Co-Optimization of Fuels and Engines
Fuel Property Team

Part 1 - Fuel Properties and Chemical Kinetics

June 9th, 2016

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1. National Renewable Energy Laboratory
2. Oak Ridge National Laboratory
3. Pacific Northwest National Laboratory
4. Sandia National Laboratories
5. Lawrence Livermore National Laboratory
6. Argonne National Laboratory

Co-Optima DOE VTO Management Team: Kevin Stork and Gurpreet Singh

a note about deviations from AMR template

- 2016 is the first time the co-optima program is being reviewed at AMR
- This three part presentation from three presenters represents an overview of the Fuel Properties-Advanced Engine Development research portfolio
  - A number of individual projects are continuing projects that pre-date co-optima
  - Several of the projects are new starts for FY16 and are in the ramp-up phase
- Relevance is not explicitly discussed, and collaborations are touched on minimally
  - Relevance and many collaborations covered in Overview presentation of Co-Optimization of Fuels and Engines (FT037)
- Limited comments to previous year reviewer comments
  - Multiple 2015 reviews feed into this portfolio overview presentation
- In some cases Collaborations are listed in Reviewer Only slides because of time limitation

Overview: Fuel Properties and Chemical Kinetics

Central Fuel Properties Hypothesis

Development of Fuel Property Database (Fioroni in collaboration with LGHG Fuels Team)

Development of Fuel Screening Criteria – Thrust I (McCormick, Szybist, Miles in collaboration with LGHG Fuels Team)

Heat of Vaporization Measurement (Fioroni)

Measurement of Autoignition Properties with Small Volumes (Fioroni/McCormick, Goldsborough, McNenly)

Fuel Structure-Property Correlations (Bays)

Fuel Property Blending Models (McCormick)

Kinetic Mechanism Development (Pitz, Zigler)

Milestones: Fuel Properties and Chemical Kinetics

Tracked Milestones:

Analysis of up to 20 molecules that represent as many functional groups as possible which will increase our capacity to understand how chemical properties (functional groups) correlate to needed fuel properties and materials compatibility. (Owner NREL, due FY16 Q2) – ***Complete***

Provide up to five fuels and 4 blending levels for blend determination studies. (Owner NREL, due FY16 Q4) – ***On Track***

Provide a report to DOE and Optima documenting the current development status and potential for each of the three small volume autoignition testing techniques. (Owner LLNL, due FY16 Q4) – ***On Track***

Develop a preliminary chemical kinetic mechanism for anisole, a compound relevant to pyrolysis oil-derived fuels. (Owner LLNL, due FY16 Q4) – ***On Track***

Central Fuel Properties Hypothesis

If we correctly identify the critical fuel properties that affect efficiency and emissions performance for downsized, boosted SI engines, then fuels that have those properties will provide optimal engine performance.
Also applies to Thrust II advanced compression ignition engines, but at a much lower level of development.

- With the correct properties, performance is a function of properties not composition or molecular structure
- Hypothesis may be true or very nearly true for petroleum-derived fuels
- Tested using engine experiments on biomass-derived fuels (oxygenates, targeted hydrocarbons) with fuel property values beyond the range exhibited by today's petroleum-derived fuels.

NREL (Fioroni) $100k: Development of Fuel Property Database (BETO)

Objectives

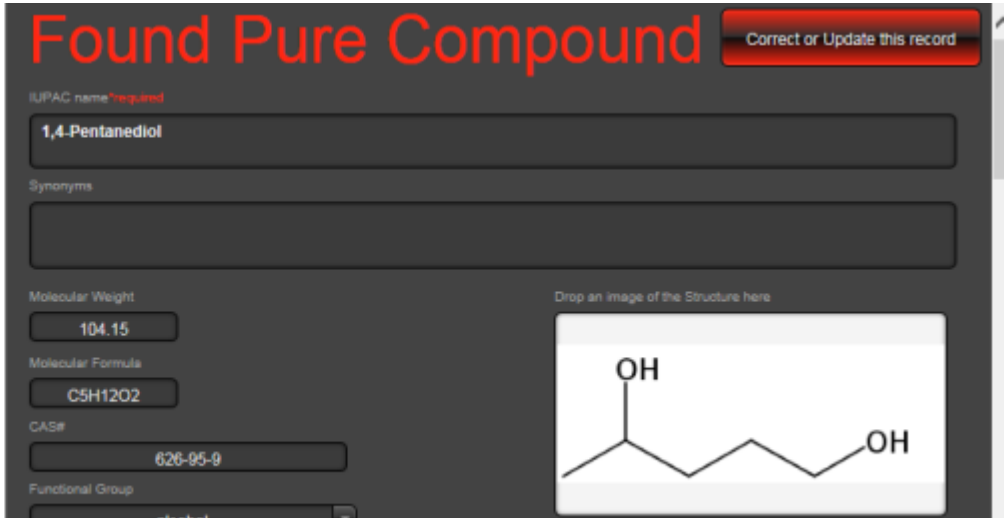
- Create a publically-accessible Fuel Property Database for conventional new candidate fuels

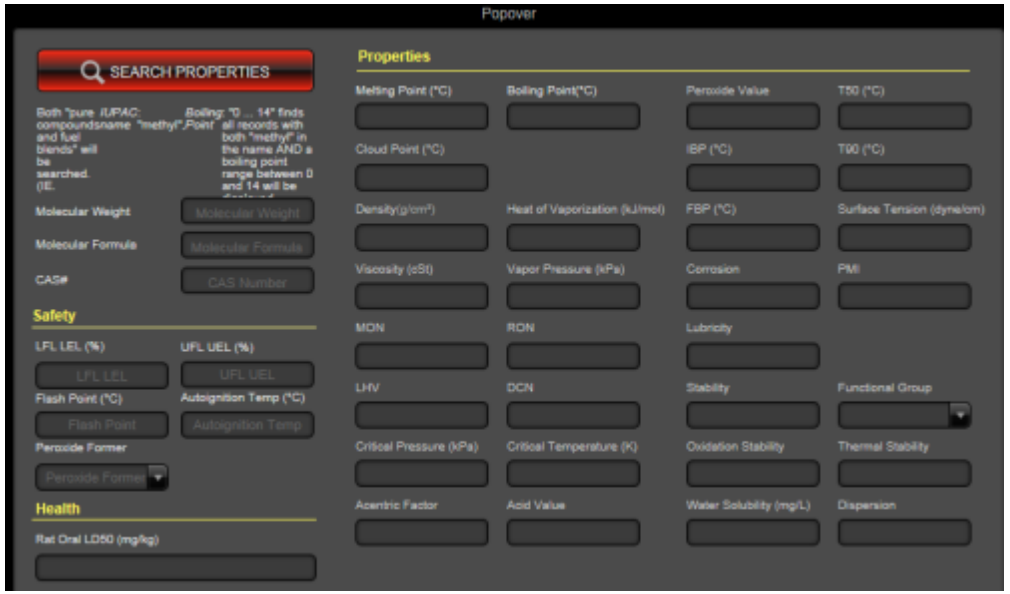
Approach

- Filemaker Pro platform with on-line access
- Fuel molecules and mixtures proposed by LGHG Fuels Team
- Data measured or from literature

Accomplishment

- 366 pure compound and 12 mixtures – so far
- Fields for 25 specific fuel properties
- Used extensively in preparing Q2 Co-Optima Milestone Report (BETO)





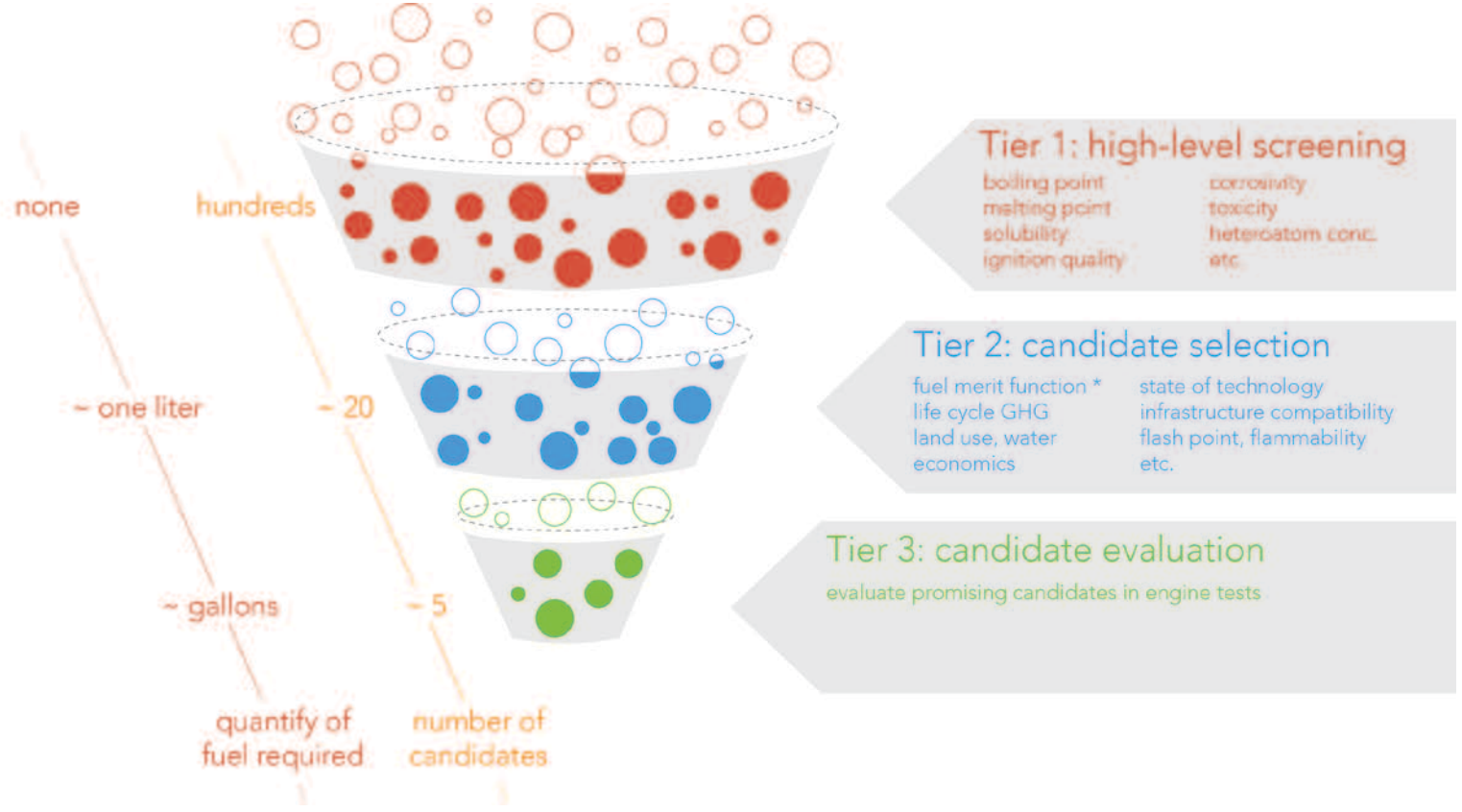
NREL (McCormick) $75k: Development of Fuel Screening Criteria (BETO)

Objectives

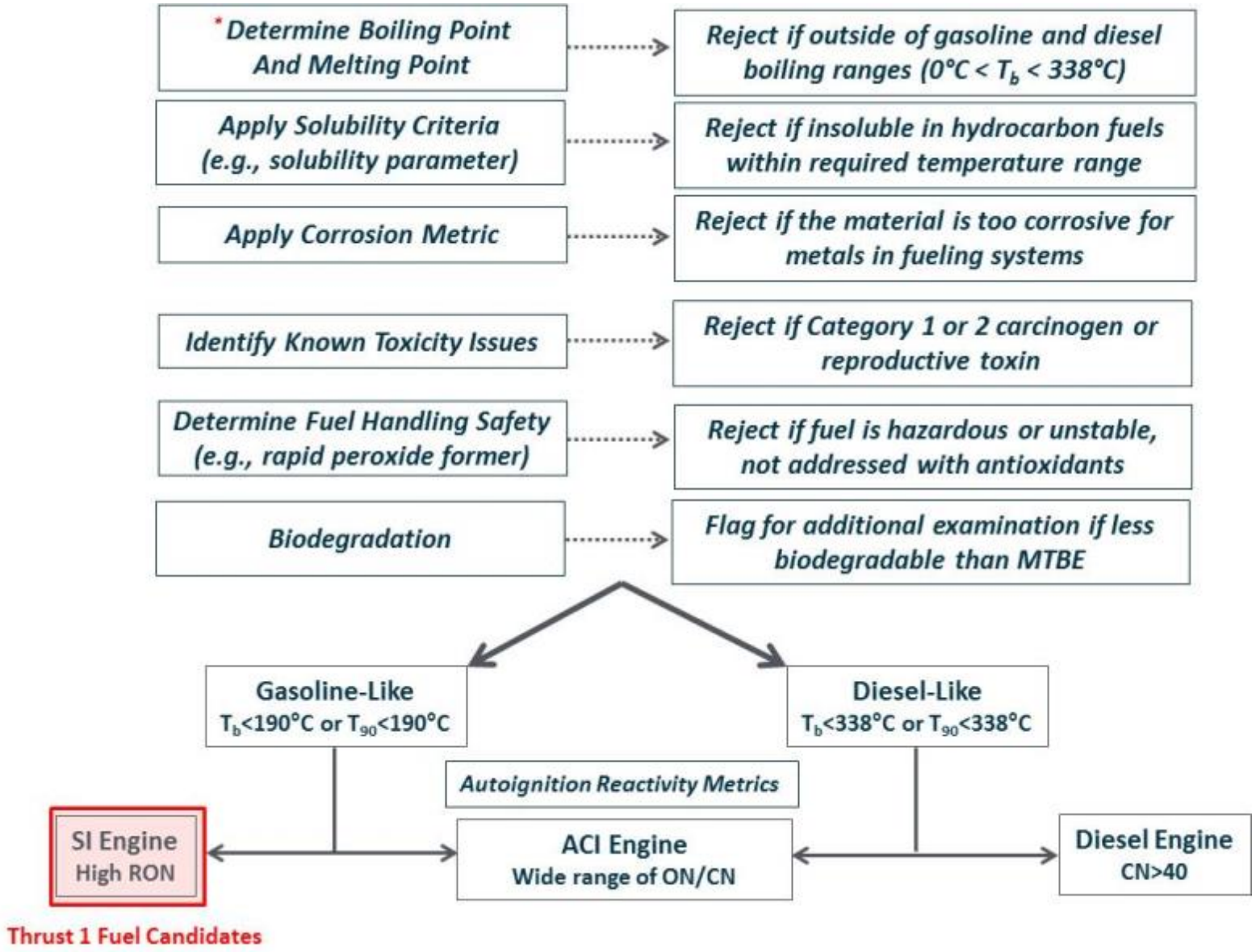
- Develop strategy for screening large numbers of candidate bio-blendstocks to select most promising based on fuel properties

Approach

- Three tier evaluation protocol



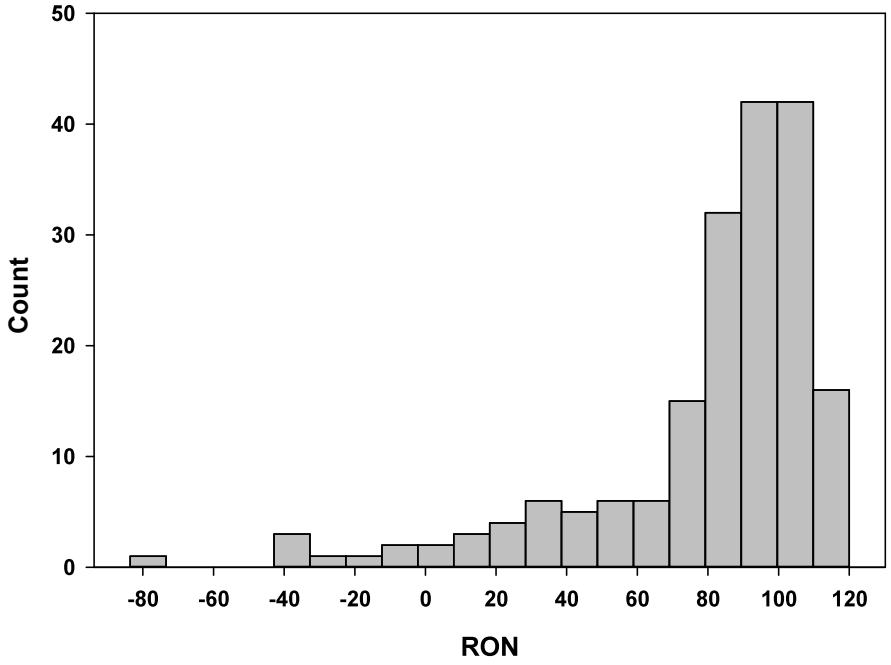
Tier 1 Screening for Thrust I Candidates



Accomplishment: Selection of Most Promising Thrust I Bio-Blendstocks

For Thrust I (advanced SI engines) apply Tier 1 Criteria:

- Melting point/cloud point below -10°C
- Boiling point between 20°C and 165°C
- Measured or estimated RON ≥ 98
- Meet toxicity, corrosion, solubility, and biodegradation requirements
- 34 promising bio-blendstocks from all functional group classes – ***strong matrix for testing central fuel properties hypothesis***



2-pentanol	6032-29-7	99.4[a]	Biochemical
Alkanes			
High-Octane Gasoline Blendstock- triptane rich		108[d]	Thermochemical
Alkenes			
4-methylene-1-(1-methylethyl)bicyclo[3.1.0]hexane (sabinene)	3387-41-5	107[c]	Biochemical
Aromatics			
1,3,5-trimethylbenzene (mesitylene)	108-67-8	>120[a]	Biochemical/Chemical
Vertifuel (60%+ aromatics)		105.7[d]	Biochemical/Chemical
Esters			
Acetic acid, methyl ester	79-20-9	>120[a]	Biochemical/Chemical
Butanoic acid, methyl ester	623-42-7	107.2[a]	Biochemical/Chemical
Pentanoic acid, methyl ester	624-	99[b]	Biochemical/Chemical
2-Methyl propanoic acid, methyl ester	547-63-7	103[c]	Biochemical/Chemical
2-Methylbutanoic acid, methyl ester	868-57-5	110.5[a]	Biochemical/Chemical
Acetic acid ethyl ester	141-78-6	118[a]	Biochemical/Chemical

