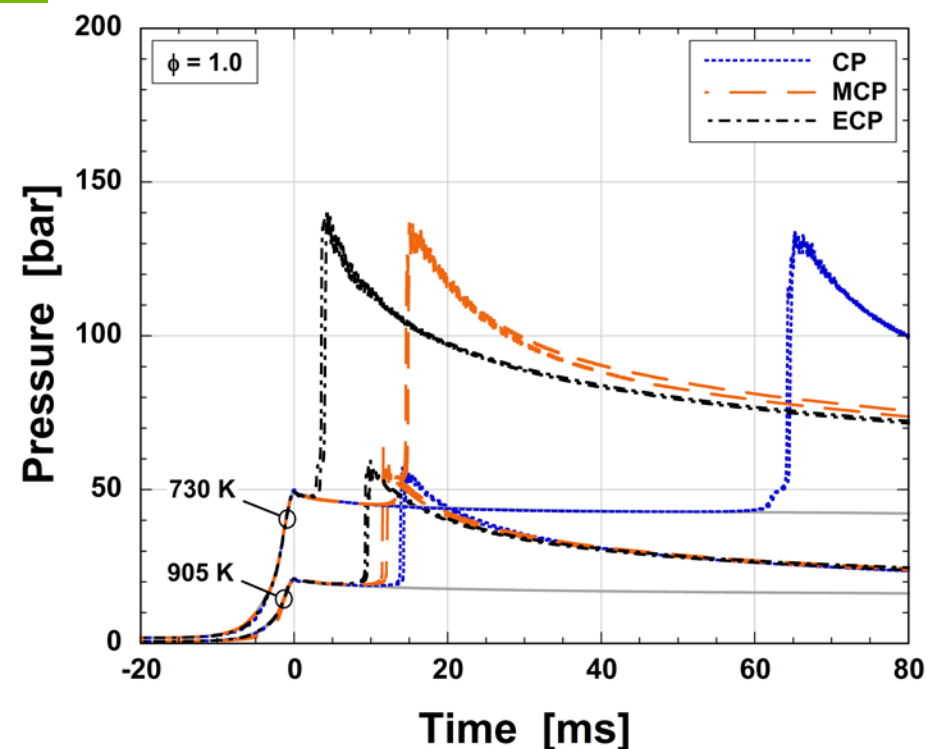
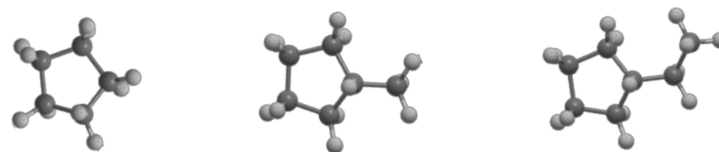
- 5-member ring naphthenes
 - Acquiring combustion data for representative hydrocarbons at LTC conditions. FY 2015/16 tests with CP, MCP and ECP;
 - Influence of ring substitution, temperature, pressure and dilution.



TECHNICAL ACCOMPLISHMENTS / PROGRESS

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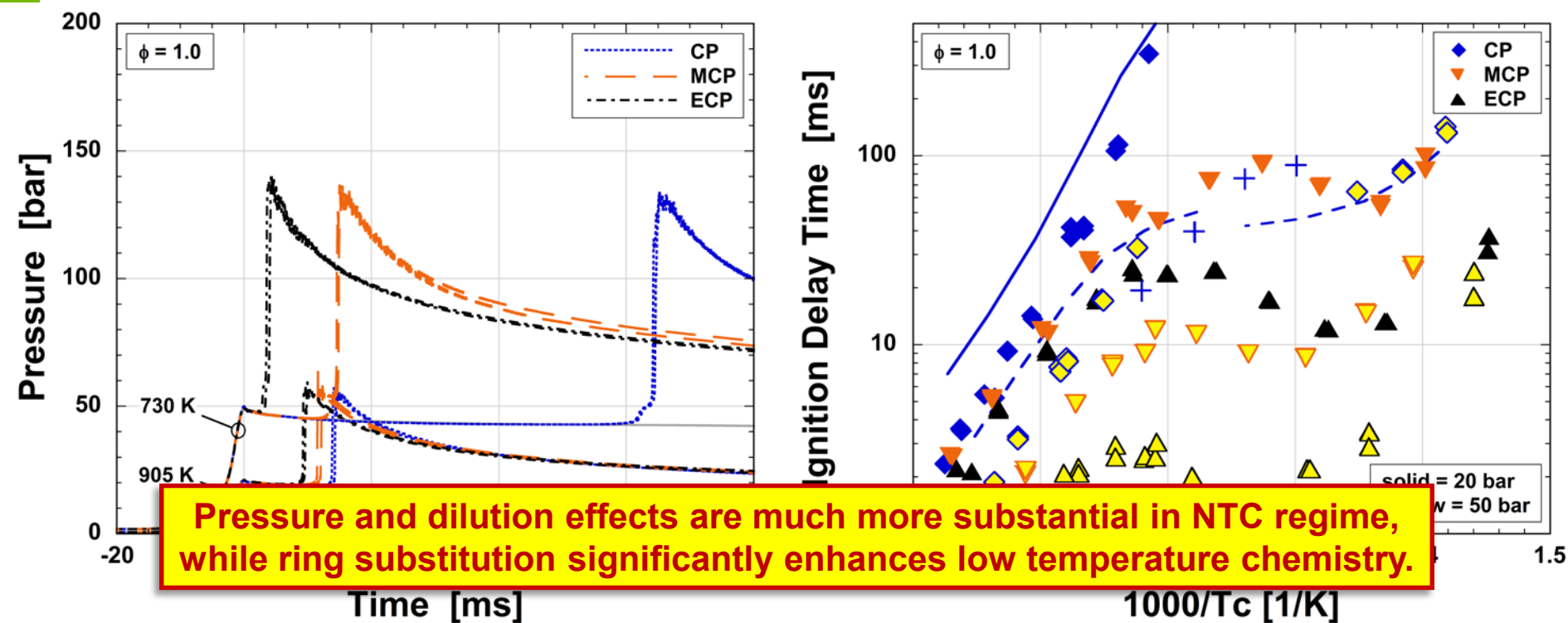
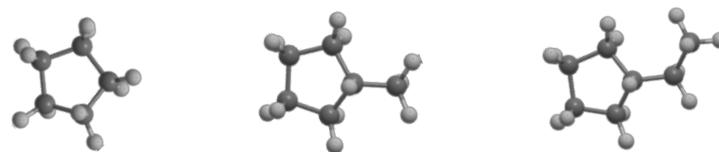
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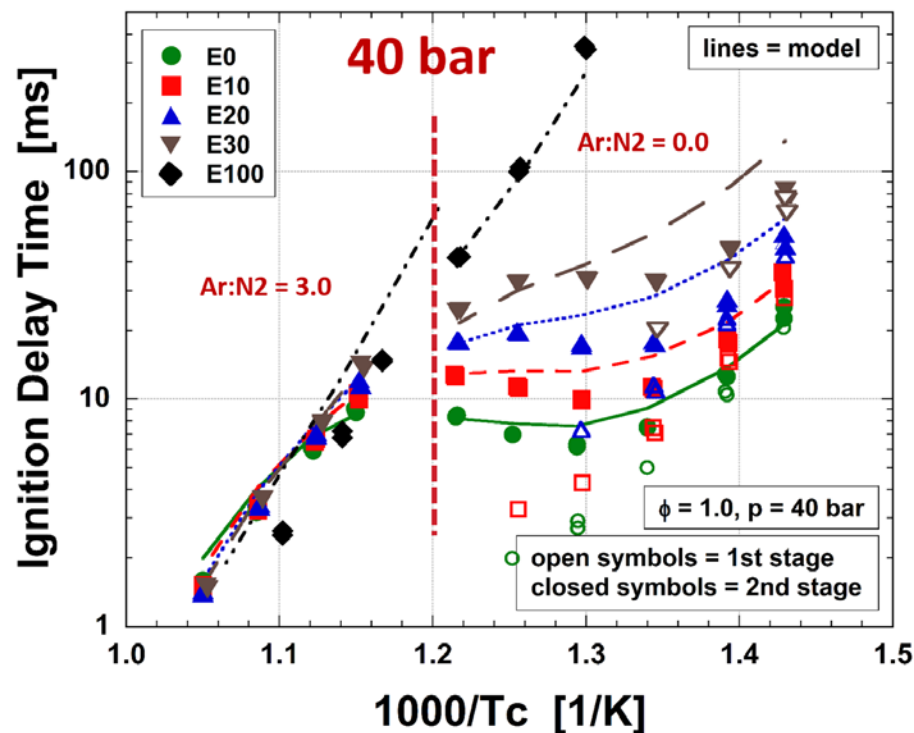
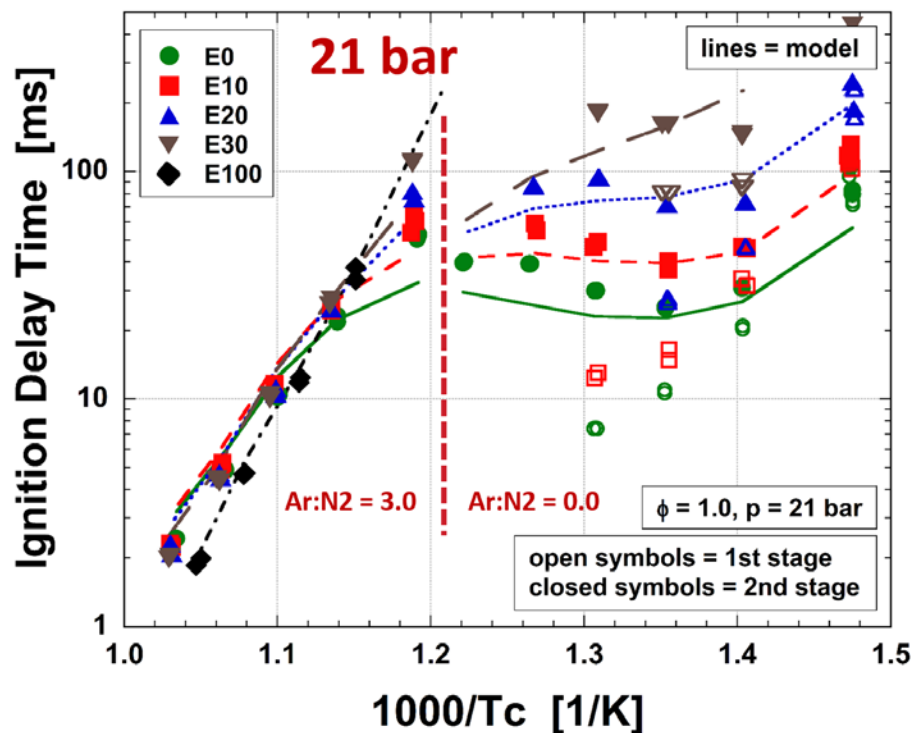
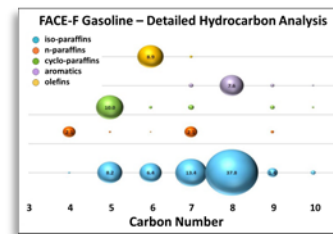
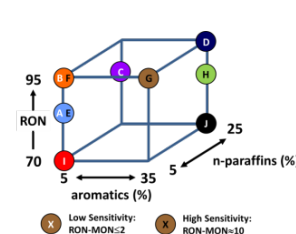
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TECHNICAL ACCOMPLISHMENTS / PROGRESS

