



Co-Optimization of  
Fuels & Engines

Project ID: FT051

## Fuel Property Characterization and Prediction

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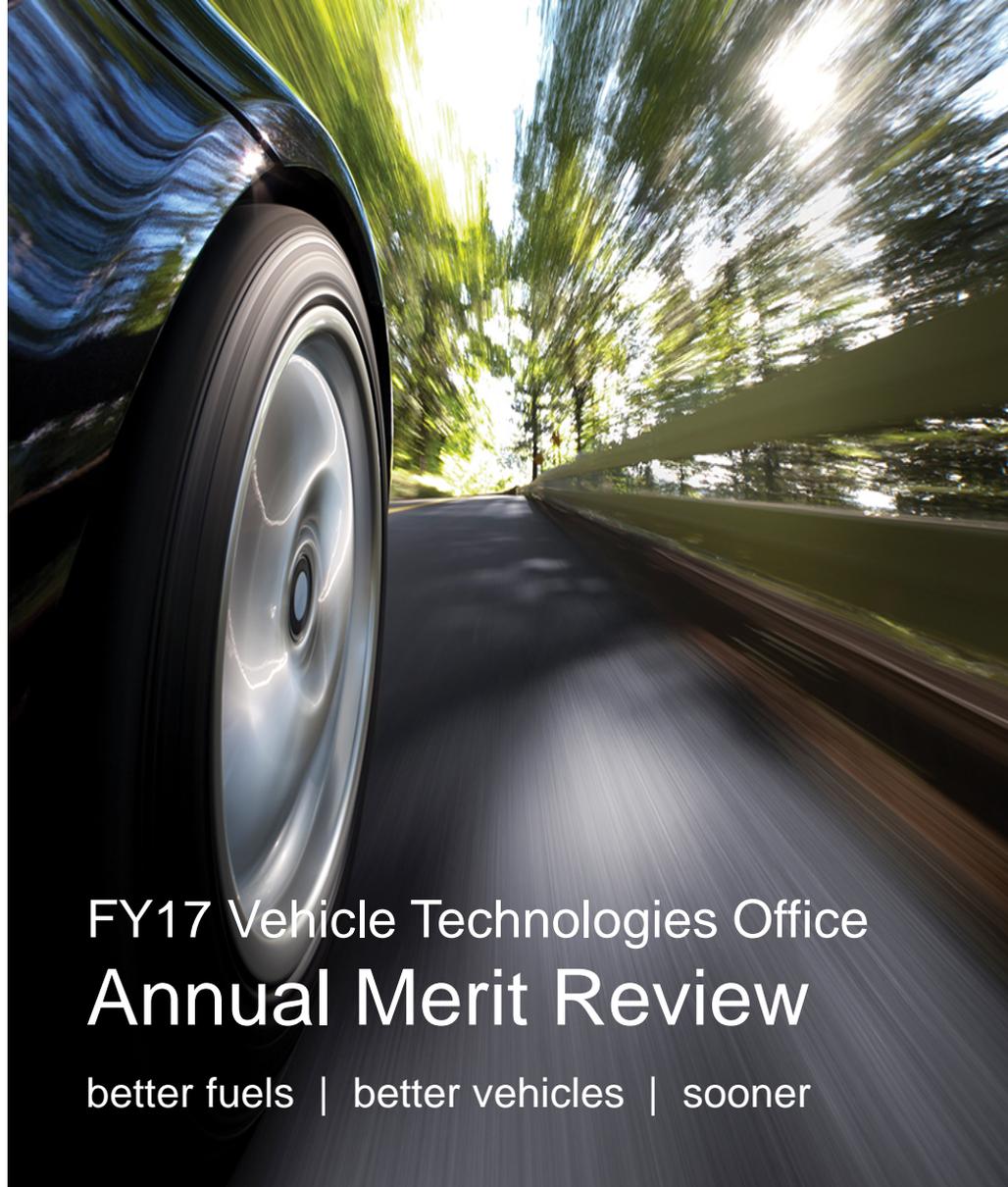
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NREL/PR-5400-68299

Washington, DC



FY17 Vehicle Technologies Office  
Annual Merit Review

better fuels | better vehicles | sooner

U.S. DEPARTMENT OF  
**ENERGY**

Energy Efficiency &  
Renewable Energy

VTO Management: Kevin Stork, Gurpreet Singh,  
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*This presentation does not contain any proprietary, confidential, or otherwise restricted information.*



## Timeline

- Project start date: 10/1/2015
- Project end date: \*9/30/2018
- Percent complete: 56%

## Budget

	FY16 Budget	FY17 Budget	FY18 Budget
VTO	\$1,247	\$1,375	\$1,375

Dollars in thousands. FY18 is request level.

## Barriers

- **Complexity:** Introduction of new fuels and vehicles involves a large number of stakeholders with competing value propositions
- **Timing:** Schedule for completing R&D and achieving market impact is extremely ambitious

## Partners

Partners include 9 national laboratories, 13 universities, external advisory board, and many stakeholders and collaborators

\*Start and end dates refer to three-year life cycle of DOE lab-call projects, Co-Optima is expected to extend past the end of FY18



- Internal combustion engines will continue to dominate the fleet for decades – and their efficiency can be increased significantly.
- Research into better integration of fuels and engines is critical to accelerating progress towards our economic development, energy security, and emissions goals.
- Improved understanding in several areas is critical for progress:
  - Fuel chemistry – property relationships
  - How to measure and predict fuel properties
  - The impact of fuel properties on engine performance
- Relevant to LD SI, MD/HD diesel, and advanced CI combustion strategies.

CI: compression ignition  
HD: heavy duty  
LD: light duty  
MD: medium duty  
SI: spark ignition

# Milestones



Month / Year	Description of Milestone or Go/No-Go Decision	Status	Lab
Sep-2017	In collaboration with Toolkit Team (at NREL) test the premise that from flow reactor measurements we can identify a TPRF fuel surrogate that behaves similarly to the fuel being tested in terms of autoignition behavior.		NREL
Dec-2016	Predict octane blending behavior of two to three classes of bio-blend stocks with two to three base fuels		LLNL
Jun-2017	Complete GDI engine tests with fuel matrix varying HOV at RON 100 and $S \approx 5$	Sep-2017	NREL

DCN: derived cetane number  
 GDI: gasoline direct injection  
 HOV: heat of vaporization  
 RON: research octane number  
 S: sensitivity

LLNL: Lawrence Livermore National Laboratory  
 NREL: National Renewable Energy Laboratory  
 PNNL: Pacific Northwest National Laboratory



## Central Fuel Hypothesis

*If we identify target values for the critical fuel properties that maximize efficiency and emissions performance for a given engine architecture, then fuels that have properties with those values (regardless of chemical composition) will provide comparable performance*