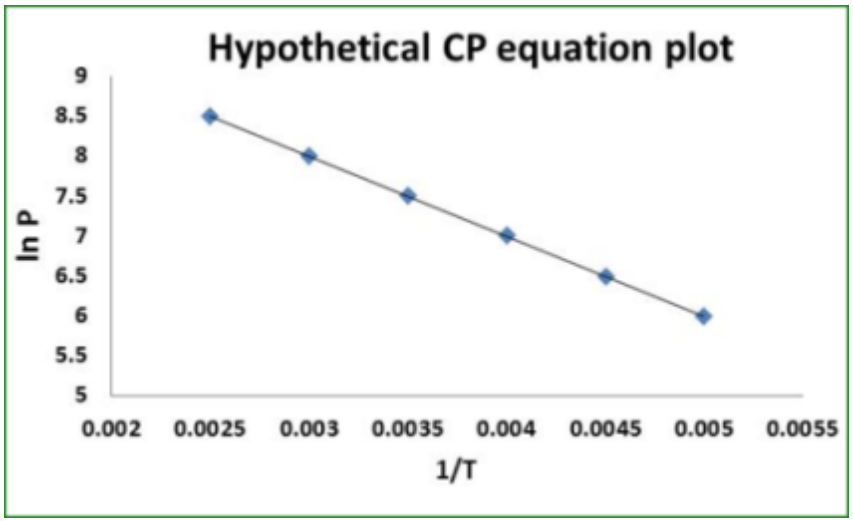
Database Future Developments

- Fully populate property data for most promising candidates
- Add capability for data on finished fuel blends

NREL (Fioroni) $250k: Heat of Vaporization Measurement

Objective

- **Develop methods for measuring heat of vaporization (HOV) of complex mixtures**
- **Measure HOV as a function of fraction evaporated**
- **High HOV fuels may extend knock limit, reduce need for spark retard beyond knock limit, reduce need for rich operation**



$\ln[P_{T1,vap}/P_{T2,vap}] = (\Delta H_{vap}/R)[1/T_2 - 1/T_1]$

P = Vapor pressure

T = temperature in Kelvin

ΔH_{vap} = HOV

R = ideal gas constant

- Pure compound HOV easily measured
  - Measure vapor pressure vs temperature and apply Clausius-Clapeyron equation
- Not applicable to blends such as gasoline

- *The vapor pressure is determined by the most volatile components of the fuel which make up only a small portion of the fuel*
- *This yields an unrealistically low value for HOV*

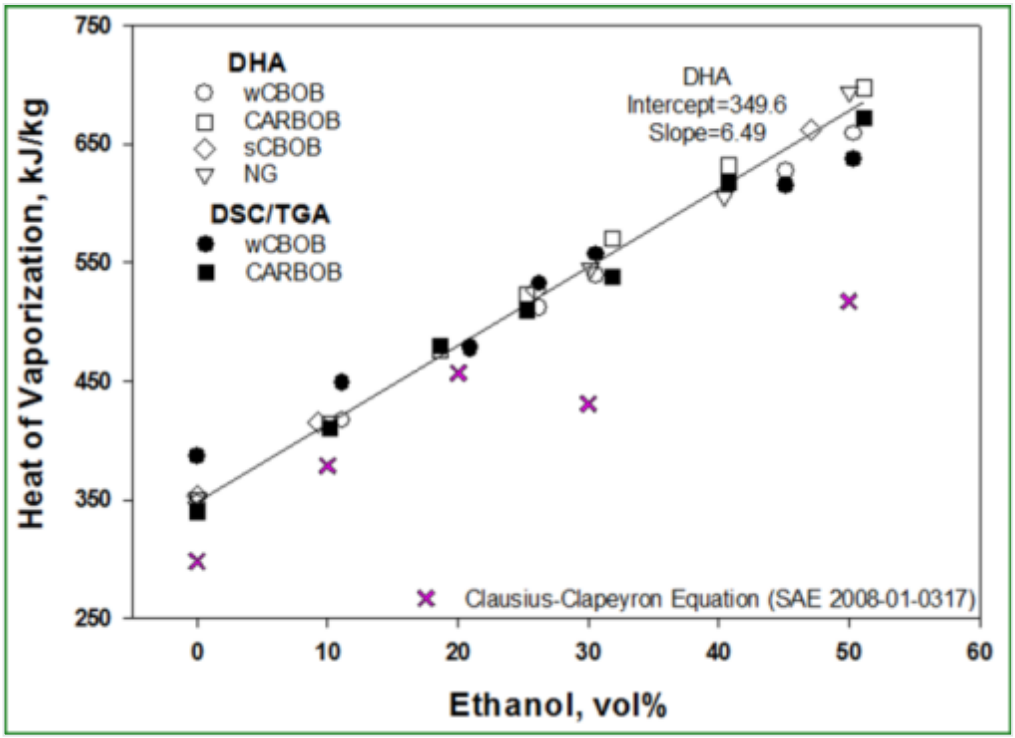
Fioroni: HOV Measurements

Approach

- Directly measure HOV by DSC/TGA
- Calculate HOV from detailed hydrocarbon analysis of gasoline (mole fraction weighted sum of pure component HOV)

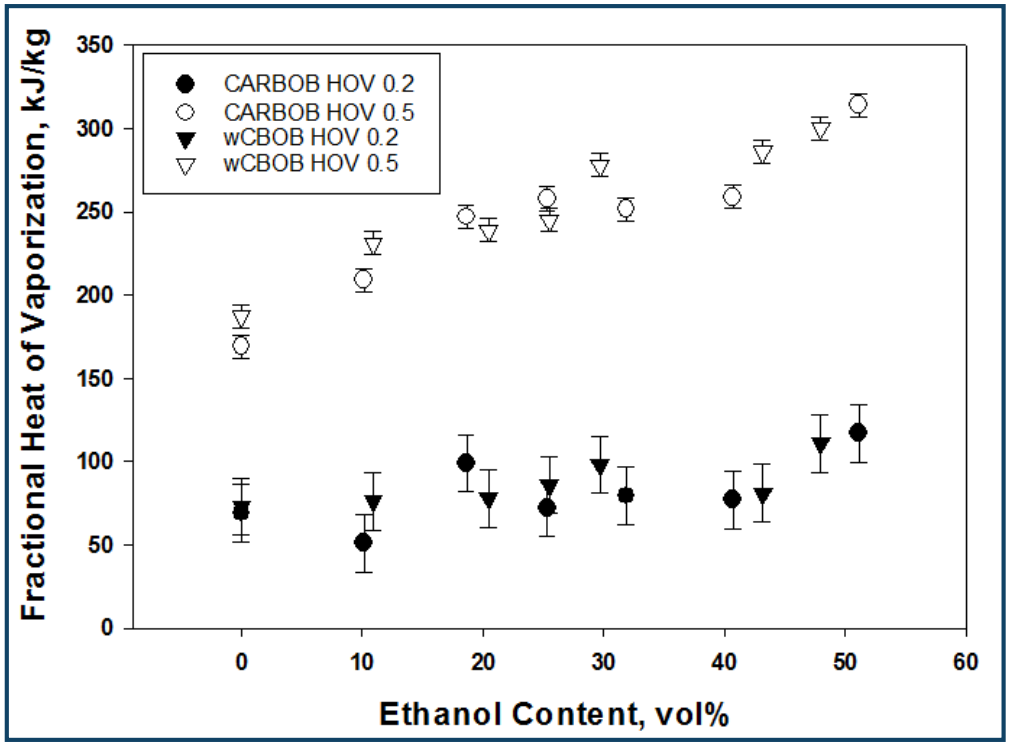
Challenge: highly volatile samples evaporate as they are loaded into the instrument

Solution: Syringe injection of sample, larger sample pans, covered with pin-hole lids



- DSC/TGA measurements agree well with DHA
- Values calculated using the CP equation fall below DSC/TGA or DHA, especially at high ethanol content
- Very similar HOV for wide range of gasolines and ethanol blends

Fioroni: HOV as a Function of Fraction Evaporated



- Effect of ethanol on HOV20 may be negligible
- Increasing ethanol has significant effect on HOV50
- Working to improve precision of this measurement under project with CRC (AVFL-27)

Collaborations:
Coordinating Research Council
University of Colorado

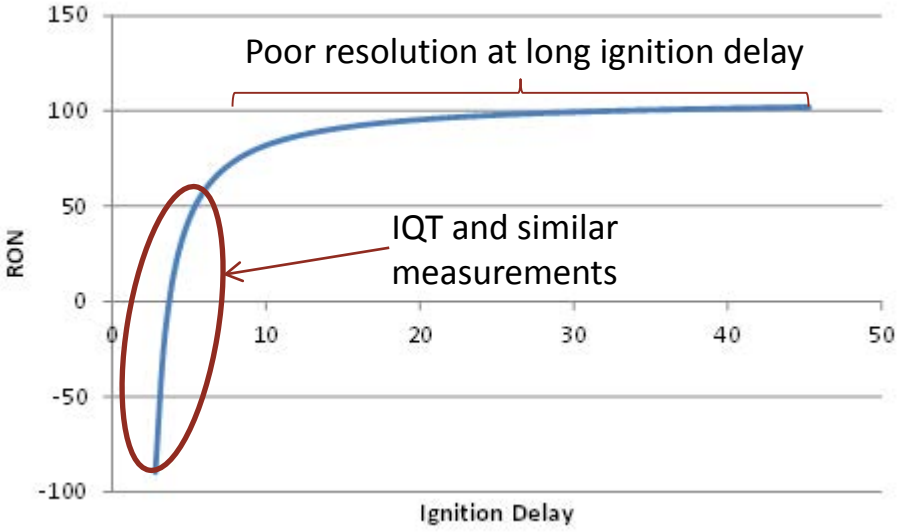
HOV Future Work FY16/17

- **Improve precision of DSC/TGA measurements**
  - **New dedicated instrument**
  - **Couple with much greater precision DSC measurements**
- **Couple with Advanced Distillation Curve experiments and DSC/TGA-MS to reveal composition as fuel evaporates**
- **Collaboration with NREL engine group on actual HOV effects**

Measurement of Autoignition Properties with Small Volumes

Background

- Providing early-stage feedback to identify promising fuel candidates, accelerate progress and eliminate effort and expense associated with unnecessary scale-up.
- Focused on using <u>milliliter volume samples</u> to characterize the autoignition behavior of fuels, the property that is the most problematic to predict.



Objectives

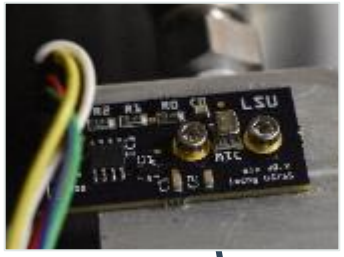
- Measure autoignition kinetics, or a variable correlated with common autoigntion metrics such as RON or CN, using a very small volume of material

Three projects in various stages:

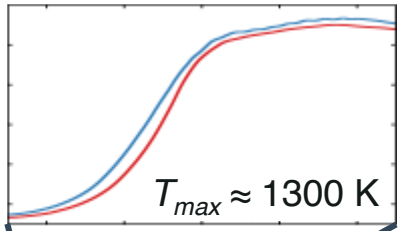
- LLNL (McNenly): Flames with Repetitive Extinction & Ignition
  - Ongoing Collaboration with Louisiana State University
- NREL (McCormick): Flow Reactor for Small Volume Autoignition Experiments
  - FY16 Start
- ANL (Goldsborough): RCM as a Small Volume Autoignition Experiment
  - FY16 Start

LLNL (McNenly) $75k: µFIT: Micro-liter Fuel Ignition Tester
Flames with Repetitive Extinction & Ignition (FREI)

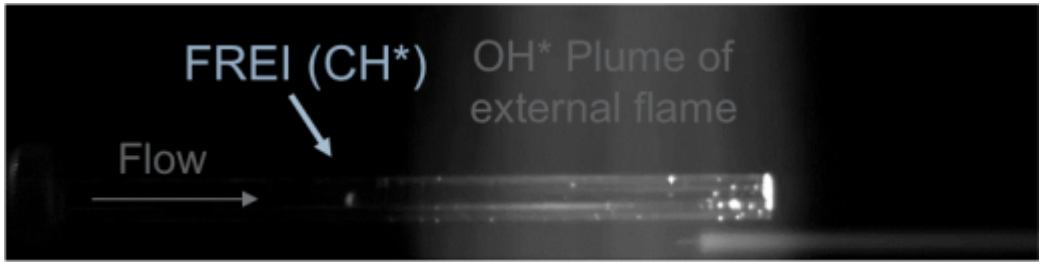
MEMS microphone



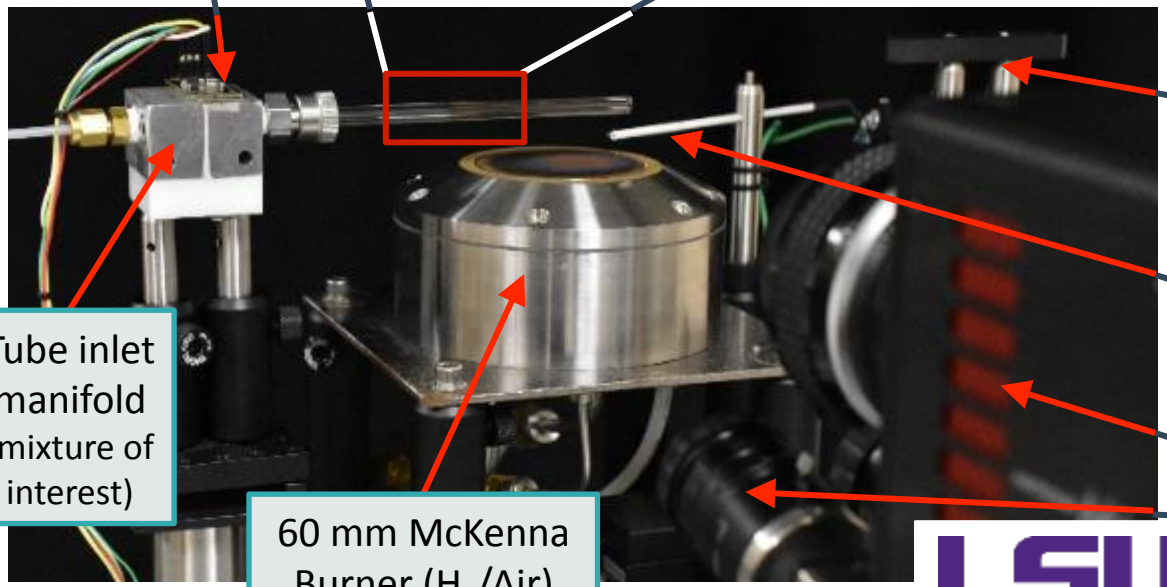
Quartz Tube
(with imposed wall temperature profile)



High Speed Videos (2000 fps; 2mm ID tube)



with 430 nm bandpass (CH*)



Translation stage for wall temperature characterization
(thermocouple not shown)

Monitoring thermocouple

High-Speed and Machine Vision Cameras

Tube inlet manifold
(mixture of interest)

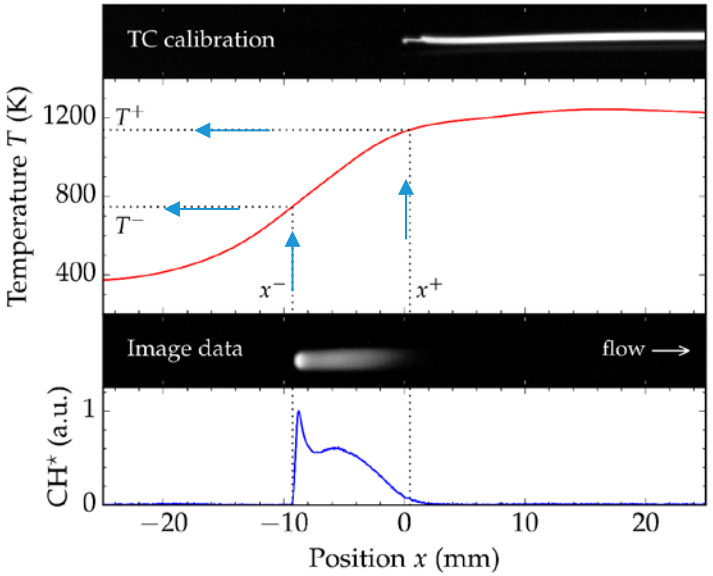
60 mm McKenna Burner (H_2/Air)
(external heating)

LSU

McNenly: µFIT: Micro-liter Fuel Ignition Tester

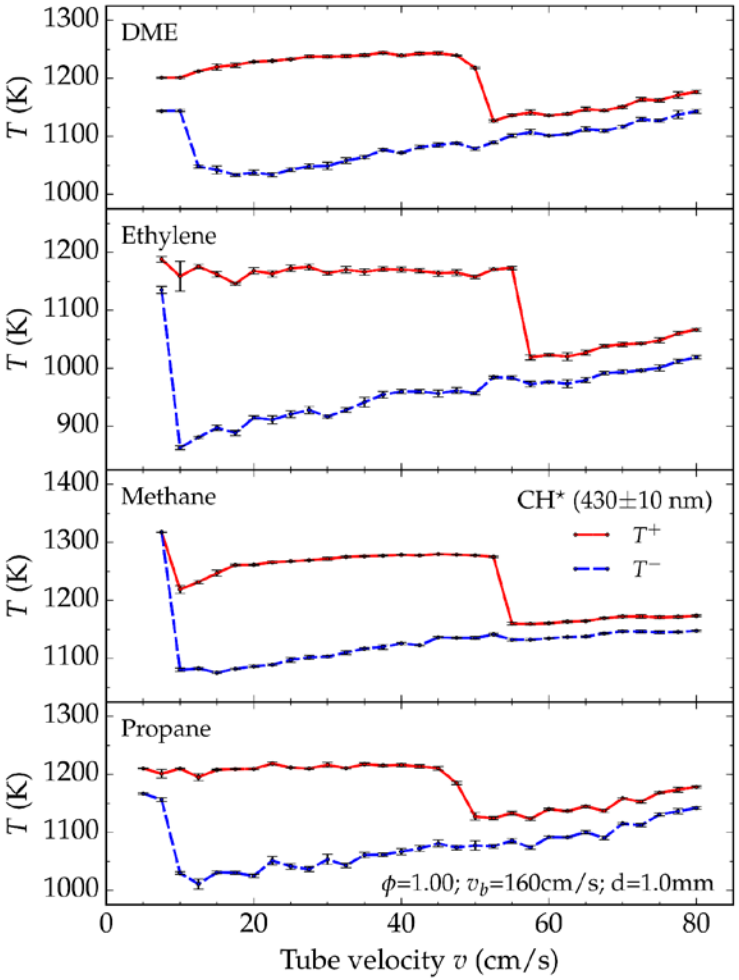
Flames with Repetitive Extinction & Ignition (FREI)

