Co-Optimization of
Fuels & Engines

# Fuel Property Experimental Kinetics

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**Presenter: G. M. Fioroni**

Date: June 3, 2020

Project # FT088

2020 DOE Vehicle Technologies Office

Annual Merit Review

better fuels | better vehicles | sooner

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

# Overview: *Experimental Kinetics*

## Timeline

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

## Budget

| Task | FY 2019 | FY 2020 |
|---|---|---|
| **F.1.4.3: *SNL***: Fuel Autoignition Behavior | $160K | $140K |
| **F.1.4.4: *NREL***: Bench-Scale Autoignition Under Engine-Relevant Conditions | $550K | $550K |
| **F.2.1.6: *NREL***: Mechanistic Basis Low and Intermediate Temperature Autoignition and Phi-Sensitivity | $150K | $200K |
| **F.2.2.3: *ANL***: ANL Kinetic Mechanism Development | $180K | $135K |
| **F.2.3.1: *ANL***: Development/Application of Multimode/ACI FQM | $115K | $160K |

## Barriers

- **Lack of fundamental knowledge about the fuel kinetics impact on multi-mode, mixing-controlled compression ignition and advanced compression ignition engine performance**
- **Need for a well-defined metric to describe phi sensitivity is still being developed**

## Partners

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

ACI: advanced compression ignition
ANL: Argonne National Laboratory
FQM: fuel quality metric
FY: fiscal year
NREL: National Renewable Energy Laboratory
SNL: Sandia National Laboratories

# Relevance: *Experimental Kinetics*

**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:**

- **Reveal underlying physical chemistry**
  - *Utilize flow reactor to validate kinetic mechanisms, interrogate soot precursor formation mechanisms, and understand the chemical basis for nonlinear blending phenomena*
- **Bench-scale experimental measurement of fuel property kinetics**
  - Small-volume autoignition at engine-relevant conditions
    - *AFIDA-based ignition delay studies for RON and S correlation*
    - *RCM-based ignition delay, heat release studies to validate, improve chemical kinetic models*
  - Mechanistic basis and molecular structure effects of ϕ-sensitivity
    - *AFIDA-based ignition delay studies to support development of a new normalized definition of ϕ-sensitivity*
    - *RCM-based autoignition measurements to facilitate development of an FQM that can capture autoignition sensitivities relevant to engine operation*

Note: phi is the fuel-air equivalence ratio, as opposed to lambda, which is the air-fuel equivalence ratio (phi = 1/lambda)

AFIDA: Advanced Fuel Ignition Delay Analyzer
MON: motor octane number
RCM: Rapid Compression Machine
RON: research octane number
S: octane sensitivity (S = RON − MON)
ϕ = phi = equivalence ratio

# Milestones: *Experimental Kinetics*

| Month/Year | Description of Milestone or Go/No-Go Decision | Status | Lab |
|---|---|---|---|
| December 2019 | Draft journal article on AFIDA correlations to RON and S in support of MM | Complete | NREL |
| March 2020 (delayed to June 2020) | Demonstrate observation of formaldehyde and acetaldehyde (by FTIR) for fuels exhibiting low-temperature and intermediate-temperature reactions at 5 bar in the flow reactor | Delayed by COVID-19 Response | NREL |
| March 2020 (delayed to September 2020) | Complete measurements of neat HPFs to validate kinetic model development | Delayed due to equipment move | ANL |
| March 2020 (delayed to September 2020) | Complete RCM testing for higher $\phi$-stratified conditions for a range fuels | Delayed due to equipment move | ANL |

FTIR: Fourier-transform infrared
HPF: high-performance fuel
MM: multi-mode

# 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 | Andrew Sutton |
| Oak Ridge National Laboratory | Mike Kass |

### Vehicle Technologies Office (VTO) Tasks

| | |
|---|---|
| NREL | Bob McCormick, Gina Fioroni, Brad Zigler, Seonah Kim, Mohmmad Rahimi, Jon Luecke |
| Lawrence Livermore National Laboratory | Bill Pitz, Scott Wagnon |
| Sandia National Laboratories | Magnus Sjoberg, Craig Taatjes, Zach Buras |
| Argonne National Laboratory | Chris Kolodziej, Scott Goldsborough |
| Oak Ridge National Laboratory | Jim Szybist, Josh Pihl, Derek Splitter |

***Highly experienced team knowledgeable in fuel property experimental kinetics***

# Approach (Technical)

## Bench-scale measurement of experimental kinetics

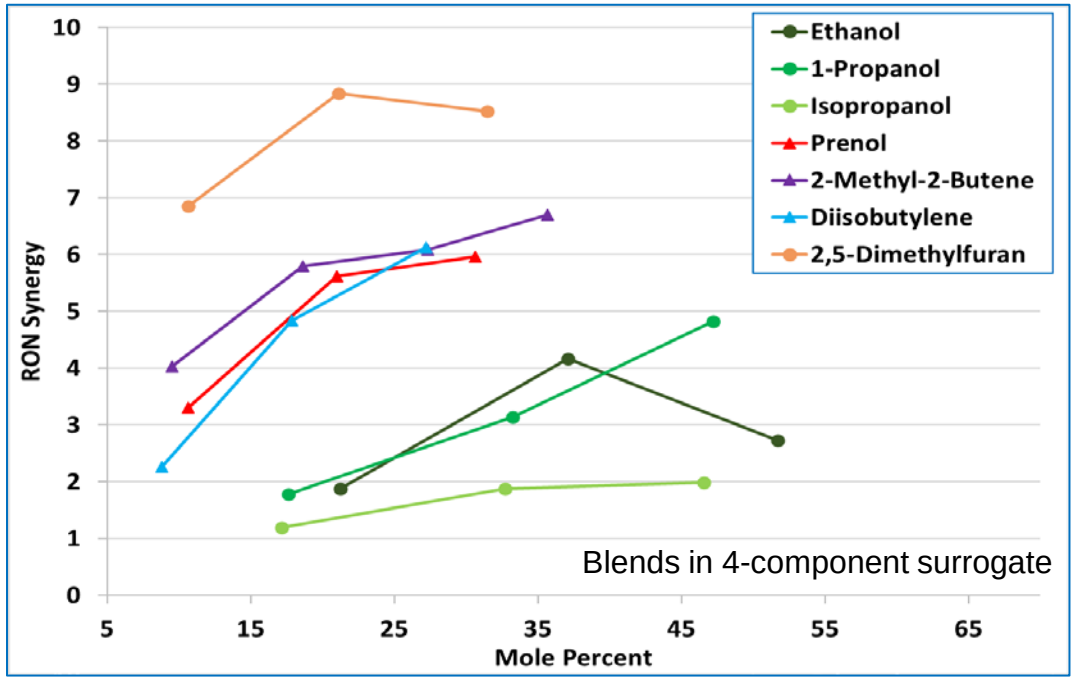
- **F.2.1.6:** Upgrade flow reactor to elevated pressure and identify and quantitate key species for developing mechanisms to explain nonlinear RON blending, soot precursor formation, and ϕ sensitivity – *NREL*
- **F.1.4.4:** Utilize AFIDA-based ignition delay studies to support early-stage fuel screening with small sample volumes via RON and S correlation: Support development of a new normalized definition of ϕ-sensitivity and investigate molecular structure effects on ϕ-sensitivity – *NREL*
- **F.1.4.3:** Employ simulations to determine structure-independent metrics that are correlated to ϕ-sensitivity – *SNL*
- **F.2.2.3:** Utilize RCM to measure ignition delay times and heat release behavior of potential top-tier fuels and blends with gasoline to validate and improve chemical kinetic models – *ANL*
- **F.2.3.1:** Utilize RCM to probe autoignition sensitivities (T, P, ϕ, EGR) towards development of engine-relevant autoignition metrics – *ANL*