Task 2 – Gasoline / Ethanol Blends

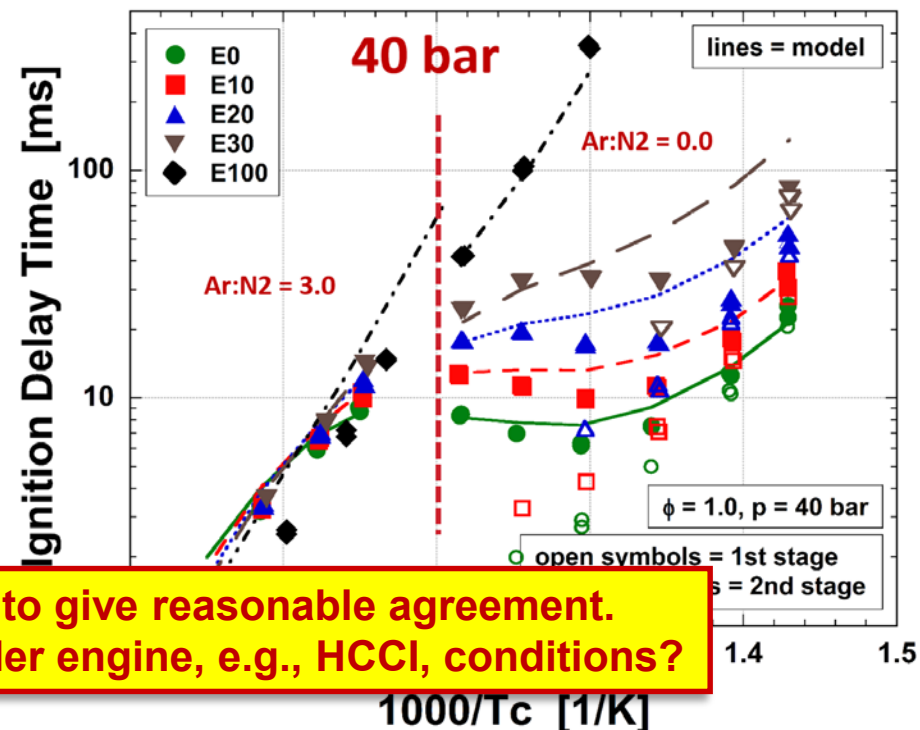
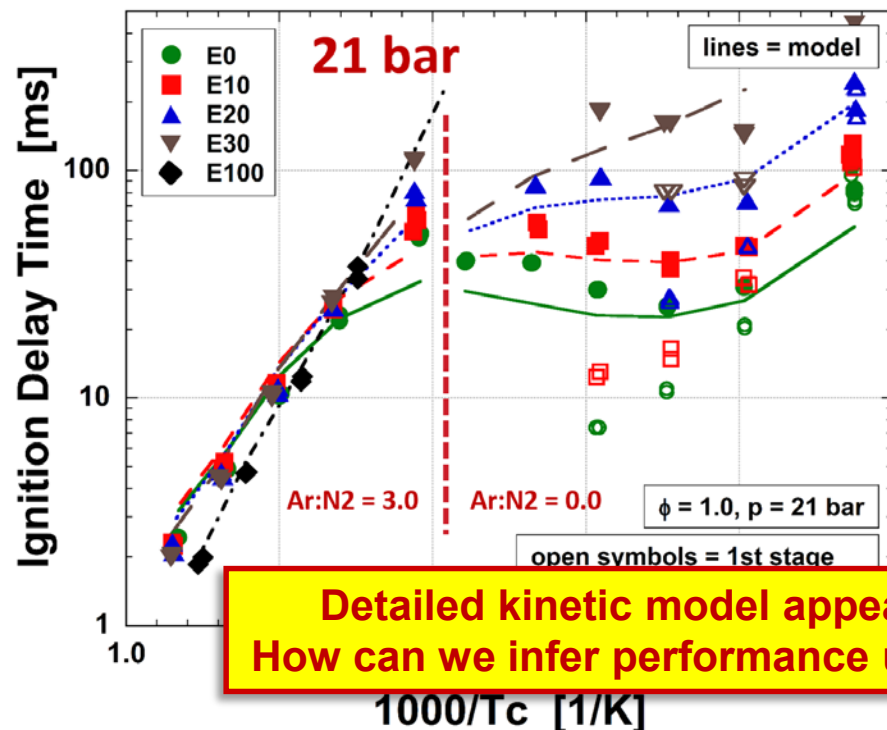
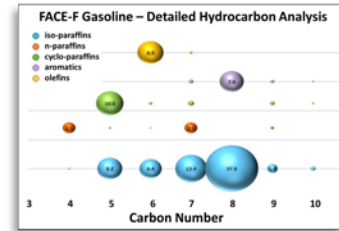
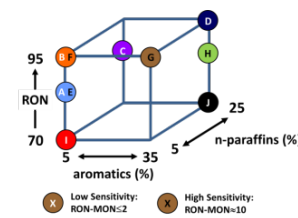
- FACE-F used as representative gasoline
 - Composition, properties well-characterized;
 - Investigating influence of ethanol blending levels (E0, E10, E20, E30, E100) on autoignition chemistry; quantifying τ , LTHR/ITHR.



