Co-Optimization of
Fuels & Engines

Multi-Mode/Multi-Mode Compression Ignition: Fuel-Property Characterization and Prediction

Presenter: Tim Bays (PNNL)

G. Fioroni (NREL)

M. McNenly and R. Whitesides (LLNL)

Date 03 June 2020

Project # FT067

2020 DOE Vehicle Technologies Office

Annual Merit Review

better fuels | better vehicles | sooner

Overview

Timeline

- Project start date: 10/1/2018
- Project end date: 9/30/2021
- Percent complete: 58%

Budget

Task	FY19	FY20
F.1.2.2a: *PNNL*: Influence of Oxygenate Clustering on Properties Affected by Distillation	$225K	$150K
F.1.3.2: *NREL*: Impact of Azeotropes on Heat of Vaporization and Species Evolution during Fuel Evaporation	$200K	$150K
G.1.1*(a)*: LLNL: Virtual Fuel Blending Models	$75K	$150K

Barriers

- Inadequate fundamental knowledge base for chemical kinetics of low temperature combustion (including multi-mode)
- Lack of fundamental knowledge about impact of fuel kinetics on kinetically controlled engine performance
- Lack of understanding of the impact of future fuels on low-temperature combustion (LTC), and whether LTC can be enabled by new fuel specifications

Partners

- Partners include nine national laboratories, 20+ universities, external advisory board, and many stakeholders

Relevance

Impact:

- ***Advance underlying science needed to develop biomass-derived-fuel and advanced engine technologies that will work in tandem to achieve significant efficiency, environmental, and economic goals***

Objectives:

- **Improved measurement of critical fuel properties relevant to engine efficiency**
  - Gasoline volatility and evaporation
  - Relationships to azeotropic behavior
  - Predictive modeling of properties which blend non-linearly
- **Reveal underlying physical chemistry**
- **Focusing on MM combustion in 2019/2020**
- **Transition to advanced CI combustion in FY20/FY21**

Milestones

Month/Year	Description of Milestone or Go/No-Go Decision	Status	Lab
December 2019	Summary report on the most synergistic and antagonistic BOBs for promising high performance fuels (HPF)	Complete	LLNL
September 2020	Using fuel property data for 2 and 4 component surrogate fuels, such as distillation and vapor pressure, relate observed changes in azeotropic behavior and oxygenate clustering to additive and additive concentrations.	On Target	PNNL

Approach (Management)

Highly Coordinated Effort Between BETO and VTO Offices

Focus of Today's Presentation

Bioenergy Technologies Office (BETO) Tasks

Pacific Northwest NATIONAL LABORATORY — Evgueni Polikarpov, Dan Gaspar

NREL NATIONAL RENEWABLE ENERGY LABORATORY — Bob McCormick, Gina Fioroni, Tom Foust, Seonah Kim, Jon Burton, Teresa Alleman

Sandia National Laboratories — Ryan Davis

Vehicle Technologies Office (VTO) Tasks

Pacific Northwest NATIONAL LABORATORY — Tim Bays, Kee Sung Han, Amity Andersen, John Linehan, Evgueni Polikarpov

NREL NATIONAL RENEWABLE ENERGY LABORATORY — Gina Fioroni, Bob McCormick, Abhijit Dutta

Lawrence Livermore National Laboratory — Matt McNenly, Russell Whitesides

Highly experienced team knowledgeable in fuel property characterization

Approach (Technical)

Measurement and understanding of gasoline-like fuel volatility

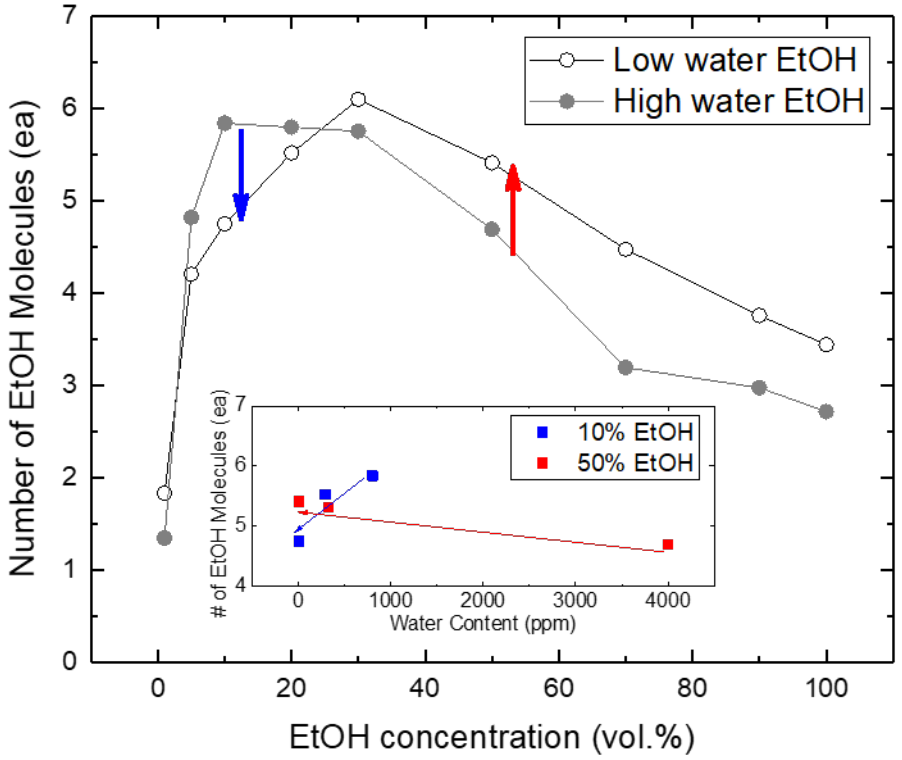
- F.1.2.2 Apply NMR diffusion measurements and molecular dynamics simulations to reveal clustering of alcohol molecules and the impact of this phenomenon on non-ideal solution behavior (RVP), relating that behavior to differences in fuel azeotropic behavior (distillation) – *PNNL*
- F.1.3.2 Utilize differential scanning calorimetry (DSC)/ thermogravimetric analysis (TGA) coupled to mass spectrometer, coupled with simulation, to quantify and understand heat of vaporization and azeotropic effects on gasoline evaporation – *NREL*