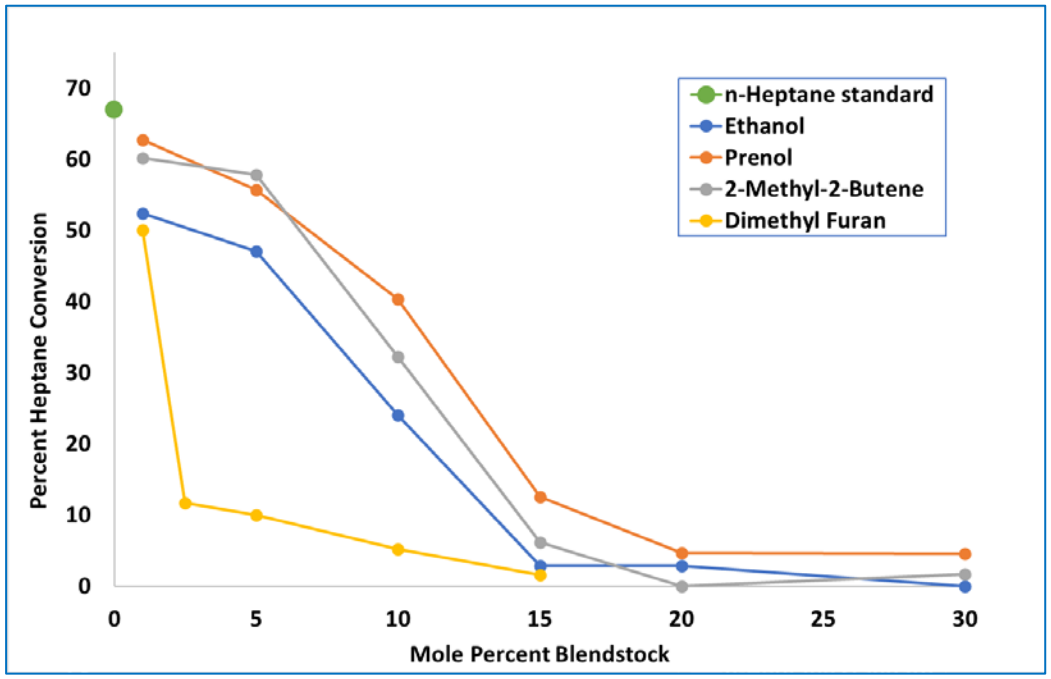
P: pressure
EGR: exhaust gas recirculating
T: temperature

# NREL (Fioroni) F.2.1.6 Mechanistic Basis Low and Intermediate Temperature Autoignition

*Accomplishment*

Flow reactor studies allow for understanding of the chemical basis for nonlinear blending effects




Flow reactor conditions:
600 K
6-second residence time
$\phi$ = 0.25

*RON Synergy = D2699 measured RON – RON linear blending model*

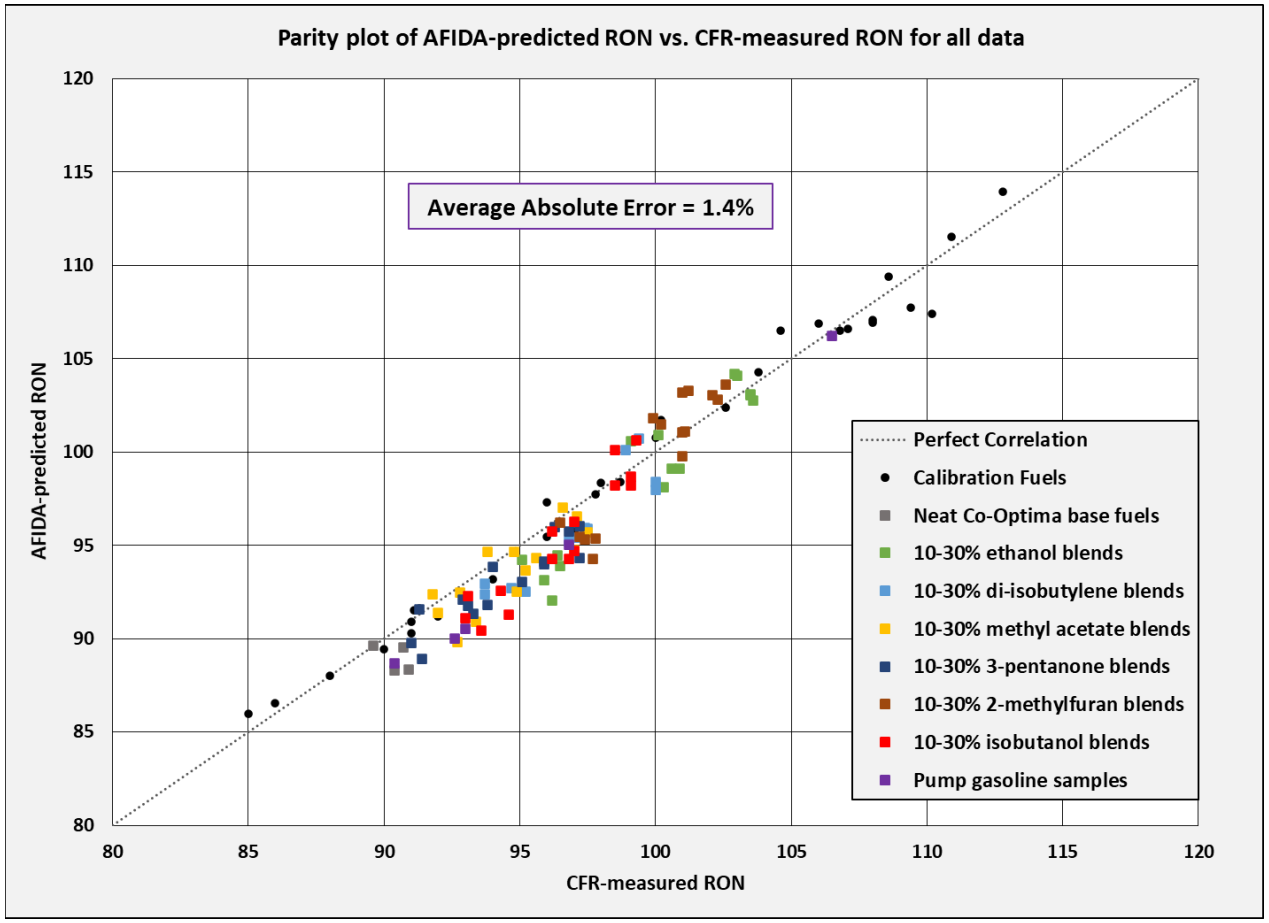
- Implemented new RON synergy metric to describe nonlinear blending behavior of various blendstocks
- Utilized flow reactor to investigate RON synergy observations and to examine intermediate species responsible for nonlinear blending trends-added FTIR to quantitate aldehyde species
- Currently working with simulations team at NREL to understand how blendstocks are affecting radical species concentrations
- Working to upgrade flow reactor to observe radical species to provide full picture of nonlinear blending behavior.