TECHNICAL ACCOMPLISHMENTS / PROGRESS

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Detailed kinetic model appears to give reasonable agreement.
How can we infer performance under engine, e.g., HCCI, conditions?

TECHNICAL ACCOMPLISHMENTS / PROGRESS

Task 2 – Gasoline / Ethanol Blends

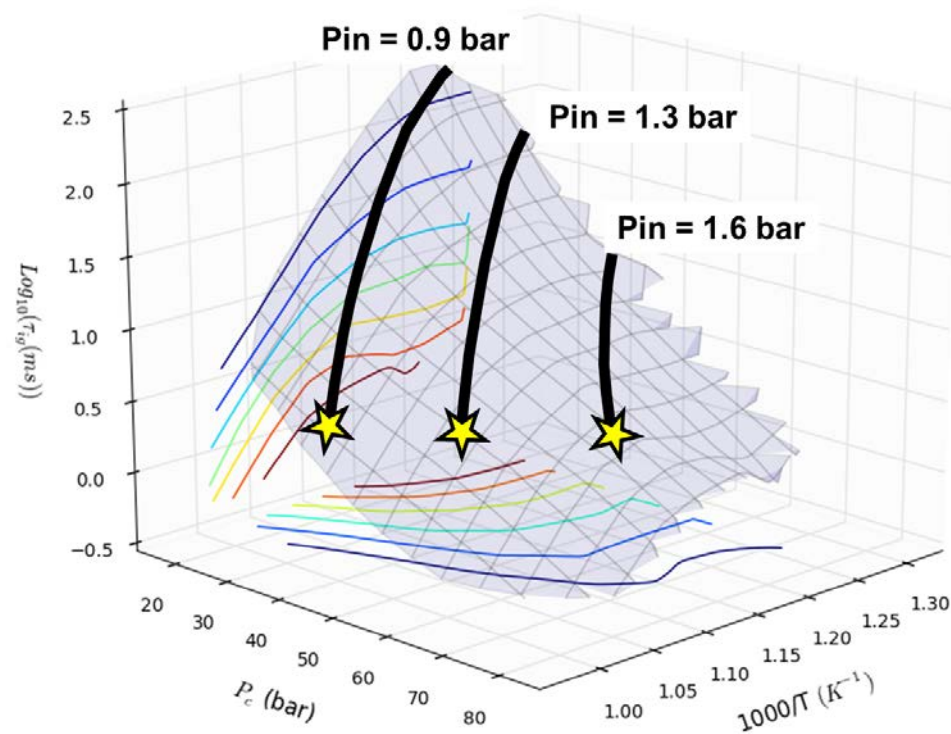
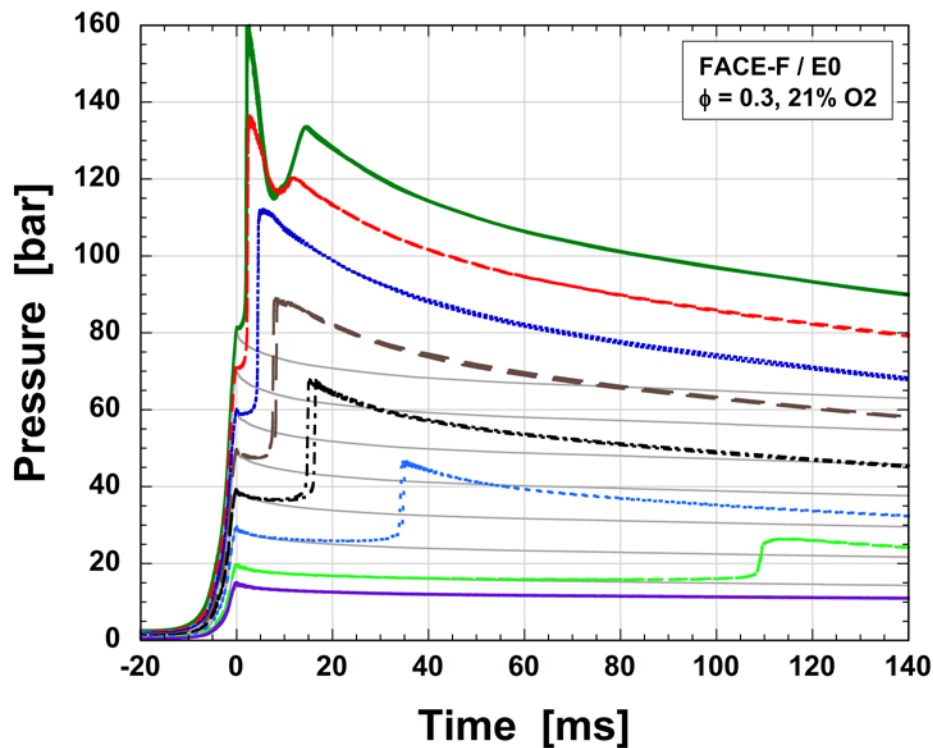
- Challenges exist comparing predictions of chemical kinetic models to LTC engine measurements
 - Many parameters in experiment (e.g., IVC) are estimated / uncertain, while in-cylinder charge contains a distribution of temperature and composition;
 - Autoignition / heat release can proceed through various modes of combustion, including sequential autoignition and deflagrative-propagation;
 - Uncertainties are inherent in chemical kinetic models due to uncertainties in rates for elementary (and lumped) reaction steps
 - Higher model uncertainties at lower IVC temperatures and retarded combustion phasing (as demonstrated in FY 2015 AMR presentation)
- New approaches developed in FY 2016 to demonstrate correlation between RCM measurements and observed engine trends, but with much lower experimental uncertainties than engine experiments
 - Measurement campaign studied changes to required intake temperature in order to maintain constant combustion phasing during HCCI combustion as intake charge is boosted, e.g., SAE 2013-01-2627