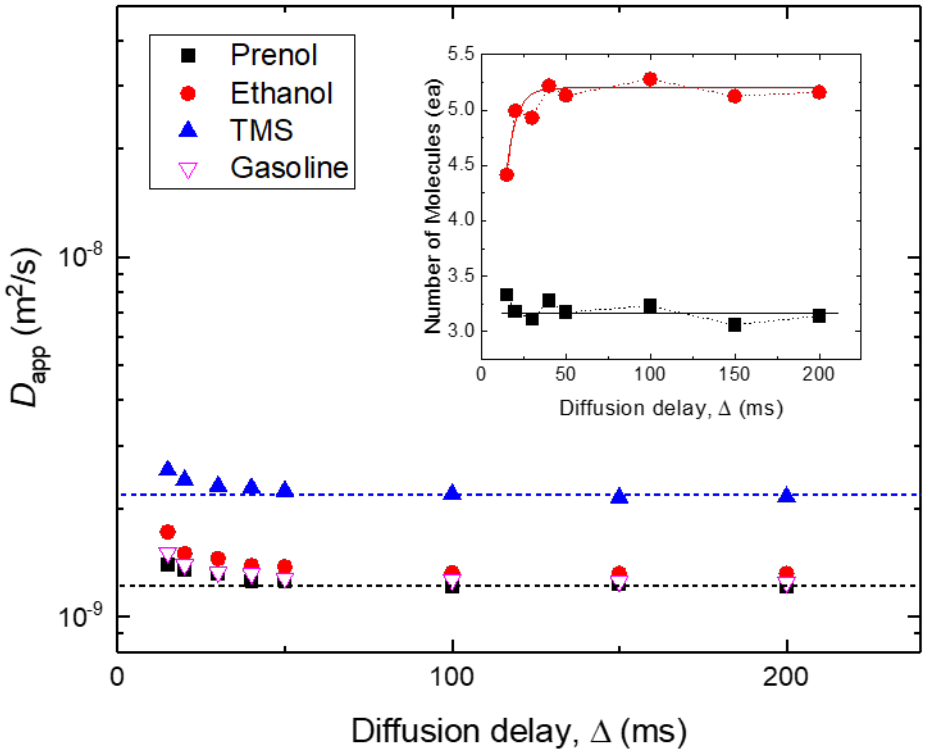
Fuel blending

- G.1.1.LLNL(a) – Use neural networks to predict key fuel properties, such as octane, for BOBs for composition-sensitive synergistic blending – *LLNL*

Technical Accomplishment: PNNL (Bays) Influence of Oxygenate Clustering on Properties Affected by Distillation

Even small amounts of water are impactful, and the identity of the hydrogen-bonding component impacts the molecular-level. This effect can be observed using vapor pressure.





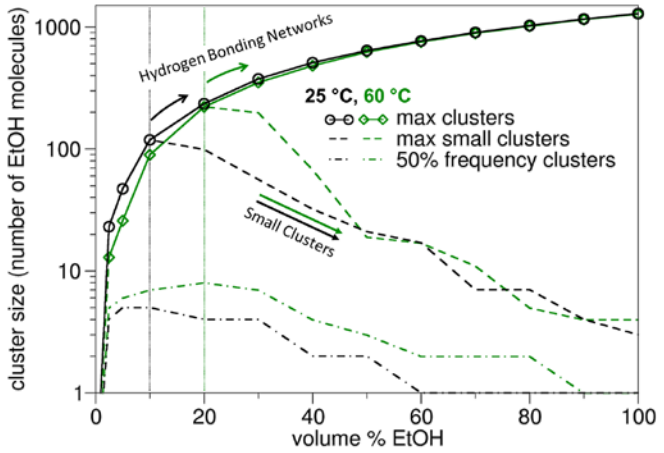
- Increasing water content changes the cluster size distribution and onset of hydrogen-bonding network formation.
- Prenol and ethanol seem to behave independently in solution. This is contrary to expectations for a homogenized solution.

Impact: Understanding how oxygenate clusters and networks contribute to vapor pressure is critical for correctly predicting fuel droplet evaporation, and effects on combustion

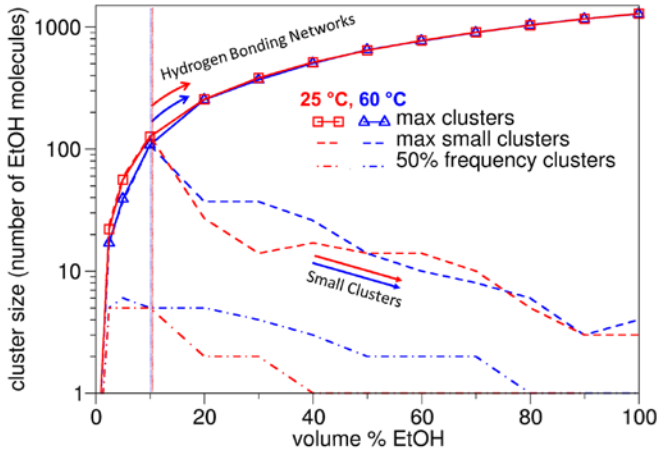
Technical Accomplishment: PNNL (Bays) Influence of Oxygenate Clustering on Properties Affected by Distillation

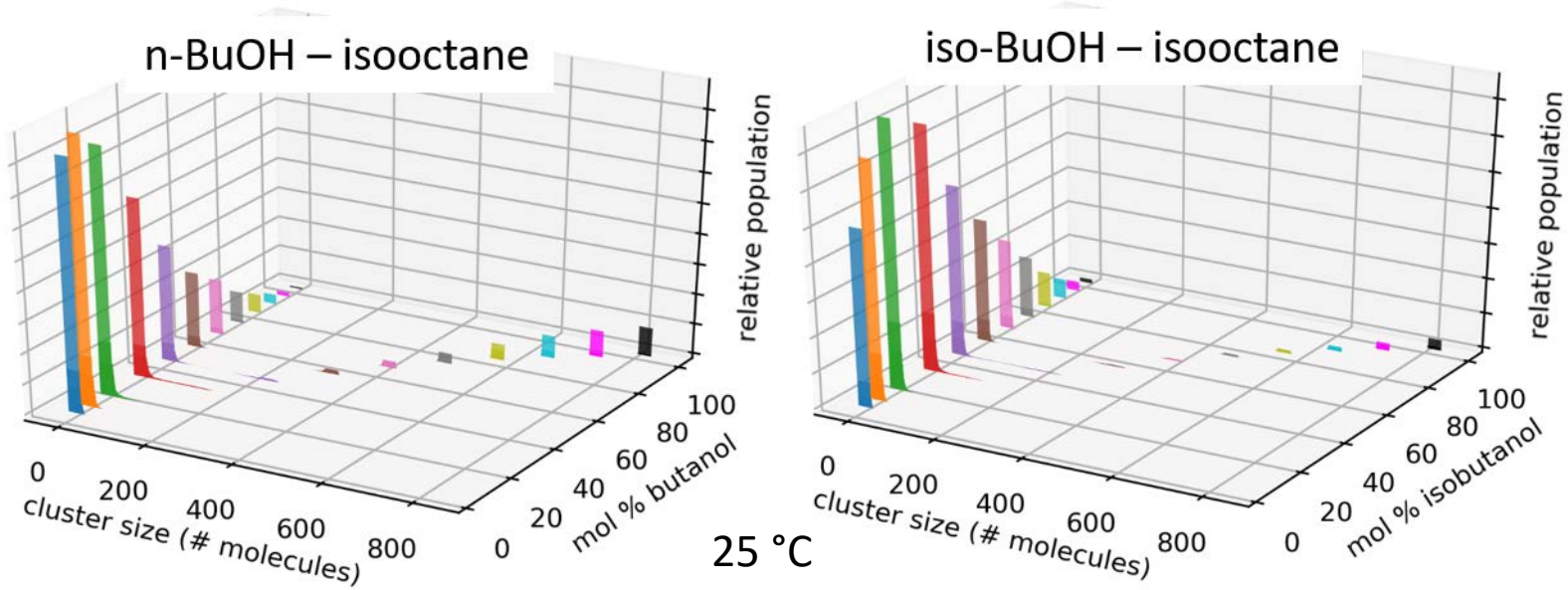
Molecular dynamics simulations show how fuel and temperature affect the transition from discrete molecular clusters to hydrogen-bonding networks