***Impact: Flow reactor allows for observation of intermediate species responsible for nonlinear blending behavior***

# NREL (Zigler) F.1.4.4: Bench-Scale Autoignition Under Engine-Relevant Conditions

*Accomplishment*

Small-volume AFIDA measurement predicts RON and S accurately over a variety of chemistries




- Continued development of an AFIDA-based small-volume (~40 mL) rapid screening (~1 hour) methodology for RON and S
- Correlations for RON and S were calibrated using 31 PRF and TRF fuels with and without ethanol, previously measured in a CFR engine over RON range of 85–113 and S range of 0–11
- RON and S correlation was validated over wide range of chemistry using 91 samples containing five blending agents at 10%–30% blend levels along with five pump gasoline samples
- Correlations developed to date:
  - RON from a single ignition delay point (10 bar, 525ºC), with an $R^2$ of 0.98 for RON = 85–113
  - S from two additional ignition delay points (10 bar, 425ºC and 475ºC) with an $R^2$ of 0.94 for S = 0–11, excellent at discerning desirable high-S fuels (S > 8)
- NREL has screened >25 fuel candidates for DOE labs and others under Co-Optima, usually for sample sizes too small to support CFR engine-based measurements
- Publication of this methodology is planned in FY 2020

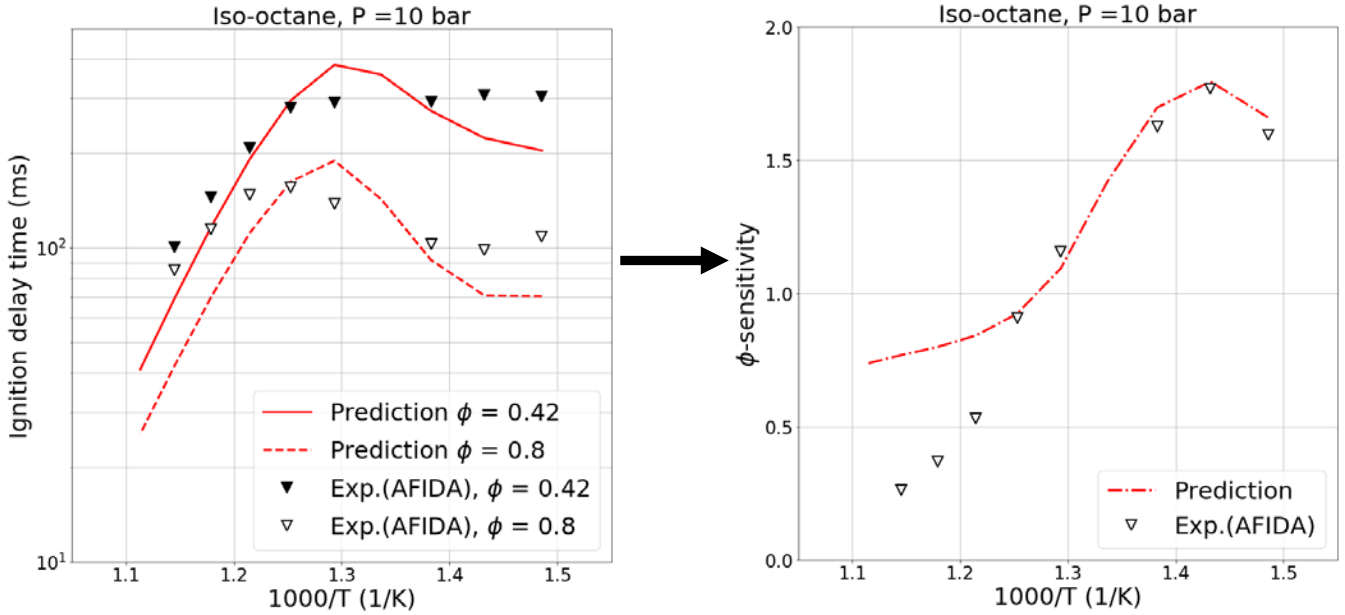
***Impact: Ability to rapidly measure RON and S with small volumes of sample will increase the pace of development of new fuels having targeted properties***

CFR: cooperative fuels research
PRF: primary reference fuel
TRF: toluene reference fuel