TECHNICAL ACCOMPLISHMENTS / PROGRESS

Task 2 – Gasoline / Ethanol Blends



- HCCI data (UC Berkeley) covering $P_{in} = 0.9$ to 1.6 bar, $T_{in} = 120$ to 60 C
- RCM experiments conducted over well-resolved T, P conditions to match those experienced by in-cylinder charge near end of piston compression
 - $P_c = 15$ – 80 bar, $T_c = 800$ – 1000 K at fuel loading of $\phi = 0.3$, 21% O_2

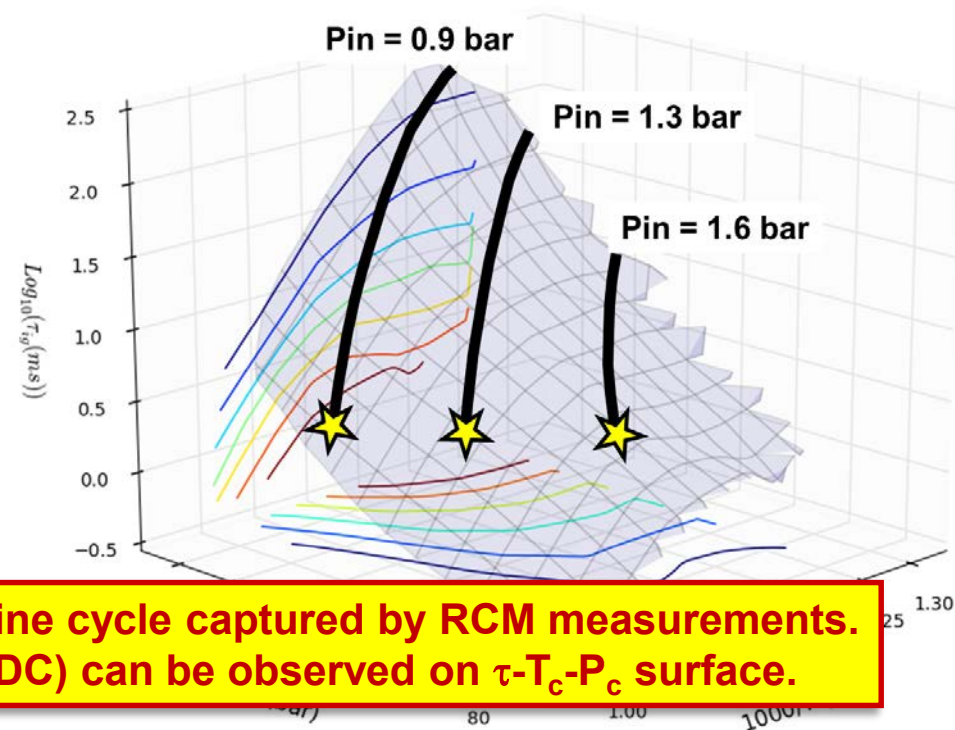
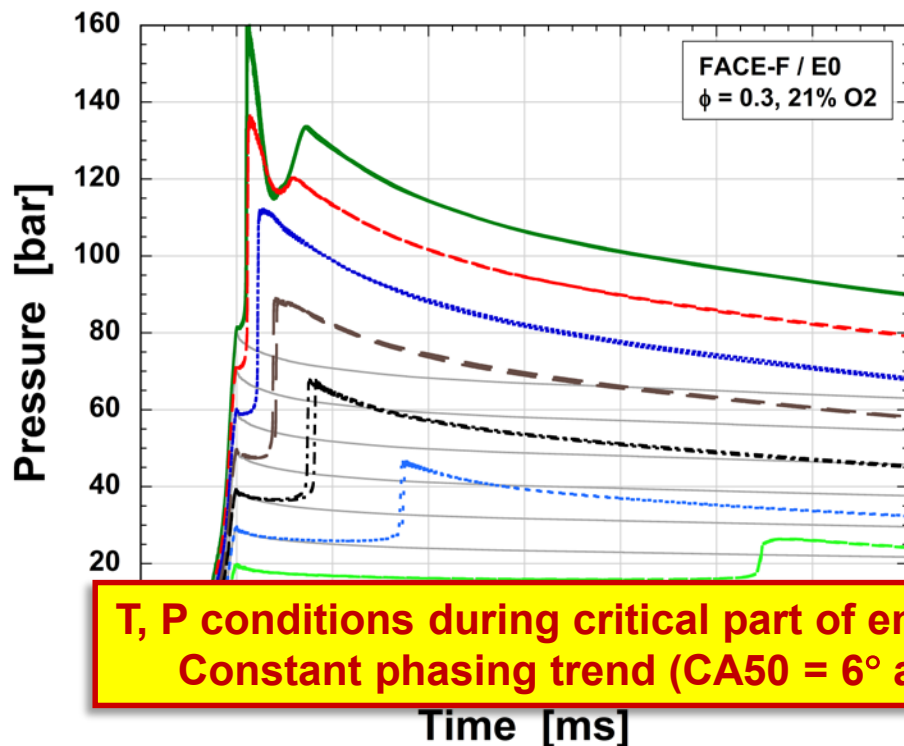