EtOH in n-Heptane



EtOH in i-Octane



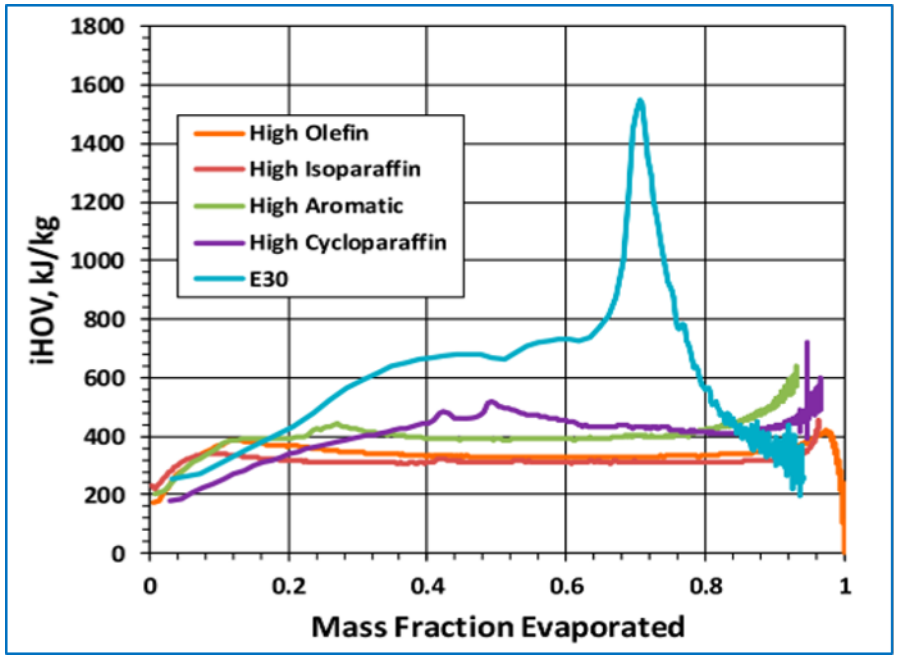


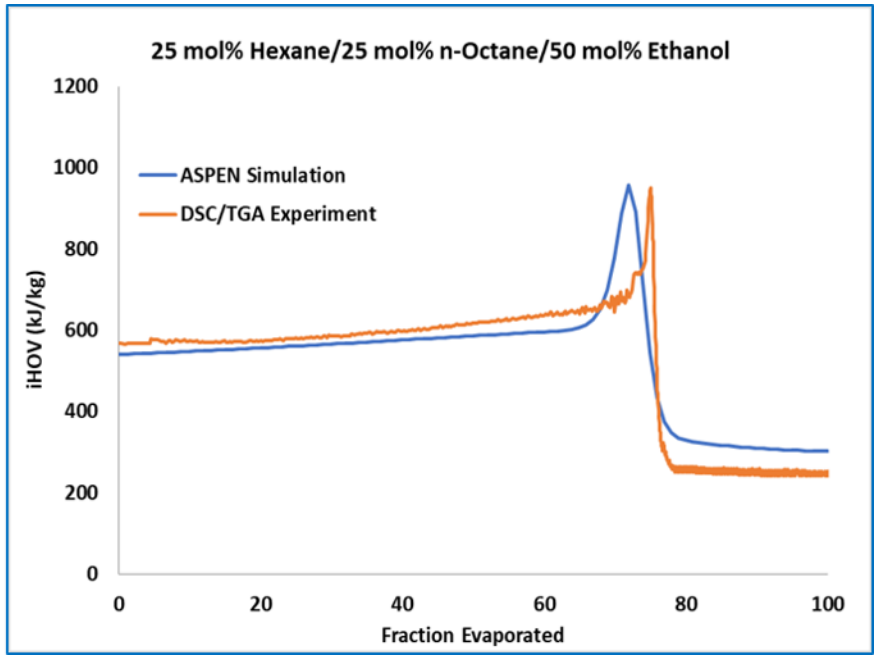
- Temperature and fuel identity determine the transition between clusters and hydrogen-bonding networks.
- Maximum butanol clustering occurs later for *iso*-butanol than for *n*-butanol, suggesting that the butanol-butanol interactions are poorer for *iso*-butanol than for *n*-butanol.