# NREL (Zigler) F.1.4.4: Bench-Scale Autoignition Under Engine-Relevant Conditions

*Accomplishment*

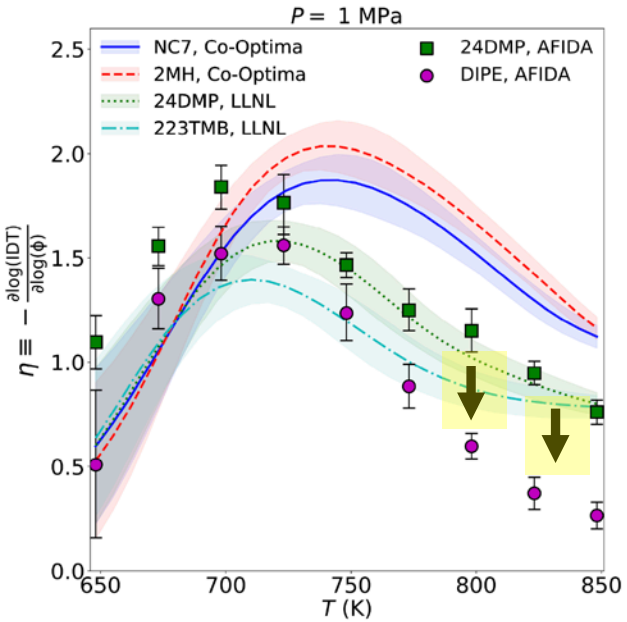
AFIDA-based studies supported development of new ϕ-sensitivity definition, enabling structure effects studies

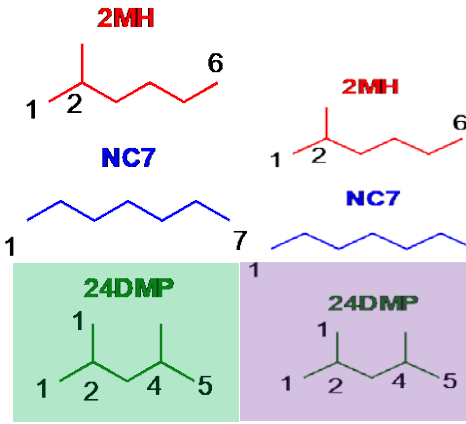



- Temperature sweeps of ignition delay across different ϕ and P supported development (by Seonah Kim's group) of new ϕ-sensitivity metric, which is primarily only a function of T and P

$$-\frac{d\log(\tau)}{d\log(\phi)}\bigg|_{T,P} = \eta$$

- This new definition was applied to compounds with developed kinetic mechanisms, and compounds of interest (without mechanisms) to study molecular structure effects on ϕ-sensitivity




Oxygen addition

***Impact: Method for rapid measurement of ϕ-sensitivity in bench-scale test will allow studies of molecular structure effects***

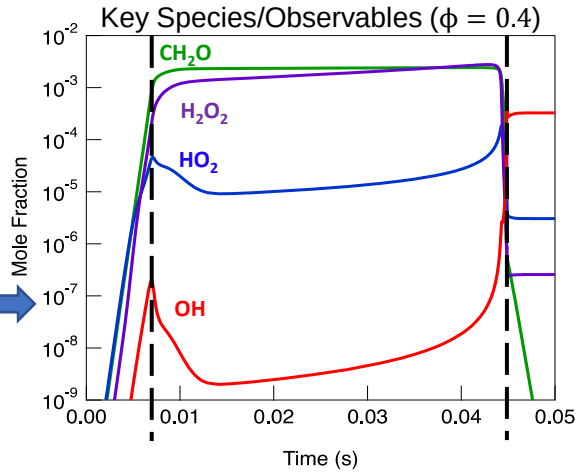
$\tau$: tau, ignition delay time

# SNL (Taatjes) F.1.4.3 Fuel Autoignition Behavior

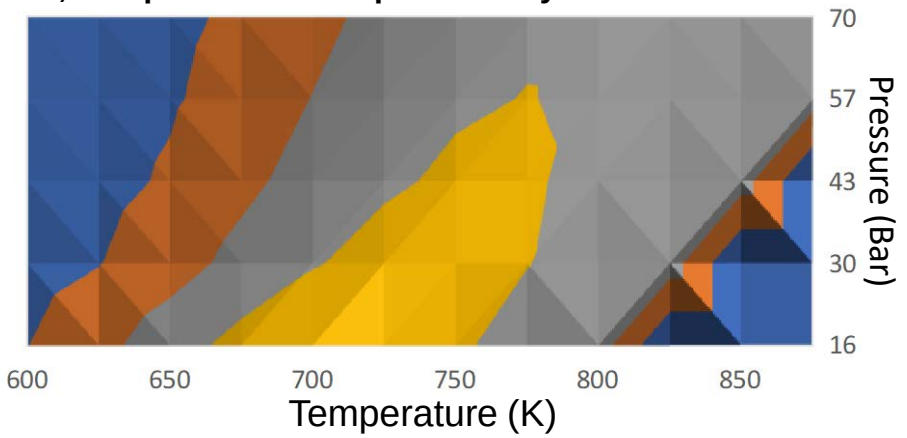
*Accomplishment*

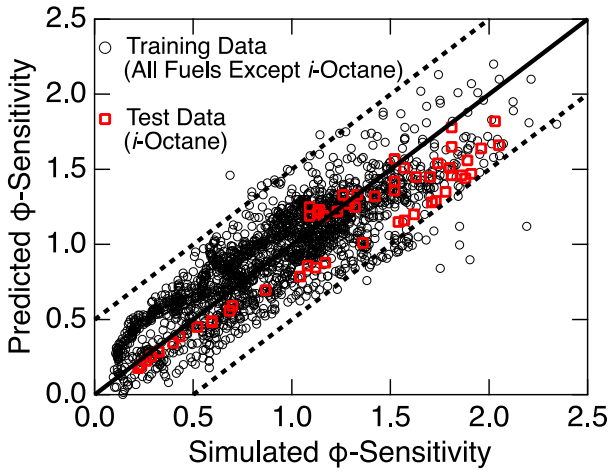
**Determine structure-independent metrics that are correlated to key ignition properties**

