Co-Optimization of
Fuels & Engines

Fuel Property Characterization and Prediction

Presenter: Gina Fioroni

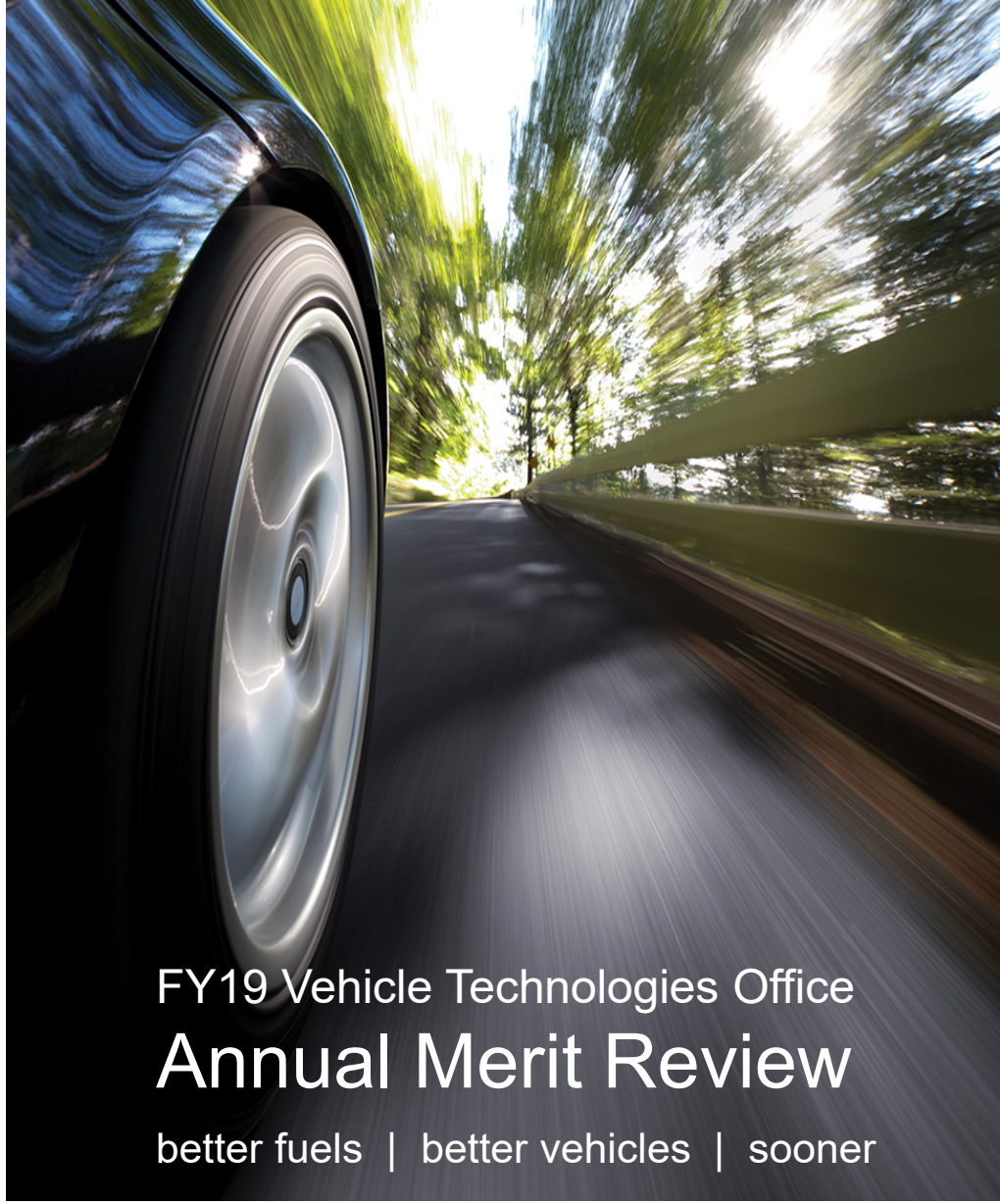
B. Zigler, J. Luecke, A. Dutta, and R.L. McCormick (NREL)

T. Bays and E. Polikarpov (PNNL)

C. Taatjes (SNL)

Date June 12, 2019

Project # FT067



FY19 Vehicle Technologies Office

Annual Merit Review

better fuels | better vehicles | sooner

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

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Quad Chart Overview
Fuel Property Characterization

Timeline

Project start date: 10/1/2018
Project end date: 9/30/2021
Percent complete: 16%

Budget

Task	FY17	FY18	FY19
F.1.3.2: *NREL*: Impact of Azeotropes on HOV MM	$200K	$200K	$150K
F.1.4.4: *NREL*: Bench-Scale Autoignition Under Engine Relevant Conditions	$0K	$0K	$550K
F.2.1.6: *NREL*: Mechanistic Basis of Phi-Sensitivity	$0K	$0K	$150K
F.1.4.3: *SNL*: Fuel Autoignition Behavior			$200K
F.1.2.5: *PNNL*: Interplay between the distillation properties and autoignition			$150K
F.1.2.2: *PNNL*: Fuel Property Blending Model	$150K	$125K	$225K

Barriers

- Inadequate fundamental knowledge base for clean diesel combustion and emissions processes
- Lack of fundamental knowledge about impact of fuel kinetics on kinetically controlled engine performance
- A well-defined metric to describe phi sensitivity is not available

Partners

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

MM: multi-mode
HOV: heat of vaporization

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
  - Bench-scale autoignition at engine-relevant conditions
  - Mechanistic basis of, and molecular structure effects of phi-sensitivity
- Reveal underlying physical chemistry
- MCCI focus with transition to MM in 2018/2019
- Transition to advanced CI combustion in FY20

CI: compression ignition
MCCI: mixing controlled compression ignition

Milestones

Month/Year	Description of Milestone or Go/No-Go Decision	Status	Lab
March 2019	Report on potential to use AFIDA to quantify phi-sensitivity for three fuels showing phi-sensitivity in published engine combustion studies	Complete	NREL
June 2019	Quantify the effect of blending acetate esters into E10 and BOB on the RVP of the finished fuel	On Target	PNNL
March 2019	Investigate the potential to use the flow reactor for observation of shifts in autoignition mechanism with phi for phi-sensitive fuels, including results of kinetic simulations	Complete	NREL
September 2019	Using data from Foong and Kolodziej, relate concentration-dependent oxygenate clustering in two and three-component reference fuels to effects on engine performance properties, specifically, RON and MON, as well as HOV measurements from NREL	On Target	PNNL

AFIDA: Advanced Fuel Ignition Delay Analyzer
BOB: blendstock for oxygenate blending
MON: motor octane number
RON: research octane number
RVP: Reid vapor pressure

NREL: National Renewable Energy Laboratory
PNNL: Pacific Northwest National Laboratory

Approach (Management)