Impact: Understanding how oxygenate clusters and networks contribute to vapor pressure is critical for correctly predicting fuel droplet evaporation, and effects on combustion

Technical Accomplishment: NREL (Fioroni) Impact of Azeotropes on Heat of Vaporization and Species Evolution

Utilize DSC/TGA in combination with simulation results to evaluate the effect of molecular structure on heat and species evolution





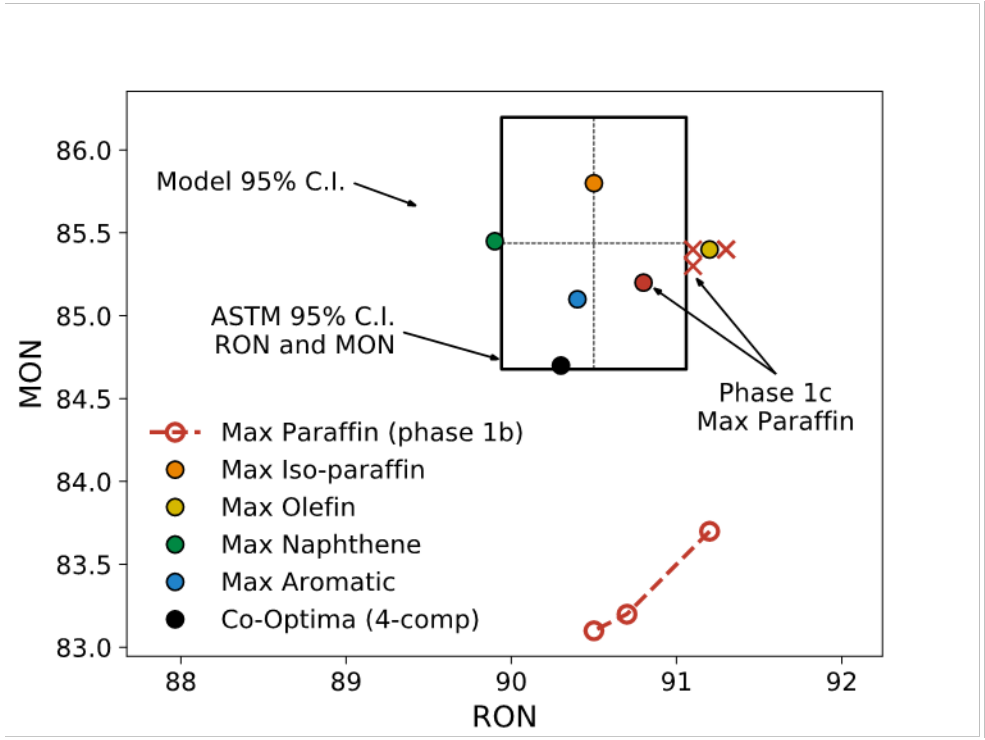
Impact: Gasoline-alcohol blend evaporation is dominated by azeotropic interactions impacting ignition timing, temperature stratification, and emissions

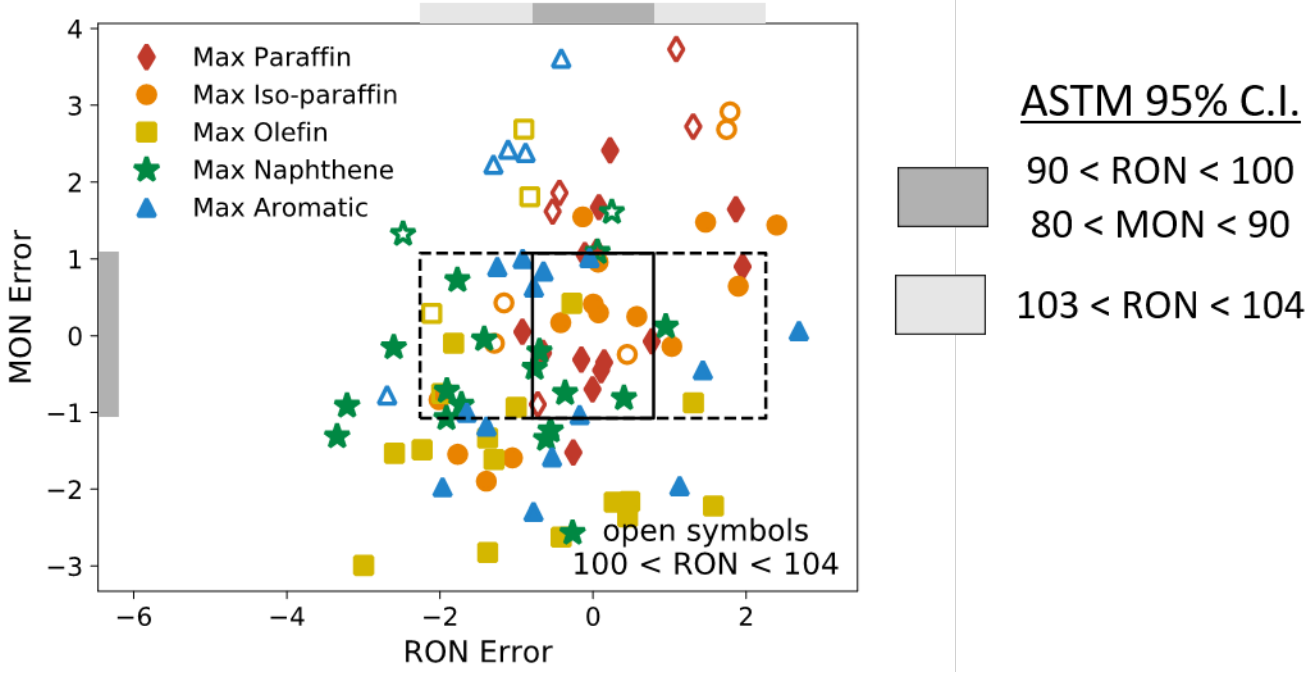
Energy Fuels 2018, 32, 12, 12607-12616

- Initially thought large spike in instantaneous heat of vaporization (iHOV) was an artifact of experiment due to offset in timing of heat flow and mass evaporated
  - ➢ ASPEN simulations show large spike in iHOV that compares well with experimental data
- Currently investigating what interactions could cause large spike in iHOV and additional cases will be simulated as needed, including more complex mixtures exhibiting this behavior

Technical Accomplishment: LLNL (McNenly) Neural network predicts octane numbers with a mean absolute error < 1.1 RON and 1.2 MON

The five new BOBs and the original Co-Optima 4-component BOB are within 0.7 RON and 0.6 MON of the cluster center





- A Bayesian blending model was created to make small, local adjustments to the physical BOB compositions to better cluster the blends and establish the probability of matching within the test budget.
- All results shown are true predictions that did not take advantage of any of the new experiments - updated neural network will be even more accurate for nonlinear blending.