Look to correlate species with $\phi$-sensitivity

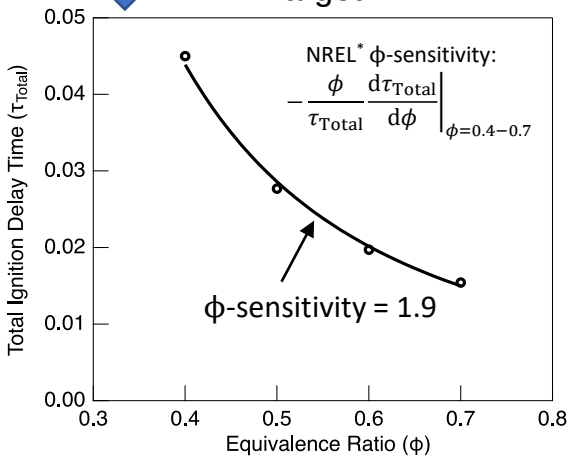



**T,P-Map of *Predicted* ϕ-sensitivity for *Iso*octane:**



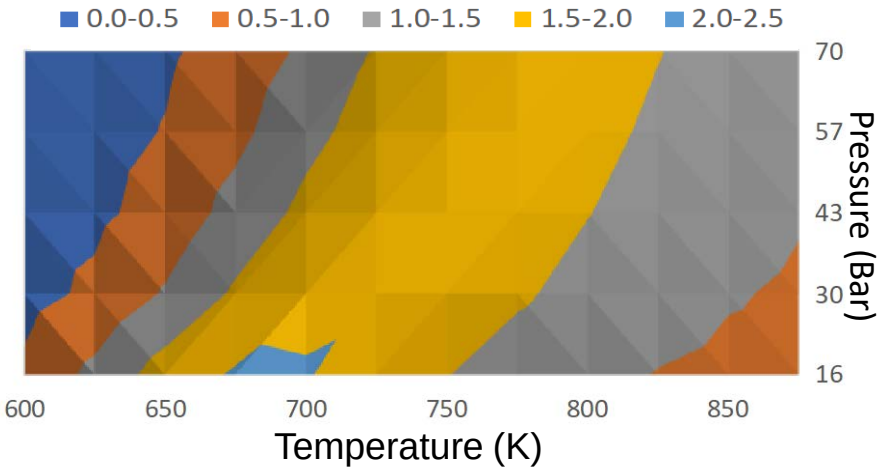

Target




*Isooctane, 700K, 30 bar*

- **2000 Simulations** = 41 fuels (alkanes, alkenes, aromatics, and oxygenates) from 2019 Co-Optima Mechanism at 600–1,000 K and 3–70 Bar
- **Polynomial Chaos Expansion** with regularization
- **Leave one fuel out test** – prediction shows similar T, P behavior but correlation not nearly as strong as observed for single stoichiometry IDT
- **Measurements of $CH_2O$, $H_2O_2$, $\tau_{1^{st}-Stage}$, $\tau_{Total}$, T, and P (at $\phi = 0.4$) can be used to predict ϕ-sensitivity with expected accuracy of ~0.25**

**T,P-map of simulated ϕ-sensitivity**

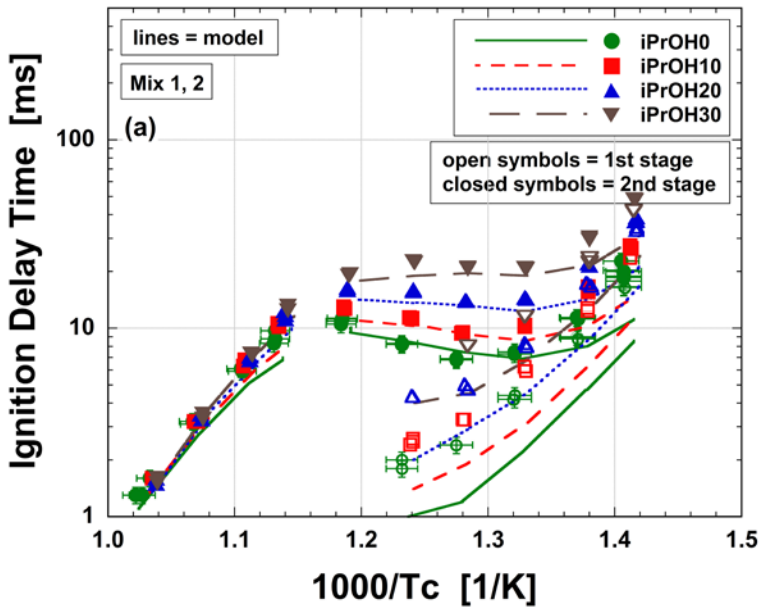


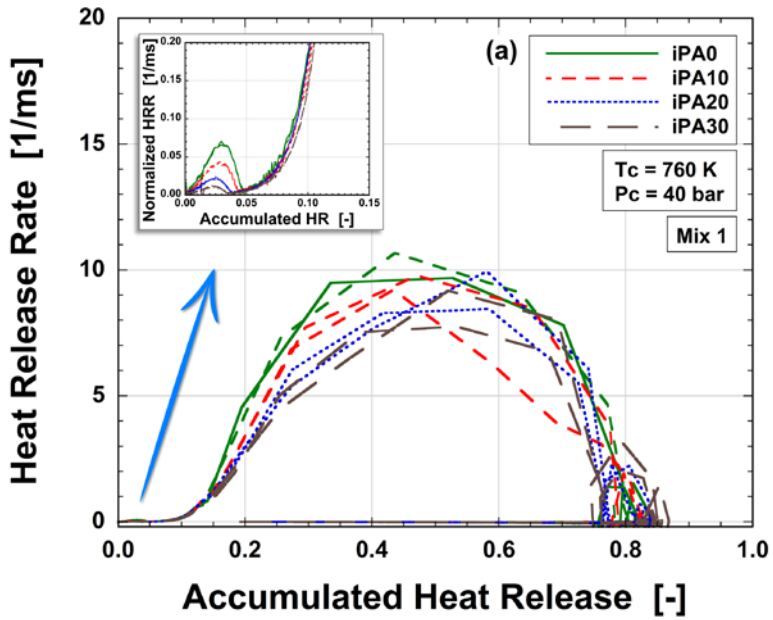

IDT: ignition delay time

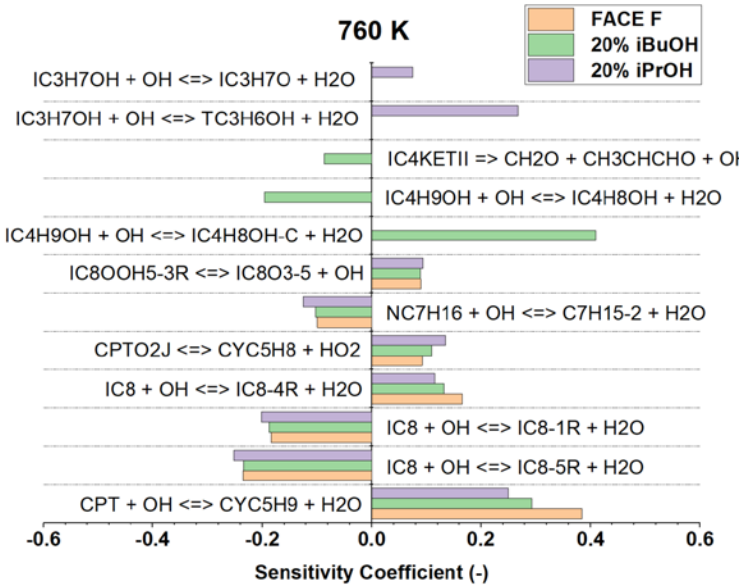
# ANL (Goldsborough) F.2.2.3 Kinetic Mechanism Development

*Accomplishment*

RCM studies identified kinetic interactions of alcohols with petroleum-derived gasoline




- Measurements using ethanol (EtOH), iso-propanol (iPrOH) and iso-butanol (iBuOH) blends into alcohol-free FACE-F can quantify effects on autoignition times, preignition heat release (LTHR, ITHR)
- Critical improvements facilitated in Co-Optima kinetic mechanism to better replicate experimental data
- Analysis with model allows kinetic interactions to be discerned, identifying reaction pathways that extend autoignition times, reduce extents of LTHR.