## Quantitative Merit Function

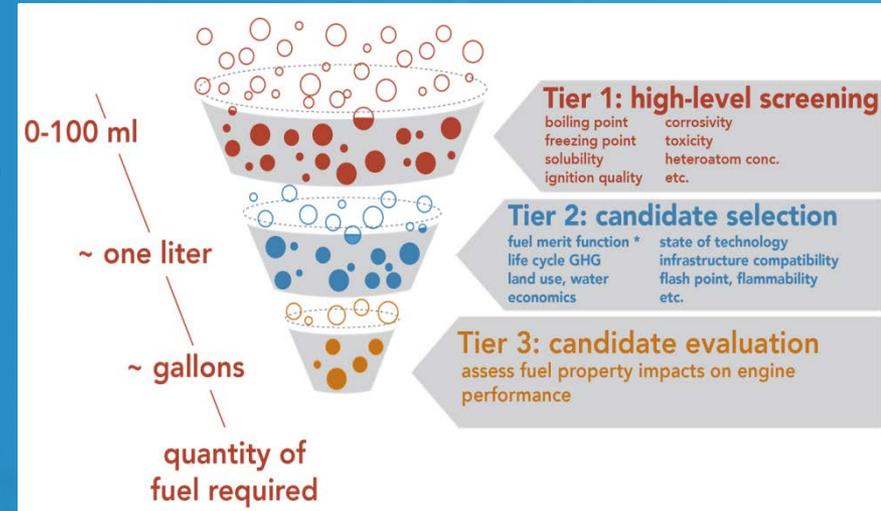
$$\begin{aligned} \text{Merit} = & \frac{(RON_{mix} - 91)}{1.6} - K \frac{(S_{mix} - 8)}{1.6} + \frac{0.085[ON / kJ / kg_{mix}] \cdot ((HoV_{fuel} / (AFR_{stoich} + 1)) - (415[kJ / kg_{fuel}] / (14.3[-] + 1)))}{1.6} \\ & + \frac{((HoV_{fuel} / (AFR_{stoich} + 1)) - (415[kJ / kg_{fuel}] / (14.3[-] + 1)))}{15.38} + \frac{(S_{Lmix} - 46[cm / s])}{5.4} \\ & - H(PMI - 1.6)[0.7 + 0.5(PMI - 1.4)] + 0.008^{\circ}C^{-1}(T_{c,90,conv} - T_{c,90,mix}) \end{aligned}$$

- Develop experimental and predictive methods for estimating the properties in the Merit Function, to refine the form of the merit function, and to test the Central Fuels Hypothesis
- Identify critical properties and allowable ranges, systematically catalog properties, and predict fuel blending behavior
- Reveal through bench and engine experiments how fuel properties that go well beyond those obtainable in conventional petroleum fuels can be leveraged to improve engine performance



### Defined desired fuel properties for mixing-controlled CI combustion

1. Cetane number (CN) > 40 (> 55 if possible)
2. Flashpoint > 52°C (or >38°C)
3. Melting point < -10°C (< -40°C if possible)
4. Soluble in low-aromatic base fuel to -10°C
5. Blends are water tolerant
6. Normal/final boiling point below 350°C
7. Toxicity lower and biodegradability similar to current fuels
8. Corrosivity equal to or lower than current fuels
9. No heteroatoms beyond O and possibly N (i.e., very low metals, S, P, etc.)
10. Oxidative stability equal to or better than those of current fuels
11. Lower heating value > 25 MJ/kg
12. Compatible with commercially available elastomers
13. Viscosity between ~0.5 and 5.0 cSt at 40°C
14. No strong odor



***Performing Tier 1 screening is the next step!***

**Co-led CRC Project AVFL-18a on diesel surrogate fuels (including solidification, see next slide); co-chaired 2<sup>nd</sup> CRC AFEE Workshop**



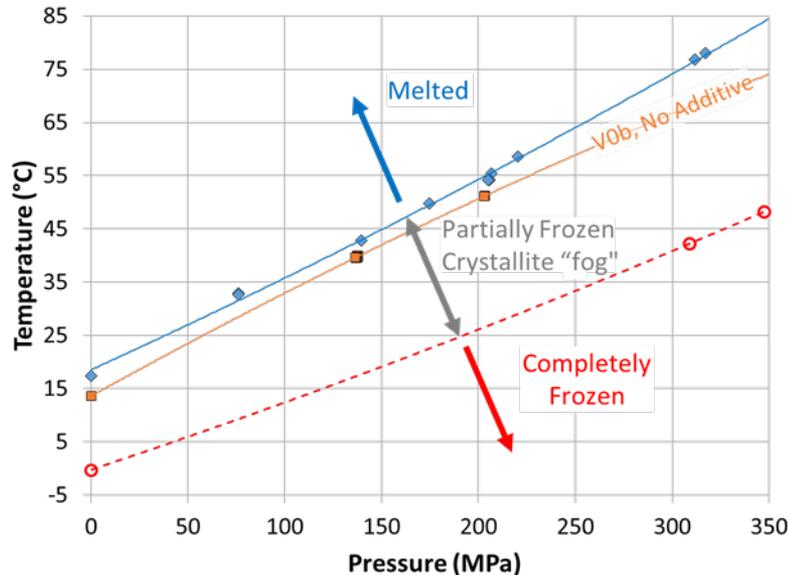
## PNNL (Bays) \$150k: Fuel Property Blending Model

### Created $^{13}\text{C}$ -NMR method to predict properties of full boiling range fuels

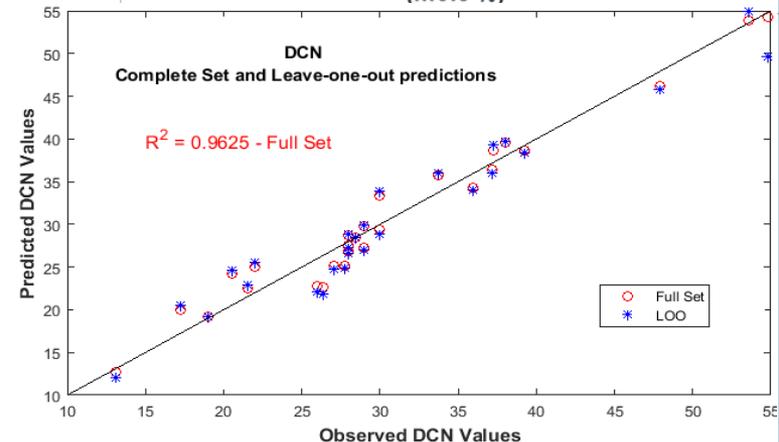
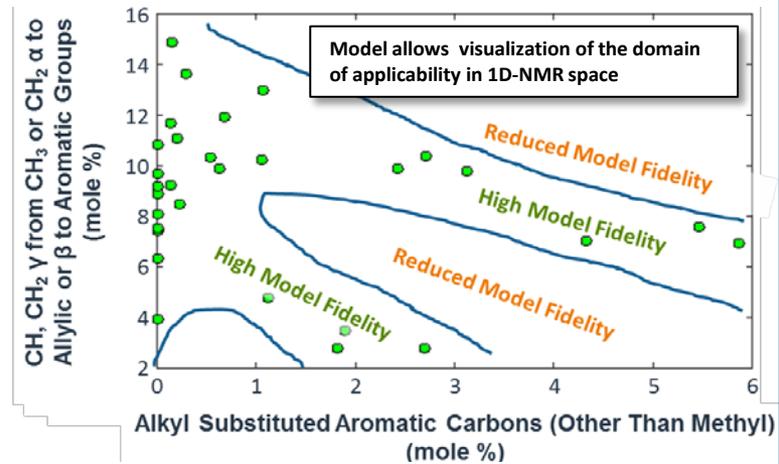
- Rapid, uses 300  $\mu\text{L}$  of fuel to predict DCN, T10, T50, and T90
- A predictive model with well defined domain of applicability was developed
- Ongoing work is focused on quantifying prediction quality outside this domain

### Developed T-P phase diagrams for fuels up to 400 MPa

- Identified T-P regions for full solidification, two-phase, and fully liquid behavior
- Phase behavior of diesel surrogate with cold-flow additive\*