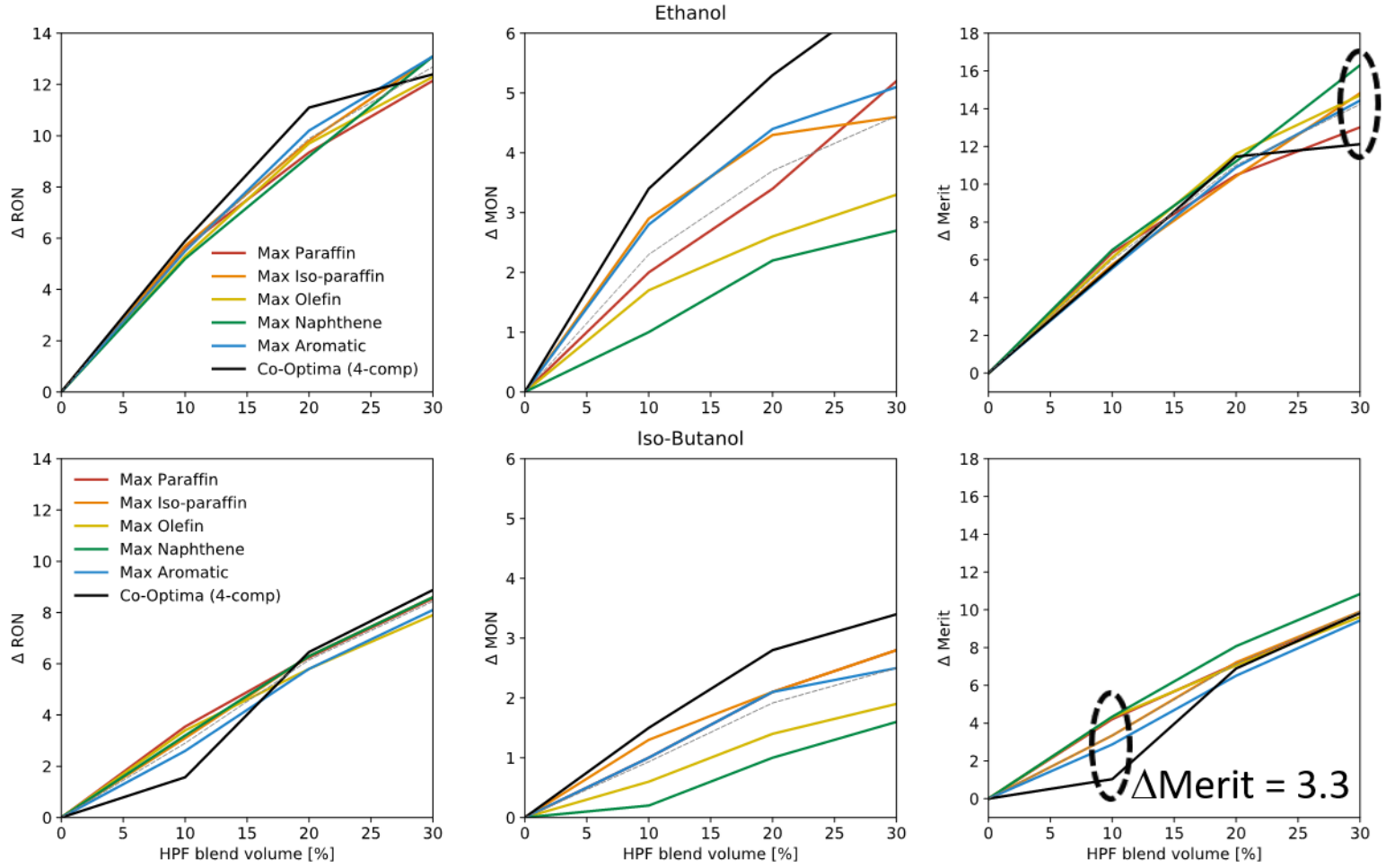
Impact: It is now possible to better predict non-linear blending and explore a broad range of compositions to elucidate the chemical reasons for synergistic blending.

Technical Accomplishment: LLNL (McNenly) Three high performance fuels show a merit score spread of 3.0 or greater

Three blendstocks show that the composition of the BOB, not just the octane rating, can change the potential engine efficiency gain by 3.0%

Ethanol

Iso-Butanol



Impact: Neural network model can be combined with blendstock cost data to optimize a BOB for certain HPFs with composition-sensitive synergistic blending.

Technical Accomplishment: LLNL (McNenly) Model predictions of merit score spread are generally greater than measured experimentally

Searching for the maximum merit score spread over a diverse collection of BOB surrogates focuses a limited number of experiments on the compositions with the greatest potential for synergistic blending optimization AND improvement to the blending model.

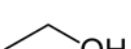
Blending Predictions (AMR 2018):

Blendstocks	Merit Score Error	RON Spread	Most Antagonistic	Most Synergistic	Sensitivity Spread	Most Antagonistic	Most Synergistic	Merit Score Spread	Most Antagonistic	Most Synergistic
2-butanol	1.1	1.9			3.1			3.6		
2-methyl-1-propanol	1.8	2.6			2.4			3.5		
ethanol	1.8	2.4			2.7			3.5		
diisobutylene mix	2.1	2.7			1.0			2.4		
methanol	1.6	2.3			3.0			3.5		
furan mix	1.2	2.3			3.5			3.4		
methoxybenzene	***4.4***	2.9			2.4			2.9		
cyclopentanone	2.3	1.6			3.1			2.5		
2-pentanone	2.9	3.2			3.8			4.4		
methylacetate	2.6	3.1			2.9			4.2		
3-pentanone	1.5	2.9			3.0			4.1		
2-propanol	0.6	2.7			2.8			3.7		
ethylacetate	3.0	2.9			2.8			3.4		
1-propanol	1.3	2.8			2.1			3.3		
2-methyl-1-butanol	1.1	1.8			1.2			1.7		
1-butanol	1.0	1.5			1.9			1.7		
3-methyl-1-butanol	0.5	1.5			1.0			1.4		

- **Max Paraffin**
- **Max Iso-paraffin**
- **Max Olefin**
- **Max Naphthene**
- **Max Aromatic**
- **Co-Optima 4-component BOB (by volume):**
  - 55% iso-octane
  - 25% toluene
  - 15% n-heptane
  - 5% 1-hexene

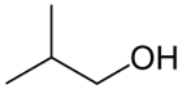
Validated HPF Blendstocks (AMR 2020):

ethanol



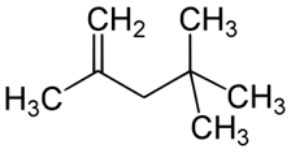
ΔMerit
pred: 3.5
meas: 4.2

iso-butanol



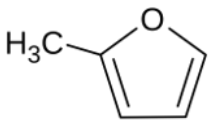
ΔMerit
pred: 3.5
meas: 3.3

diisobutylene



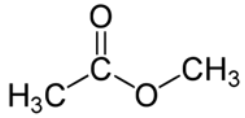
ΔMerit
pred: 2.4
meas: 2.2

2-methylfuran



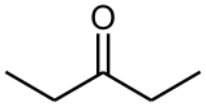
ΔMerit
pred: 3.4
meas: 2.4

methyl acetate



ΔMerit
pred: 4.2
meas: 1.9

3-pentanone



ΔMerit
pred: 4.1
meas: 3.0

Impact: Validated neural network octane model can be used to ensure a minimum high-load performance when screening potential blends for multi-mode engine applications.