***Impact: ANL RCM can replicate engine conditions (T, P, ϕ, EGR, and ignition times)***

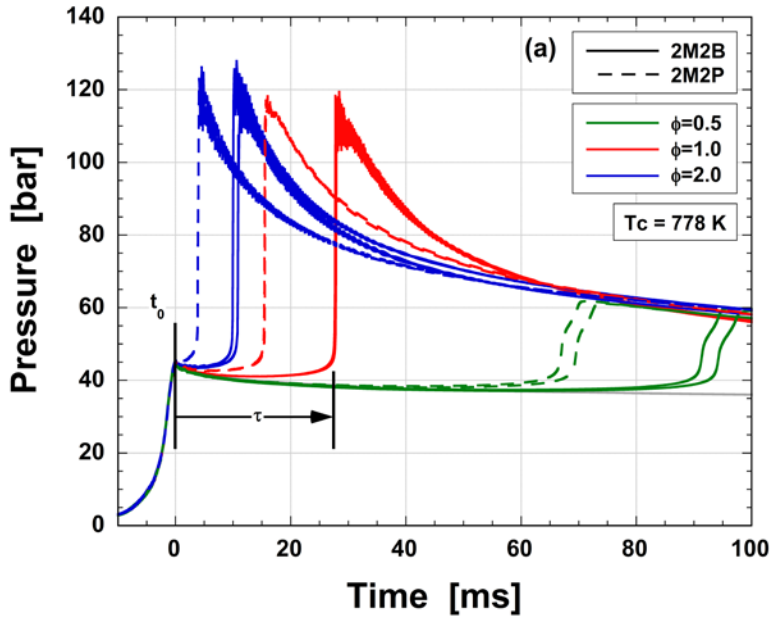
FACE: fuels for advanced combustion engines
ms: milliseconds

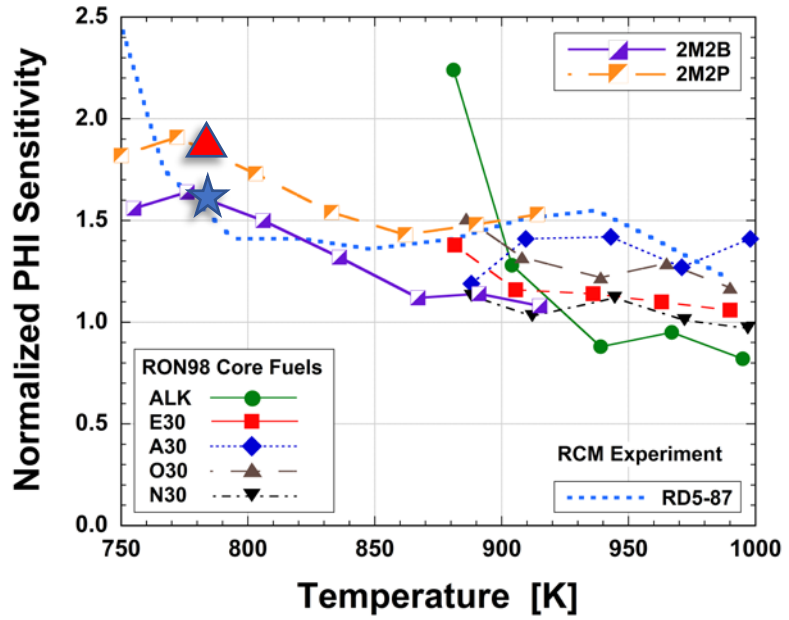
ITHR: intermediate-temperature heat release
LTHR: low-temperature heat release

# ANL (Goldsborough) F.2.3.1 Development / application of MM/ACI Fuel Metric

*Accomplishment*

RCM studies facilitating development of high ϕ-sensitive, HPF iso-olefin fuels




- PNNL highly branched Mix 1
- PNNL less branched Mix 2
- PNNL CoOptima 8 (planned)
- PNNL CoOptima 9 (planned)

NREL* ϕ-sensitivity:

$$\eta \equiv \frac{\phi}{\tau_{\mathrm{Total}}} \frac{\mathrm{d}\tau_{\mathrm{Total}}}{\mathrm{d}\phi}\bigg|_{\phi=varies}$$

- RCM measurements of PNNL "green" iso-olefin mixtures compared against growing database of full boiling-range fuels (Co-Optima Core Fuels, RD5-87), blended fuels, and individual components to assess and rank based on ϕ-sensitivity
- Early screening enables insight into structural features in complex mixtures that determine ϕ-sensitivity and allow modifications in fuel production techniques to enhance this autoignition property.

***Impact: Platform availability to screen fuel candidates, rank fuels for ACI engine schemes***

# Response to Previous Year Reviewers' Comments

The reviewer remarked that this project is aimed at measuring key fuel properties that underlie the entire Co-Optima project. This is a key and critical project for the entire effort. *The Zigler work on small-volume methods for autoignition under engine-relevant conditions is extremely interesting and of great value.*

- ***The small-volume prediction to RON and S has continued, with improved correlations. This work is presently being prepared in a journal article submission. Additionally, an energy company industry partner has shared fuel samples with high RON and S to support this development.***

The AFIDA is showing good ability to explain gasoline sensitivity and octane numbers but it requires 40 milliliters (mL) of fuel to accomplish a sweep of test conditions. *According to the reviewer, that is an enormous amount of fuel in relation to what bench-scale fuel production experiments typically achieve. The reviewer wanted to know how does the amount of fuel required for these bench-scale experiments connect with the BETO exploratory fuel production activities.*

- ***NREL is considering how early-stage screening measurements may be made with smaller amounts (<<40 mL). But the RON and S correlation has so far been successfully applied under Co-Optima to small sample volumes produced by PNNL and other sources.***

The reviewer said that proposed future research looks appropriate, *but was concerned about the ability, or timeframe, to develop and refine a fuel metric for mixed-mode ACI given that experimental studies on mixed-mode ACI are only starting and are highly divergent in approaches*.