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



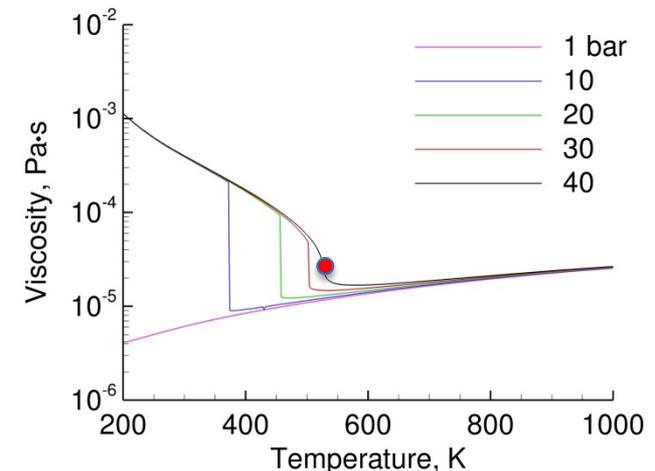
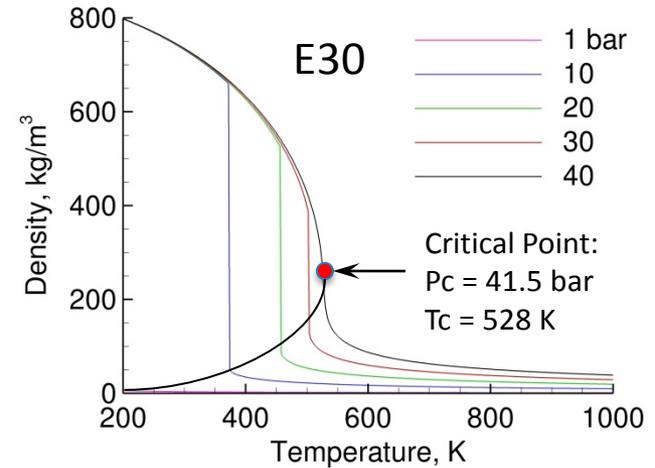
# Technical Accomplishments and Progress SNL (Oefelein, Lacaze) \$75k: Thermophysical Properties of Fuels



Estimate properties of fuel blends to parameterize engine simulations

Completed detailed treatment of thermodynamic and transport properties for multicomponent fuels:

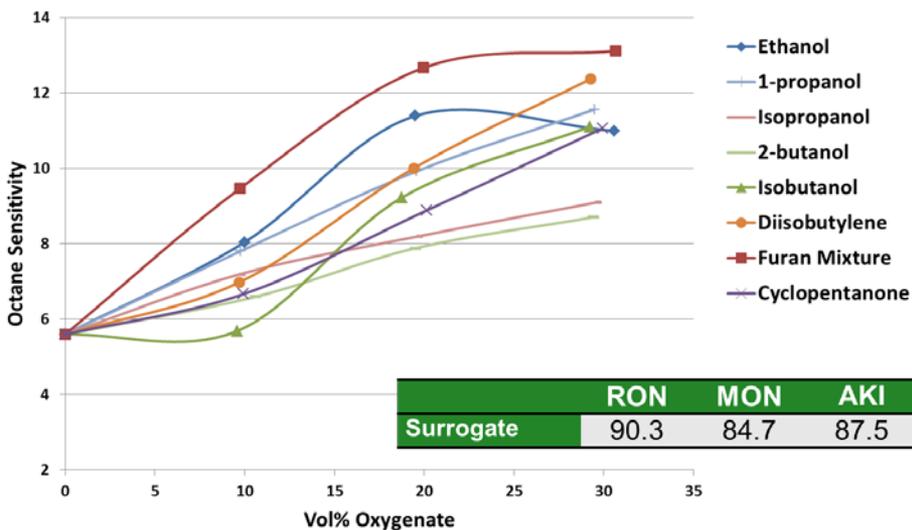
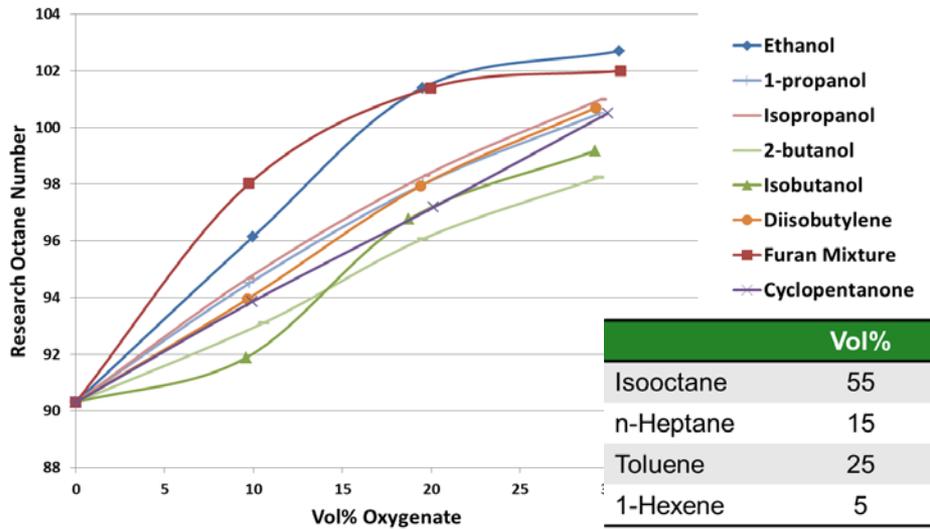
- Real-fluid mixture properties obtained using Extended Corresponding States model
- Multicomponent formulation using cubic (PR/SRK) or BWR equations of state
- Generalized to treat wide range of fuel blendstocks (fuel/oxidizer/products)
- Provide tabulated input for project codes: Viscosity, Surface Tension, Enthalpy of Vaporization, Vapor Pressure, Thermal Conductivity, Density, Specific Heat.



Accurate estimation of liquid fuel properties is key to correctly simulate spray dynamics, fuel-air mixing and combustion necessary evaluate fuel performances

# Technical Accomplishments and Progress

## NREL (McCormick, Fioroni) \$400k: Fuel Property Database and Blend Property Testing



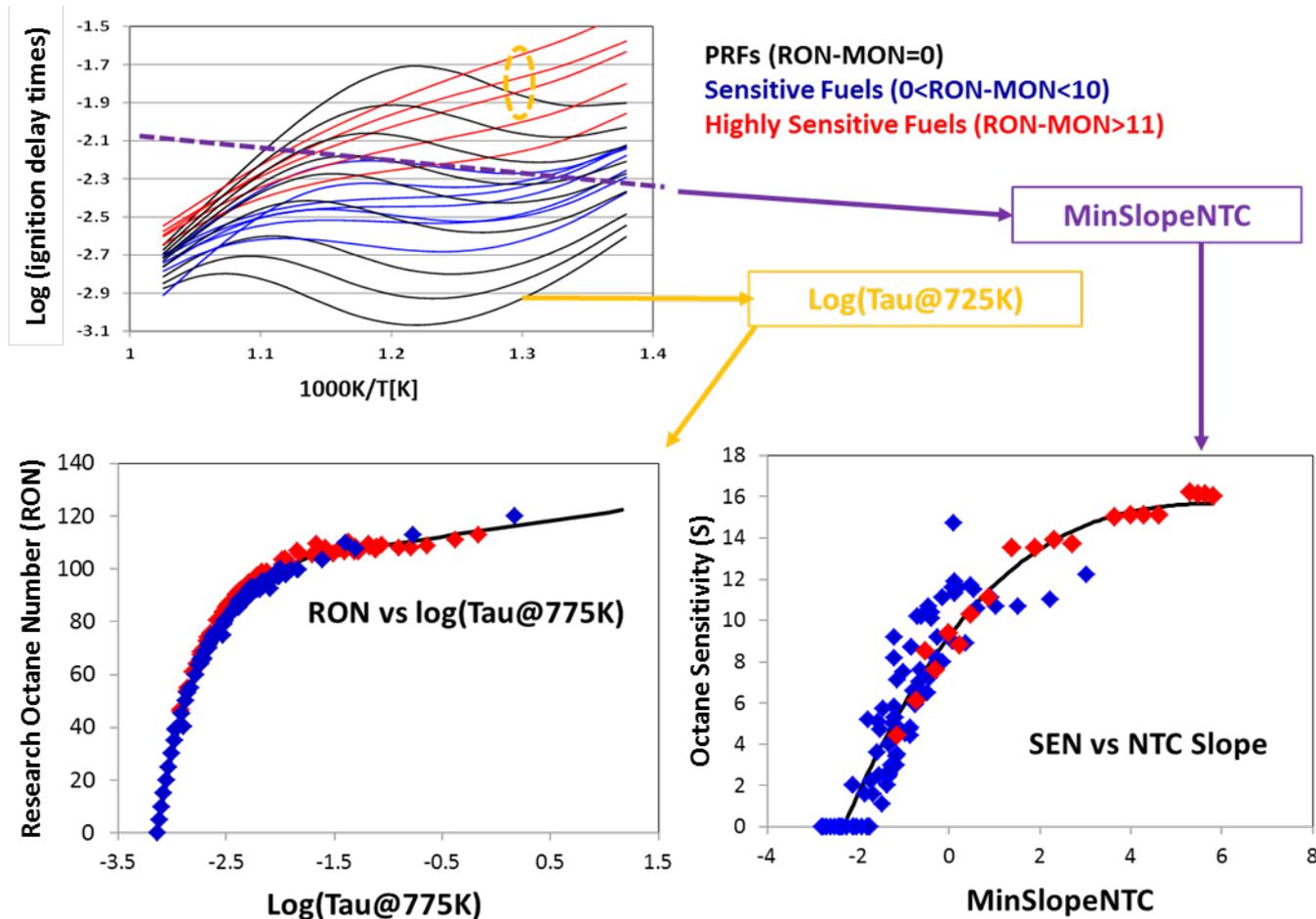
### Completed blend property testing and Tier 2 screening for SI combustion