Responses to Previous Year Reviewers' Comments (Vaporization)

Several reviewers indicated a desire to link the work on clustering and iHOV/azeotropic behavior more closely to engines, sprays, and spray modeling. *Summarized comments and responses:*

- ***A missing connection seems to be to real spray behavior.***

  RESPONSE: We agree and have been working to address them. Proposed work in FY21 will perform droplet evaporation modelling of systems that we have investigated (iHOV, azeotropic behavior, clustering). In FY20 we are running parallel experiments (DSC/TGA, NMR-clustering) to determine whether water has a strong heat effect in the DSC/TGA experiments, and do multi-alcohol systems behave in the same manner as single alcohol systems. Do these affect the size of the spike in the iHOV that was noted in DSC/TGA experiments and ASPEN simulations? How do changes in clustering affect distillation azeotropes?

- …**whether work has begun to translate this fundamental behavior [oxygenate clustering] into evaporation modeling.**

  RESPONSES:

  – We are working to link our clustering work and evaporation modeling efforts more closely in FY20 and in proposed work for FY21. We believe this to be very important.

  – We appreciate the Reviewer's references to research by C. Hasse and co-workers, as well as suggesting that modeling leverage standard fuel injectors used in the ECN.

Responses to Previous Year Reviewers' Comments (Vaporization)

- The reviewer stated that development and improvement of new testing methods for characterization of fuels is central to developing increased understanding of fuels and fuel properties. The reviewer would like to have seen a more comprehensive discussion of why these specific fuel parameters were studied and what specific technical barrier is being addressed.

  RESPONSE: Fuel droplet evaporation, distillation, and azeotropic behavior resulting from alcohols has the potential to affect ignition delay and fuel stratification, and address the barriers noted for understanding combustion kinetics.

Responses to Previous Year Reviewers' Comments (Simulations)

- "**According to the reviewer, the approach of this work is fantastic.** It was nice seeing an effort to develop rapid screening tools for combustion properties of fuel blends that so nicely couples with the central fuel hypothesis. Because this work's foundation is solidly rooted in the two hypotheses outlined by the Co-Optima program, the directions taken by the program have significantly impacted the overall program."

  RESPONSE: Thanks reviewer 1!

- In predicting RON, MON, and blending effects, the fidelity of the simulation was not clear to the reviewer. Dependencies blending effects upon engine operating condition, and for a mixed-mode direct injection spark ignition (DISI) engine, flame propagation subject to mixture stratification is essential. These were not sufficiently addressed.

  RESPONSE: The RON and MON are predicted using a neural network that takes single reactor ignition delay calculations from the detailed gasoline mechanism as well as other molecular structure and readily available thermophysical properties as inputs. The training data are actual ASTM experimental measurements, so the neural network has the flexibility to correct errors in the underlying mechanism used for the ignition delay inputs. The new models developed for Task G.5.3 will have the ability to capture both flame propagation and mixture stratification.

Responses to Previous Year Reviewers' Comments (Simulations)

- Although this reviewer indicated that the project seemed to be on track toward its overall goal, the reviewer expected to see results on uncertainty quantification of the simulation, suitable accommodation of mixing and flame propagation in the computationally efficient metric, as well as validation against DISI engine experiment in the future. Additionally, a more suitable performance metric has to be defined for other modes such as ACI and mixed-mode for fuel screening. The fact that fuels with the same RON and MON can perform differently does not necessarily invalidate the central fuel hypothesis because it is probable the key fuel property has yet to be correctly identified.

  RESPONSE: We agree that different engine performance for blends with identical octane ratings is evidence than a new property or dimension should be considered for the Central Fuel Hypothesis to hold. One of the goals of the new models developed for Task G.5.3 is to identify missing metrics that rely on charge preparation, stratification, mixing and flame propagation. Once the models are validated, they can be used to assess for uncertainty quantification. These tasks were originally planned for late FY19, but had to be delayed to accommodate a funding shortfall.

Collaboration and Coordination with Other Institutions

- ***Collaboration among nine national laboratories***
- ***LLNL - Collaboration across VTO programs -*** *(Virtual fuel models are designing the gasoline surrogate for the $12M/yr Partnership to Advance Combustion Engines (PACE) Program)*
- **NREL - Pennsylvania State University** (Kinetic and Molecular Dynamics Simulations)
- **NREL - Colorado State University** (*Advanced Distillation and Droplet Evaporation Simulations*)
- **PNNL - NREL - Coordinating Research Council** (*HOV Measurements-AVFL-27-2 and diesel fuel surrogates-AVFL-18a*)
- **PNNL - Yale University** *(Yield Sooting Index)*
- **LLNL - Penn State University** *(Yield Sooting Index Advanced Flame Solver)*
- **LLNL - Louisiana State University** *(Microliter Flow Reactor)*

<u>Coordination:</u>

- Monthly team meetings, quarterly face-to-face leadership planning meetings, and an annual all-hands meeting
- Monthly stakeholder updates including technical highlights and deep-dive presentations – more than 85 individuals at 46 organizations across industry and other non-DOE governmental agencies

AVFL: Advanced Vehicle/Fuel/Lubricants
DOE: Department of Energy

Remaining Challenges and Barriers

- **Lack of fundamental knowledge of the key reaction species that explain phi-sensitivity and non-linear octane blending**
- **A well defined metric to describe and measure phi-sensitivity for a broad range of fuel molecular structures is needed**
- **Fuel-Engine experiments and high-fidelity simulations can not generate enough data to discover hidden fuel properties using unsupervised learning (data mining)**
- **Absence of foundational understanding about the fuel ignition and soot formation mechanisms as well as the kinetics impact on dilute gasoline, low-temperature, and clean diesel combustion**
- **The effect of chemical composition on the evaporation process for gasoline-like fuels is not accounted for in current models, including effects of HOV, alcohol clustering, and non-idealities such as azeotrope formation. Work to investigate the impact of properties of fuel blends and associated molecular structure on spray evaporation is lacking.**

Proposed Future Research

- **Fundamental research on understanding the key reaction species that explain phi-sensitivity and non-linear octane blending. (G.1.1.LLNL(a))**
- **Use unsupervised machine learning to cluster simulated chemistry features to uncover hidden correlations between lower fidelity engine models and engine performance. (G.1.1.LLNL(a))**
- **Perform multi-component spray droplet vaporization simulations to translate the impact of increased heat of vaporization with alcohol vaporization, observed in DSC/TGA experiments and ASPEN simulations, on mixture stratification due to spray evaporation. (F.1.2.5 and F.1.2.2a)**
- **Quantify the relationship between distillation properties and autoignition (octane) to take advantage of synergistic effects to develop high-sensitivity blendstocks for multi-mode combustion. (F.1.2.5)**
- **Continue work in FY20 that determines the influence of small molecules on clustering. (F.1.2.2a)**
- **Develop methods to control and optimize fuel component vapor-liquid partitioning, through modification of distillation azeotropes, use small molecules, to improve distillation-dependent properties, such as ignition timing, charge temperature and stratification, and emissions. (F.1.2.2a)**