TC data plus low-speed images yield temperatures



FREI characteristics (T^+ and T^-) depend on fuel

Fuel consumption:
gases: 1-10 sccm/min
liquids: 1-5 µl/min



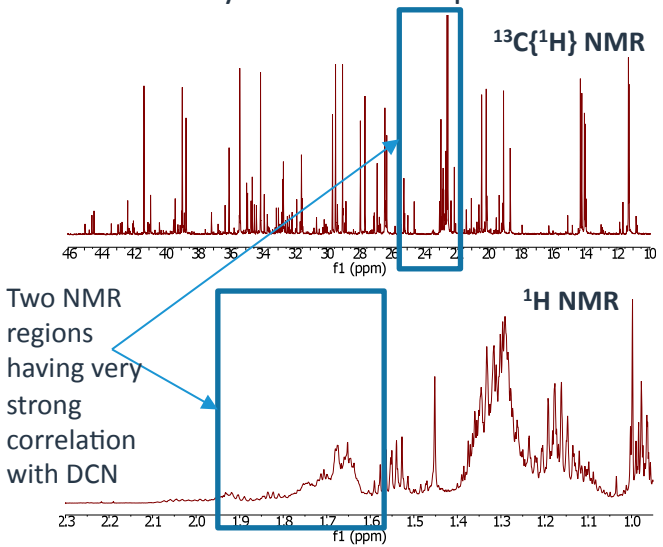
Remaining work plan for FY 2016:

- Reduce temperature measurement uncertainty
- Continue and improve measurements for liquid reference fuels (iso-octane, n-heptane & toluene)
- Redesign burner to prepare for experiments at elevated pressures

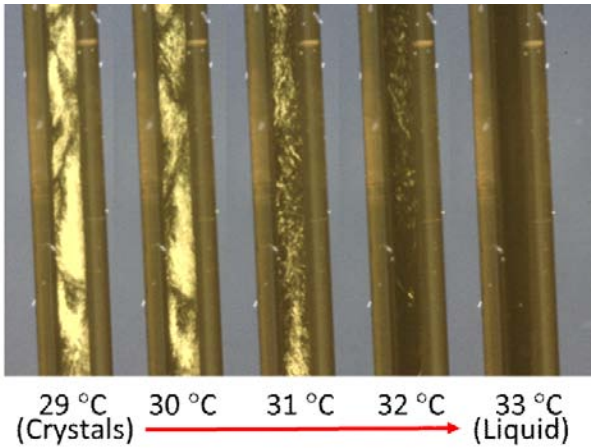
PNNL (Bays) 150k: Fuel Structure-Property Correlations

- Objective – Correlate fuel performance properties to chemical & solution structures in complex fuels
- Impact – Achieve the ability to *rapidly predict properties, like DCN, from < 1 mL of fuel*
- Approach
  - Use NMR/2D-GC to investigate fuel structure-property correlations, emphasizing DCN/RON prediction
  - Understand high-pressure phase behavior of fuels
- Future Work
  - Correlations to other properties, e.g., distillation or P_{vap}
  - P-T behavior beyond diesel surrogate fuels to fuels relevant to Co-Optima

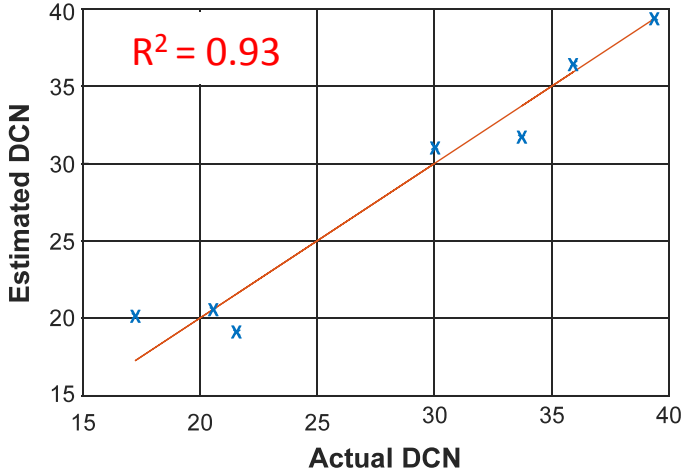
^{13}C and ^{1}H NMRs of an Upgraded Biomass Hydrothermal Liquefaction Oil



Final Melting Point of *n*-Octadecane Crystals in Surrogate 3 at 10,000 psi*



DCN Prediction from a *Single* ^{13}C NMR Region (24.5-22 ppm)



*Results are preliminary. Final results are expected to be within 10% of presented values.

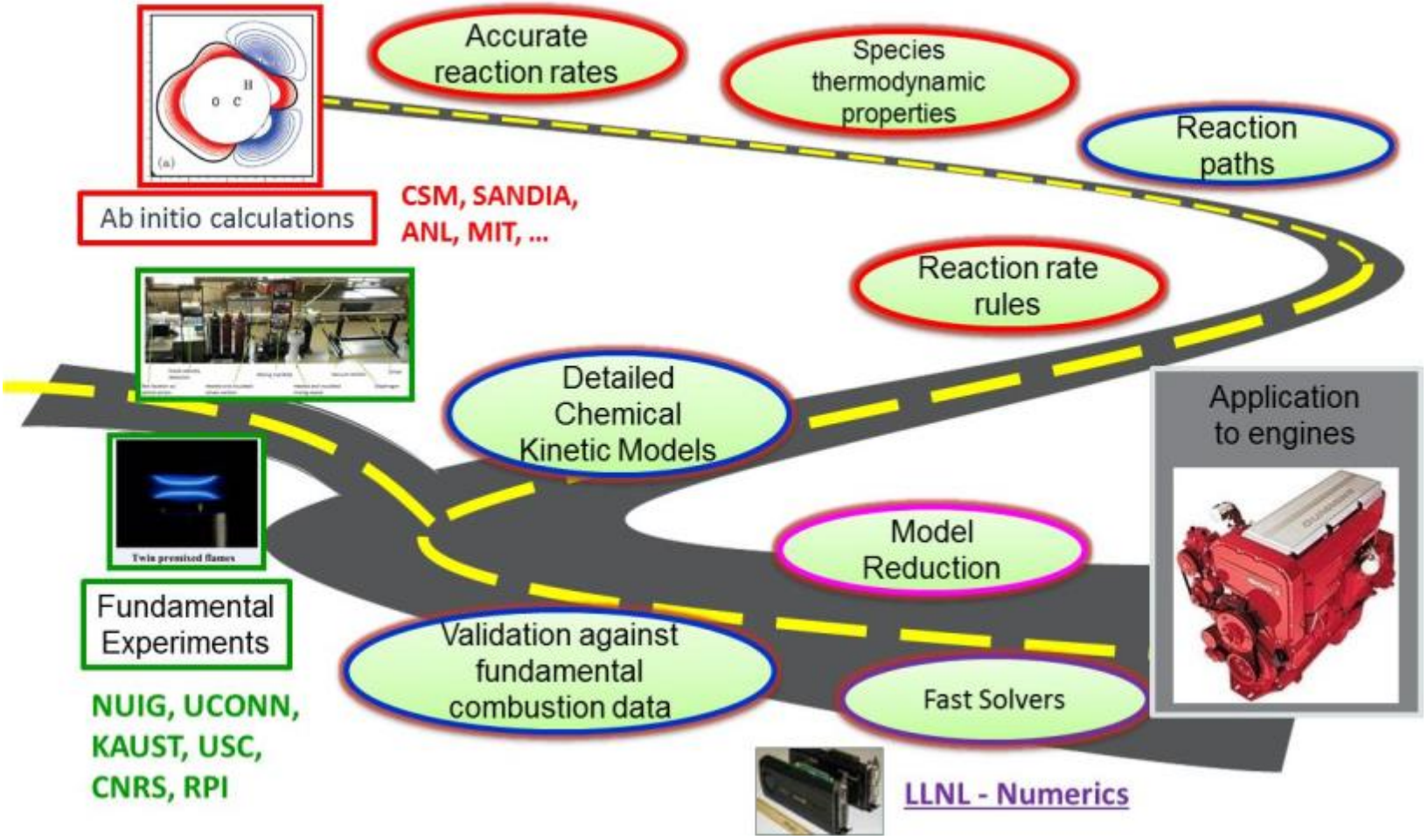
Work conducted in collaboration with CRC Project AVFL-18a.

LLNL (Pitz) $500k: Kinetic Mechanism Development

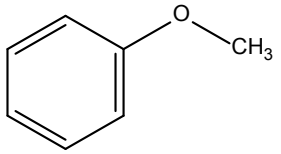
Objective:

- **Develop and validate chemical kinetic models for various bio-blendstocks and fuel surrogates**

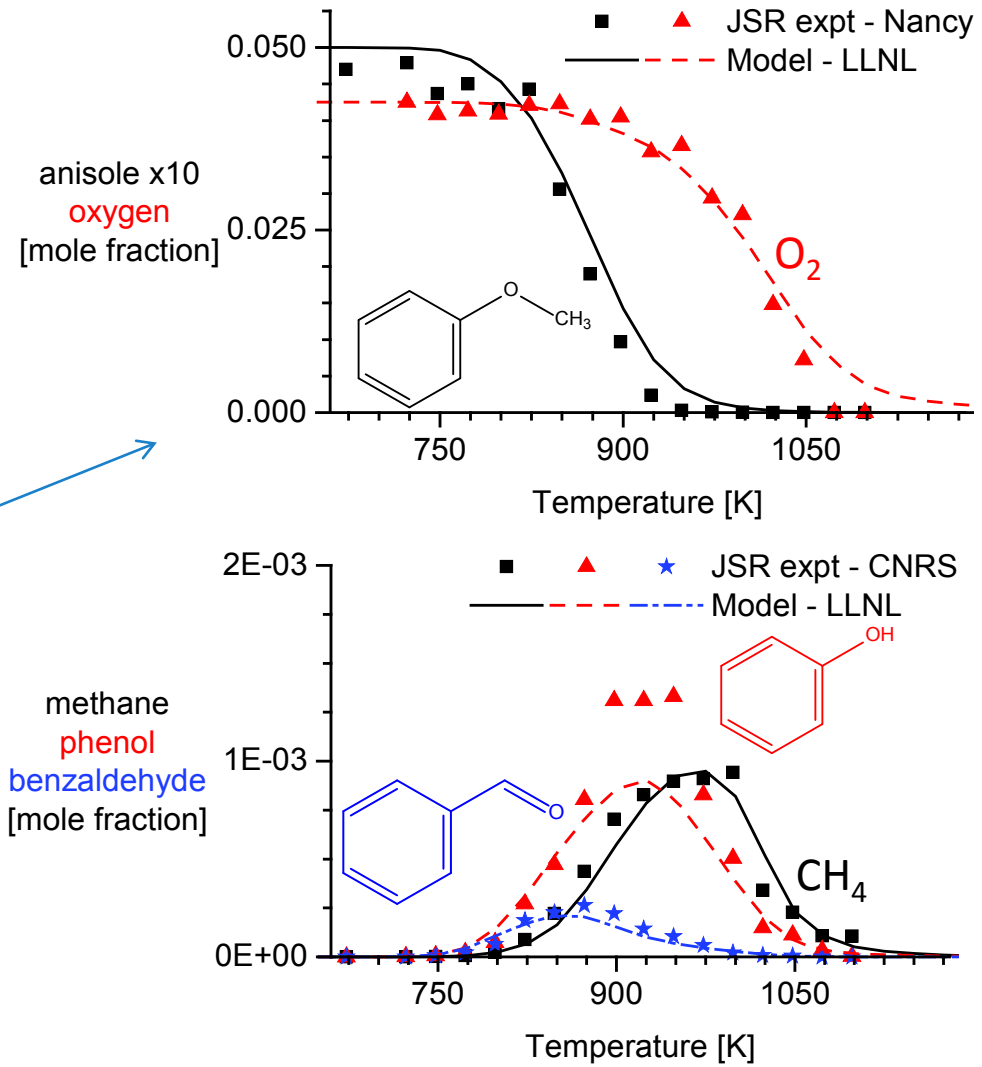
Approach:



Pitz: Development of kinetic mechanism for anisole, a bio-derived fuel



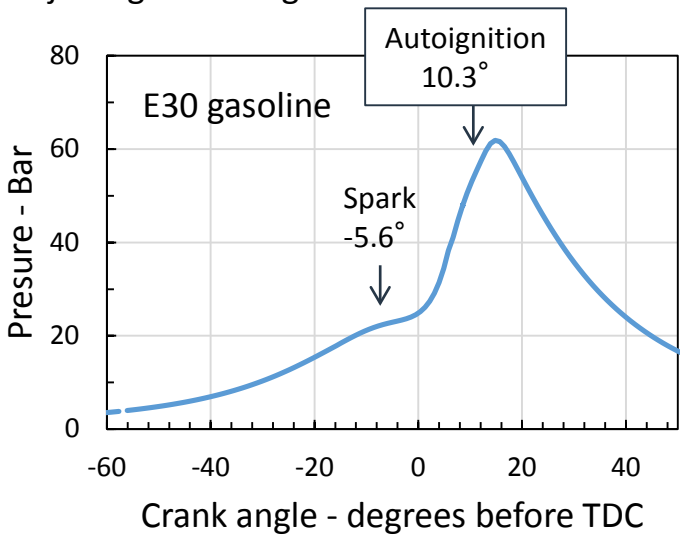
- Surrogate for methylated phenolics stream produced from biomass
- On Co-Optima list of most promising Thrust I candidates
- RON = 119, Sensitivity = 21
- LLNL preliminary mechanism complete
- Comparison of mechanism with intermediate species data
- Collaborators measuring ignition delay times (NREL), laminar burning velocities (Lund Univ.) and more intermediate species at high pressure (CNRS, Orleans) for additional validation

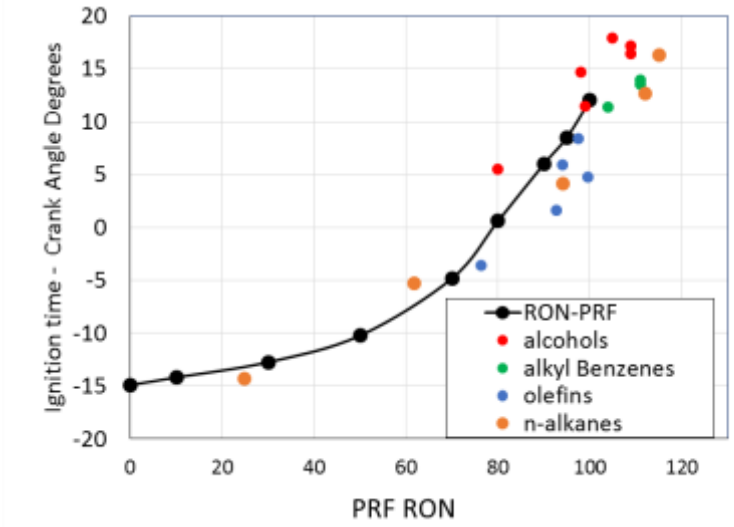


Jet stirred reactor experimental data:
Nowakowska, Herbinet, Dufour, Glaude, Combust. Flame (2014)

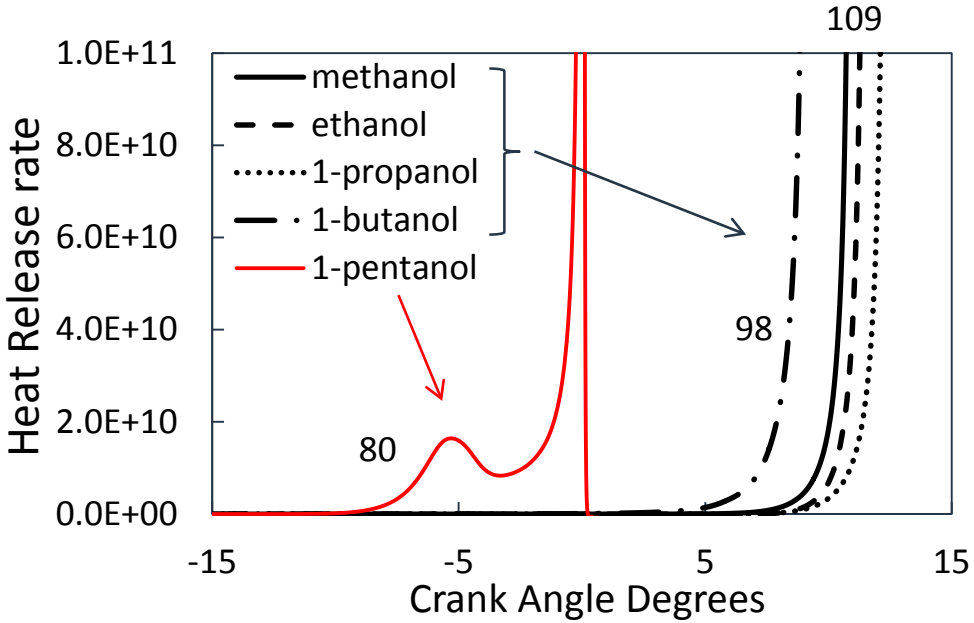
Pitz: Investigation of the effect of molecular structure on ignition behavior at RON-like engine conditions

- RON-like pressure history from Magnus Sjöberg's DISI engine at Sandia





- Heat release curves for different alcohol chain-lengths for a RON-like engine pressure trajectory:

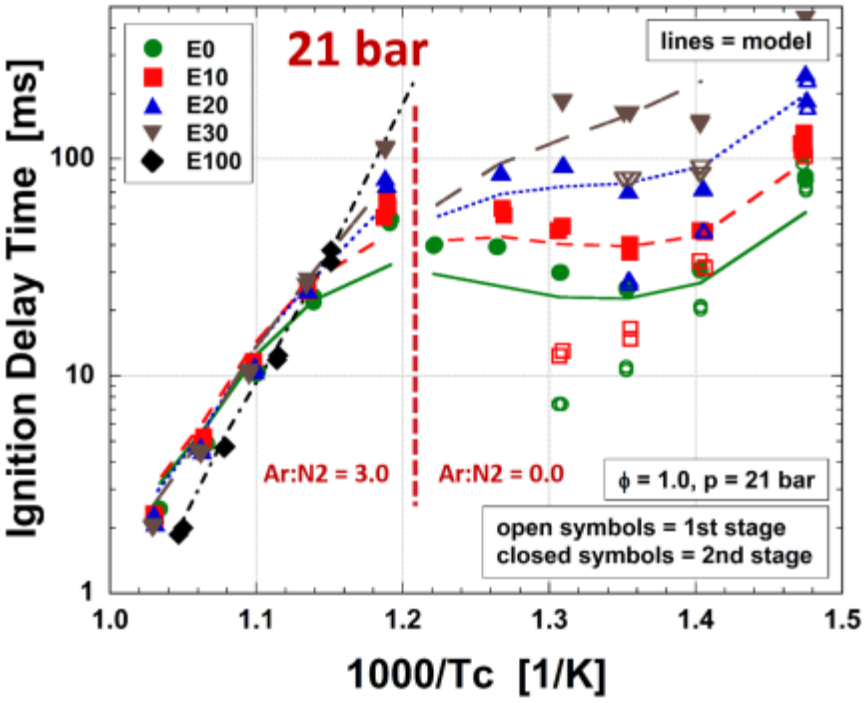


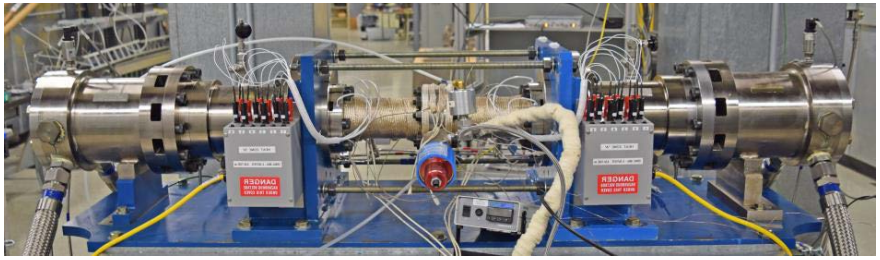
(Numbers on plot are RON values)

- RON predictions for a series of fuels in different chemical classes using RON-like pressure history

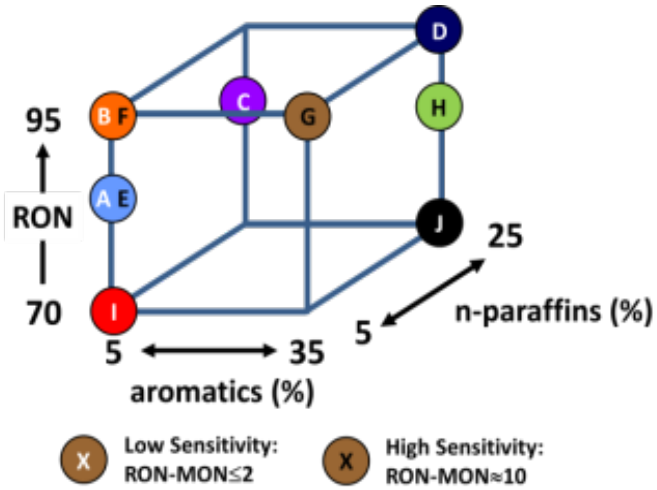
ANL (Goldsborough) $250k: Rapid compression machine (RCM) investigation of gasoline mixtures with ethanol and validation of surrogate mechanism

- ANL rapid compression machine
- CRC FACE-F / Ethanol blends (E0–E30, E100)
- LLNL kinetic mechanism for gasoline surrogate





Ignition Delay Time [ms]



Fuels for Advanced Combustion Engines (FACE)-F:

- RON = 94.4
- Sensitivity = 5.6
- Aromatics: 8.6%
- n-Paraffins: 4.2%
- Naphthenes: 11.0%
- Olefins: 8.9%

ANL (Goldsborough) $250k: Rapid compression machine (RCM) investigation of gasoline mixtures with ethanol and validation of surrogate mechanism

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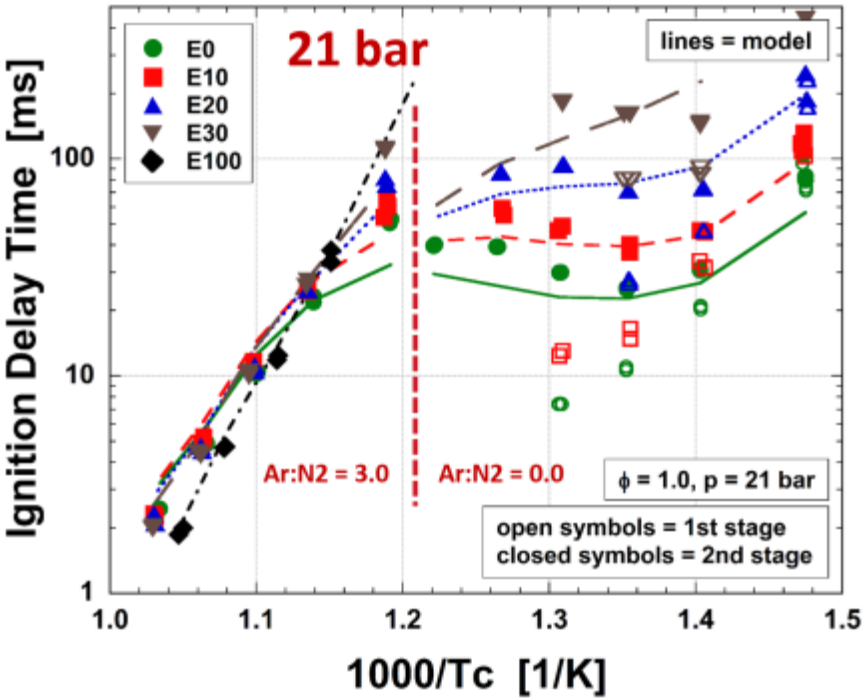
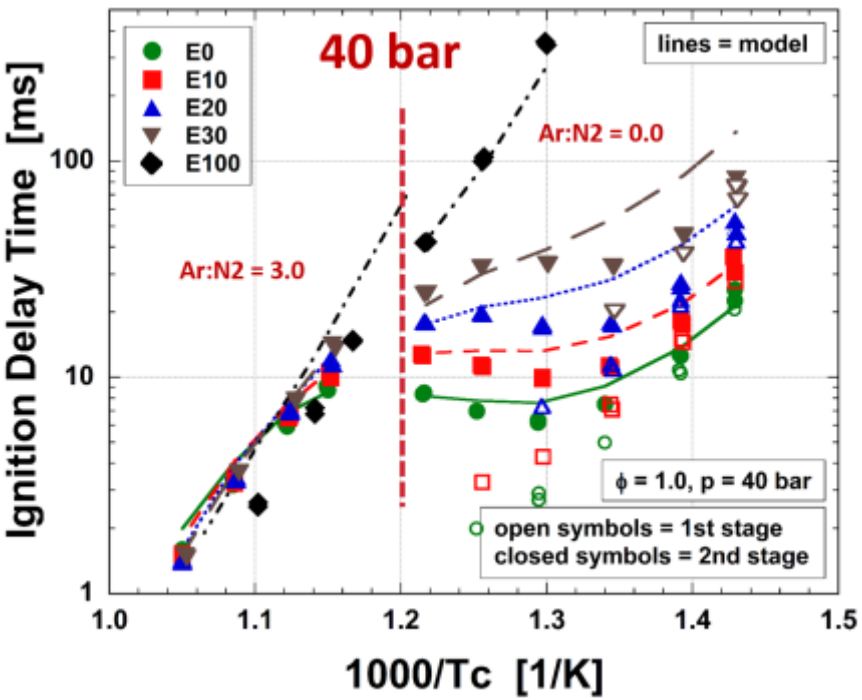
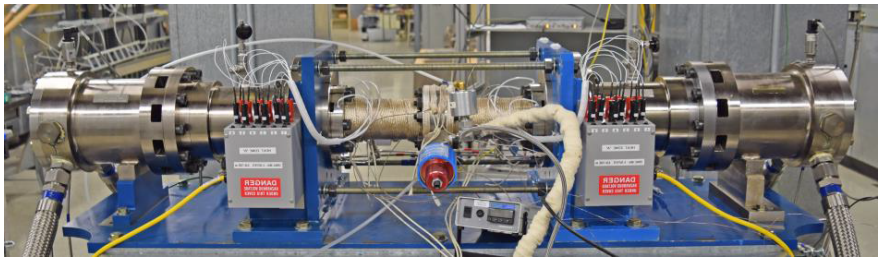






NREL (Zigler) $550K: Chemical Kinetics and SI Autoignition Behavior

Objectives

- Assist in *development and validation of chemical kinetic mechanisms for blends* through ignition delay experiments and simulations.
- Combine bench-scale autoignition studies with engine experiments to *more extensively quantify fuel blend ignition performance* than possible with RON and MON.

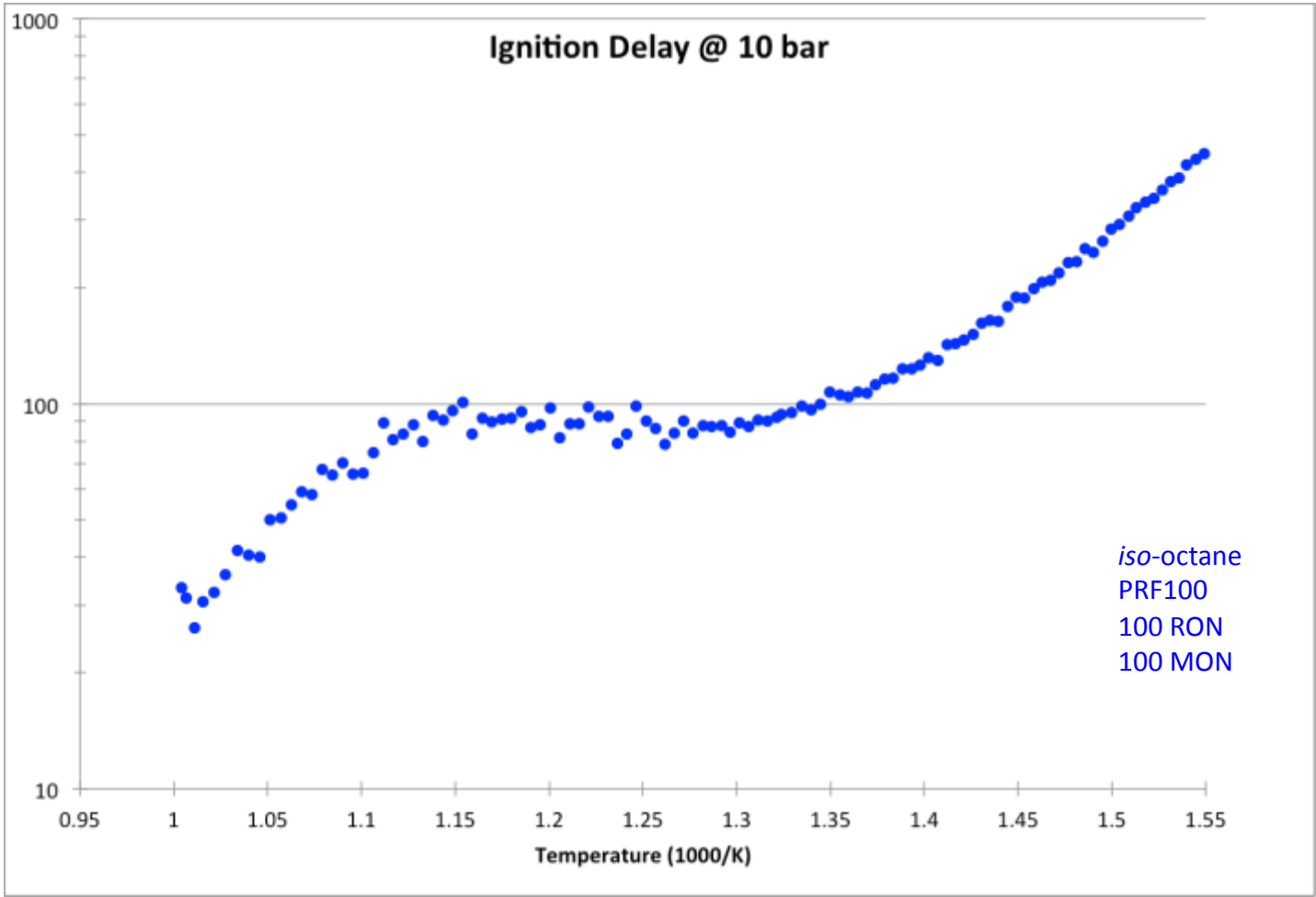
Approach

- Employ a modified Ignition Quality Tester (IQT) to measure ignition performance of biofuel compounds blended into both key simple surrogate mixtures, and more complex gasoline range research fuels.
- Perform computational fluid dynamics (CFD) simulations of IQT to evaluate reduced kinetic mechanisms for blends against experimental data.
- Evaluate IQT-based data to highlight key kinetic behavior related to how ignition delay increases at low temperatures in relation to increased octane sensitivity.
- Characterize all fuels used in NREL's engine experiments (and several engine studies from other labs, including gasoline compression ignition) with the IQT.
- Begin correlation of IQT data to fuel chemistry and engine results.

Zigler: Ignition delay experiments assist in development of kinetic mechanisms for biofuel blends

- Temperature sweeps at several fixed pressures provide experimental data to develop accurate *kinetic mechanisms for blends* of biofuels into key gasoline surrogates.
- Simulations of IQT enable a development feedback loop for validation of mechanisms against engine-relevant experimental data.

- The critical negative temperature coefficient (NTC) region is mapped.



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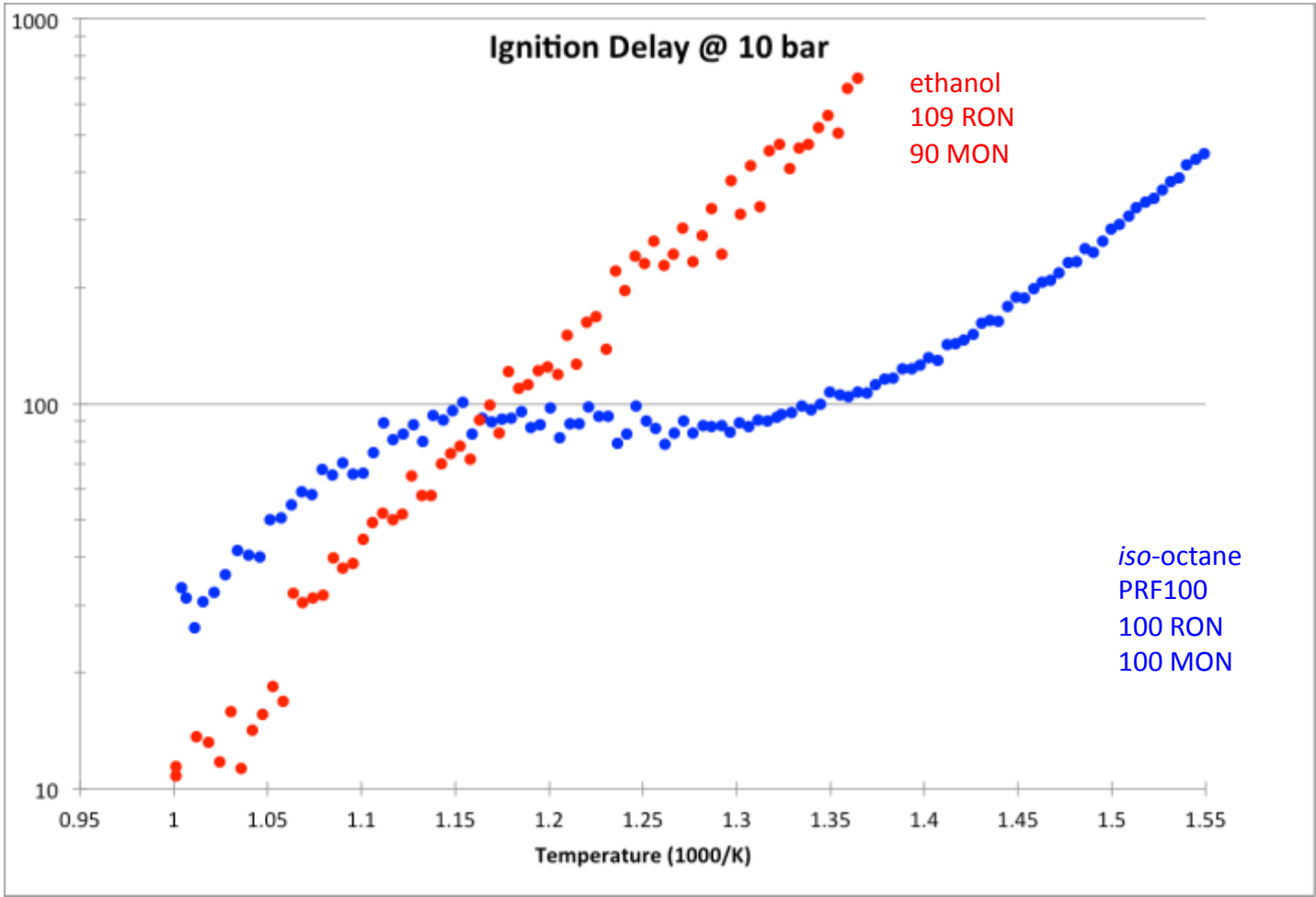
- Temperature sweeps at several fixed pressures provide experimental data to develop accurate *kinetic mechanisms for blends* of biofuels into key gasoline surrogates.
- Simulations of IQT enable a development feedback loop for validation of mechanisms against engine-relevant experimental data.