- LD SI engine blendstocks screened based on blending properties
- RON and MON in a 4-component surrogate
- RON  $\geq 98$ , S  $\geq 8$
- **Blend RON and sensitivity shown for preliminary set of the most promising**
- RVP, distillation, stability assessed in RBOB
- RVP effect less than ethanol
- Distillation meeting D4814 and less of an effect than ethanol
- Note that the furan mixture and cyclopentanone oxidized on stability test – potential issue



## From Model Prediction to Octane Rating

New correlations were developed bridging fundamental ignition delay time measurements and engine metrics (RON and S).





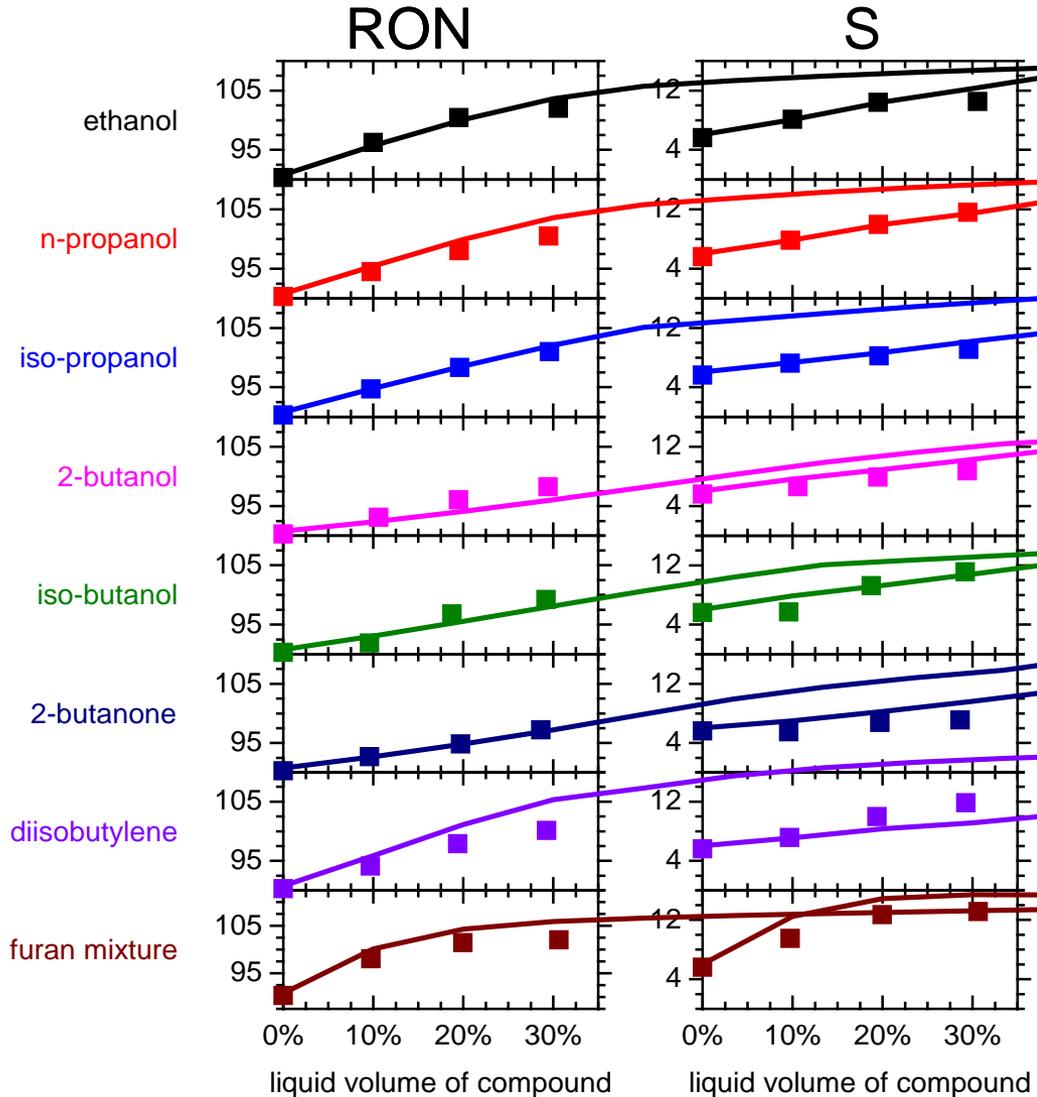
### Gasoline surrogate kinetic model used to simulate blends from Tier 2 screening

- Octane number data for blends of the Co-Optima LD SI engine blendstocks into a four component surrogate was developed by NREL.
- A surrogate was selected to allow kinetic models to be used for comparison
- Here we show comparison of simulated RON and S for the most promising blendstocks