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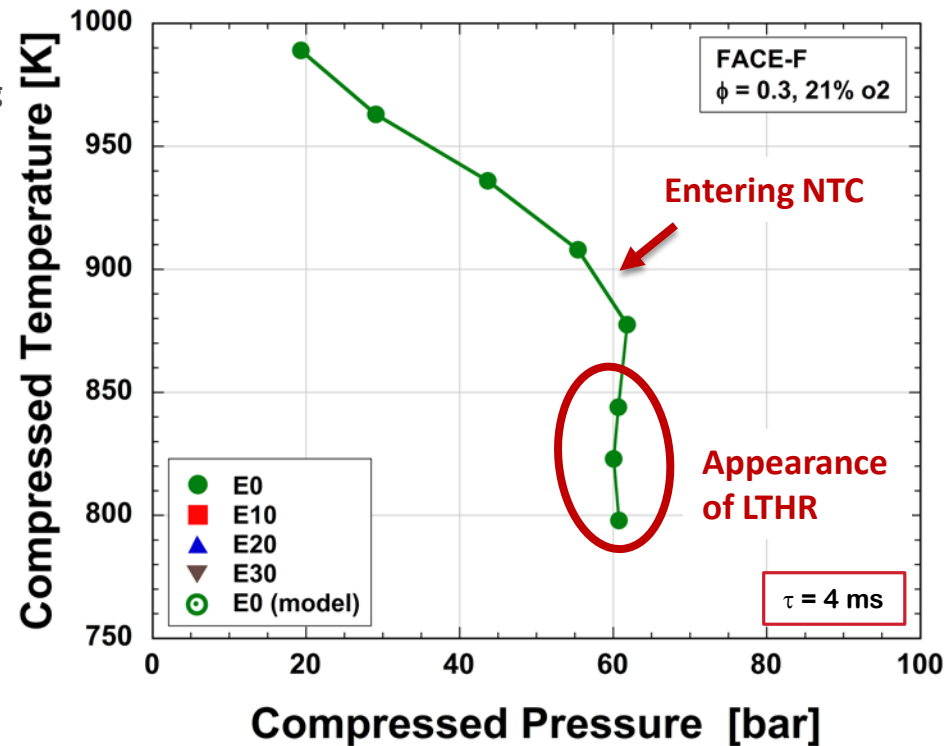
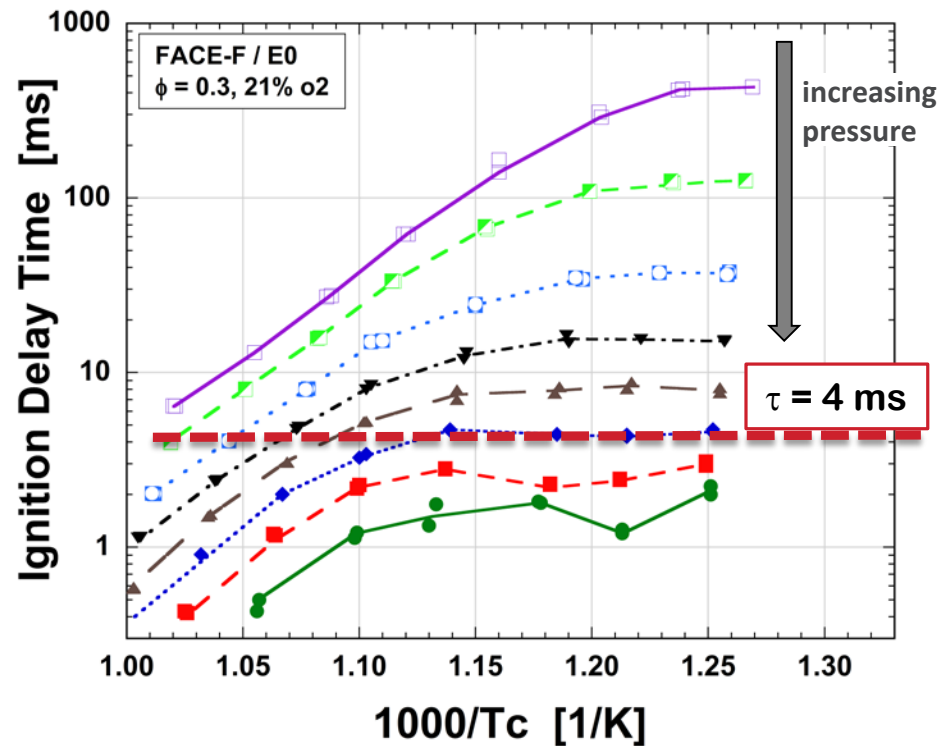


T , P conditions during critical part of engine cycle captured by RCM measurements. Constant phasing trend ($CA_{50} = 6^\circ$ aTDC) can be observed on τ - T_c - P_c surface.

TECHNICAL ACCOMPLISHMENTS / PROGRESS

Task 2 – Gasoline / Ethanol Blends

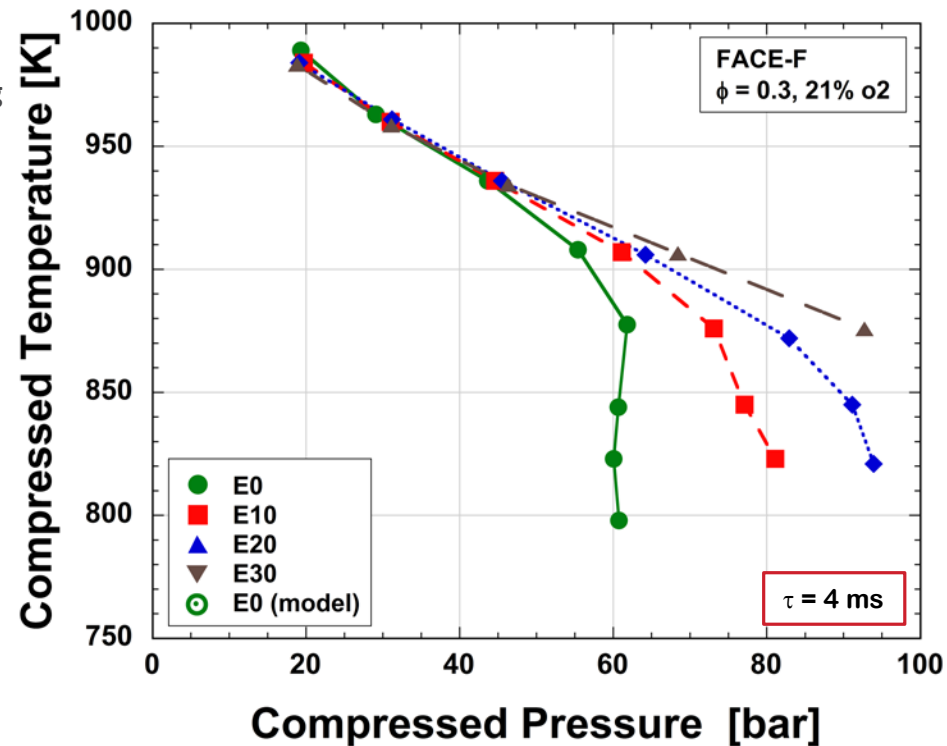
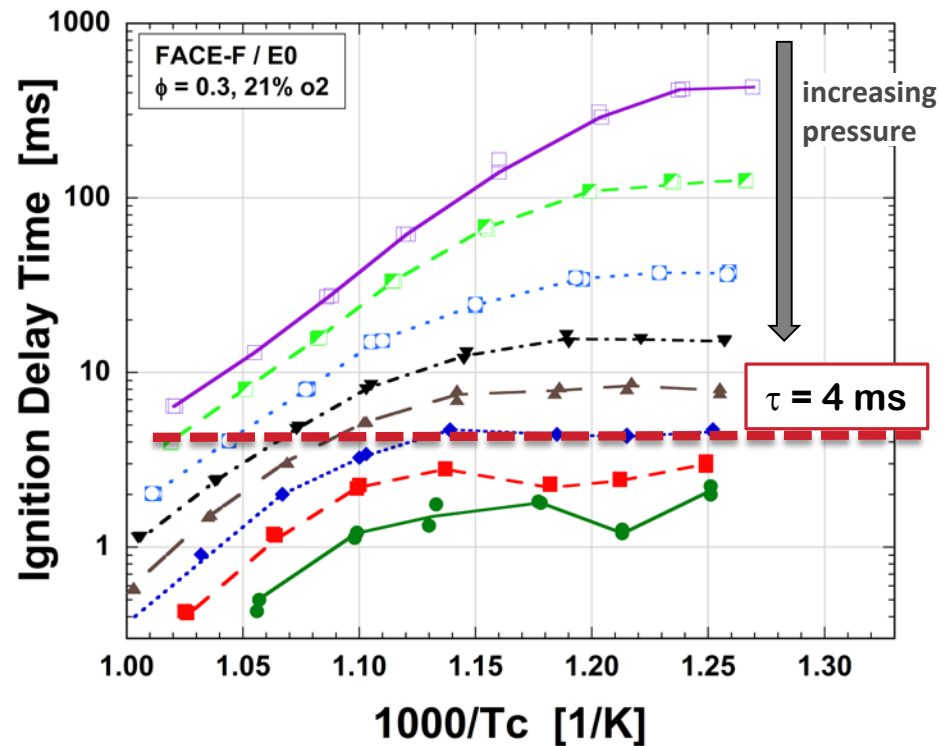
- Constant combustion phasing in RCM indicated by iso- τ line. T_c , P_c at ($\tau = 4$ ms) are close to those seen at TDC in UC Berkeley HCCI engine, trend with T_c - P_c very similar to that observed in T_{in} - P_{in} engine data.
- Influence of NTC chemistry and appearance of LTHR clearly evident.