Any proposed future work is subject to change depending on funding levels

Summary

- Implemented NMR diffusion experiments and molecular dynamic simulations to evaluate alcohol cluster size as a function of alcohol, temperature, and fuel.
  Impact: Understanding how oxygenate clusters and networks contribute to vapor pressure is critical for correctly predicting fuel droplet evaporation, and effects on combustion.
- Implemented significant method improvements to DSC/TGA HOV method to reduce sample loss and improve precision.
  Impact: Method improvements allow for better accuracy: understanding how fuel evaporation phenomena can impact autoignition, mixing, and pollutant formation.
- Utilized DSC/TGA/MS in combination with simulation results to evaluate molecular structure effects on species evolution during evaporation.
  Impact: Gasoline-alcohol blend evaporation is dominated by azeotropic interactions impacting ignition timing, temperature stratification, and emissions.
- Synergistic blending test campaign completed for 5 new BOBs and 6 HPF blendstocks (95 measurements).
  Impact: Chemical composition of the BOB accounted for a merit score spread greater than 3.0 for three blendstocks (ethanol, iso-butanol and cyclopentanone) suggesting synergistic blending may be optimized.

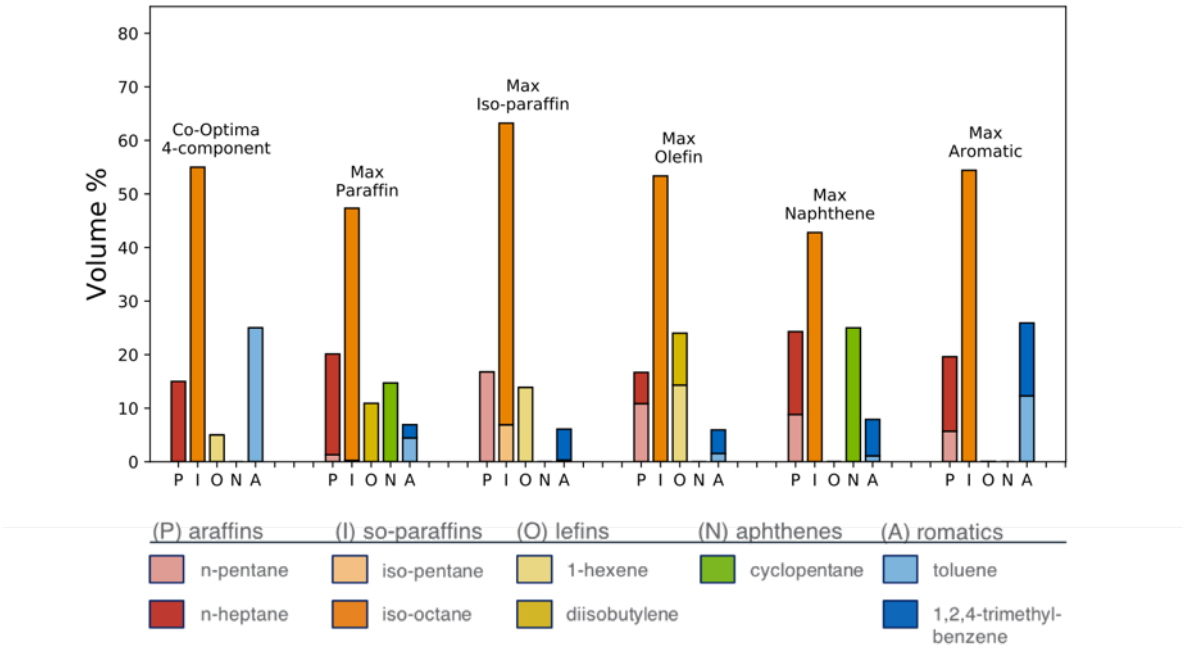
List of Acronyms and Abbreviations

ACI: advanced compression ignition
AKI: anti-knock index
AMR: Annual Merit Review
ASTM: ASTM International
AVFL: Advanced Vehicle/Fuel/Lubricants
BETO: Bioenergy Technologies Office
BOB: blendstock for oxygenate blending
BuOH: butanol
CI: compression ignition
C.I.: confidence interval
D_{app}: apparent diffusion coefficient
DISI: direct injection spark ignition
DSC: differential scanning calorimetry
DOE: Department of Energy
ea: each
E30: gasoline containing 30 volume percent ethanol
ECN: Engine Combustion Network
EtOH: ethanol
HOV: heat of vaporization
HPF: high-performance fuel
i-: *iso-*
iHOV: instantaneous heat of vaporization
K: Kelvin
LLNL: Lawrence Livermore National Laboratory
LTC: low-temperature combustion
meas.: measured
MCCI: mixing compression controlled ignition
MM: multi-mode
MON: motor octane number
m: meters
ms: milliseconds
mol.%: percent by mole
MS: mass spectroscopy
NMR: nuclear magnetic resonance
NREL: National Renewable Energy Laboratory
PNNL: Pacific Northwest National Laboratory
pred.: predicted
PrOH: propanol
RON: research octane number
RVP: Reid vapor pressure
s: seconds
S: sensitivity (S= RON-MON)
TGA: thermogravimetric analysis
TMS: tetramethylsilane
vol.%: percent by volume
VTO: Vehicle Technologies Office