#### Kinetics Surrogate

iso-octane, 55.8%  
 toluene, 25%  
 n-heptane, 14.8%  
 1-hexene, 4.4%

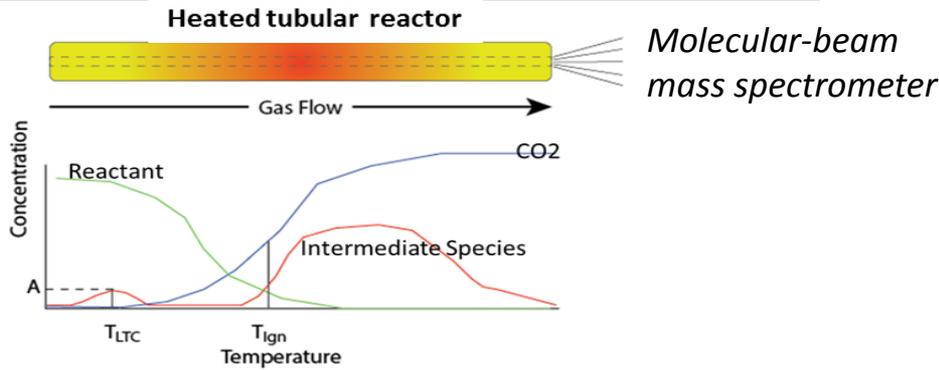
RON	MON	AKI
90.3	84.7	87.5





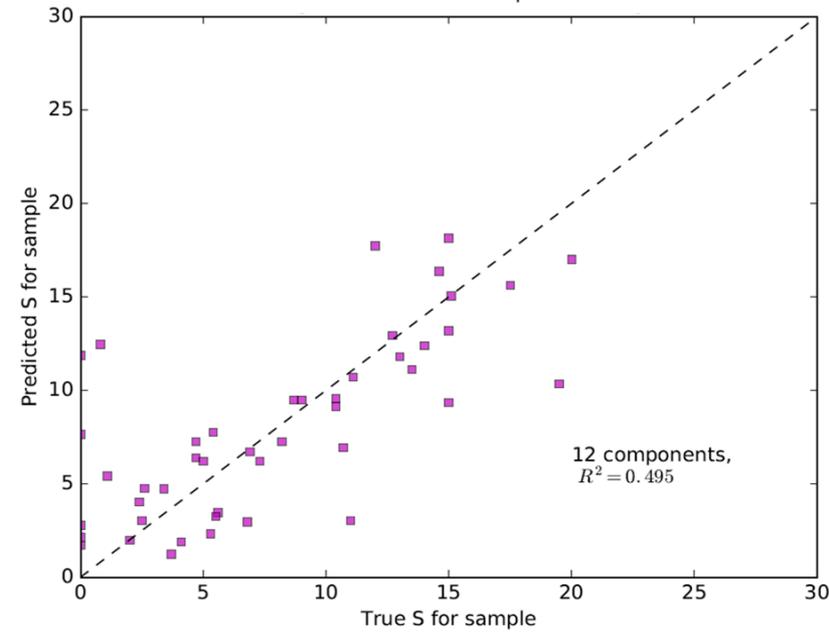
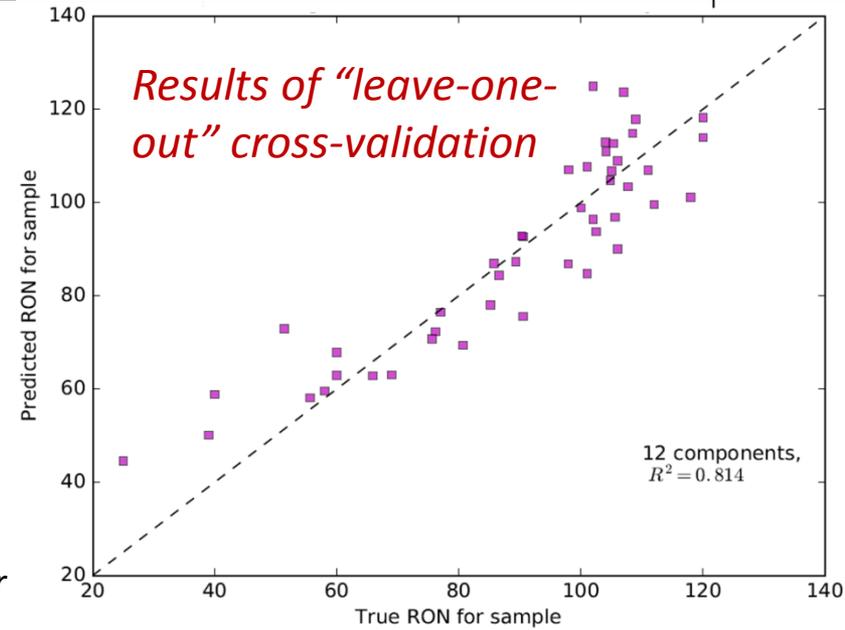
## Demonstrated potential to predict RON and S using small sample volume in a flow reactor

- Concept: predict RON and S using a small volume (< 500  $\mu\text{L}$ ) of material
- Oxidized in a small flow reactor. RON and S predicted from correlation with species profiles observed for a training set



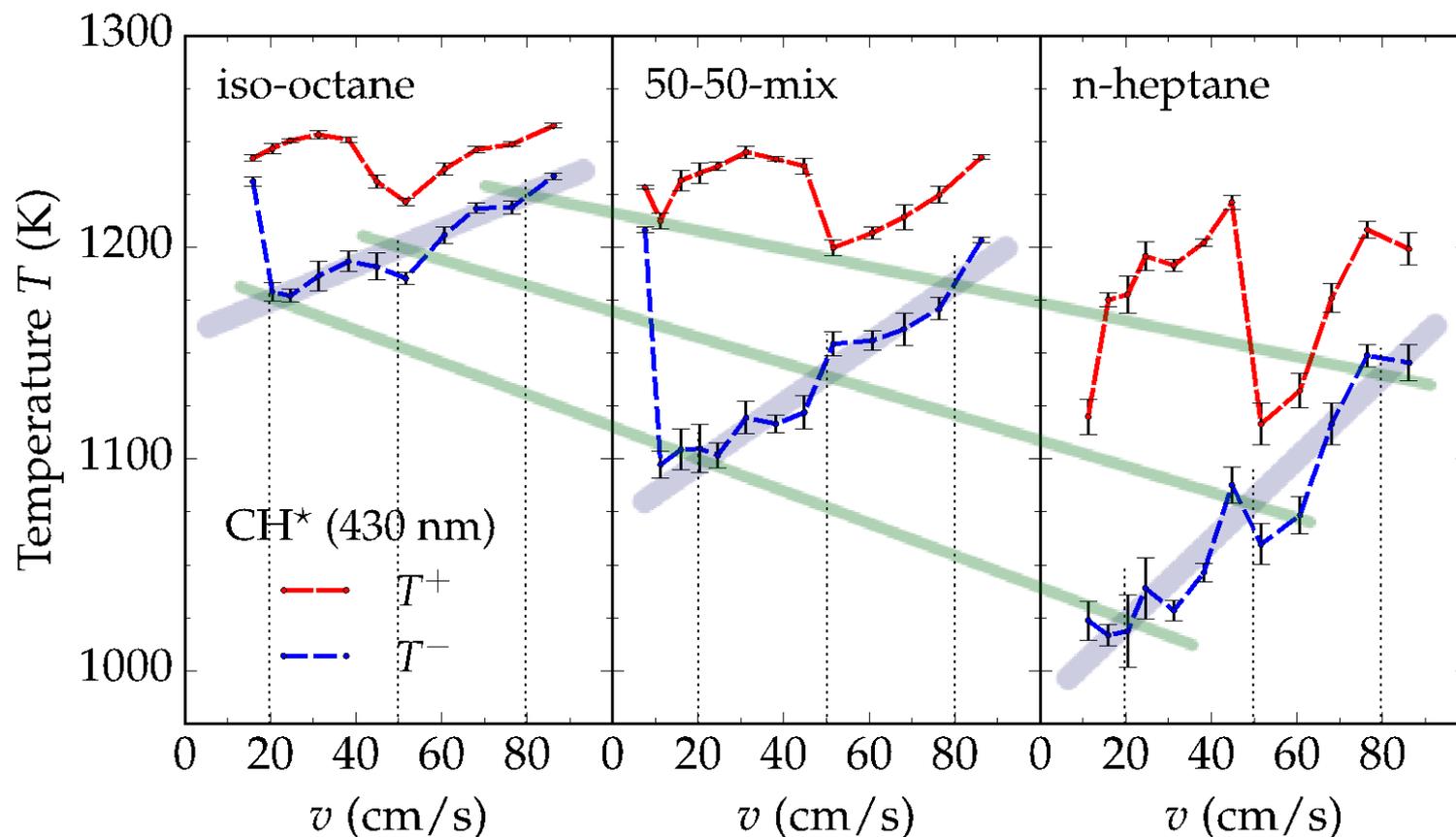
$$\text{Ignition metric} = \alpha \cdot A \cdot T_{\text{LTC}} + \beta \cdot T_{\text{Ign}}$$

- Principal component analysis of runs for 46 “fuels” at three temperatures
- PRF, ethanol-PRF, TRF, and range of pure oxygenates
- Much broader range of oxygenates need to be included in dataset