TECHNICAL ACCOMPLISHMENTS / PROGRESS

Task 2 – Gasoline / Ethanol Blends

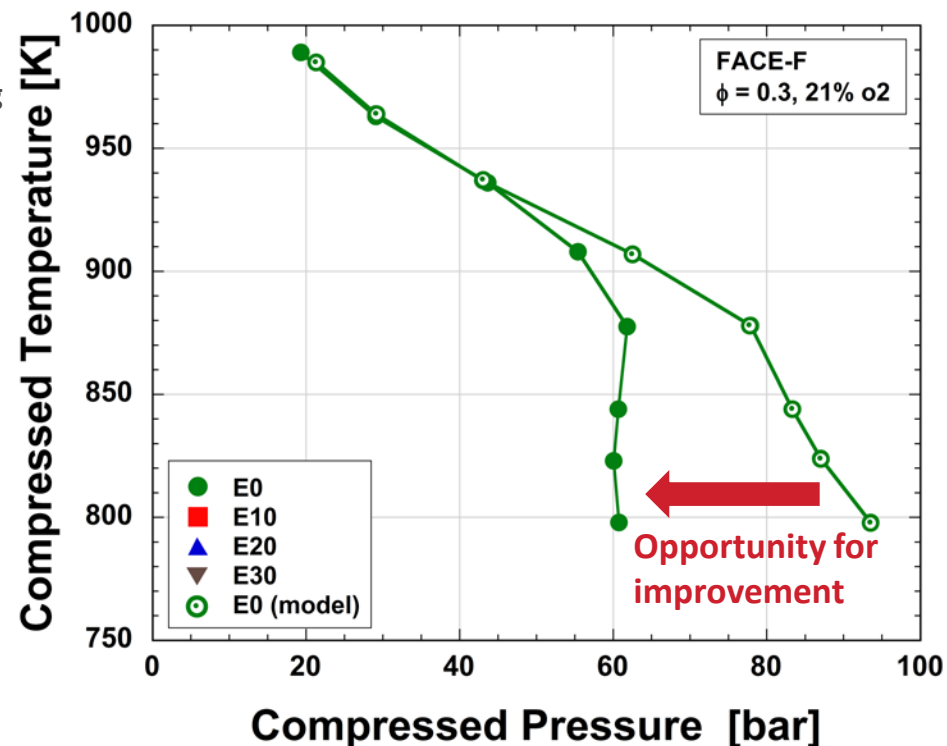
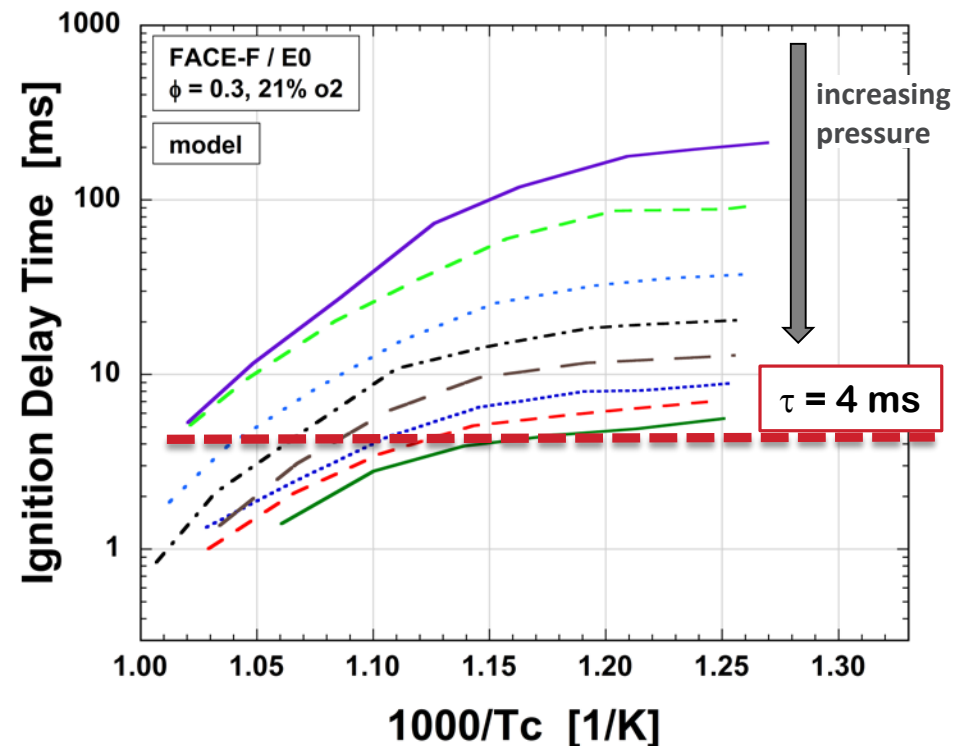
- Ethanol-blended gasoline exhibits suppressed reactivity, most prominently at high pressure and low temperature, e.g., in boosted LTC range. This is consistent with observations of $P_c = 20, 40$ bar experiments.