Highly Coordinated Effort Between BETO and VTO Offices

Focus of Today's Presentation

Bioenergy Technologies Office (BETO) Tasks

NREL	Bob McCormick, Gina Fioroni, Tom Foust, Seonah Kim, Jon Burton, Teresa Alleman
Pacific Northwest National Laboratory	Evgueni Polikarpov, Dan Gaspar
Los Alamos National Laboratory EST. 1943	Andrew Sutton
Oak Ridge National Laboratory	Mike Kass

Vehicle Technologies Office (VTO) Tasks

NREL	Bob McCormick, Gina Fioroni, Matt Ratcliff, Abhijit Dutta, Brad Zigler
Pacific Northwest National Laboratory	Evgueni Polikarpov, Tim Bays
Lawrence Livermore National Laboratory	Bill Pitz
Sandia National Laboratories	Magnus Sjoberg, Craig Taatjes, Scott Skeen
Argonne National Laboratory	Chris Kolodziej, Scott Goldsborough
Oak Ridge National Laboratory	Jim Szybist, Josh Pihl, Derek Splitter

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 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 performance in an engine (HOV, RON, MON) - *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 effects on gasoline evaporation – *NREL*

Fuel autoignition mechanisms

- F.1.4.4 Utilize expanded bench-scale ignition delay and heat release studies of ignition kinetics along ACI and MM relevant P-T trajectories to understand blending effects, especially ϕ sensitivity – *NREL*
- F.2.1.6 Employ flow reactor to identify and quantitate key species in autoignition mechanisms that can be used to explain ϕ sensitivity – *NREL*

NMR: nuclear magnetic resonance
ACI: advanced compression ignition
P-T: pressure-temperature

ϕ = phi = equivalence ratio

NREL (Fioroni) Heat of Vaporization Measurement Precision Quantified and Improved

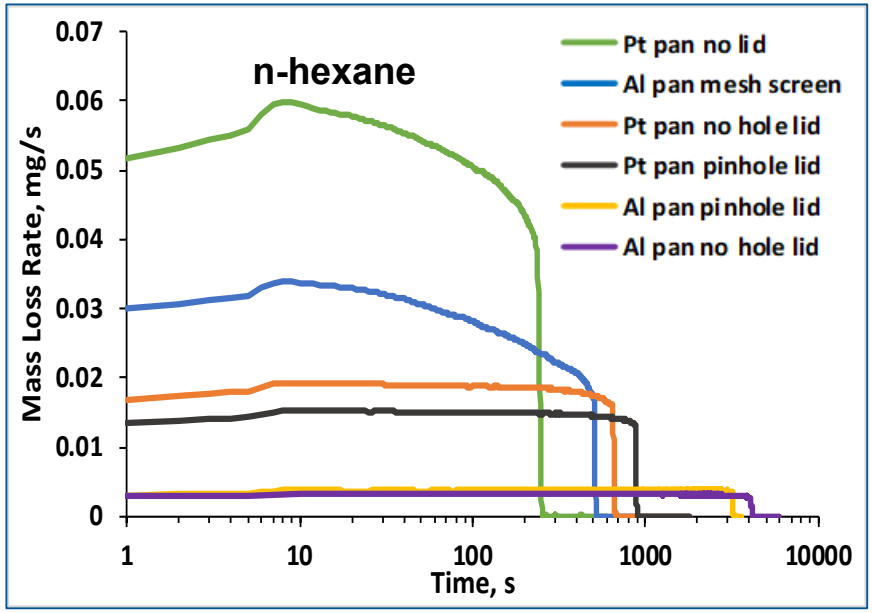
Accomplishment

Sample loss and factors affecting precision of DSC/TGA HOV method quantified and minimized

Measured HOV of n-hexane using various pan/lid configurations

Pan/Lid Configuration	%Initial Mass Loss	HOV (kJ/kg)	% Difference
Pt/no lid	11.0	379	3.5
Pt/pinhole lid	5.7	376	2.7
Al/pinhole lid	5.5	374	2.2
Al/pinhole lid (manual door)	1.8	361	-1.4

Literature value hexane HOV = 366 kJ/kg from *J. Phys. Chem. Ref. Data* **2003,** *32,* 519-878



Energy & Fuels, **2018**, *32(12)*, pp 12607-12616

- Examination of n-hexane evaporation using several DSC/TGA pan/lid configurations showed initial sample loss can be reduced
- Implementing manual closure of DSC/TGA instrument door reduced sample loss further
- Accurate total HOV measurements achieved regardless of rate of sample loss

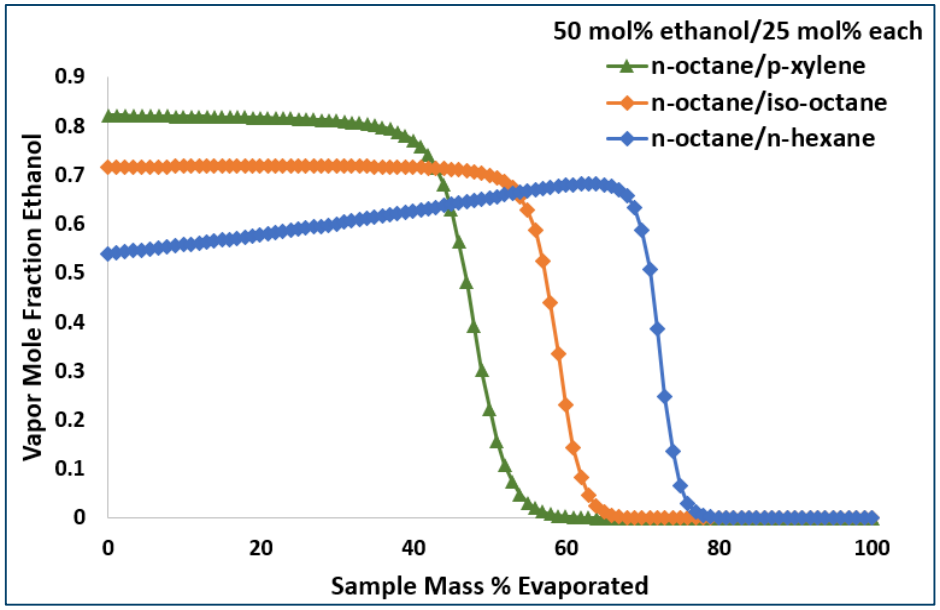
Al: aluminum
Pt: platinum

Impact: Understanding how fuel evaporation phenomena can impact autoignition, mixing, and pollutant formation