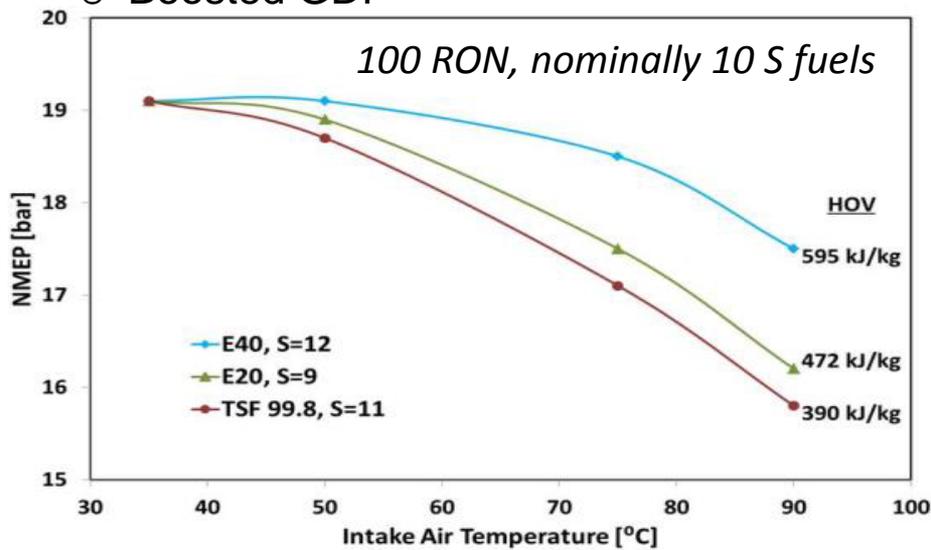
## Microliter Fuel Ignition Tester ( $\mu$ FIT) shows correlation of extinction temperature with PRF RON



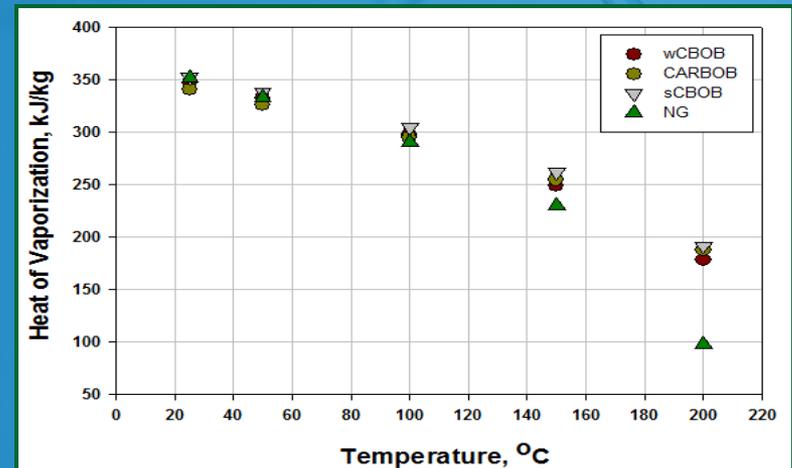


## NREL (Fioroni, McCormick) \$500k: HOV Measurement and Impacts

- HOV can affect knock resistance, particle emissions, and other aspects of engine efficiency
- Recent work shows this is a function of engine operating conditions
- Under some conditions HOV is a component of S, but as intake temperature is increased it can affect the knock limit
  - Knock-limited loads at late combustion phasing: CA50 = 20.5 CAD ATDC
  - Boosted GDI



- Have developed methods for measuring total and partial HOV
  - Differential scanning calorimetry (DSC)/thermogravimetric analysis (TGA)
  - Calculation from detailed hydrocarbon analysis (DHA)
- DHA accurately estimates total HOV for full boiling range gasolines – including effect of temperature
- Working to improve DSC/TGA precision and on methods for partial HOV



Chupka, G.M., et al., "Heat of Vaporization Measurements for Ethanol Blends Up To 50 Volume Percent in Several Hydrocarbon Blendstocks and Implications for Knock in SI Engines" *SAE Int. J. Fuels Lubr.* 2015, doi:10.4271/2015-01-0763.



### Significant improvements in HOV measurement precision

- **Reduced error for standards from 10% to less than 1% in some cases**
  - New DSC/TGA instrument set up with tighter environmental and vibration controls
  - Platinum pans provide better heat transfer and precision. Better fitting pan lids.
- Issues with high vapor pressure compounds:
  - Toluene 2.3 kPa at 20°C – 1.2%
  - Hexane 17.6 kPa at 20°C – 4.9%
  - Evaporation too rapid for accurate heat flow measurement
- Using lids with no pin-hole slowed evaporation rate and produced an improvement in precision

#### Old Method (HOV in kJ/kg):

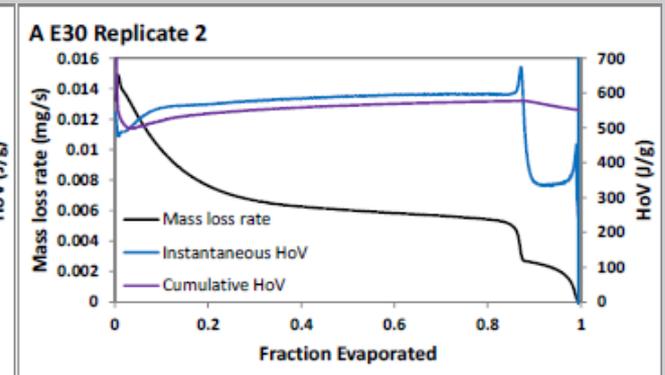
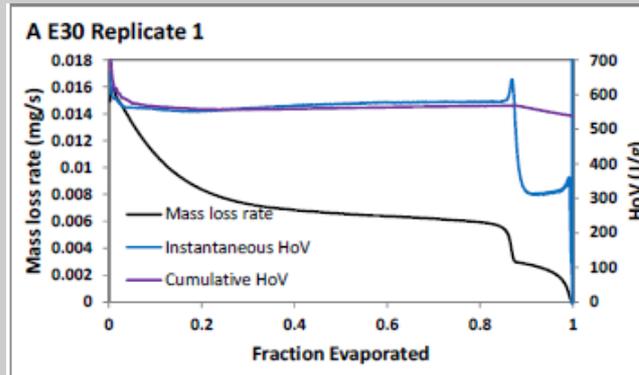
Compound	Literature	Measured	% Error
Toluene	412	450.4	9.3
Hexane	365	405.7	10.8
Isooctane	308	323.2	4.9
ethanol	924	1033.3	11.8

#### New Method (HOV in kJ/kg):

Compound	Literature	Measured	% Error
Toluene	413	408	1.2
Hexane	366	384	4.9
Isooctane	308	307	0.3
Ethanol	924	928	0.4
2-Methylpentane	347	362	4.3
Hexane	366	375	2.7

### Completed CRC Project AVFL-27 measuring HOV of full boiling range gasolines

- Improved data analysis method for DSC/TGA data – instantaneous HOV

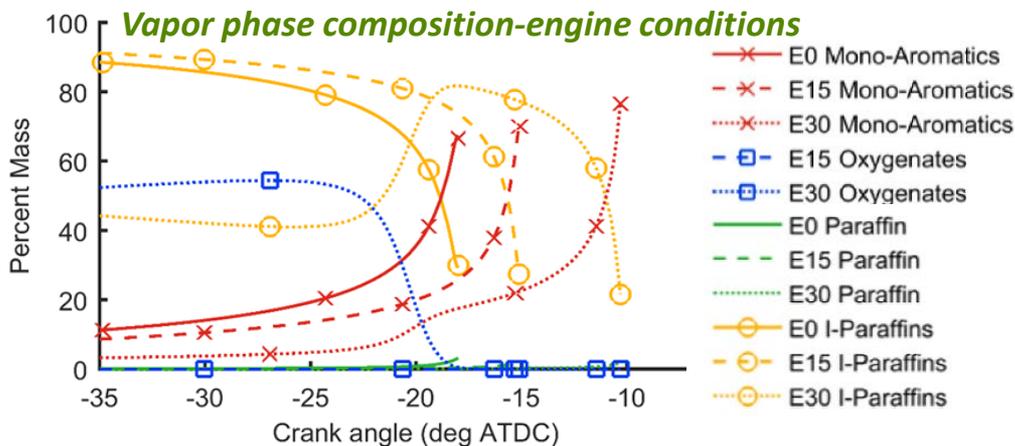
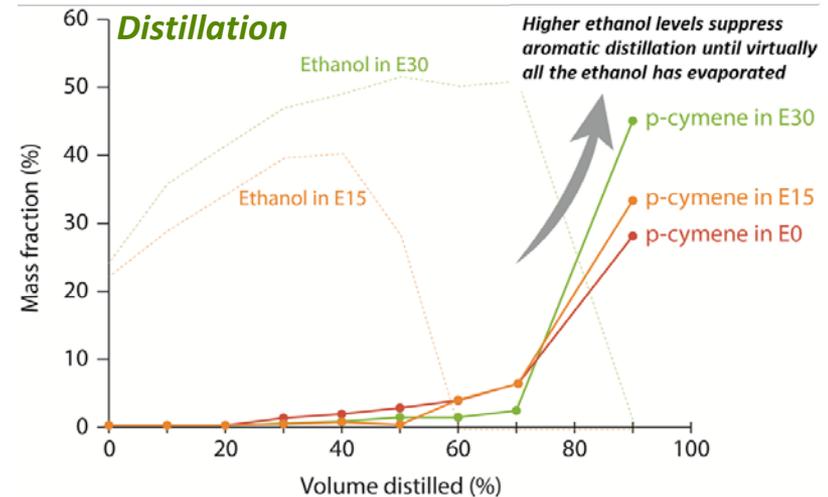