TECHNICAL ACCOMPLISHMENTS / PROGRESS

Task 2 – Gasoline / Ethanol Blends

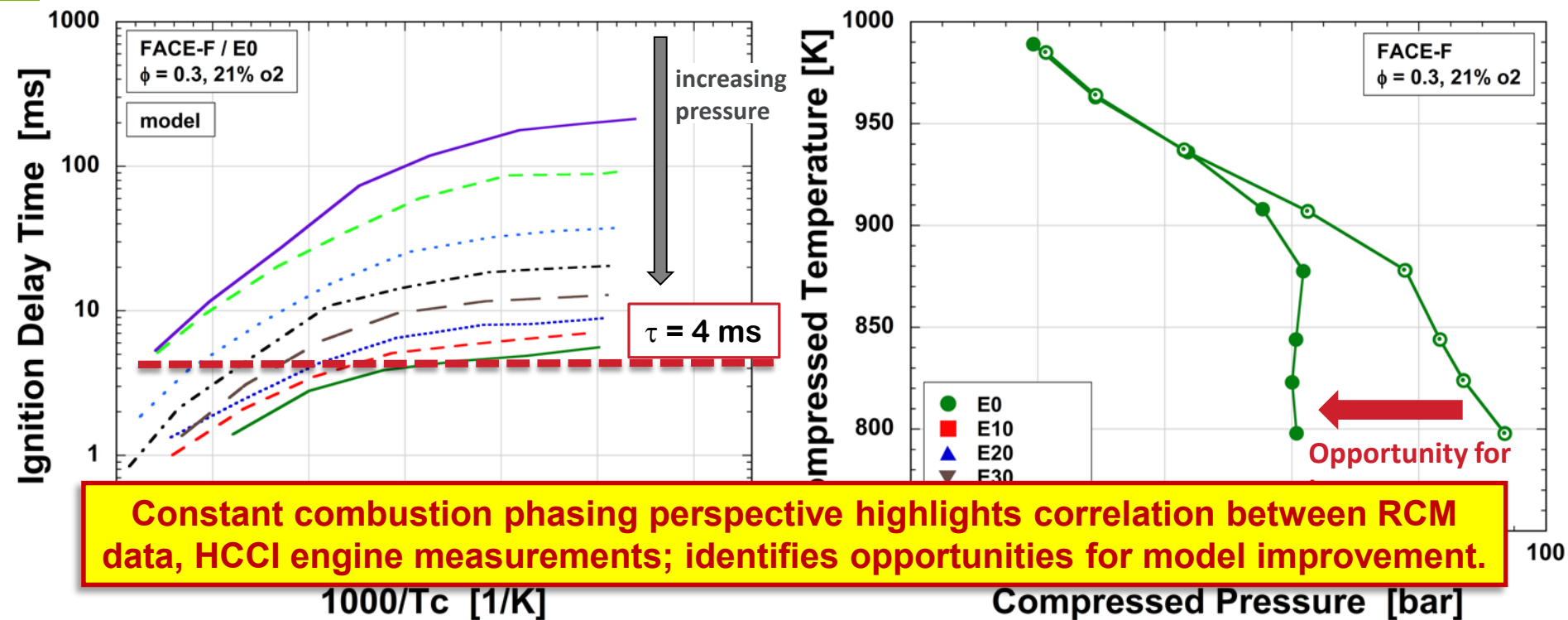
- Predicted ignition delay times for LLNL 5-component gasoline surrogate model are reasonably good, but evolution of low temperature (i.e., peroxide) chemistry, and associated LTHR at higher pressures not adequately captured.



TECHNICAL ACCOMPLISHMENTS / PROGRESS

Task 2 – Gasoline / Ethanol Blends

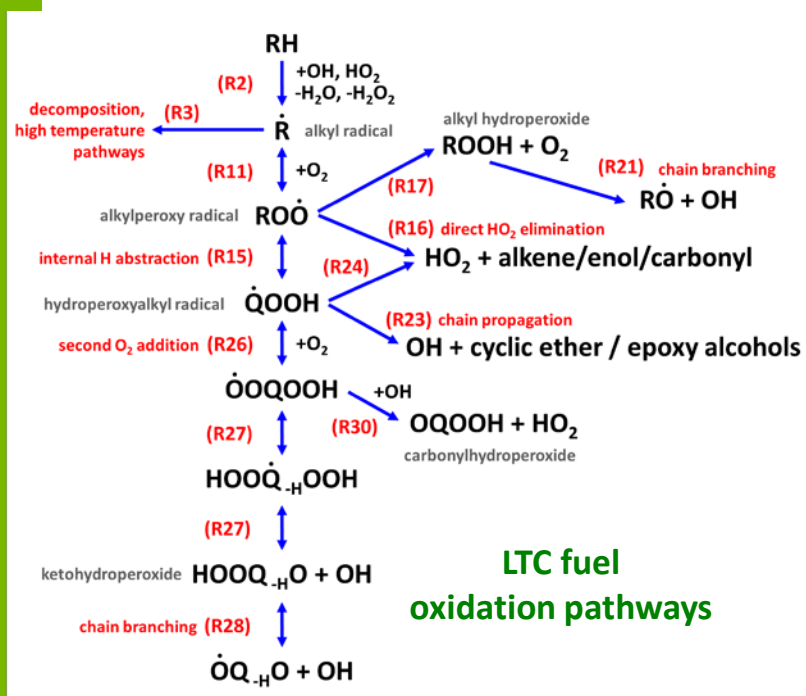
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TECHNICAL ACCOMPLISHMENTS / PROGRESS

Task 4 – UQ/GSA for Gasoline Surrogate Model

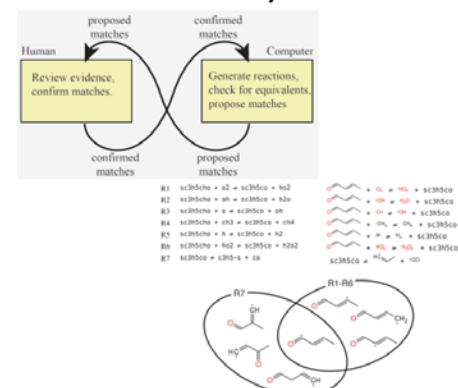
- Methodology developed to implement UQ/GSA with LLNL model
 - ~10⁴ correlated uncertainties. Apply UFs based on: (a) foundational (C₀-C₄) chemistry (AramcoMech), or (b) reaction class (where 'rate rules' are used)
 - Detailed accounting of 7,366 reactions necessitates automated means to identify, classify and appropriately perturb individual reactions



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 ₃ O ₂ , and C ₂ H ₅ O 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 ₂ O ₂ = ROOH + HO ₂ .	5
19	ROO + CH ₃ O ₂ = RO + CH ₃ O + 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 = OOOQOOH).	4
27	Isomerization of OOOQOOH 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.



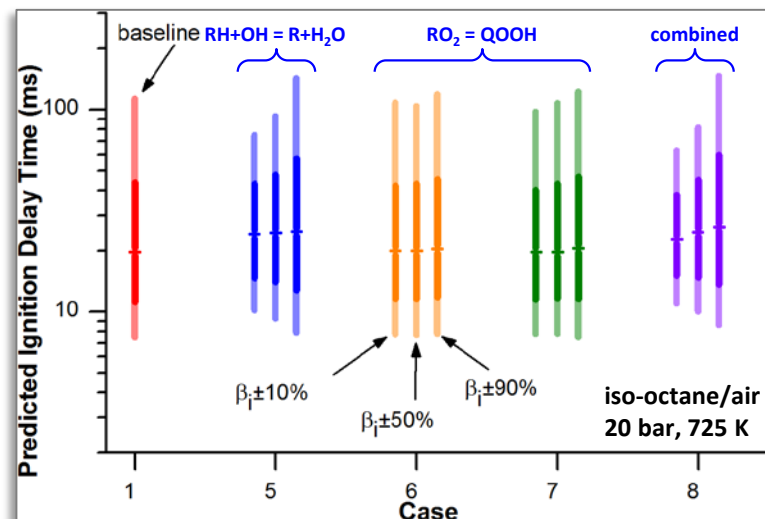
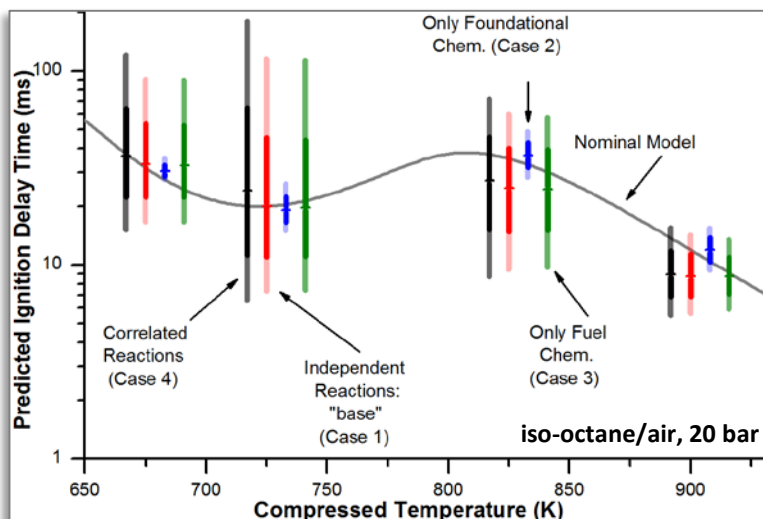
B. Classify reactions in existing model via comparison with reactions generated by RMG using new species 'dictionary'.