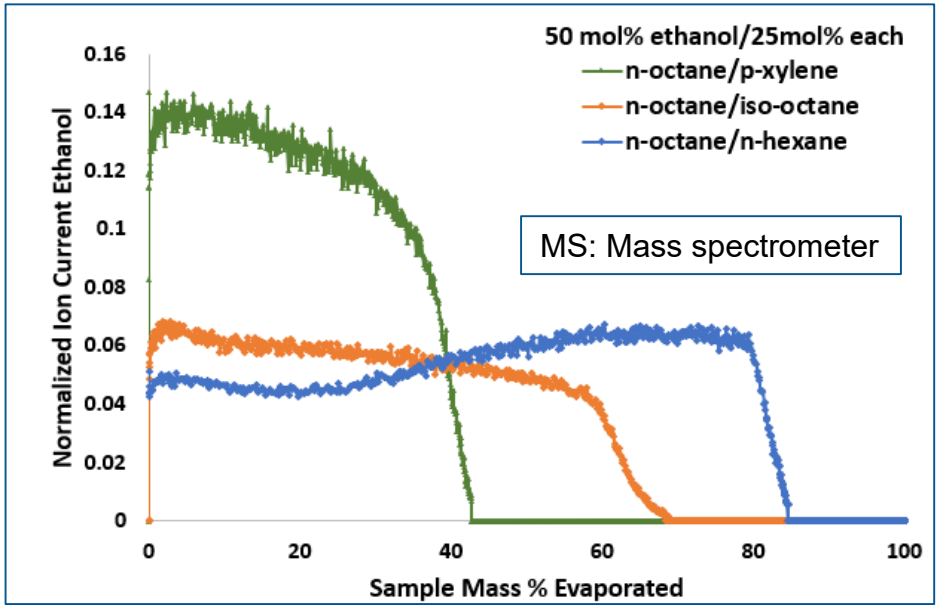
NREL (Fioroni) Impact of Azeotropes on Heat of Vaporization

Accomplishment

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



Aspen simulation of ethanol evaporation



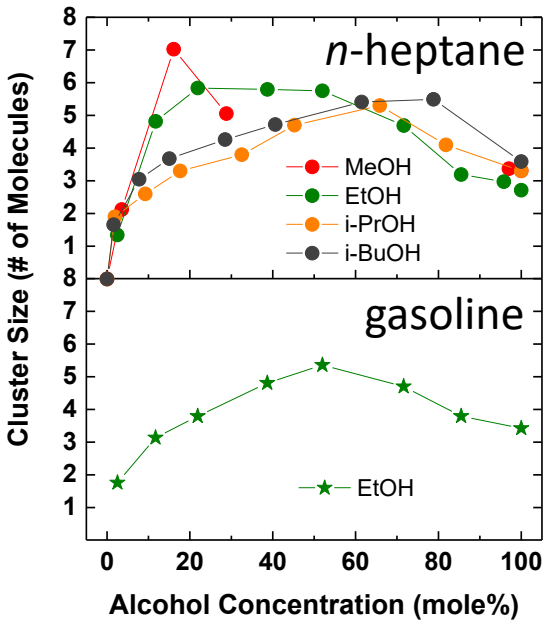
DSC/TGA/MS measured ethanol evaporation

- Simulation closely matches measured results: Demonstrates effect of hydrocarbon molecular structure on evolution of ethanol evaporation
  - ➢ Change in base composition shifts ethanol evaporation and consequent cooling effect
- Applying methods to several combinations of gasoline components and various alcohols
- ***Identify the most important azeotropic interactions between alcohols and gasoline components***

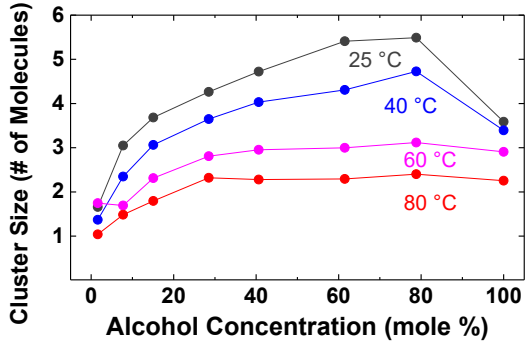
Impact: Gasoline-alcohol blend evaporation is dominated by azeotropic interactions impacting ignition timing, temperature stratification, and emissions

Alcohol cluster size depends upon the alcohol, temperature, and fuel

Alcohol Clusters at 25 ºC



Temperature Dependence of *i*-BuOH Clusters in *n*-Heptane



MeOH: methanol, EtOH: ethanol, i-PrOH: *iso*-propanol, i-BuOH: *iso*-butanol

- **Alcohol:** Larger alcohols require higher concentrations to achieve maximum cluster size:

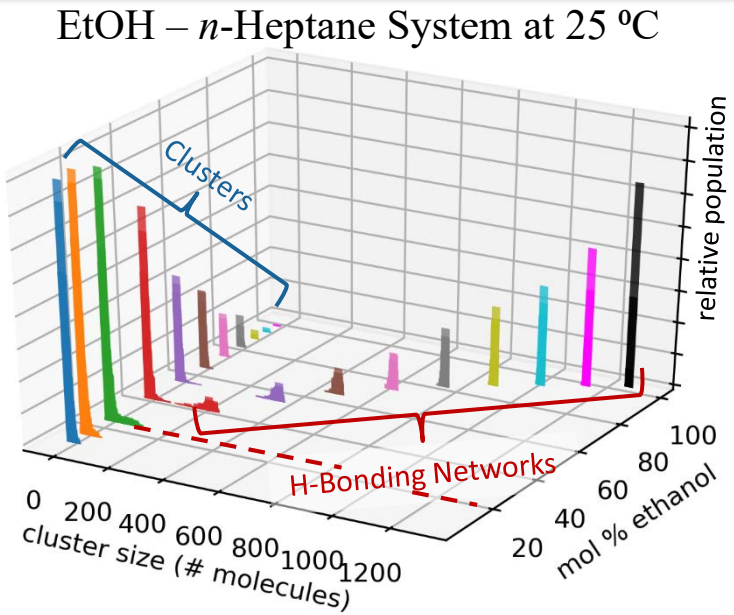
  MeOH > EtOH > *i*-PrOH > *i*-BuOH

  - Concentration at maximum average cluster size increases from 16 to 79 mol% in the same order
  - Decreasing hydrogen-bond strength between alcohols and increasing interaction between the alcohol and *n*-heptane
- **Fuel:** Maximum EtOH cluster size (5-6 molecules)
  - Blending in gasoline rather than *n*-heptane reduces max cluster size and shifts the maxima from 22 mol% to 52 mol% in gasoline by disrupting EtOH-EtOH interactions
- **Temperature (T):** Increasing T decreases cluster size
  - Max cluster size for all four alcohols decreases with T (*i*-BuOH results shown)

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

Accomplishment

Molecular dynamics simulations show transition from clustering to hydrogen-bonding networks



Bimodal Distribution:

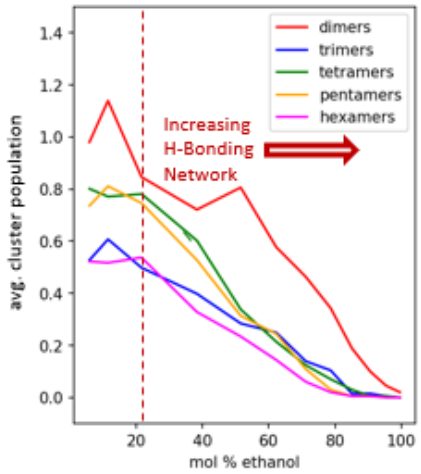
- Small clusters dominant at < 20 mol% EtOH
- Large clusters forming a hydrogen-bonding network become distinct at > 20 mol% EtOH
- Network may be considered a distinct region, constituting a second phase within the system

Cluster Types:

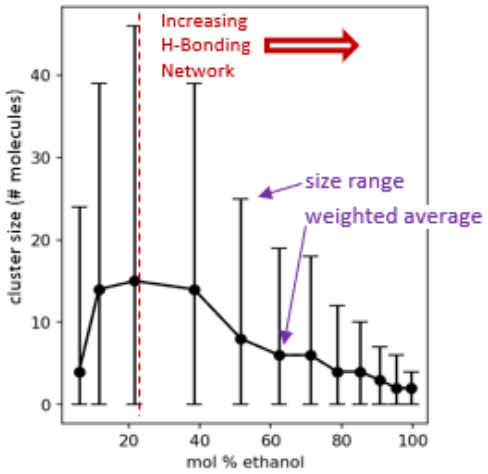
- Population declines support network formation
- Distribution of cluster sizes, dimers-to-hexamers. Populations do not steadily decrease with increasing cluster size

- **Cluster Sizes:**
  - Size ranges show dynamic nature of the system
  - Weighted averages qualitatively align with NMR experiments

Cluster Types



Cluster Sizes

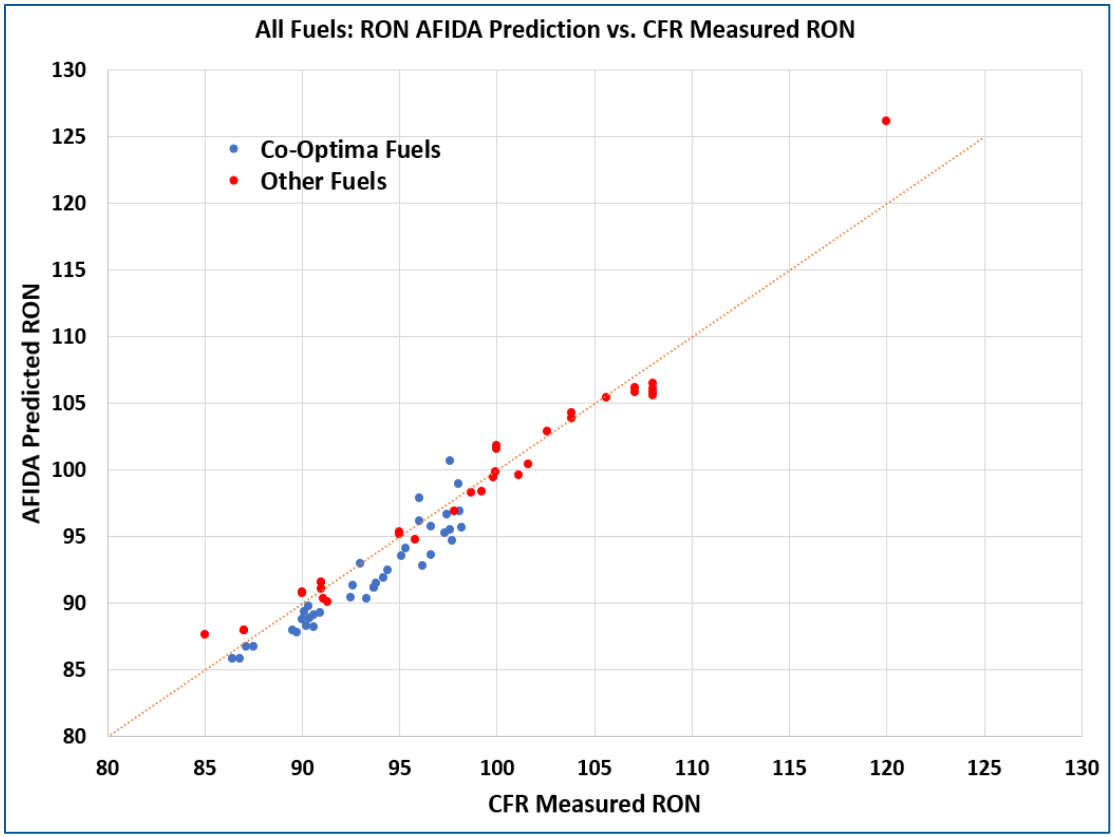


Impact: Understanding how oxygenate clusters and networks contribute to vapor pressure is critical for correctly predicting fuel droplet evaporation, and effects on combustion

NREL (Zigler) Bench Scale Autoignition Under Engine Relevant Conditions

Accomplishment

Small volume AFIDA measurement predicts RON to within 2%



- 20 mL of sample for RON
- 20 minutes experiment time
- Single P-T point
- Correlation based on 65 surrogate blends, from 85 to 120 RON, with $R^2 = 0.95$

A second empirical correlation to predict S (0-12) is under development using a second temperature point: Requires 40 mL fuel and 1 hour (total for RON + S)

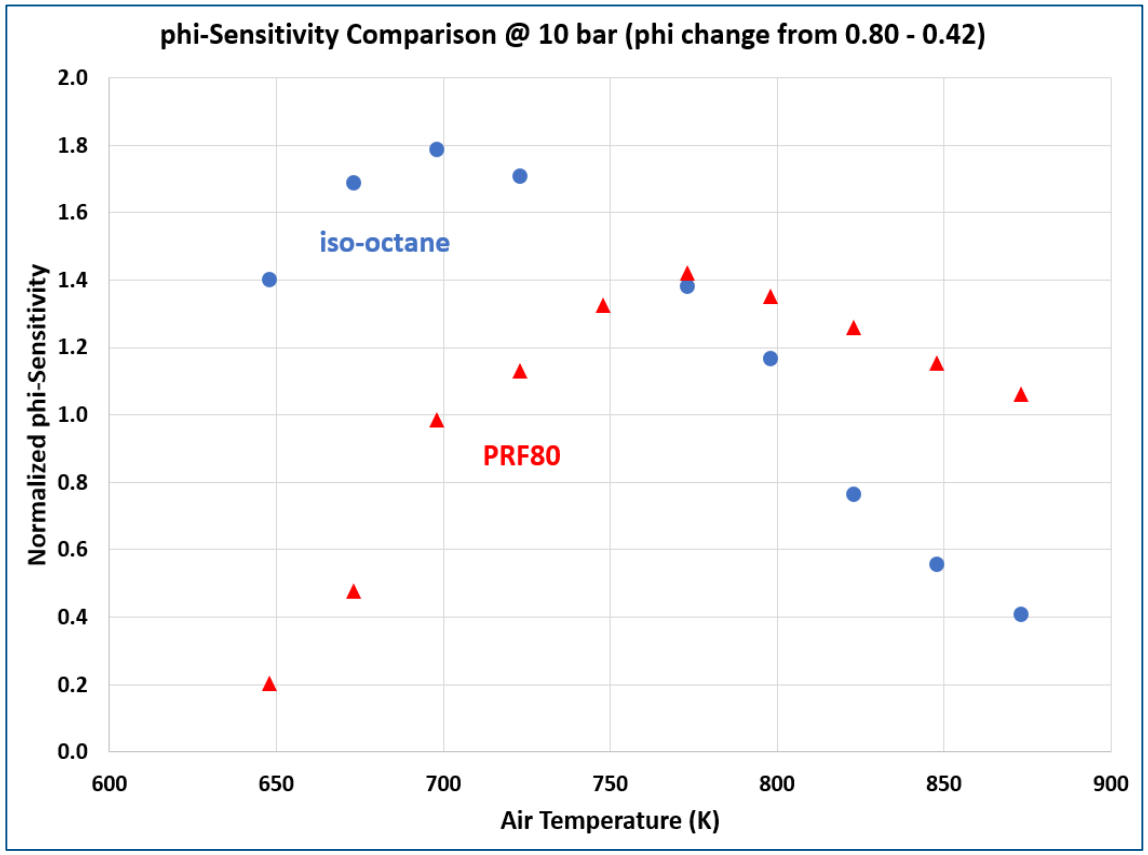
CFR: cooperative fuel research (engine)
S: sensitivity (S= RON-MON)