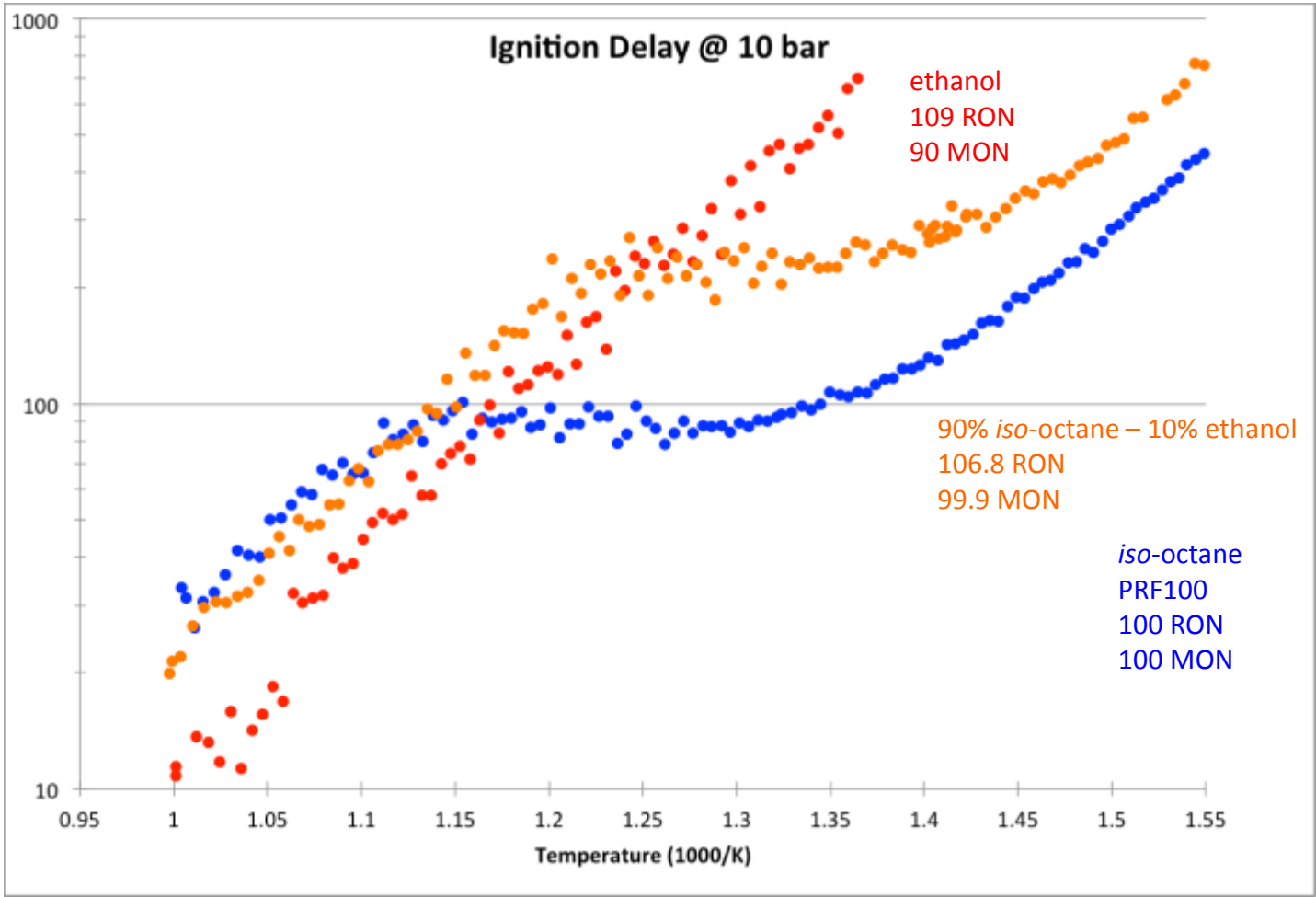
- The critical negative temperature coefficient (NTC) region is mapped.
- Note ethanol (109 RON) has shorter ignition delay at high T than *iso*-octane (100 RON).



Zigler: Ignition delay experiments assist in development of kinetic mechanisms for biofuel blends

- Temperature sweeps at several fixed pressures provide experimental data to develop accurate *kinetic mechanisms for blends* of biofuels into key gasoline surrogates.
- Simulations of IQT enable a development feedback loop for validation of mechanisms against engine-relevant experimental data.

- The critical negative temperature coefficient (NTC) region is mapped.
- Note ethanol (109 RON) has shorter ignition delay at high T than *iso*-octane (100 RON).
- A 10% ethanol blend increases ignition delay while maintaining NTC behavior,



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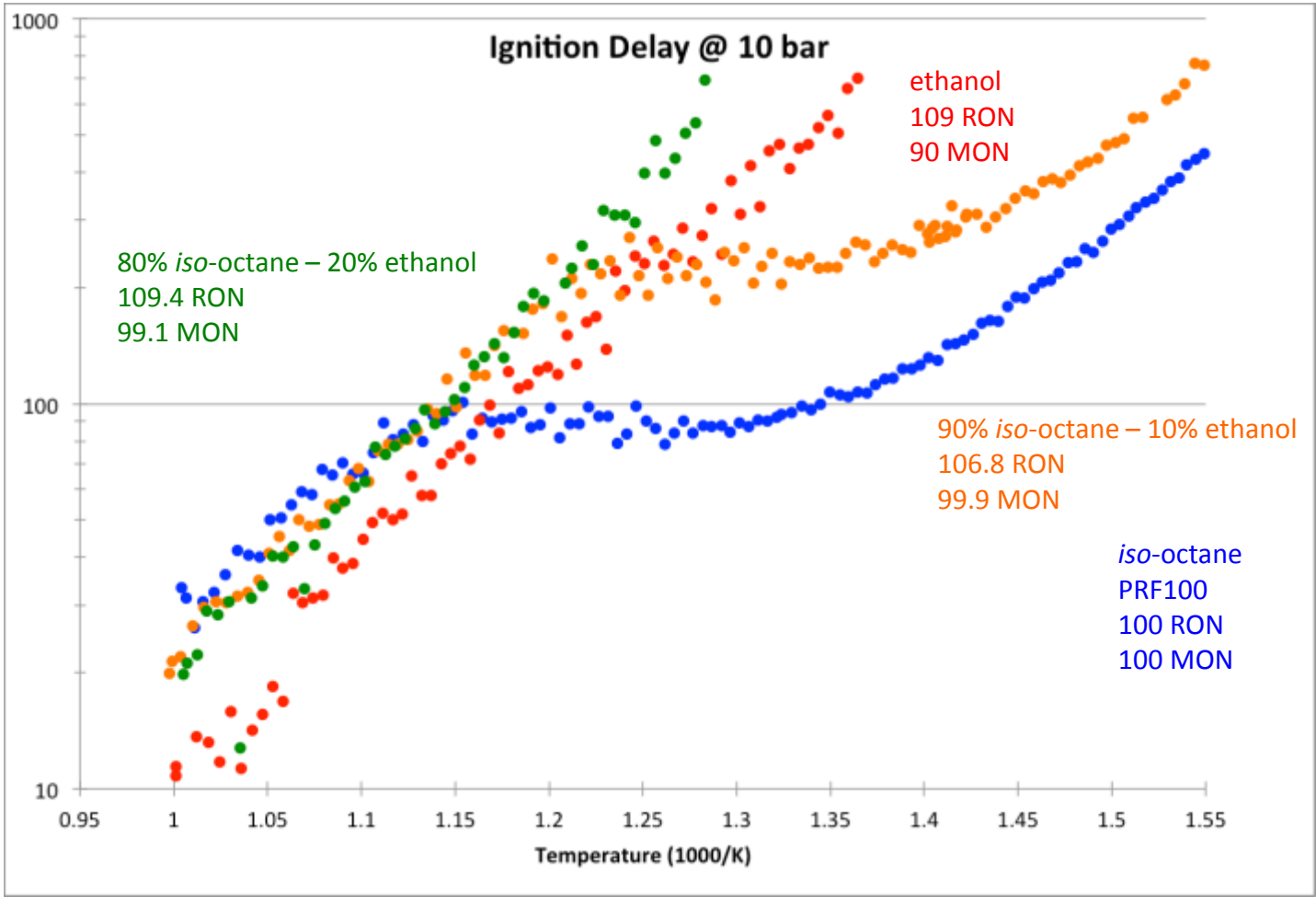
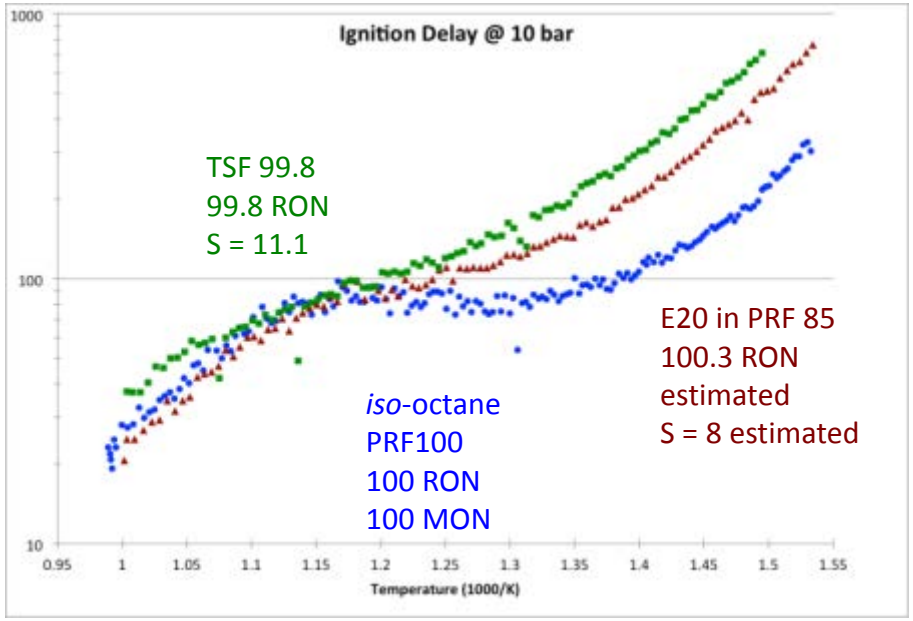
- Note ethanol (109 RON) has shorter ignition delay at high T than *iso*-octane (100 RON).
- A 10% ethanol blend increases ignition delay while maintaining NTC behavior,
- But a 20% ethanol blend eliminates NTC behavior while increasing ignition delay over neat ethanol in that region.

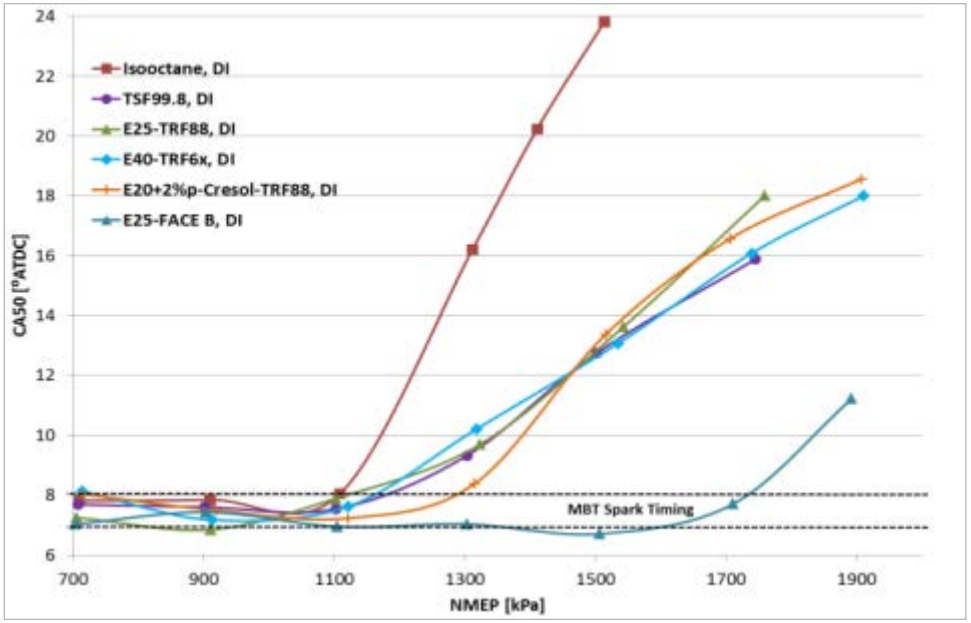


Zigler: Ignition delay experiments provide more insight to engine results beyond RON and octane sensitivity

- Temperature sweeps at several fixed pressures provide experimental ignition delay data (rather than just RON or MON), including *how ignition delay increases at low temperatures in relation to increased octane sensitivity (S)*.
- The IQT data *will be correlated with engine data* focusing on load extension possible using spark retard with high S fuels.

- In this study of ~100 RON fuels, increasing octane sensitivity correlates with increased ignition delay at lower temperatures.
- IQT data offer insight why increased load is possible with retarded spark timing, where end-gas follows lower temperature trajectory with increased ignition delay times.
- Engine studies show that higher S enables increased load via spark retard (following presentation).

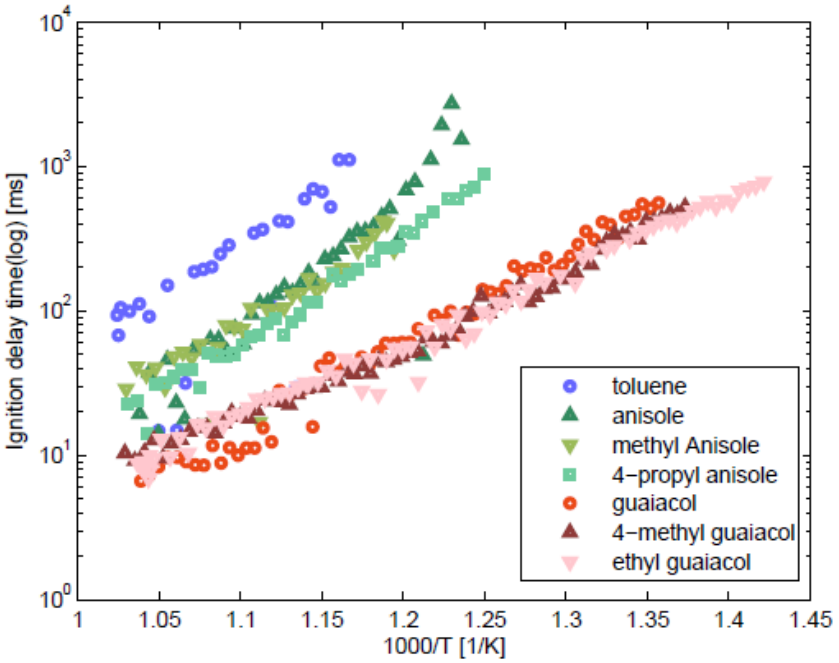


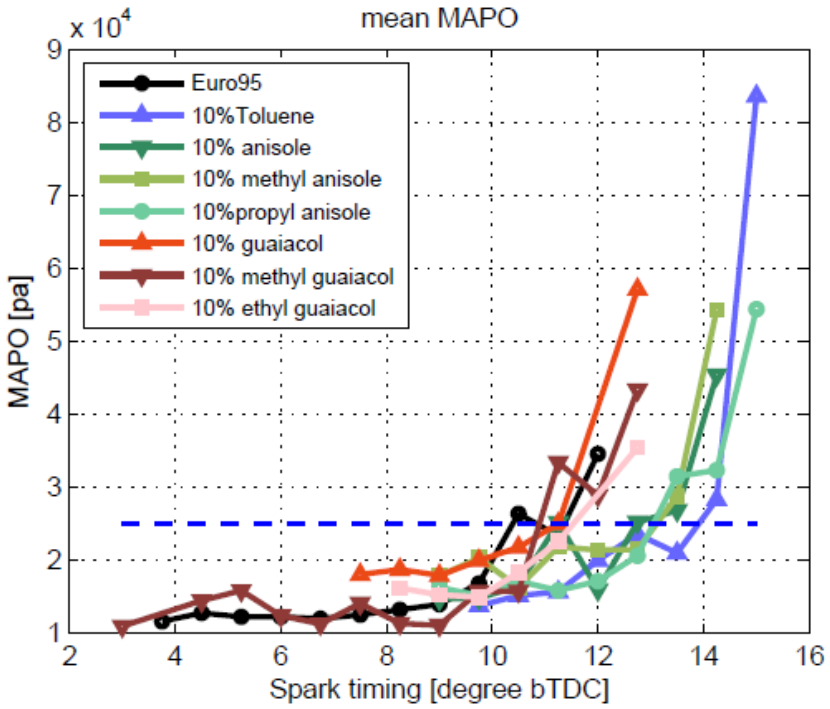


NREL: Ignition delay experiments assist in development of kinetic mechanisms for biofuel blends

- Temperature sweeps at several fixed pressures provide experimental ignition delay data (rather than just RON or MON), to examine biomass-oxygenate structure effects on engine knock resistance.
- IQT data is being correlated with engine data to explain oxygenate structure effects.

Tian, M., Ratcliff, M., McCormick, R.L., Luecke, J., Yanowitz, J., Glaude, P.-A., Cuijpers, M., Boot, M.D., "Evaluation of Lignin Based Octane Boosters in a Spark Ignition Engine" submitted.





Future work: kinetics

Pitz

- Develop surrogate mixture models for gasoline fuels to be used in Co-Optima:
  - Three RON 98 reference gasoline fuels: alkylate, reformate and ethanol-containing
  - Base fuel(s) selected for blending with bio-derived blendstocks
- Simulate SI and CI engine experiments :
  - with RON 98 gasolines for
    - constant octane sensitivity obtained from aromatics or ethanol
    - octane sensitivity varied
  - using basefuel(s) combined with Tier 2 bio-derived blendstocks
- Use kinetic models to investigate high-sensitivity fuels deriving octane sensitivity from aromatics or olefins. Is there a significant difference autoignition resistance at Thrust 1 conditions?
- Develop/validate component kinetic models to represent missing chemical classes in Tier 2 blendstocks (ketones and methyl furan)
- Investigate blendstocks that can probe the most beneficial fuel properties (resistance to autoignition and high flame speed) for Thrust 1 conditions.

Zigler

- Expand IQT ignition kinetics studies of key surrogate blends beyond ethanol to include other biofuel compounds of interest, in coordination with kinetics sub-team (within FP team), and AED and LGGF teams
- Incorporate IQT-based parametric ignition delay data in engine simulation knock integral calculations to correlate to engine-based experimental data
- Focus more experimental studies and kinetic model simulations on relationship between octane sensitivity, increased ignition delay time at lower temperatures, and engine load extension possible with spark retard and high S (includes tighter collaboration with LLNL)
- Expand collaboration with other labs on studying fuels used in their engine experiments in the IQT (e.g., collaboration with ANL on gasoline compression ignition)
- Begin industry collaboration (including via CRC) of using IQT-based experimental studies to provide more ignition performance data for fuel / engine studies

Fuel Properties Team Research Summary

Relevance

Fuel Properties research is the crucial link between fuel production (LGHG Fuels Team) and engine combustion (Advanced Engine Development Team) and testing of the central fuel properties hypothesis investigated within “Co-Optima.”