- ***The project team is leveraging multiple apparatuses and approaches within the Co-Optima portfolio this FY towards the development of a fuel autoignition metric applicable to ACI, using new and existing experimental and computational databases to provide needed insight.***

The reviewer greatly appreciated efforts to increase the pressure of the reactor setup

- ***An elevated pressure design is complete, and the system is currently being brought online.***

# Collaboration and Coordination with Other Institutions

- ***Collaboration of nine national laboratories***
- **University of Connecticut** (*Kinetic Simulations*)
- **Pennsylvania State University** (Kinetic and Soot Precursor Simulations)
- **University of Illinois-Chicago** (*Ignition Delay Measurements*)
- **Oakland University** (*Ignition Delay Measurements*)
- **Yale University** *(Yield Sooting Index Measurements)*
- **Colorado School of Mines** *(AFIDA Ignition Delay Mapping of EGR Species Effects)*
- **Massachusetts Institute of Technology** *(Kinetic Model Development)*
- **University of Central Florida** *(Ignition Delay, CO-Time-History Measurements)*
- **PNNL** *(Small-Volume Screening RON/S Correlation; Production of $\phi$-Sensitive iso-Olefin Fuels)*
- **LLNL** *(Kinetic Simulations)*
- **ANL** *(Rapid Compression Machine Measurements)*


**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 100 individuals at 80+ organizations across industry and other non-DOE governmental agencies

# Remaining Challenges and Barriers

- AFIDA-based ignition delay measurements for high-reactivity fuels and high-temperature/high-pressure conditions (representing some engine-relevant conditions) are significantly affected by mixing physics, requiring use of CFD simulation (instead of 0D approximation). This limits conditions where AFIDA may provide experimental data feedback for full kinetic mechanism development, and tie points to other more fundamental devices (such as rapid compression machine) are required.
- Completion of elevated pressure flow reactor system has been delayed by COVID-19 response. Additional experiments needed to prove proof of concept in utilizing FTIR in optical flow reactor system to detect unstable intermediate species.
- RCM and other bench-scale apparatuses considered towards development of autoignition metrics can better isolate autoignition chemistry from complex environment within engine combustion chamber, and use small quantities of fuel, but mapping of measurements to ACI combustion in operating engines is still underway.

CFD: computational fluid dynamics

# Proposed Future Research

- **F.2.1.6:** *Complete upgrade of flow reactor to operate under elevated pressures and introduce higher-boiling, diesel-range fuels—Investigate options for observing intermediate radical species such as hydroxyl (OH) and hydroperoxyl (OOH) radicals to further understand nonlinear blending behaviors-supports completion of June 2020 milestone*
- **F.1.4.4:** *Ignition delay mapping of EGR species effects for kinetic mechanism development feedback with LLNL*
- **F.1.4.4:** *Phi-sensitivity studies are being expanded beyond LD multi-mode fuels to MD/HD advanced compression ignition fuels*
- **F.1.4.3:** *Determine if the correlation between formaldehyde/hydrogen peroxide ($CH_2O/H_2O_2$) and $\phi$-sensitivity still holds if the species are measured under dilute-fuel conditions, such as in a jet-stirred reactor or flow reactor*
- **F.2.2.3:** *Measurements for MD/HD prototypical ACI fuels and fuel blends*
- **F.2.3.1:** *Correlations of ignition times and preignition heat release to ACI engine conditions to map fuel behaviors*

*Any proposed future work is subject to change based on funding levels*

HD: heavy duty
LD: light duty
MD: medium duty

# Summary: *Technical Accomplishments and Impact*

- Utilization of flow rector to review chemical basis for nonlinear blending
  *Impact: Flow reactor allows for observation of intermediate species responsible for nonlinear blending behavior*
- Flow reactor studies improve kinetic mechanisms and reveal chemical species responsible for soot precursor formation
  *Impact: A simple yet powerful tool for validating kinetic simulations and soot precursor mechanisms, which can be rapidly applied to a wide range of systems*
- 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*
- RCM-based autoignition measurements provide critical targets for chemical mechanism validation
  *Impact: ANL RCM can replicate engine conditions (T, P, $\phi$, EGR, and ignition times)*
- RCM-based autoignition measurements achieve engine-relevant conditions useful for developing relevant fuel autoignition metrics
  *Impact: Platform availability to screen fuel candidates, rank fuels for ACI engine schemes*

# Overall Summary: *Fuel Property Experimental Kinetics*

| | |
|---|---|
| **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** |
| **Approach** | • Leveraged highly experienced team knowledgeable in fuel property kinetics<br>• Utilized unique bench-scale capabilities to measure and reveal the underlying chemistry and unique species responsible for nonlinear blending effects and $\phi$-sensitivity |
| **Technical Progress** | • Employed flow reactor for observation of intermediate species responsible for nonlinear blending behavior and developed parallel higher-pressure flow reactor system<br>• Utilized flow reactor to improve kinetic mechanisms and in conjunction with QM simulations, interrogate the mechanisms responsible for soot precursor formation<br>• Small-volume AFIDA measurements were used to predict RON to within 2%<br>• AFIDA-based studies provided bench-scale measurement of phi-sensitivity<br>• Determined structure-independent metrics that are correlated to key ignition properties<br>• Identified kinetic interactions of alcohols with petroleum-based gasoline |
| **Collabo-rations** | • Highly coordinated effort of 120+ researchers across nine national laboratories, 20+ universities, 80+ organizations across industry and other non-DOE governmental agencies, and two DOE offices |
| **Future Work** | • Targets remaining technical barriers and focuses on advancing AFIDA and RCM-based measurements toward MD/HD ACI fuels to map fuel behaviors |