Impact: Ability to rapidly measure RON and S with small volumes of sample will increase the pace of development of new fuels having targeted properties

NREL (Zigler) Bench-Scale Autoignition Under Engine Relevant Conditions

Accomplishment

AFIDA–based studies provide bench scale measurement of ϕ-sensitivity



- Temperature sweeps of ignition delay for ϕ-sensitive fuels shows ignition delay differences from ϕ = 0.80 – 0.42
- Plotting normalized ϕ-sensitivity $(1/\tau)(d\tau_{ign}/d\phi)$ compares between fuels at a fixed pressure
- The AFDIA can rapidly sweep ignition delay for ϕ-sensitivity studies across temperatures at up to 40 bar

PRF: performance reference fuel

Impact: Method for rapid measurement of phi-sensitivity in bench-scale test will allow studies of molecular structure effects on mechanism and kinetics of this poorly understood kinetic phenomenon

NREL (Fioroni) Mechanistic Basis of Phi Sensitivity

Accomplishment

Changes in reaction chemistry with phi observed, but higher pressures required to observe phi-sensitivity relevant to engine conditions

- PRF80 demonstrated phi-sensitivity in HCCI engine studies
- PRF80 was examined in atmospheric pressure flow reactor at 600 K – 1000 K and phi of 0.25, 0.5, and 1
- Small changes in reactivity with phi were observed, however higher pressures are required to observe low-temperature and intermediate-temperature reactions believed to be related to phi-sensitivity
- Reactor modifications are underway to increase pressure to the 5 to 10 bar range and to allow more precise quantification of formaldehyde
- Future improvements proposed to achieve even higher pressures

HCCI: homogeneous charge compression ignition

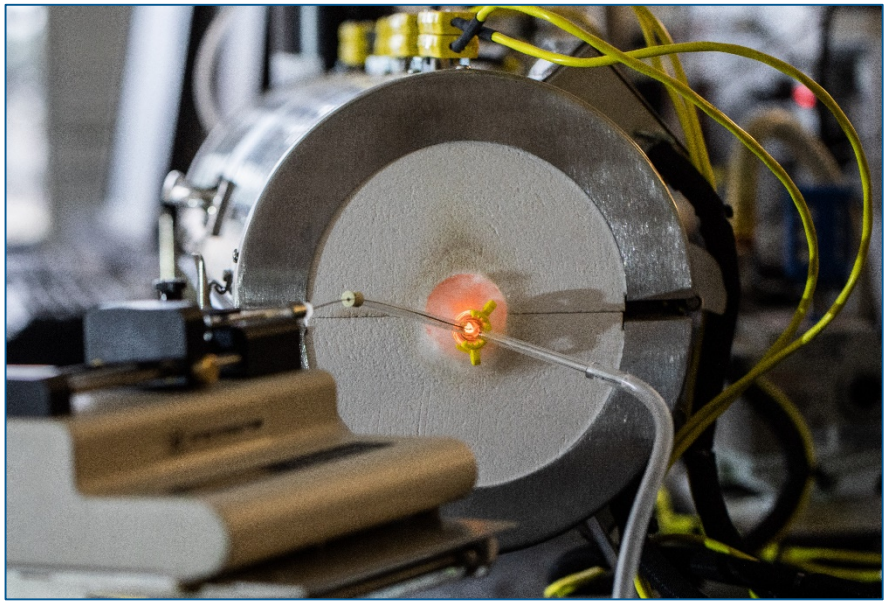


Photo by Werner Slocum, NREL 56025

Impact: With modifications to achieve higher pressure, flow reactor experiments can be utilized to identify and quantitate key species in autoignition mechanisms that can explain phi-sensitivity

Response to Previous Year Reviewers' Comments

The reviewer complimented this project for having developed exceptional methods for better measuring/predicting fuel properties and generating valuable data for mechanism validation. The reviewer stated that the project could be significantly better if the flow reactor can be upgraded to be capable of operating at higher pressure, which is critical to validate reaction mechanisms at conditions closer in ICEs.

We thank the reviewer for complimenting the progress of the project to date. We strongly agree that upgrading the flow reactor to operate at elevated pressures is an important task and have begun to take steps to increase our pressures to 5-10 atmospheres (atm). In addition, we are working on a white paper proposing to operate to even higher pressures of up to 50 atm.

ICEs: internal combustion engines

Collaboration and Coordination with Other Institutions

- ***Collaboration of nine national laboratories***
- **University of Connecticut** (*Kinetic Simulations*)
- **Pennsylvania State University** (Kinetic and Molecular Dynamics Simulations)
- **Colorado State University** (*Advanced Distillation and Droplet Evaporation Simulations*)
- **Coordinating Research Council** (*HOV Measurements-AVFL-27 and diesel fuel surrogates-AVFL-18a*)
- **Ford Motor Company** (*HOV Measurements in CRC AVFL-27*)
- **University of Illinois-Chicago** (*Ignition Delay Measurements*)
- **Oakland University** (*Ignition Delay Measurements*)
- **Yale University** *(Yield Sooting Index)*

Coordination:

- 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
- 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, non-idealities such as azeotrope formation, and composition evolution over the evaporation process