Approach

Careful measurement of fuel properties, development of new fuel property measurement methods, and targeted engine experiments directed at revealing fuel property effects – all based on a fuel matrix designed to go well beyond the chemistry represented by conventional petroleum-derived fuels.

Accomplishments

- In collaboration with LGHG Fuels Team, a fuel property database was constructed and populated
- A three tier fuel screening process was developed. Tier 1 screening for Thrust I (SI) fuels was performed and a list of most promising advanced SI engine bio-blendstocks developed
- New methods for measuring fuel heat of vaporization were developed and are being refined
- Small volume autoignition testers are being developed for rapid fuel screening using milliliter volumes
- Correlations between easily measured chemical parameters and fuel properties are being developed
- Validated combustion kinetic models for important bio-blendstocks and fuel surrogates are being developed based on RCM and IQT kinetic data

Collaborations

- “Co-Optima” has 9 National Labs, stakeholder engagement, and external advisory board
- Projects presented also represent extensive collaborations with industry and universities

Future Work – A portfolio of ongoing and future work is described

Co-Optimization of Fuels and Engines
Fuel Property and Advanced Engine Development Team

Thrust I engine projects

June 9th, 2016

Jim Szybist,[1] Scott Sluder, [1] Matt Ratcliff, [2] Thomas Wallner, [3] Derek Splitter, [1] Andrew Ickes, [3] Christopher P. Kolodziej,[3] Bob McCormick,[2] Paul Miles [4]

1. Oak Ridge National Laboratory
2. National Renewable Energy Laboratory
3. Argonne National Laboratory
4. Sandia National Laboratories

Co-Optima DOE VTO Management Team: Kevin Stork and Gurpreet Singh

overview: thrust I engine projects

Thrust I engine projects focus on Spark Ignition combustion strategies with a focus of understanding the effects of fuel properties

Overarching Fuel Property Hypothesis: If we understand the ***critical fuel properties*** correctly, then fuels with those properties will provide comparable performance regardless of the chemical composition.

Merit Function	
Efficiency Benefits of High Octane Fuels	**ORNL Sluder**
Effects of RON, HoV, and Octane Sensitivity	**NREL Ratcliff** ANL Kolodziej/Ickes
Dilution Limits on SI Combustion	**ORNL Szybist** ANL Kolodziej/Wallner
Fuel Effects on LSPI	ORNL Splitter

milestones for Thrust I engine projects are either complete or on-track

Tracked co-optima milestones

Q2. Quantify vehicle fuel efficiency gains from the use of a ~98 RON gasoline in combination with increased compression ratio using the Ford 1.6L engine (ORNL Sluder) **Complete**

Q3. Determine the strengths and deficiencies that exist in using flame speed to predict dilution tolerance through experimental and kinetic modelling studies (ANL Kolodziej/Wallner) **On-track**

- **Additional project level milestones are also on-track**

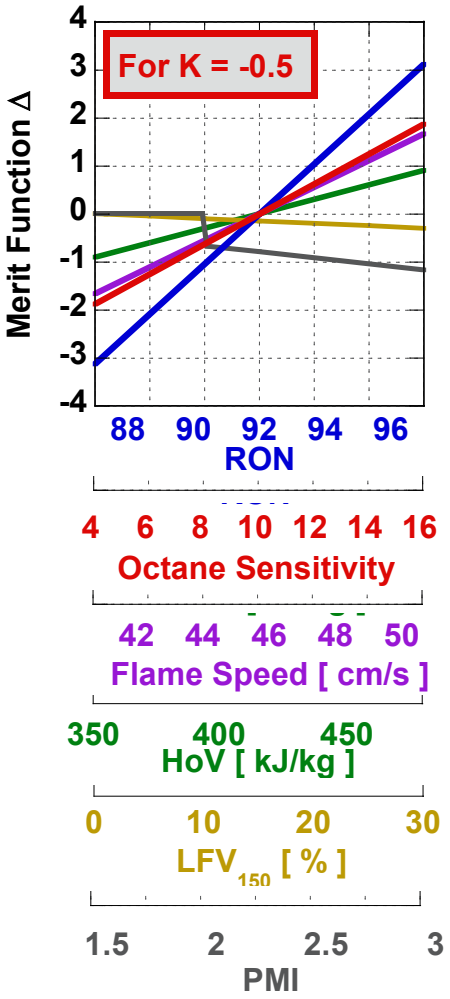
purpose of efficiency merit function for thrust I: tool to rank promising candidates for further study

$$Merit = \sum \frac{(RON_{mix} - 92)}{1.6} - K\frac{(S_{mix} - 10)}{1.6} + \frac{(S_{L\,mix} - 46[cm/s])}{3} + \frac{0.01[ON/kJ/kg](HoV_{mix} - 415)[kJ/kg]}{1.6} + \frac{(HoV_{mix} - 415)[kJ/kg]}{130} - LFV_{150} - H(PMI - 2.0)[0.67 + 0.5(PMI - 2.0)]$$

RON | Octane Sensitivity | Flame Speed | Heat of Vaporization | Distillation | Particulate Emissions

The goal of Thrust 1 engine research is to develop a robust and quantitative understanding on how efficiency is impacted by fuel properties.

- This is an **approach** on how to value properties for efficiency
- This is not a finished product, the merit function will continuously evolve
- We are working to determine if these are the right fuel properties whether we adequately understand their impacts
- The fuel property hypothesis will be tested with biofuels that introduce different chemistry (structures and functional groups)



ORNL (Sluder) $500k: efficiency benefits of high octane fuels

Objectives

- Quantify fuel efficiency impacts of octane number
- Test central fuel property hypothesis using fuels with different chemistry

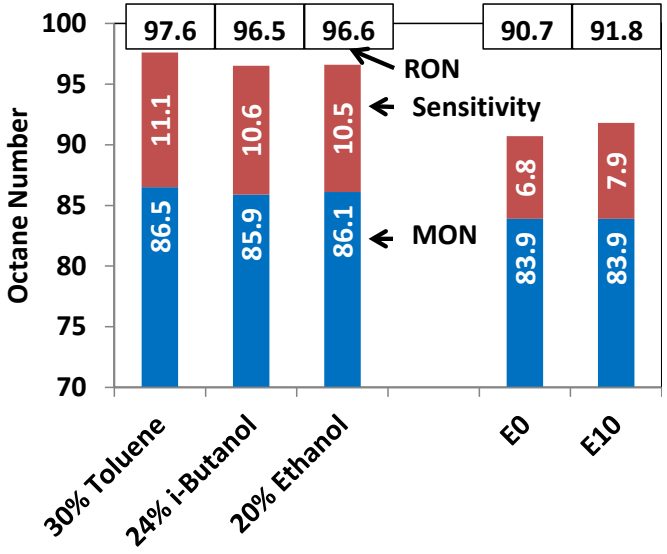
Approach

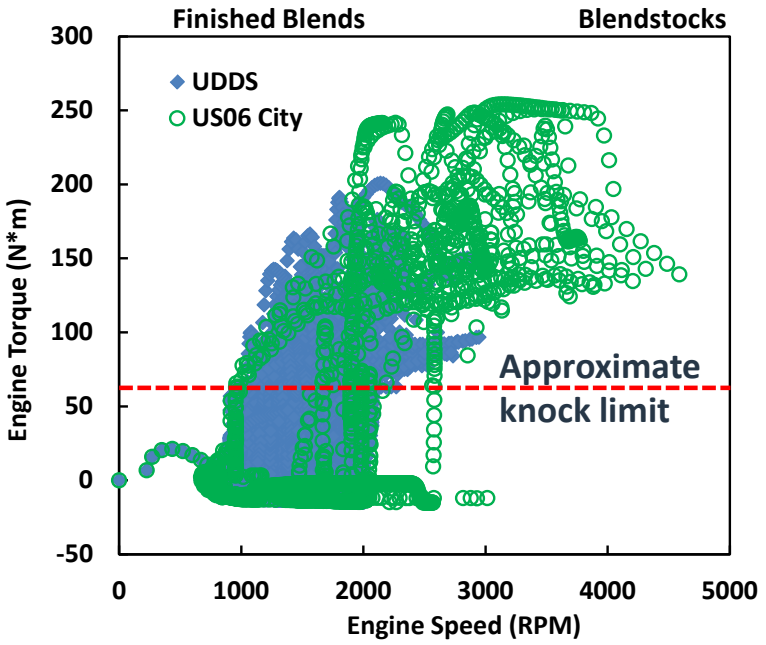
Engine Experiments

- Experiments with a 1.6L Ecoboost engine using three different compression ratios (10:1 (stock), **12:1**, and 13:1)
- Map engine performance with multiple fuel formulations

Vehicle Simulations

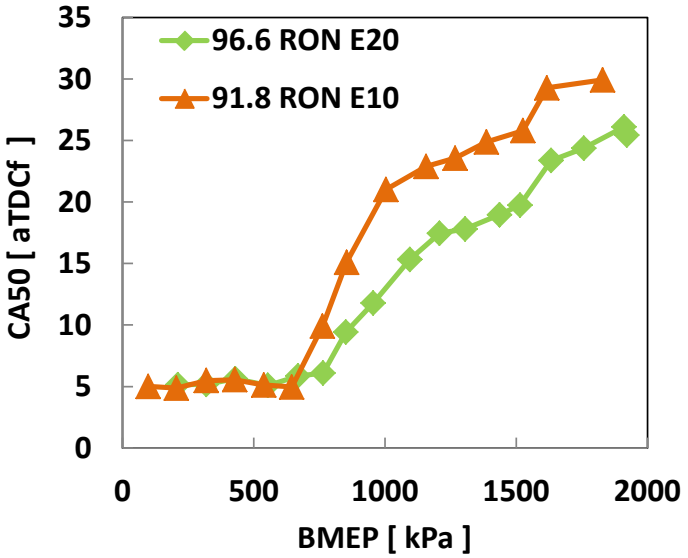
- Experimental data used in Autonomie vehicle simulations to quantify vehicle energy consumption and fuel economy

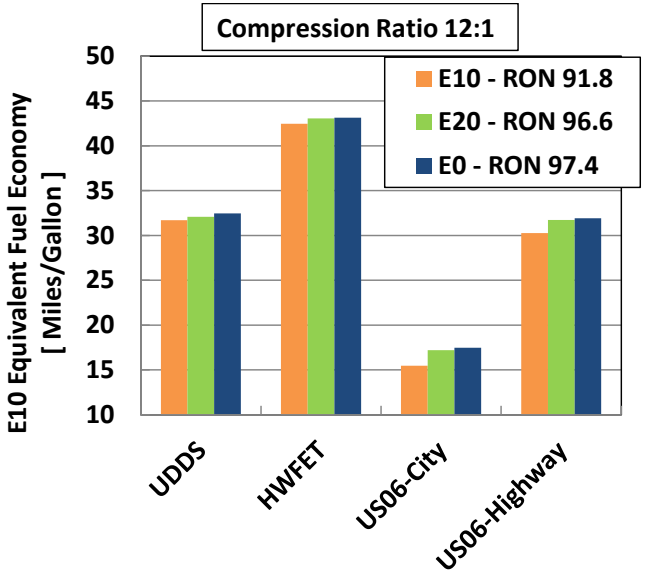




at fixed compression ratio, the benefit of increased octane rating for high-torque cycles can be significant

- Increasing octane rating reduces spark retard for knock avoidance
  - Improvement is limited to knock-limited load range
- Important to match RON to CR with desired torque
  - Downsizing/downspeeding trend demands increasing torque
- Energy consumption improvement for 5 RON points
  - UDDS cycle (light load): 2%
  - US06 city portion (higher load): 11%
- 3.5% energy consumption decrease needed to achieve volumetric fuel economy parity for E20 compared to E10





ORNL and NREL collaboration: HoV can be thought of a contributor to octane sensitivity

ORNL - Sluder (3/3)

- Inconsistencies in literature regarding HoV impact on knock propensity
  - HoV effect only been observed when covariant with octane sensitivity
- Expanded with new experimental results from ORNL and NREL
- Main conclusion: HoV is a thermal contributor to sensitivity
  - Aligns the findings of seemingly contrary literature findings
  - Consistent with the vaporization effects in the RON and MON tests

2016-01-0836
Published 04/05/2016
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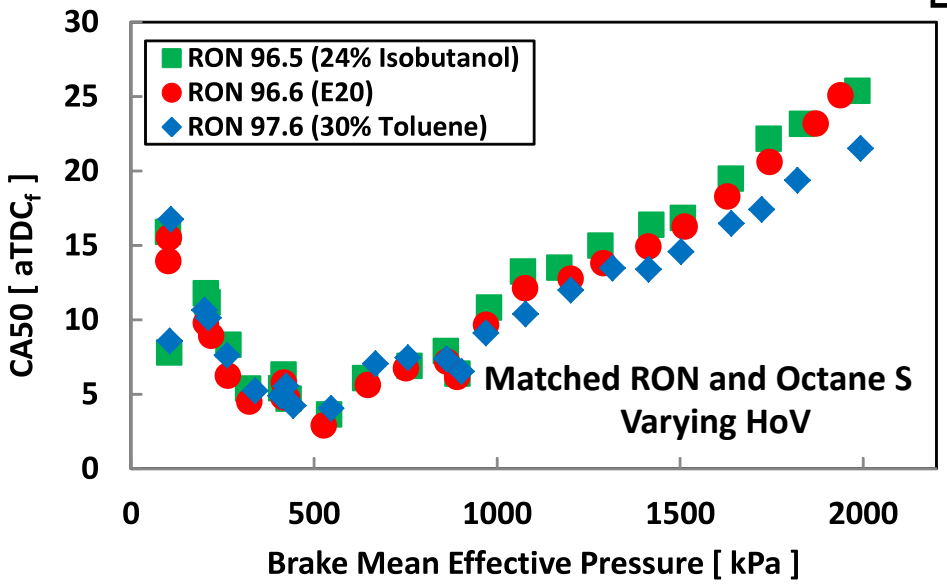
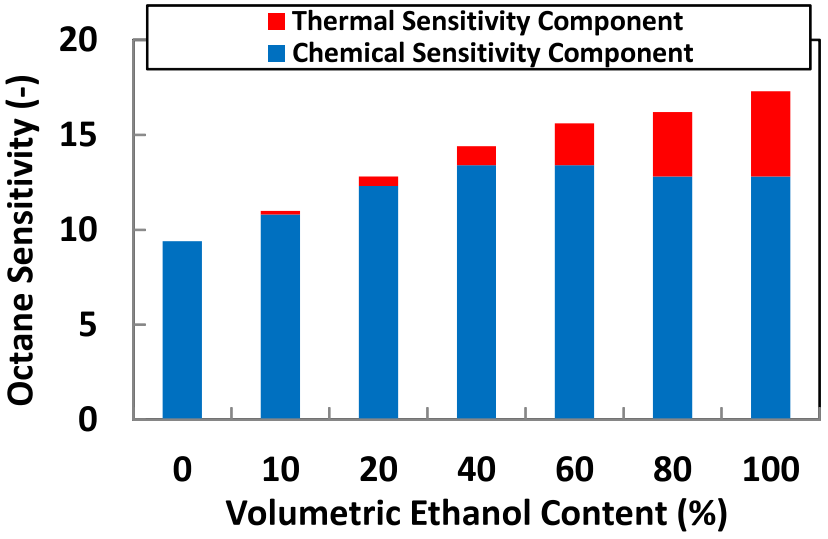
doi:10.4271/2016-01-0836
saefuel.saejournals.org

Exploring the Relationship Between Octane Sensitivity and Heat-of-Vaporization

C. Scott Sluder and James P. Szybist
Oak Ridge National Laboratory

Robert L. McCormick, Matthew A. Ratcliff, and Bradley T. Zigler
National Renewable Energy Laboratory





NREL (Ratcliff) $250k: effects of S, HoV and RON on GDI Performance

Objectives

- Test null hypothesis: At a given octane sensitivity, HoV impact on knock resistance is included in S

Approach

- Single cylinder version of GM Ecotec 2.0L, 9.2: CR
- Side-mounted DI or upstream fuel injection
- Load sweeps at an intake manifold temp of 50 ° C
- Sweep intake manifold T for max load at 2 different CA50 phasing

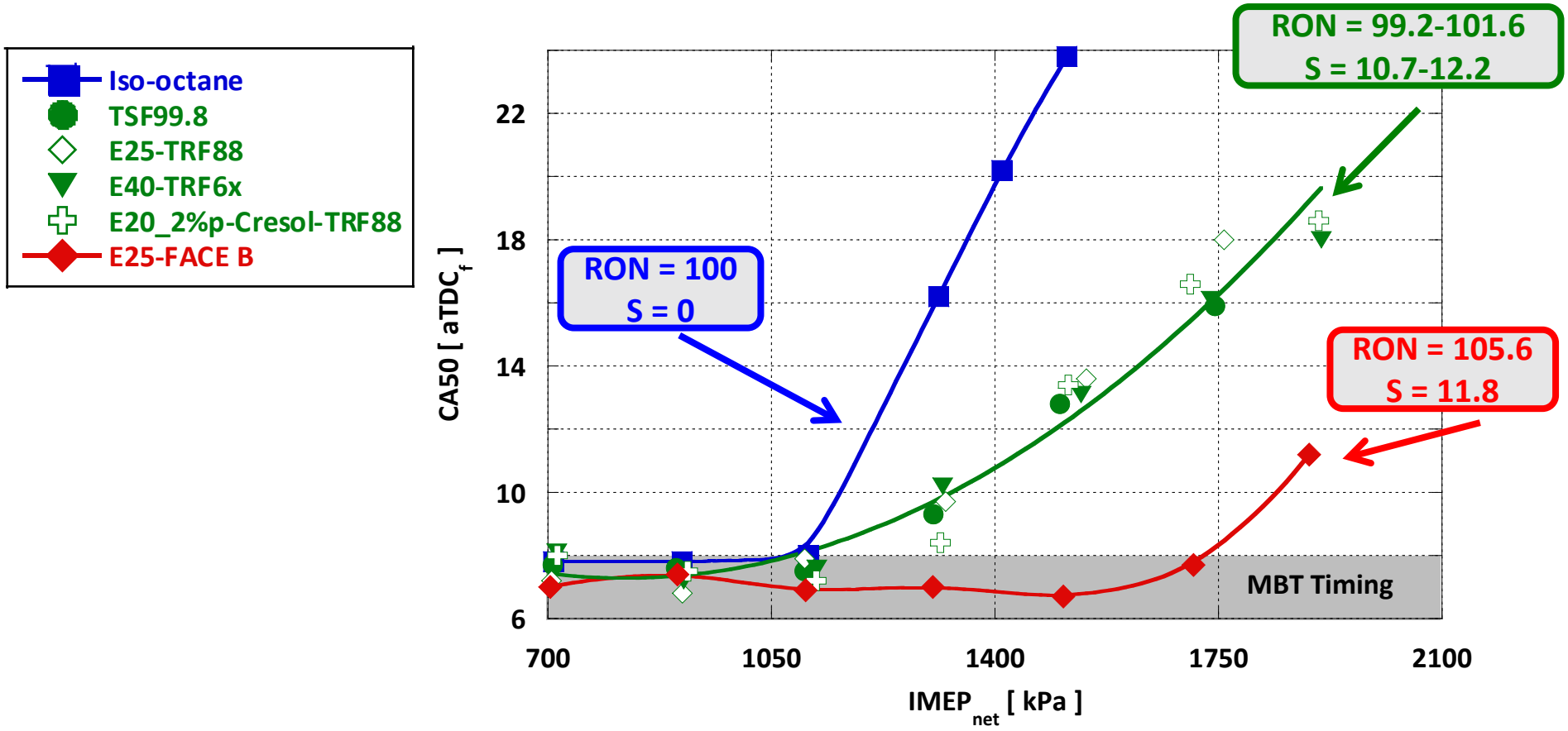
Fuel Matrix

- Matched RON and S at variety of HoV
- Fuels with different S and RON included to bound results