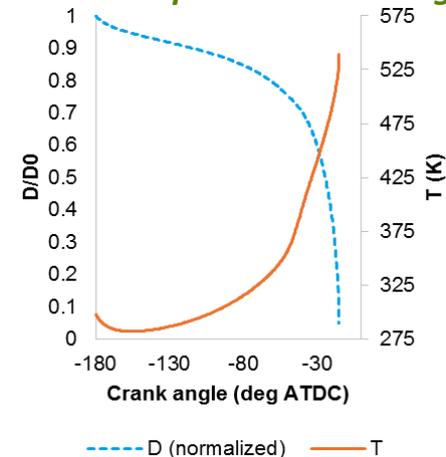
### Droplet vaporization model developed to explore ethanol's (HOV) effect on evaporation

- Evolving droplet composition modeled as a distillation process
  - Composition and distillation curves validated by experiments
  - Distillation measurements show suppression of aromatic evaporation
- Droplet evaporation simulations show:
  - The presence of ethanol reduces droplet temperature and slows evaporation rate
  - Non-ideal vapor-liquid equilibrium and increased HOV alter droplet composition evolution
  - Longer droplet lifetimes predicted at higher ethanol levels and under ramped temperature conditions

**Collaboration with Colorado State University:** Burke, S., Ratcliff, M., McCormick, R.L., Rhoads, R., Windom, B. "Distillation-based Droplet Modeling of Non-Ideal Oxygenated Gasoline Blends: Investigating the Role of Droplet Evaporation on PM Emissions" *SAE Int. J. Fuels Lubr.* 10(1):69-81, 2017, doi:10.4271/2017-01-0581.



### Temperature and droplet diameter-engine conditions





“fuel properties and chemical kinetics, as well as the Thrust I engine projects, are very relevant to helping DOE meet the objectives of petroleum displacement because a major goal is to develop a robust and quantitative understanding of how efficiency is impacted by fuel properties” Response: *We are grateful that the reviewers recognize the importance of the project*

“fuel candidates are being selected without substantial grading by production cost or difficulty....this is the ultimate determinant of the relevancy of the project” Response: *Production cost is being evaluated for the candidates that have passed Tier 2 screening*

“if given the well-acknowledged risks associated with Thrust II engine concepts, whether there is overwhelming evidence that the only barrier remaining for Thrust II engines is the lack of a co-optimized fuel.” Response: *While a co-optimized fuel may not be the only remaining barrier, the lack of focus on a co-optimized fuel for ACI has been a major weakness of prior research*



- Collaboration of nine national laboratories
- Army Research Laboratory
- CanmetENERGY
- Colorado School of Mines
- Colorado State University
- Coordinating Research Council
- Louisiana State University
- National Research Council Canada
- National Institute of Standards and Technology
- University of Connecticut
- Yale University

# Remaining Challenges and Barriers



## **LD SI**

- Recent studies show that RON and S are not fully predictive of autoignition under highly boosted conditions
- While progress has been made, prediction of RON and S for unknown candidates requires significant additional development
- HOV effects on knock, efficiency, and particle emissions remain poorly understood

## **MD/HD Diesel**

- The best potential diesel-range molecules have not yet been identified
- Fuel effects on diesel combustion cannot yet be accurately simulated

## **Lean SI/Mixed Mode ACI**

- How fuel effects differ for lean conditions has not been widely investigated
- Fuel effects on stratified lean SI PM emissions are poorly understood
- Development of fuels with optimal properties for both SI and ACI modes remains challenging

## **MD/HD Full Time ACI**

- Critical fuel requirements for ACI in general are only vaguely understood

# Proposed Future Research



## **LD SI**

- Fundamental research to reduce uncertainty in LD SI merit function, specifically in the areas of improved knock resistance parameters, particulate matter index accounting for the effects of oxygenates, fuel effect on LSPI and catalyst light off

## **MD/HD Diesel**

- Perform Tier 1 and Tier 2 screening of candidate diesel blendstocks
- Research on how the broad range of fuel chemistry accessible in Co-Optima affects the NOx-PM tradeoff, PM reactivity in-cylinder and in diesel particle filter
- Develop a merit function for this combustion mode

## **Lean SI/Mixed Mode ACI**

- Investigate fuel effects on autoignition and PM formation for lean and stratified lean conditions, as well as ACI conditions
- Develop a merit function for this combustion mode

## **MD/HD Full Time ACI**

- Covering a broad range of fuel properties, investigate the magnitude of fuel property effects in this combustion mode
- Develop a merit function for this combustion mode

Proposed future work is subject to change based on funding levels



## Relevance

- Better integration of fuel and engine research critical to accelerating progress towards economic development, energy security, and emissions goals

## Approach

- Reveal through bench and engine experiments how fuel properties that go well beyond those obtainable in conventional petroleum fuels can be leveraged to improve engine performance
- Develop quantitative merit function for fuel effects on efficiency for various combustion strategies

## Accomplishments

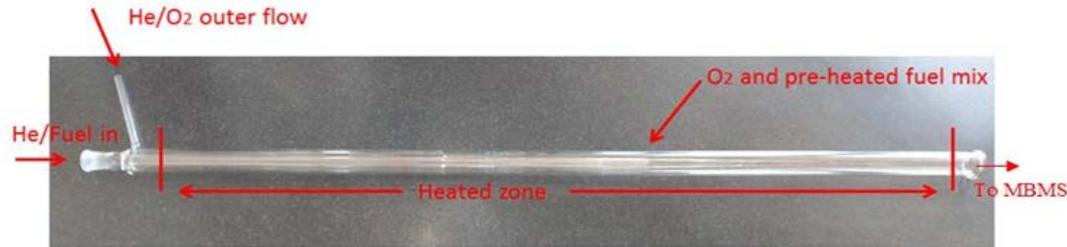
- Defined desired fuel properties for mixing-controlled CI combustion
- Created  $^{13}\text{C}$ -NMR method to predict cetane number of full boiling range fuels
- Completed detailed treatment of thermodynamics and transport properties for multicomponent fuels
- Completed blend property testing and Tier 2 screening for SI combustion
- Developed new correlations bridging fundamental ignition delay time measurements and engine metrics (RON and OS)
- Simulated blends from Tier 2 Screening using gasoline surrogate kinetic model
- Demonstrated potential to predict RON and S using small sample volume in flow reactor
- Microliter Fuel Ignition Tester (mFIT) shows correlation of extinction temperature with PRF RON
- Made significant improvements in HOV measurement precision
- Developed droplet vaporization model to explore ethanol's HOV effect on evaporation

## Collaborations

- "Co-Optima" has nine National Labs, stakeholder engagement, and an external advisory board as well as extensive collaborations with industry and universities