Proposed Future Research

- Effect of molecular structure, blend composition, and reaction conditions (T, P, ϕ) on autoignition mechanisms
- Fundamental research on understanding the key reaction species that explain phi-sensitivity and non-linear octane blending
- Correlate AFIDA-based ϕ sensitivity to ACI engine data with the goal of developing a rapid bench-scale phi sensitivity measurement
- Foundational research on fuel evaporation and mixing with air, and how this is impacted by fuel chemistries well beyond those in conventional petroleum fuel
- 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)
- Utilize comprehensive kinetic mechanisms to provide the framework for discovering fuel-independent correlations (F.1.4.3)

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

Summary: Technical Accomplishments and Impact

- 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
- 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
- Small volume AFIDA measurement predicts RON to within 2%
  Impact: Ability to rapidly measure RON and S with small volumes of sample will increase the pace of development of new fuels having targeted properties
- AFIDA–based studies provide bench scale measurement of ϕ-sensitivity
  Impact: Method for rapid measurement of ϕ-sensitivity in bench scale test will allow studies of molecular structure effects on mechanism and kinetics
- Changes in reaction chemistry noted with changes in phi in flow reactor
  Impact: With modifications to achieve higher pressure, flow reactor experiments can be utilized to identify and quantitate key species in autoignition mechanisms that can explain ϕ-sensitivity

Overall Summary: Fuel Property Characterization and Prediction

Overview

- Focused on identifying, and measuring or predicting critical fuel properties; as well as understanding quantitatively how these properties can be exploited to improve engine performance and meet environmental and economic goals

Approach

- Leverage highly experienced team knowledgeable in fuel property characterization
- Utilize unique capabilities to measure and understand gasoline-like fuel volatility, and to reveal the underlying chemistry and unique species responsible for non-linear blending effects and phi-sensitivity

Technical Progress

- Employed improved DSC/TGA/MS in combination with simulation results to evaluate the effect of blendstock molecular structure on heat and species evolution during evaporation
- Determined that alcohol cluster size depends on the alcohol, the temperature, and the fuel
- Utilized molecular dynamic simulations to show transition from alcohol clustering to hydrogen-bonding networks
- Small volume AFIDA measurements were used to predict RON to within 2%
- AFIDA-based studies provide bench scale measurement of phi-sensitivity
- Flow reactor was utilized to observe changes in reaction chemistry versus changes in phi

Relevance

- **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**

List of acronyms

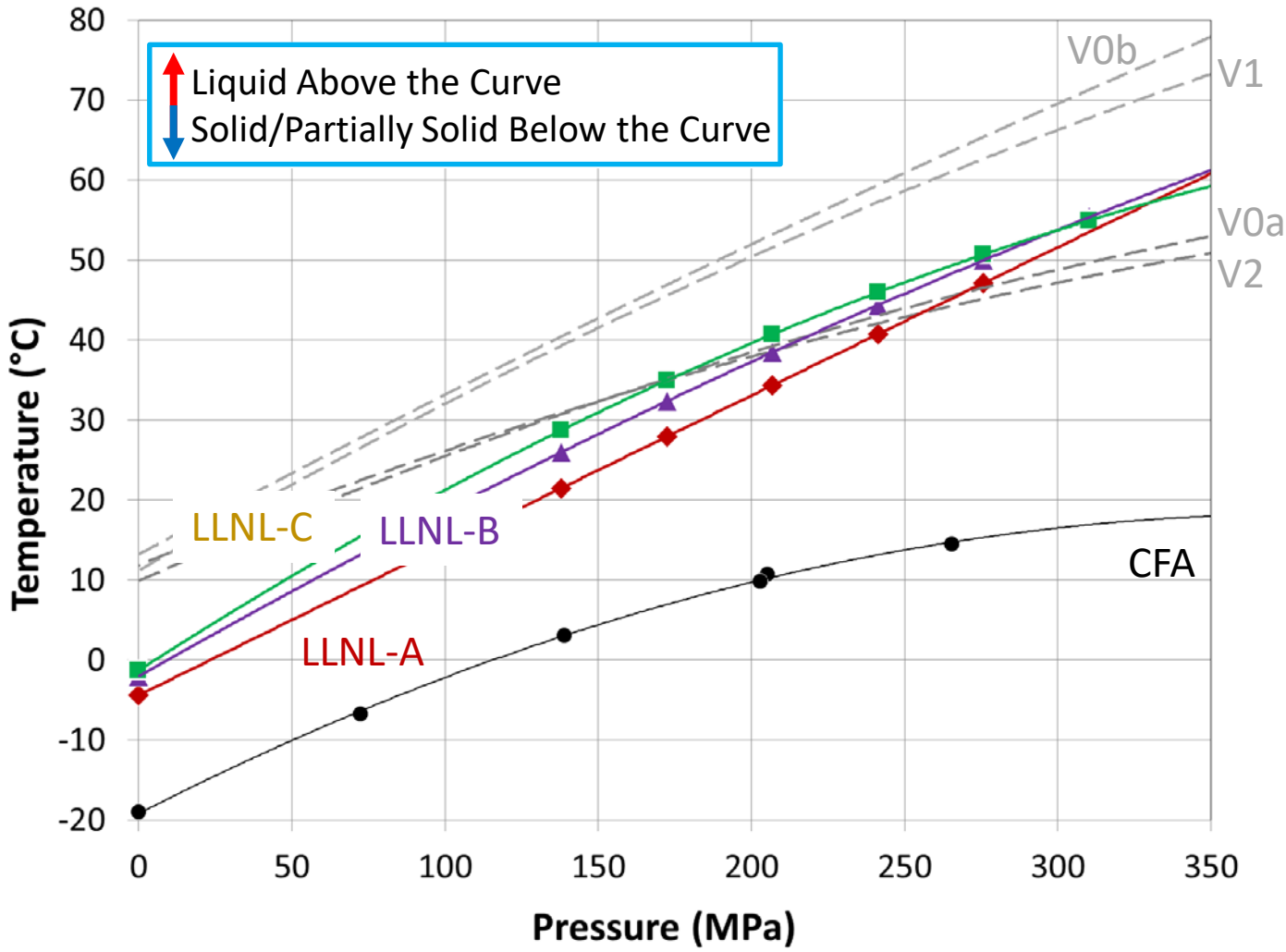
ACI: advanced compression ignition
AFIDA: advanced fuel ignition delay analyzer
AVFL: Advanced Vehicle/Fuel/Lubricants
BETO: Bioenergy Technologies Office
BOB: blendstock for oxygenate blending
CFR: cooperative fuel research
CI: compression ignition
DSC: differential scanning calorimeter
DOE: Department of Energy
EtOH: ethanol
HCCI: homogeneous charge compression ignition
HOV: heat of vaporization
i-BuOH: *iso*-butanol
i-PrOH: *iso*-propanol
K: degrees Kelvin
MCCI: mixing compression controlled ignition
MeOH: methanol
MM: multi-mode
MON: motor octane number
MS: mass spectrometer
NMR: nuclear magnetic resonance
NREL: National Renewable Energy Laboratory
PNNL: Pacific Northwest National Laboratory
PRF: performance reference fuel
P-T: pressure-temperature
RON: research octane number
RVP: Reid vapor pressure
SNL: Sandia National Laboratories
S: sensitivity (S= RON-MON)
TGA: thermogravimetric analysis
VTO: Vehicle Technologies Office

Technical Back-Up Slides

PNNL (Bays) Measured solidification of diesel surrogate components at fuel injection pressures up to 300 MPa

Accomplishment

Diesel fuel surrogates show lower melting points than previous surrogate formulations.