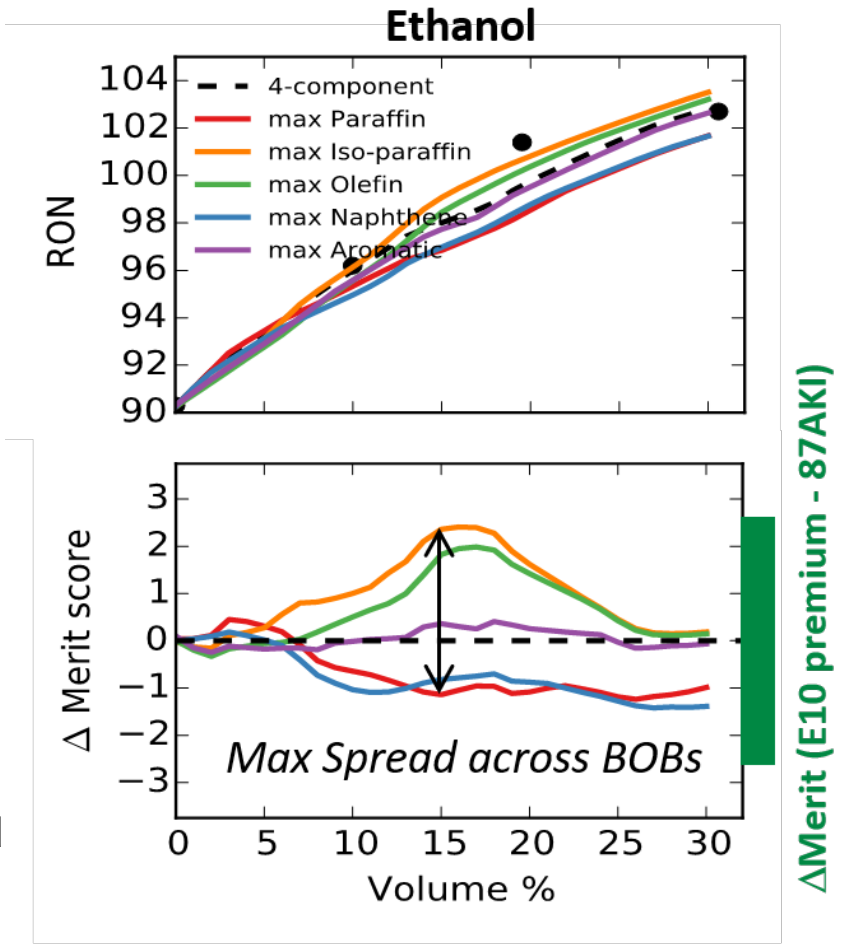
Technical Back-Up Slides

Technical Accomplishment: LLNL (McNenly) Test campaign completed to validate neural network octane model predictions for synergistic blending

Variation in merit score predicted by the neural network is 60% of the efficiency benefit switch from regular to E10 premium for six HPF blendstocks.



- Each new BOB designed to maximize one PIONA class and match the Co-Optima BOB octane rating
- 95 new RON and MON tests with ethanol, iso-butanol, 2-methylfuran, 3-pentanone, methyl-acetate, and diisobutylene mixed in each BOB.



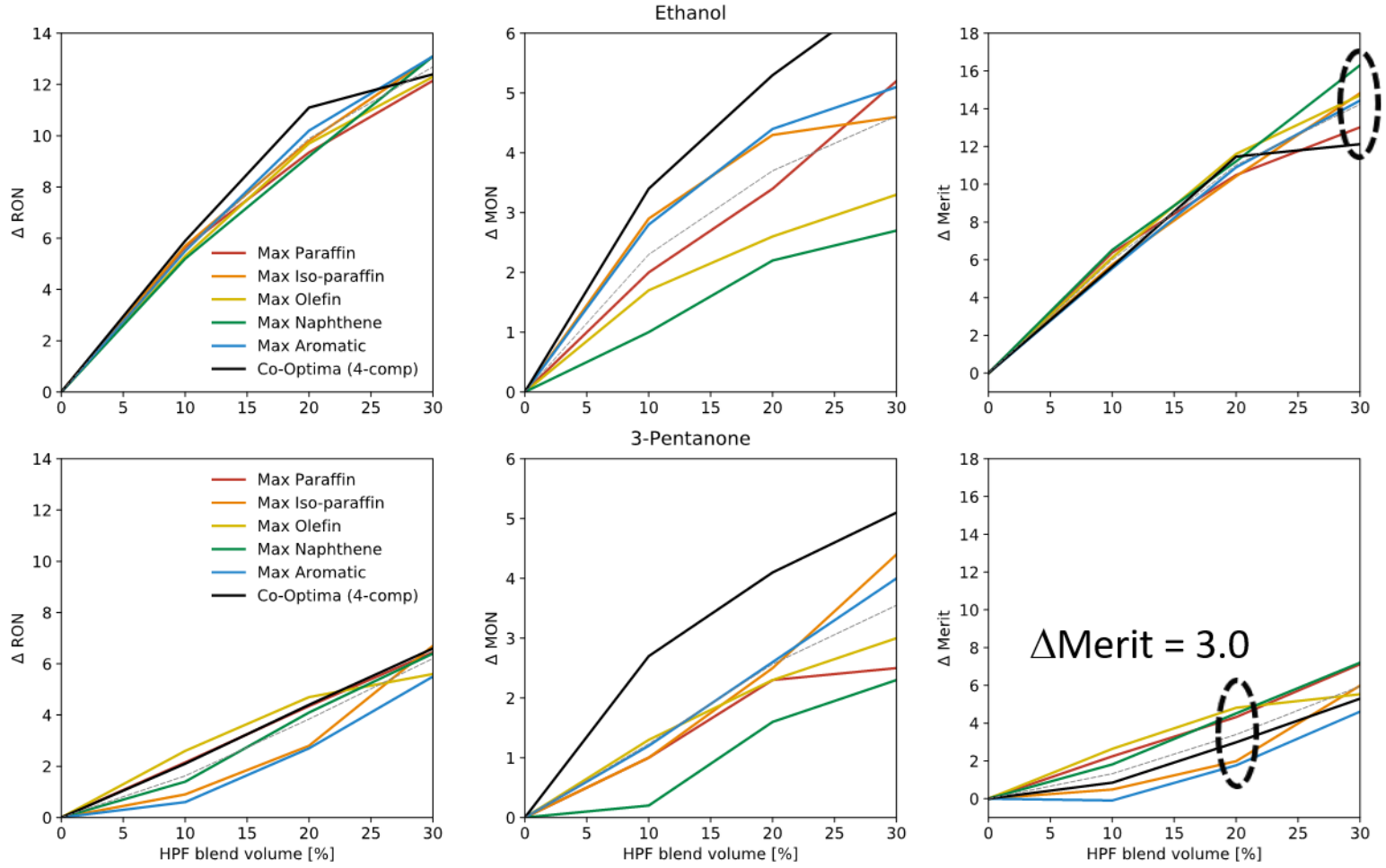
Impact: Determine if a composition property needs to be considered for HPF octane blending performance for the Central Fuel Hypothesis to be valid.

Technical Accomplishment: LLNL (McNenly) Three high performance fuels show a merit score spread of 3.0 or greater

Three blendstocks show that the composition of the BOB, not just the octane rating, can change the potential engine efficiency gain by 3.0%

Ethanol

3-Pentanone



Impact: Neural network model can be combined with blendstock cost data to optimize a BOB for certain HPFs with composition-sensitive synergistic blending.