Fuel	RON	S	HOV [kJ/kg]	Oxygen wt%
Isooctane (PRF 100)	100	0	303	0
TSF99.8 (74% Toluene)	99.8	11.1	390	0
E25 in TRF88 (23% Toluene)	101.6	10.7	489	24.6
E40 in TRF6x (24% Toluene)	99.2	12.2	595	40.3
E20 + 2% p-Cresol in TRF88	100.3	10	472	22.4
E20 + 6% Anisole in TRF88	99.9	11	472	26.5
E25- FACE B	105.6	11.8	485	26.3

load sweeps reveal that performance of fuels with matched RON and S is independent of HoV

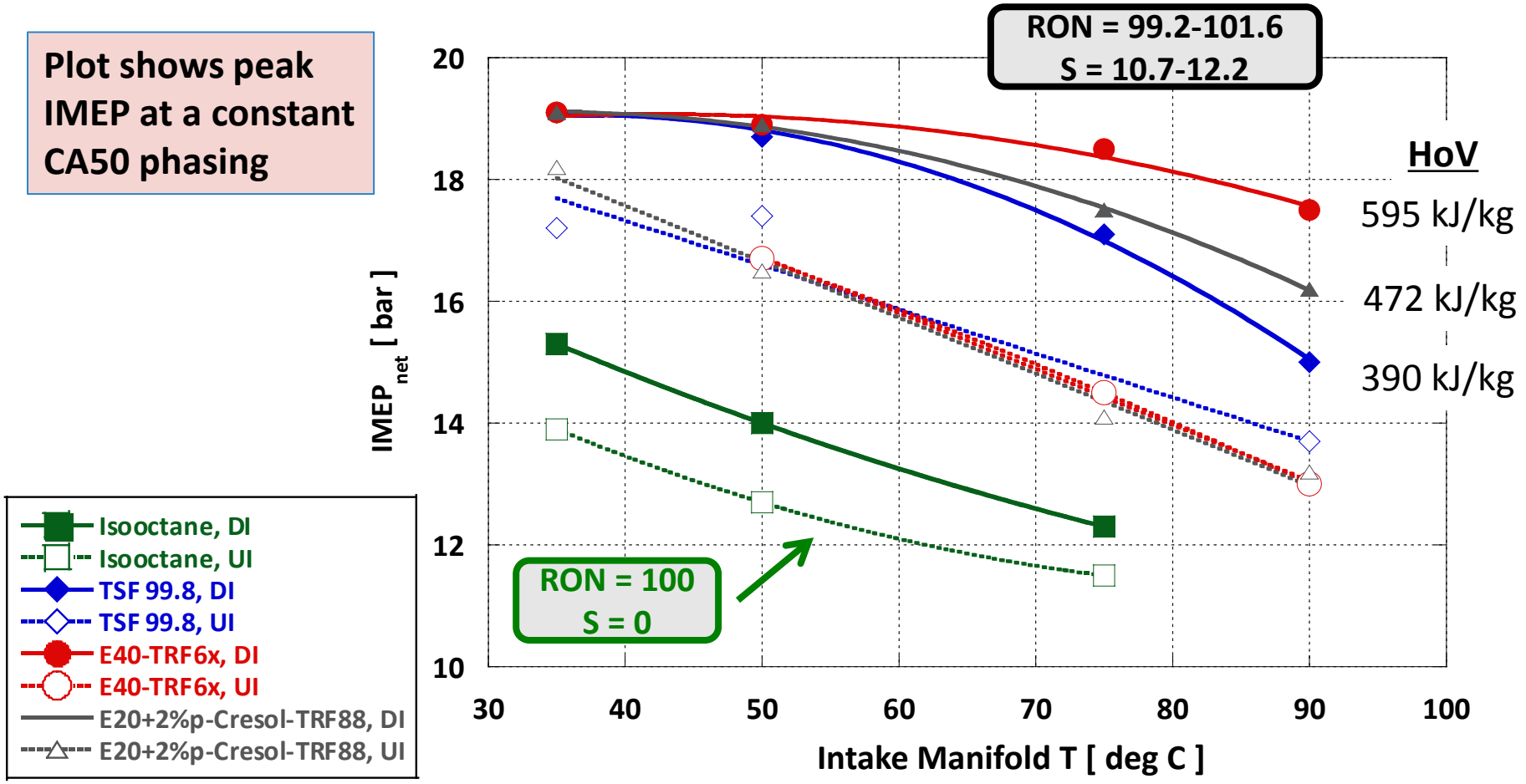
- Using direct injection (DI) all 100 RON, S ≈ 11 fuels have similar knock-limited performance gains over isooctane; no evident HoV benefit
- S ≈ 11 allows more than half the combustion phasing advance available with 106 RON fuel, between 1200 – 1500 kPa NMEP



HoV appears to improve performance at elevated intake air temperatures

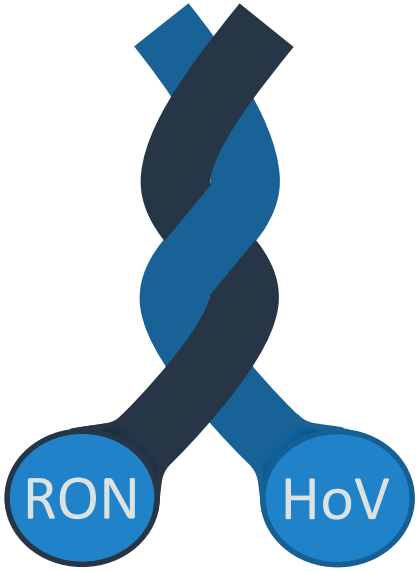
- Increasing HoV improves DI performance at late combustion phasing and intake manifold temperatures greater than 50 ° C
- Performance of upstream injected (UI) 100 RON, S ≈ 11 fuels is significantly higher than DI of isooctane

Plot shows peak IMEP at a constant CA50 phasing



ANL (Wallner) $300k: studies of research octane number (RON) and heat of vaporization (HoV)

- **Objectives**
  - Develop a better understanding of how fuel properties, particularly RON and HoV, impact auto-ignition for conventional, stoichiometric SI combustion
  - Isolate effects of entangled fuel properties, such as RON and HoV, on SI combustion and knock



- **Project Plans**
  - Use the well-established CFR engine (identifies fuel RON and MON) as a research platform to develop scientific understanding of isolated fuel effects on SI combustion
  - Investigate HoV effects on RON as a function of operating parameters (intake air temperature, compression ratio, and spark timing) for a range of fuels

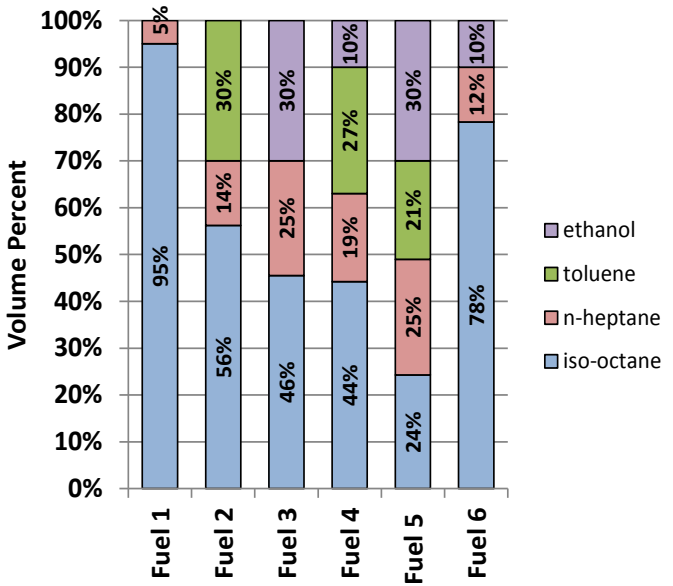
collaborations established, CFR engine and test cell prep nearing completion

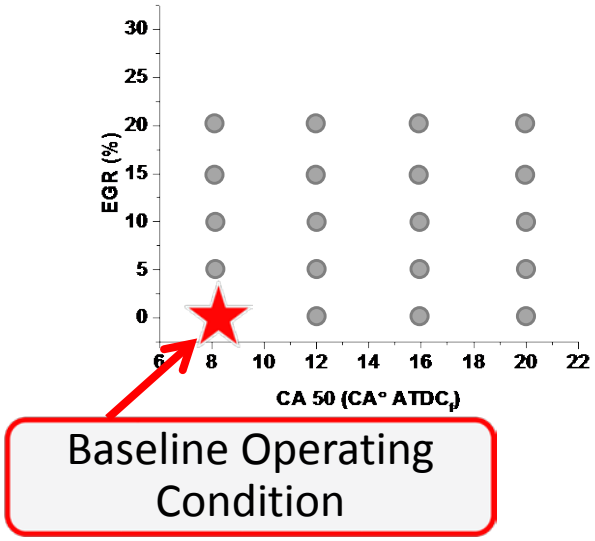
- **Progress**
  - Collaboration established with Marathon Petroleum Corporation
  - CFR engine refurbished and installation underway
  - Test cell data acquisition installed
  - Test matrix and analytical method defined

- **Deliverables**
  - Completion of initial test matrix by Sep 30, 2016
  - Boundary conditions of CFR engine for modeling to toolkit team
  - Development of a two-parameter knock behavior characteristic which takes HoV into account is a potential outcome of this work

ORNL (Szybist) $300k: fuel effects on the limits of EGR dilution for SI engines

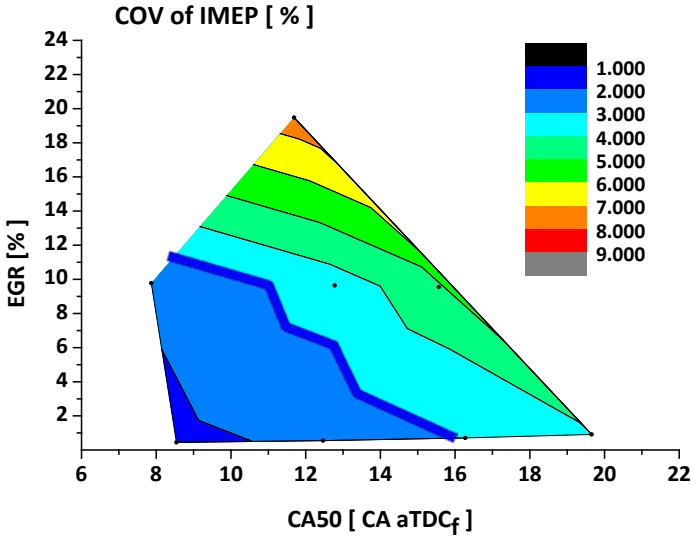
- **Objectives**
  - Determine the magnitude and causes of fuel-specific differences in extending the EGR dilution limit
- **Methodology**
  - Single cylinder version of GM Ecotec 2.0L, 9.2: CR
    - 2000 rpm, nominal load of 3.5 bar $IMEP_g$
  - Side-mounted DI, laboratory air handling with external cooled EGR loop
  - 6 fuel blends from pure components designed to vary flame speed, enable kinetic modeling
  - Dilution limit defined by stability metric (COV) through EGR/combustion phasing space
- **Future Work:** Continuing work will be focused on high load dilution tolerance and pressure effects (>15 bar)



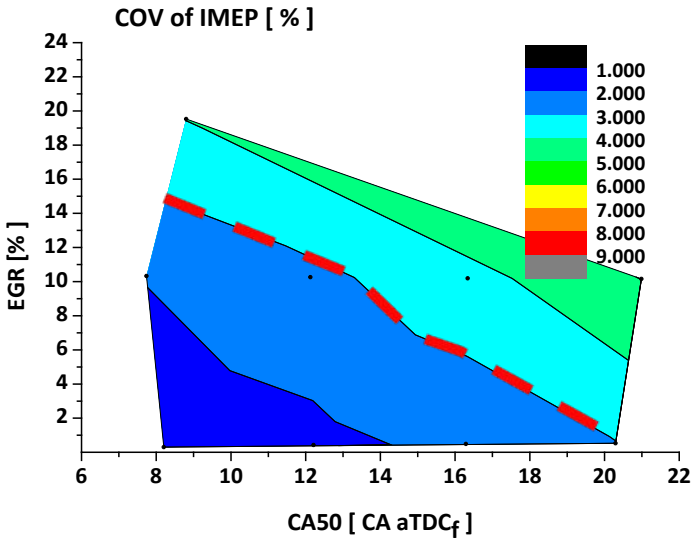


EGR dilution tolerance is defined by combustion stability, fuel specific differences are observed

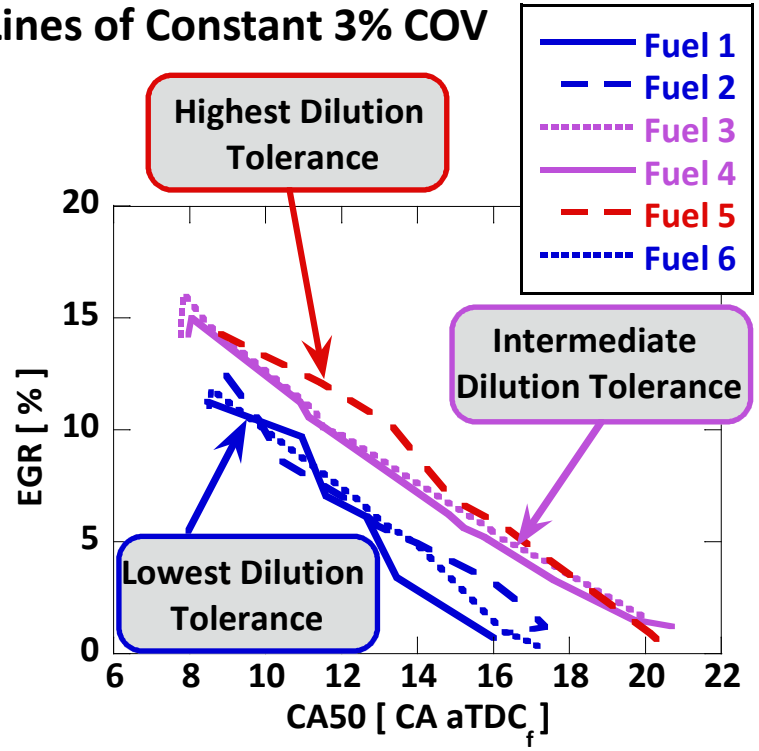
Fuel 1
95% iso-octane, 5% n-heptane



Fuel 5
24% iso-octane, 25% n-heptane, 21% toluene, 30% ethanol



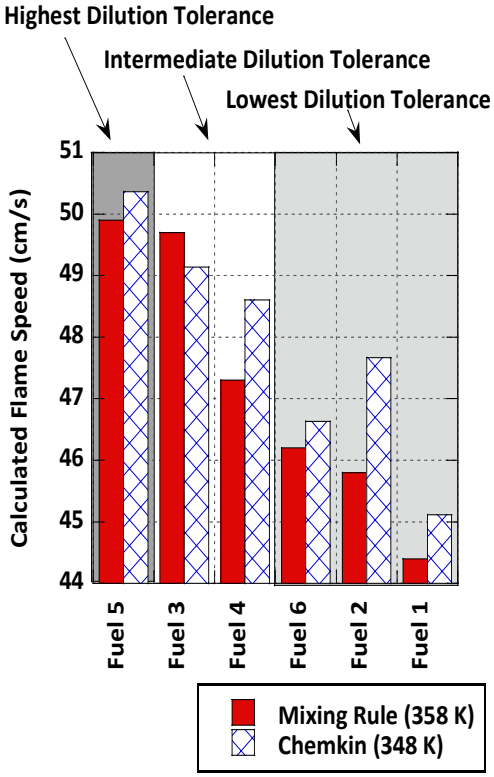
Lines of Constant 3% COV



- Response to EGR is the similar for all fuels (similar slopes)
- Fuels-specific differences are due to different starting points

highest dilution tolerance fuels have highest flame speed

- Dilution tolerance correlates to laminar flame speed
  - Energy fraction mixing rule and kinetic calculations agree
  - Kinetics allow flame speed calculations at relevant temperature and pressure conditions
- Flame speed at ignition provides a good indication of spark-to-CA5, combustion stability
  - Experimental spark-to-CA5 to represents early flame growth
  - Rapid early flame kernel growth critical for combustion stability
  - Calculated flame speed in excellent agreement with experimental spark-to-CA5