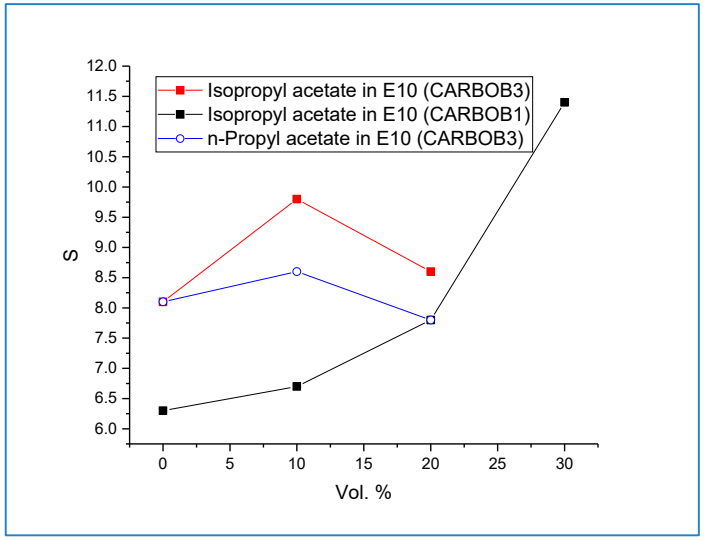
- Measured solidification of diesel surrogate components at fuel injection pressures up to 300 MPa
- P-T curves show the final melting point data (FMP) for three new diesel surrogates, (LLNL-A -C).*
- Developed to reduce propensity for solidification in fuel lines of test systems, while being compositionally rigorous for kinetic modeling.
- About 12 ºC reduction in FMP realized at atmospheric pressure, and maintained over V0b & V1, but the slopes cross V0a and V2** at common rail pressures.

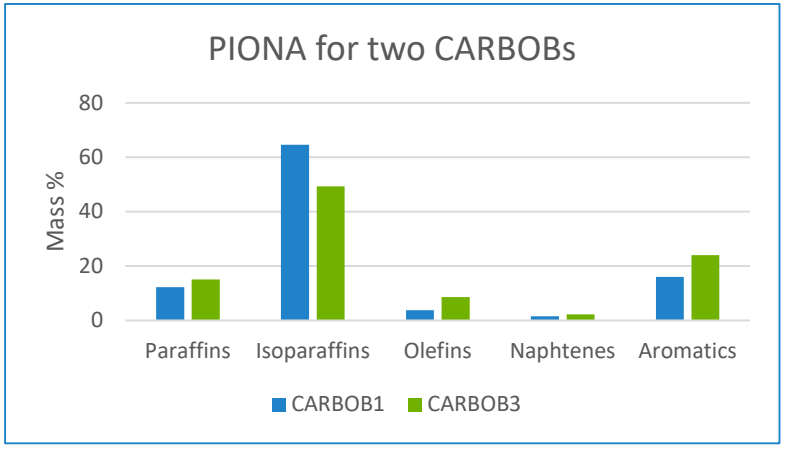
Impact: Improvements in diesel fuel surrogate formulation reduce the propensity for pressure-freezing in diesel fuel injectors, allowing testing to assist with kinetic modeling

PNNL (Polikarpov): Interplay Between the Distillation Properties and Autoignition

Ongoing Work

Quantify the relationship between distillation properties and autoignition in multi-mode fuels by blending acetate esters as octane sensitivity boosters





- Perform simulated distillation (SimDis), octane and RVP measurements to establish autoignition relationship on various blend levels of esters in BOB and E10
- Investigate effect of blending sensitivity-boosting acetate esters of varied molecular weight into BOB and E10 on the distillation curve of resulting fuel mixtures
- *RON/MON tests of ester bends in E10 indicate that BOB composition plays critical in non-linear blending effects:* Synergistic blending of isopropyl acetate was observed in E10 blends on one CARBOB, but not another
  - Two of five additional BOBs acquired
  - Contract lab testing to begin
  - Vapor pressure test set up on order

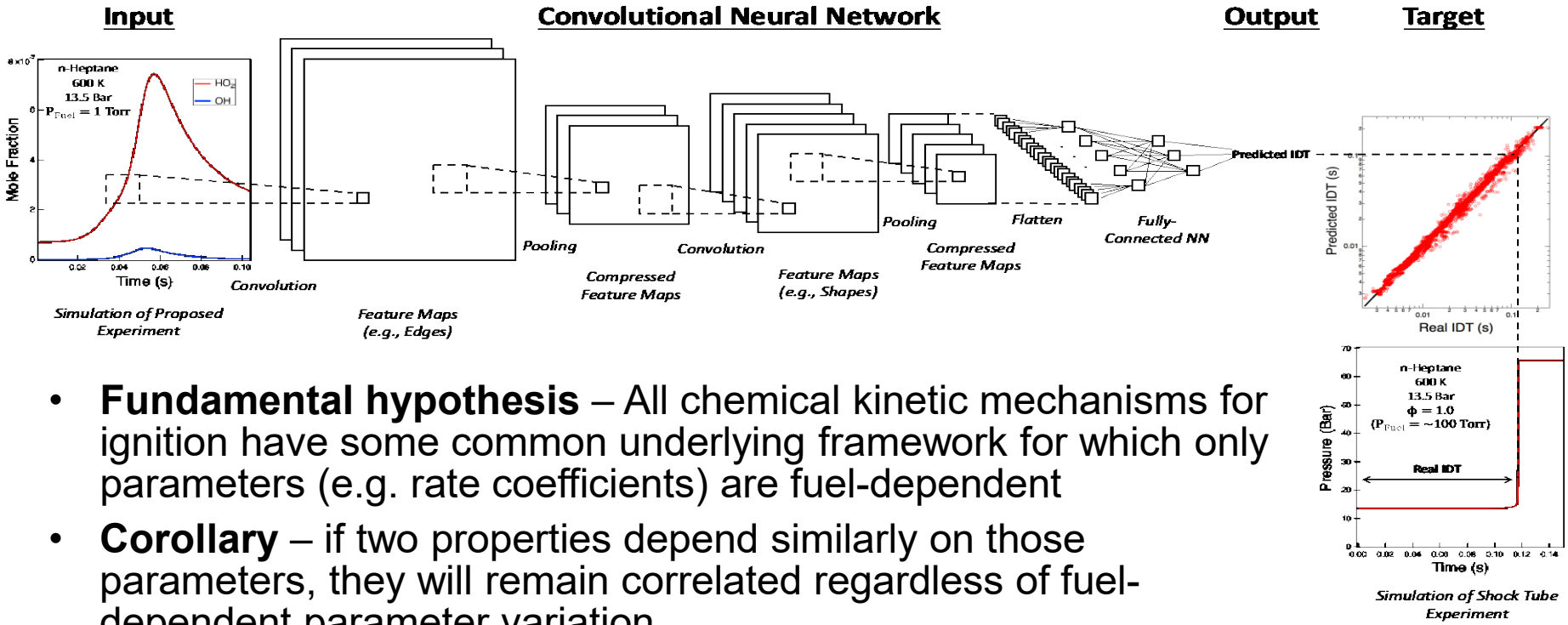
CARBOB: California air resources blendstock for oxygenate blending