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

# Technical Back-Up Slides

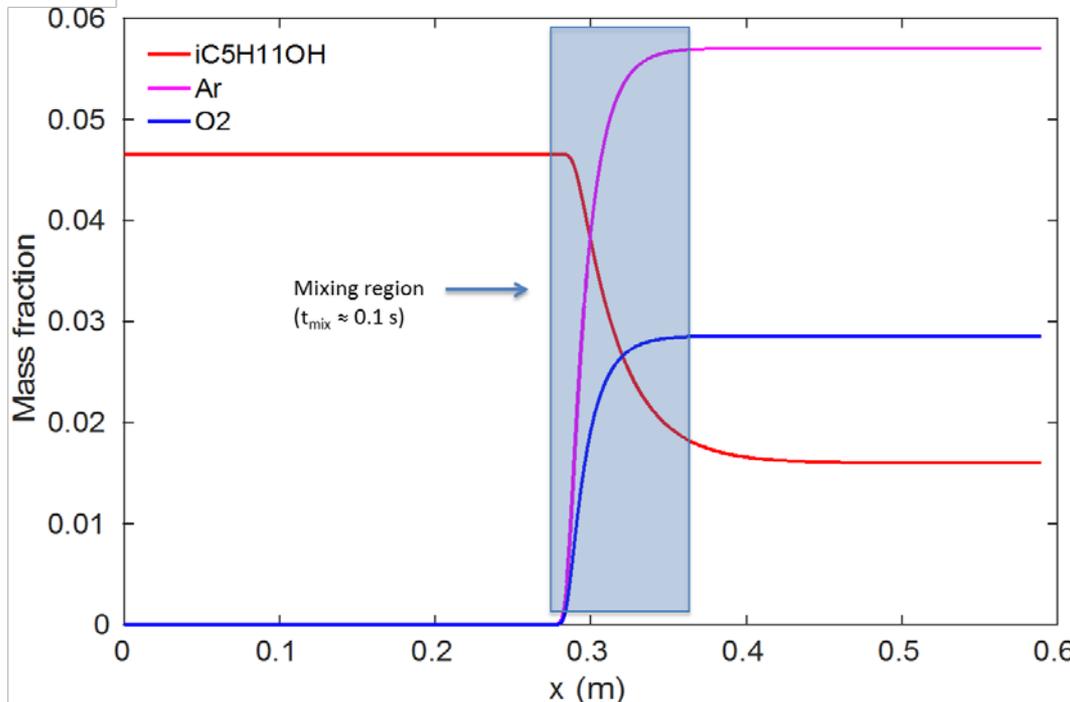
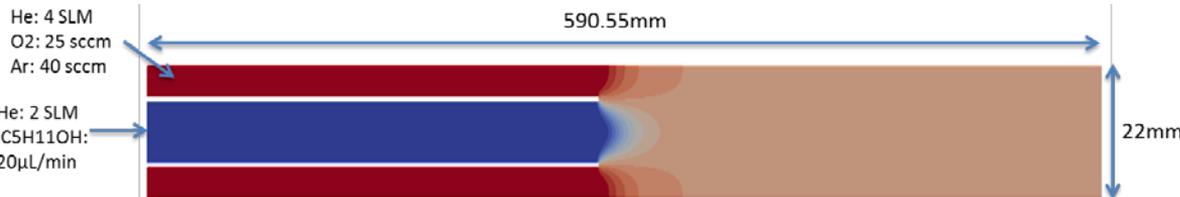


Leave-one-out cross-validation plots show that the predictive model is fairly good within the applicability domain defined by the fuels actually tested.

This test set of 37 fuels was heavily weighted towards PRF, ethanol-PRF, and toluene-PRF blends – although it also included:

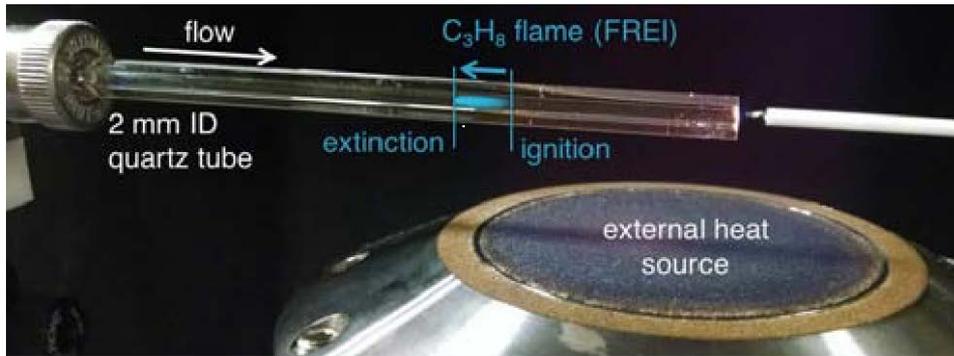
- 5 additional alcohols
- 3 esters
- 2 ketones
- The furan mixture
- One olefin (Diisobutylene)
- Triptane
- A high aromatic blend (Vertifuel)

The LOO cross-validation suggests that with a test set including a wider range of functionality and improved precision a robust model can be obtained.



# Technical Accomplishments and Progress – Backup Slide

## Support $\mu$ -FIT Experimental Design



ID – inside diameter

Figure 1. Experimental setup for  $\mu$ FIT operating with a propane and air flame in the unsteady FREI mode. The time needed for the flame to propagate from the ignition point to the extinction point is much less than the exposure time resulting in the appearance of a broad flame.

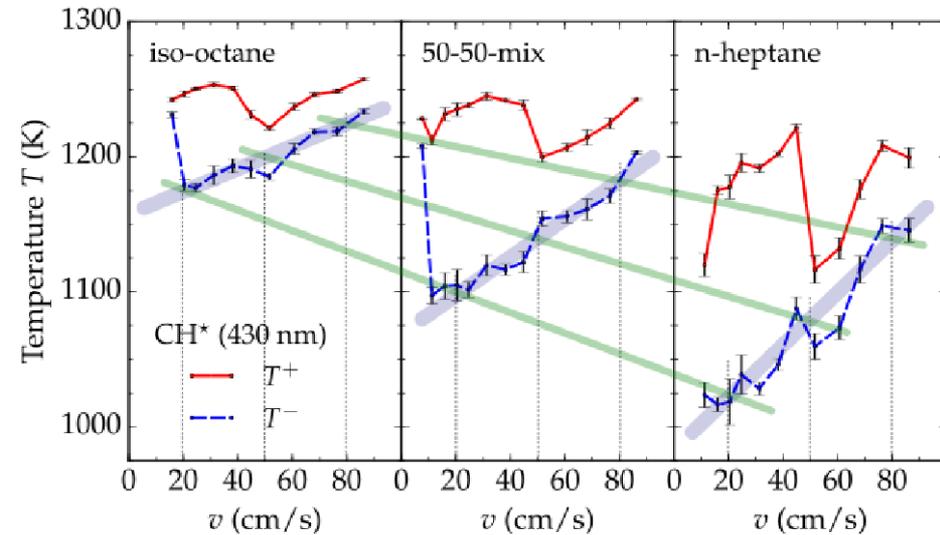


Figure 2. Ignition (red =  $T^+$ ) and extinction (blue =  $T^-$ ) temperatures as a function of the mass-averaged inlet velocity for three PRF mixtures. The green lines illustrate that the extinction temperature at a given velocity appears to increase linearly with increasing iso-octane fraction.



## Heat of Vaporization Measurement and Impacts

### • Droplet evaporation – engine model

- Non-ideal interactions between oxygenates and hydrocarbons by UNIFAC group contribution theory
- Composition and distillation curves were validated by experiments
- With composition calculated throughout the distillation, the changing HOV and other physical properties can be found using reference data.
- The droplet modeled in terms of energy transfer, which in turn provides the transient mass transfer, droplet temperature, and droplet diameter.

Vapor composition – 1000 rpm