TECHNICAL ACCOMPLISHMENTS / PROGRESS

Task 4 – UQ/GSA for Gasoline Surrogate Model

- Efforts in FY 2016 focused on further development / refinement of approach and conditions considered
- Conducted detailed review of uncertainties in foundational chemistry model (AramcoMech, 253 species, 1542 reactions)
 - Previously estimated with conservatively low uncertainty factors (UF = 2);
 - Realistic bounds are now considered for each reaction.
- Refined techniques to account for ‘correlations’ within the model
 - Application to ‘rate rules’ for analogous reaction steps;
 - ‘Branching ratios’ that specify reaction rates with multiple product channels.



RESPONSE TO REVIEWER COMMENTS

- The project has developed an excellent approach to overcome technical barriers of inadequate chemical kinetic modeling capability for LTC, and combustion data are acquired at pressures closer to actual in-cylinder conditions, which is important. The project is well designed in terms of systematic experiments and analysis for various fuels and surrogate blends and the approach seems feasible. The success of this endeavor will surely benefit the entire engine community. Furthermore, the RCM Workshop is an excellent way to engage labs, universities, energy companies and engine manufacturers. The project needs to continue to apply techniques and results to engine level attributes, covering more surrogate components and real fuels, while it would be appropriate to be more forward thinking and examine performance of other gasoline blends, such as gasoline with butanol.
 - New experimental measurements are reported this FY, with efforts that explicitly illustrate correlations between constant volume conditions in the RCM, and variable volume conditions seen in engines, critically at engine-representative pressures. Plans for future fiscal years cover more gasoline types and surrogate formulations, while efforts in the Co-Optima program cover next-generation biofuels.
- UQ/GSA tools aid chemistry development, while challenges and improvements in terms of accounting for correlated uncertainties are properly identified. The technical accomplishments are clearly aligned to the overall project objectives of improving chemical kinetic modeling capability, and the overall U.S. DOE goal of predictive engine simulations. It is unclear however, why ignition delay time is used exclusively as the metric for mechanism validation / improvement, when other measurements such as laminar flame speed, extinction strain rate, etc. should be considered. It would be beneficial to clearly identify how the kinetic model will be improved based on the measurements.
 - Parameters derived from RCM measurements, such as ignition delay time, LTHR/ITHR and intermediate species concentrations are just a few that should be considered for kinetic model evaluation, and iterative improvement through sub-mechanism refinement. It should be noted that metrics such as flame speed are important for SI combustion, but are often dominated by small-molecule chemistry, and not as significantly influenced by the molecular structure / composition of the fuel.

COLLABORATIONS

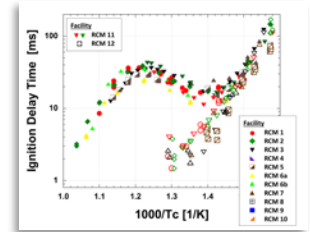
Ongoing Interactions (Inside / Outside VTO)

- **DOE Working Groups on LTC engines**: share data at meetings of AEC MOU, participate on ACEC Fuels Roadmap Subteam
- **CRC FACE Working Group**: participate in meetings, test CRC fuels
- **ANL**: gasoline LTC engine via FT045, refine UQ/GSA approaches and target reactions for mechanism improvement
- **LLNL**: gasoline model development / validation, formulation of gasoline surrogates, ToolKit development / testing
- **KAUST / Chevron**: provide FACE fuels, cyclopentane mechanism development
- **UC Berkeley, SNL**: share HCCI engine data, tests with surrogate molecules
- **Northeastern U.**: utilize NU's novel mechanism diagnostics / analysis
- **Other organizations**: NUI Galway (kinetic models); Vrije Universiteit Brussel (reduced-order physical models); U. Leeds (UQ/GSA approaches); U. Michigan / U. Connecticut / UL1ST / U. Cambridge (RCM review paper)

COLLABORATION

Community-wide Activities

- ANL-led, International RCM Workshop: patterned after ECN to better understand LTC phenomena using RCMs, especially autoignition 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 29 July 2016 at Yonsei University, Seoul, KOREA (in conjunction with International Combustion Symposium)



REMAINING CHALLENGES / BARRIERS

- 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 multiple-component (3-10) 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, like direct measurement of important chemical intermediates, could improve development / validation efforts;
- Mild ignition, which is initiated due to local perturbations in the gas temperature, can complicate autoignition measurements under some conditions and needs further understanding, as well as approaches to mitigate this.

PROPOSED FUTURE WORK

FY 2016 and beyond

- Coordinate surrogate blend formulation for FACE-F with LLNL and conduct tests with multiple-component surrogates
 - Utilize various techniques to select component molecules and blending ratios, including blends with ethanol;
 - Conduct additional tests with surrogate components and full boiling-range gasoline as needed.
- Conduct RCM tests with RD-587 (E10 certification gasoline)
 - Coordinate with SNL to target LTGC engine conditions
 - Coordinate with LLNL to formulate and test surrogate blends for RD-587, along with single-component fuels as necessary
- Design, fabricate gas sampling / integrated analytical unit (GCxGC) for new single-piston RCM
 - Conduct detailed measurements with iso-octane and other surrogates at LTC conditions to quantify intermediate species concentrations of important cyclic ethers and olefins formed / consumed during ignition delay period
 - Collaborate with LLNL reduce uncertainty in rate controlling reactions and improve model predictions

PROPOSED FUTURE WORK

FY 2016 and beyond

- Conduct tests with unique surrogate molecules, e.g., cycloheptadiene, in collaboration with Combustion Chemistry group at SNL CRF
 - Quantify influence of peroxide intermediates, e.g. QOOH, which have been directly measured by CRF, on autoignition behavior at engine-relevant conditions (T , P , ϕ , $\%O_2$) via RCM measurements and kinetic modeling

SUMMARY

- Objective
 - Acquire data, validate / improve models for transportation-relevant fuels at advanced engine conditions
- Project Approach
 - Utilize ANL's RCM and novel analysis tools, leverage expertise of BES-funded researchers to synergistically improve predictive models
- Technical Accomplishments / Progress
 - Acquired data to understand autoignition behavior of 5-member ring naphthenes and FACE-F gasoline blended with ethanol
 - Improved / refined UQ/GSA using LLNL detailed gasoline surrogate model
- Collaborations
 - National labs, universities and industry; International RCM Workshop
- Future Work
 - Additional testing with gasoline surrogate components, blends and full boiling range gasolines
 - Improvements to UQ/GSA, covering additional conditions / fuels

An aerial photograph of the Argonne National Laboratory campus, showing various buildings, parking lots, and a large circular structure, all overlaid with a semi-transparent blue filter.

THANK YOU