Impact: Understanding of non-linear blending and the relationship between distillation and octane will help take advantage of synergistic effects to develop high-sensitivity blendstocks for multimode combustion

Ongoing Work

Identify performance needs for multimode combustion and determine structure-independent metrics that are correlated

- Fuel metrics must be independent of fuel molecular structure



- **Fundamental hypothesis** – All chemical kinetic mechanisms for ignition have some common underlying framework for which only parameters (e.g. rate coefficients) are fuel-dependent
- **Corollary** – if two properties depend similarly on those parameters, they will remain correlated regardless of fuel-dependent parameter variation
- *Work for another sponsor has demonstrated such correlations*
- ***Robust correlations will allow structure-independent metrics for fuel performance characterization***

Comprehensive Kinetic Mechanisms Provide the Framework for Discovering Fuel-Independent Correlations

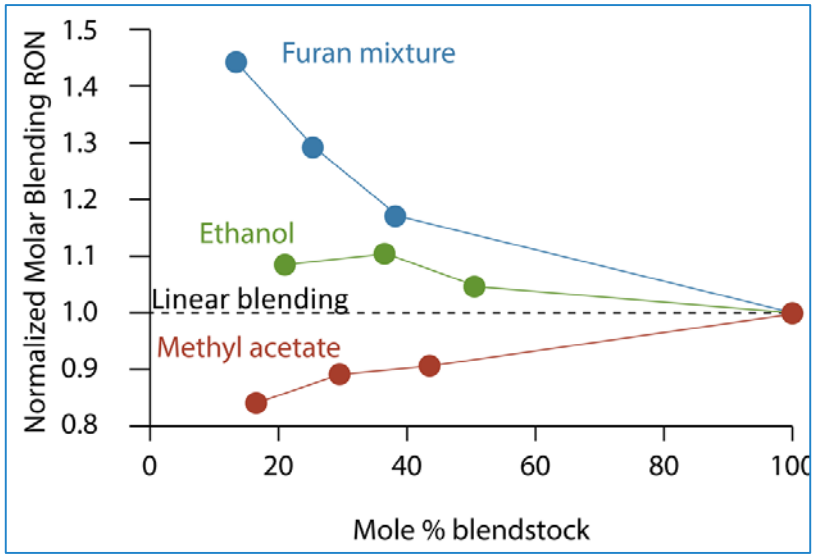
Same computational machinery is being used to characterize new correlations

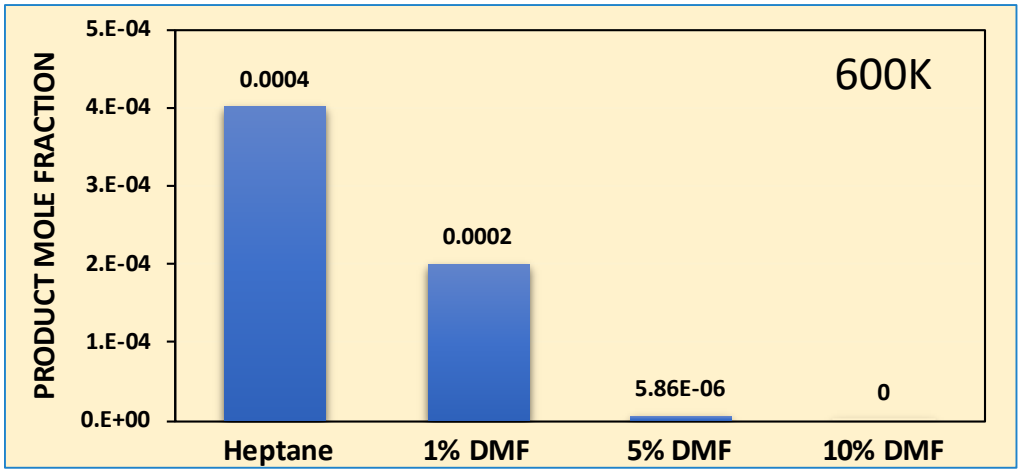
- Beyond RON /beyond MON (parameterized by K) conditions probe reactivity on different areas of the pressure-temperature space
- Dimensions besides P & T also important in multimode operation
  - Φ-sensitivity for response to fuel stratification
  - ΔT sensitivity for response to temperature stratification
  - Nitrous Oxide (No_x) sensitivity for response to exhaust gas recycling
  - Intermediate temperature heat release (ITHR) / low temperature heat release) LTHR profiles
- Need to ensure that mechanisms are complete enough to capture these dimensions – may not be true for NO_x sensitivity
- Test correlations with experiments of other Co-Optima participants

NREL (Fioroni)
Reveal Chemistry for Non-Linear Blending Effects

Goal: Understand chemical basis for synergistic and antagonistic blending for RON.

- Blended various synergistic and antagonistic compounds with a radical generator (heptane)
- Autoignition at 600 Kelvin (K)
- Synergistic compounds shut down low-temperature autoignition at low blend levels
- Identified potential common fragment in synergistic compounds that may be responsible for synergistic blending effects





DMF = dimethyl furan

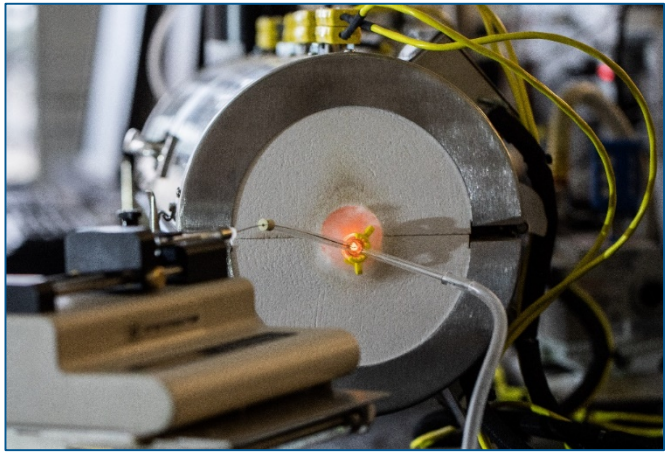


Photo by Werner Slocum, NREL 56025

Impact: Revealing the mechanism of non-linear blending for octane number will allow design of molecules with desired blending octane behavior.