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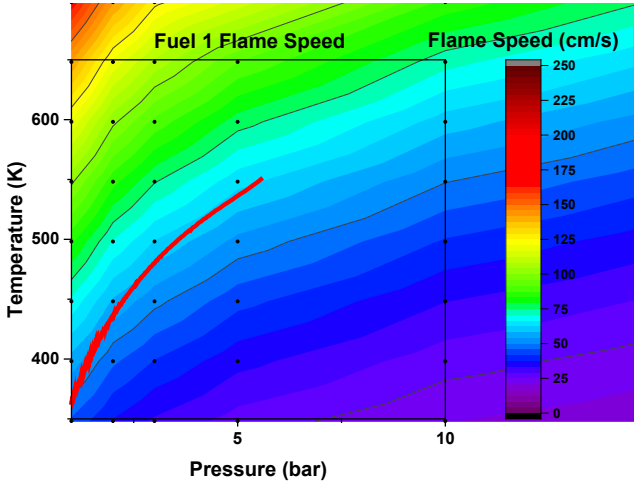
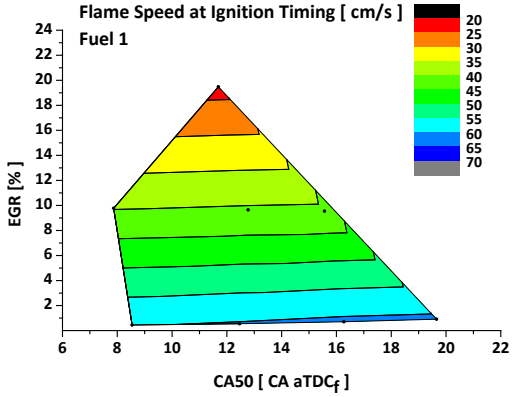
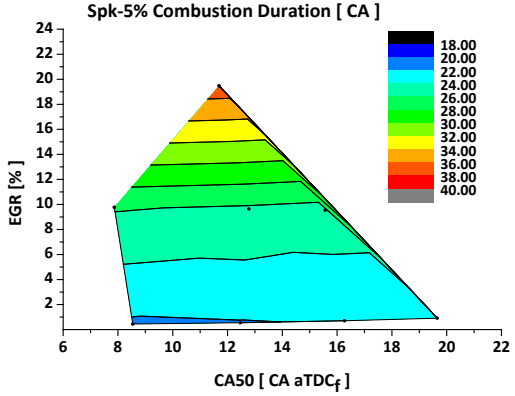


Calculated Flame Speed at Ignition Timing is Insensitive to Spark Timing

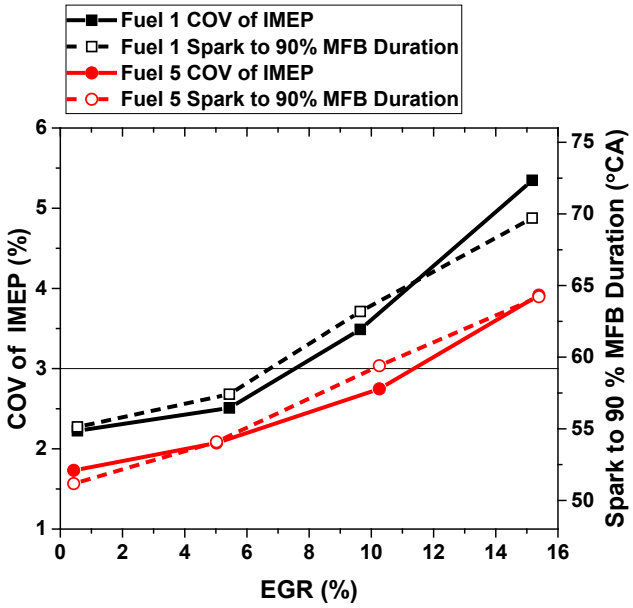


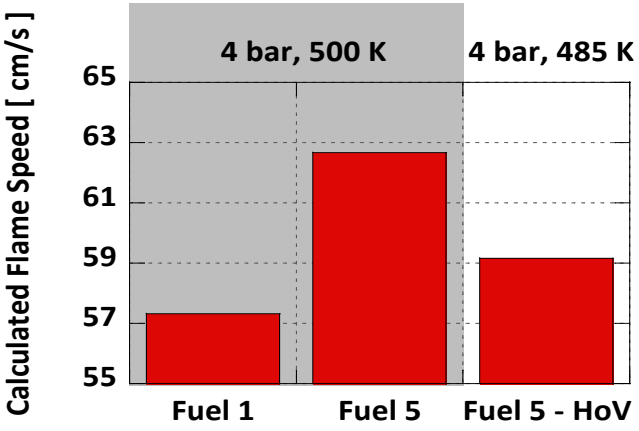
Agrees with Experimental Results of Spark-to-CA5 duration



fuel-specific effects can be significant, HoV identified as possible dilution tolerance detractor

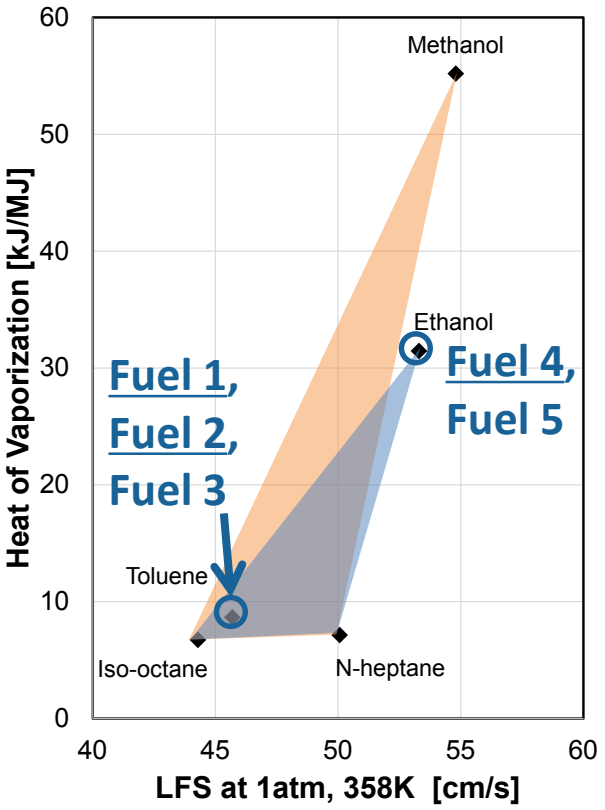
- Fastest flame speed fuel enables a 50% relative increase in EGR at a constant COV of 3% compared to the slowest flame speed fuel
  - 8% EGR to 12% EGR
  - Absolute EGR dilution tolerance will change with engine design and operating condition
  - Relative ranking between fuels is expected to remain for all homogeneous SI engines
- HoV may detract from dilution tolerance
  - Flame speed is a function of temperature
  - Up to 15 C of additional charge cooling expected for 30% ethanol
  - Flame speed calculations reveals this temperature reduction has a large impact on flame speed
- This project to move to high loads FY16 FY17
- ANL to investigate flame speed effects





ANL (Wallner) $200k: fuel effects on EGR and lean dilution limits on SI combustion

- **Objectives**
  - Identify the influence of fuel properties on SI combustion lean and EGR dilution tolerance
  - Quantify the relative impact of fuel properties on dilution tolerance compared to engine design parameters
- **Methodology**
  - Single cylinder version of Ford engine, 0.63L, 12.2:1 CR
    - 1500 rpm, loads of 3.2 and 5.6 bar IMEP, constant combustion phasing (8 CA aTDC$_f$)
  - PFI and DI fueling
- **Project Plans**
  - Evaluate hypothesis that laminar flame speed (LFS), at nominal conditions, can be used to predict dilution tolerance (lean and EGR) of a fuel in SI combustion
  - Determine the impact of HoV on dilution tolerance
  - Compare fuel LFS lean/dilute tolerances against engine design parameters

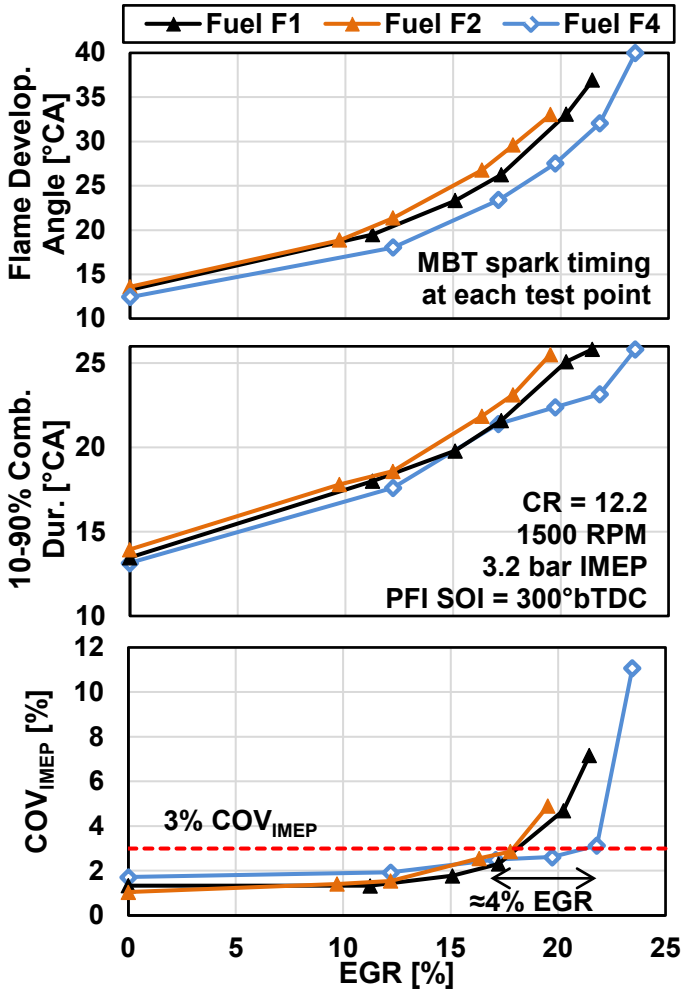


Fuel Components	1	2	3	4	5
iso-octane		X	X	X	
n-heptane		X	X		X
toluene	X				
ethanol		X		X	
methanol			X		X

fuel matrix is isolating effects of LFS and HoV in preliminary data

- **Progress**
  - Developed a method to identify fuel blends with target HoV and flame speed
  - Derived fuel matrix and test program
  - Preliminary results confirm positive correlation of flame speed with dilution tolerance

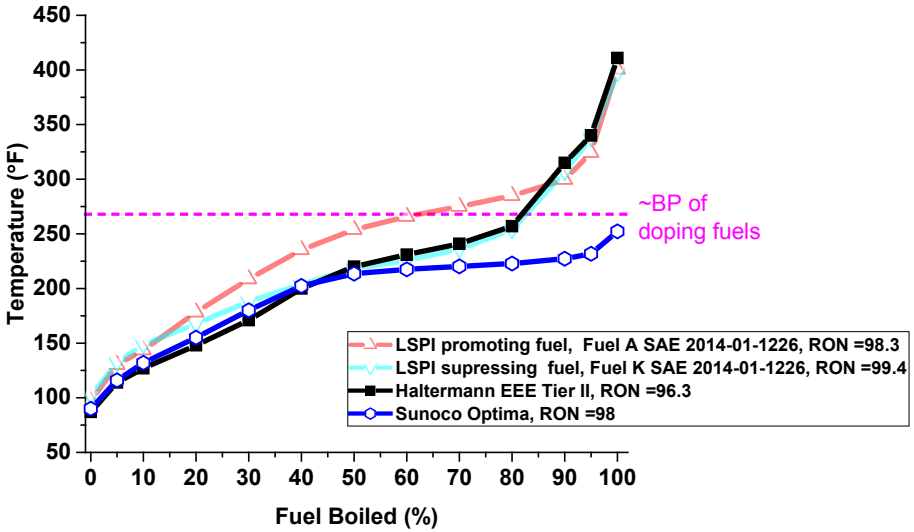
- **Deliverables**
  - Comparison of fuel and engine design parameters on SI combustion lean dilution tolerance
  - Completion of LFS hypothesis testing by June 30, 2016

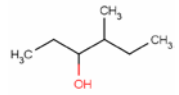
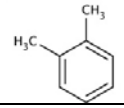
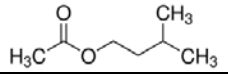
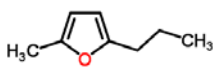
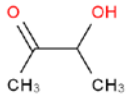


Fuel F1: Low LFS, Low HOV (toluene)
Fuel F2: Low LFS, Low HOV (mixture)
Fuel F4: High LFS, High HOV (mixture)

ORNL (Splitter) $150k: fuel effects in low speed pre-Ignition

- **Objectives**
  - To improve the understanding of fuel properties on low speed pre-ignition (LSPI)
- **Project Plans**
  - Single cylinder version of Ford1.6L Ecoboost engine
    - Dedicated LSPI engine
    - Leverages lubricants LSPI activity
    - Automated LSPI test cycle
  - Initial work focused on boiling point, HoV, and fuel structure on LSPI
    - Input to fuel merit function and co-optima down selection
  - Extend focus to down selected co-optima fuels



Molecule Type	Bio-blendstock	Structure	BP (°C)	RON (-)	HoV (kJ/kg)	Planned
Alcohol	4-Methylpentan-3-ol		148	95.9	423	
Alkane	(1S, 4S)-1,7,7-trimethylbicyclo [2.2.1]heptane		144.6	95.3	268	
Aromatic	o-Xylene		144	120	409	X
Ester	3-Methylbutyl acetate		142	100.6	291	X
Furan	2-methyl-5-propyl furan		138	93.9	295	
Ketone	3-hydroxy-2-butanone		148	107.5	506	X

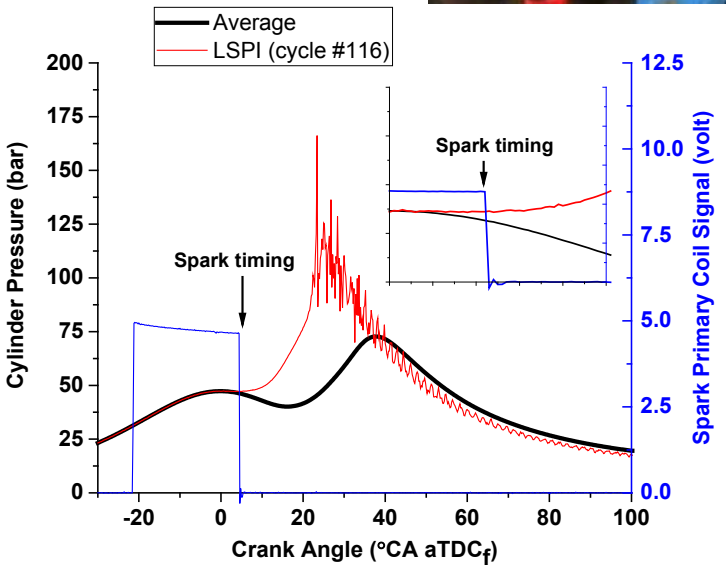
engine system is operational, on-track to meet Q4 project-level milestone

- **Progress**
  - Initial scoping fuels identified
  - DAQ system collecting 15,000 consecutive cycles is operational through the leveraged lubricant project
  - Engine failure occurred under LSPI conditions
    - New engine installed and operational

- **Deliverables**
  - Initial molecular structure effects on LSPI tests Sept 30 2016
  - Feed forward of findings into fuels merit function

FY 2016 Q1

FY 2016 Q2



comments to last years reviewers 2015 projects included: FT002 (Zigler), and FT008 (Szybist)

Reviewers commented on the selection process of bio and conventional fuels being studied.

Fuel choices moving forward will be guided by multi-lab "Co-Optima" effort. This includes coordination with BETO "Co-Optima" effort through the Low Greenhouse Gas Fuels Team, through stakeholder engagement, and alignment on fuels amongst the various National Laboratories

Reviewers commented on the need to better understand the role of fuel properties as it relates to engine behavior. Specific examples include determining the chemistry-specific contribution to RON (FT008).

This comment is in-line with the overarching fuel hypothesis of the "Co-Optima" effort. We are seeking to understand whether knowing fuel properties are sufficient, or if the chemical composition of the fuel is critical to understanding performance aside from the fuel properties.

- **Specific to FT008: Regarding the high-octane study, the reviewer asked what is the impact of revised piston geometry on fuel spray volatility and wall impingement, fuel pool fires, etc.**

  Fuel injection events for this study are early in the intake stroke, providing lengthy evaporation and mixing times and reducing the importance of jet-piston interactions. While the piston geometries are not optimal for cold start and transients, discussion of the designs with industry stakeholders have provided confidence that they are adequate for research applications.

numerous overarching and portfolio-level collaborations additional project-level collaborations

- **Co-Optimization of Fuels and Engines** brings together expertise from across the National Laboratory system, working toward a common purpose. This effort has stakeholder engagement at a high level to ensure relevance.
  - 9 laboratories, engines, fuels, kinetics, simulation, biofuel development, LCA& TEA, market transformation
  - Monthly stakeholder engagement phone calls, industry listening days, external advisory board
- Projects presented at the semi-annual AEC program review meetings
- Engagement with ACEC Tech Team activities

Additional project-level collaborations with industry and academia

Sluder
Ford – Hardware and technical guidance
USDRIVE Fuels Working Group – multiple OEMs and energy companies

Szybist
FCA – Cody Baldwin-Squibb
University of Michigan – Yan Chang (student)

Splitter
Driven Racing Oils – custom lubricants

Kolodziej/Ickes
Marathon Oil – Hardware, fuels, technical guidance

Kolodziej/Wallner
Ford - Hardware

Ratcliff
General Motors – Hardware and Technical Guidance

summary

Relevance

Thrust I engine experiments are critical to understanding the role of fuel properties on efficiency. This information is critical to knowing how to value various fuel properties within “Co-Optima.”

Approach

Perform engine experiments that test the overarching “Co-Optima” fuel property hypothesis. Provide quantitative results that will aid in refining the Thrust I merit function. Interact with other teams within “Co-Optima” for modeling support, fuel selection, and fuels critical to the overall goal of reduced GHG emissions.

Accomplishments

- Once octane sensitivity has been accounted for, the role of HoV on KLSA is significantly diminished
- Multi-lab effort provided insight into the role of HoV as a thermal component to octane sensitivity
- EGR dilution tolerance is dominated by flame speed, related to early flame kernel growth

Collaborations

- “Co-Optima” has 9 National Labs, stakeholder engagement, and external advisory board
- Projects presented at AEC semi-annual program review, engaged with ACEC TT
- Numerous other project-level collaborations

Future Work

Continue to test the overarching “Co-Optima” fuel property hypothesis by incorporating biofuels with a wide range of chemical compositions into experiments, with support from modeling and kinetics efforts, in coordination with additional “Co-Optima” teams.