# List of Acronyms

ACI: advanced compression ignition
AFIDA: advanced fuel ignition delay analyzer
ANL: Argonne National Laboratory
BETO: Bioenergy Technologies Office
CFD: computational fluid dynamics
CFR: cooperative fuels research
$CH_2O$: formaldehyde
DOE: Department of Energy
EGR: exhaust gas recirculation
EtOH: ethanol
FACE: fuels for advanced combustion engines
FTIR: Fourier-transform infrared
FQM: fuel quality metric
$H_2O_2$: hydrogen peroxide
HD: heavy duty
HPF: high performance fuel
IDT: igniton delay time
ITHR: intermediate-temperature heat release
*i*-BuOH: isobutanol
*i*-PrOH: isopropanol
LD: light duty
LLNL: Lawrence Livermore National Laboratory
LTHR: low-temperature heat release
MD: medium duty
MM: multi-mode
MON: motor octane number
NREL: National Renewable Energy Laboratory
OH: hydroxyl
OOH: hydroperoxyl
P: pressure
$\phi$ = phi = equivalence ratio
1-PE: 1-phenyl ethanol
2-PE: 2-phenyl ethanol
PNNL: Pacific Northwest National Laboratory
PRF: primary reference fuel
QM: quantum mechanical
RCM: rapid compression machine
RON: research octane number
S: sensitivity (S = RON – MON)
SNL: Sandia National Laboratories
T: temperature
$\tau$: tau, ignition delay time
TRF: toluene reference fuel
VTO: Vehicle Technologies Office
YSI: Yield Sooting Index

# Thank You

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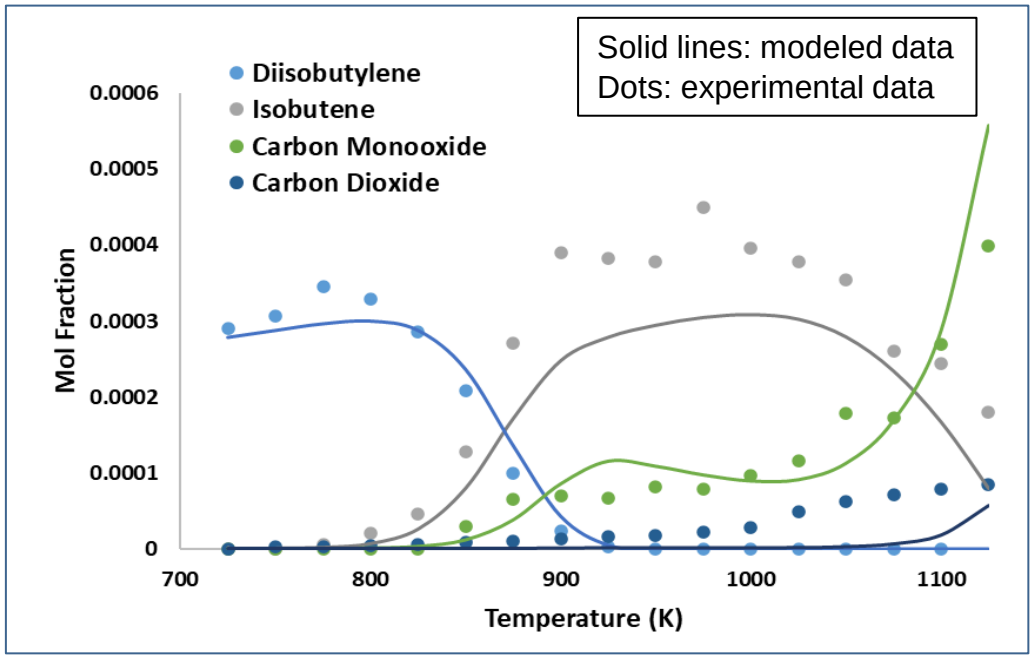
# Technical Back-Up Slides

# NREL (Fioroni) F.2.1.4 Flow Reactor Autoignition Kinetic Mechanism Development and Validation

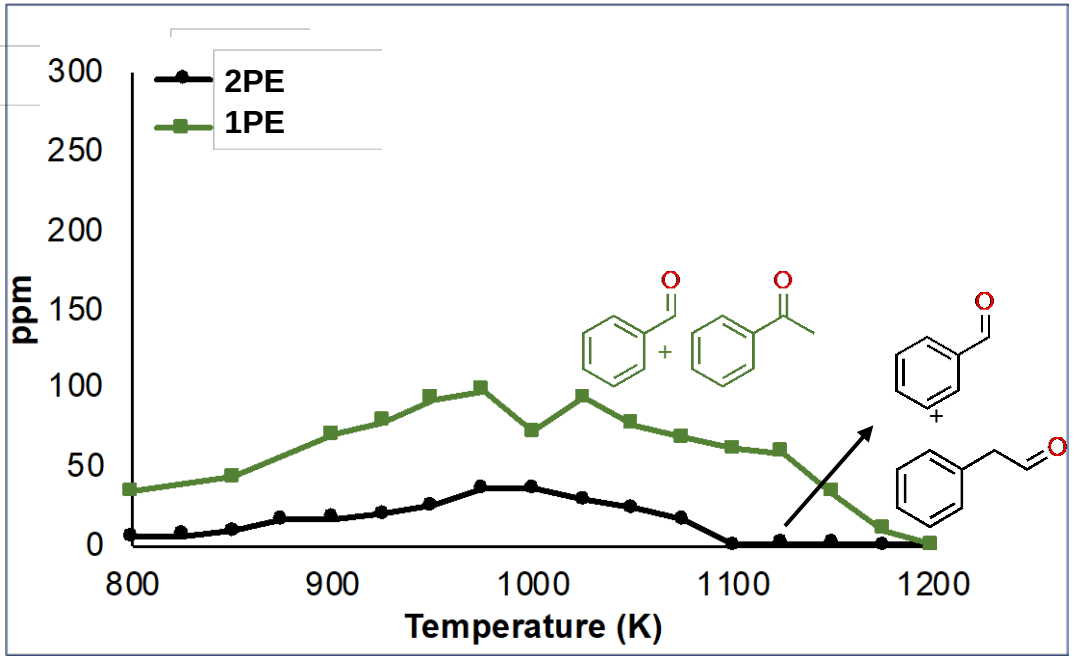
*Accomplishment*

**Flow reactor studies validate kinetic and soot precursor formation mechanisms**

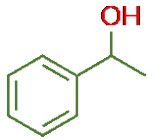
*Diisobutylene Autoignition Species Profiles*




*Soot Precursor Formation: Validation of Oxygenated Aromatics Formation*

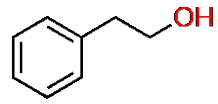



**1-phenylethanol (1PE)**




**YSI = 142**

**2-phenylethanol (2PE)**




**YSI = 207**

- Provided species profiles from flow reactor to validate kinetic mechanisms in collaboration with LLNL
  - Diisobutylene isomers and the three isomers of methyl-butenes data utilized to improve kinetic models
- Utilized quantum mechanical (QM) calculations from Seonah Kim's group in conjunction with flow reactor experiments to explain differences in sooting tendency of different isomers of phenyl ethanols and ethyl phenols.

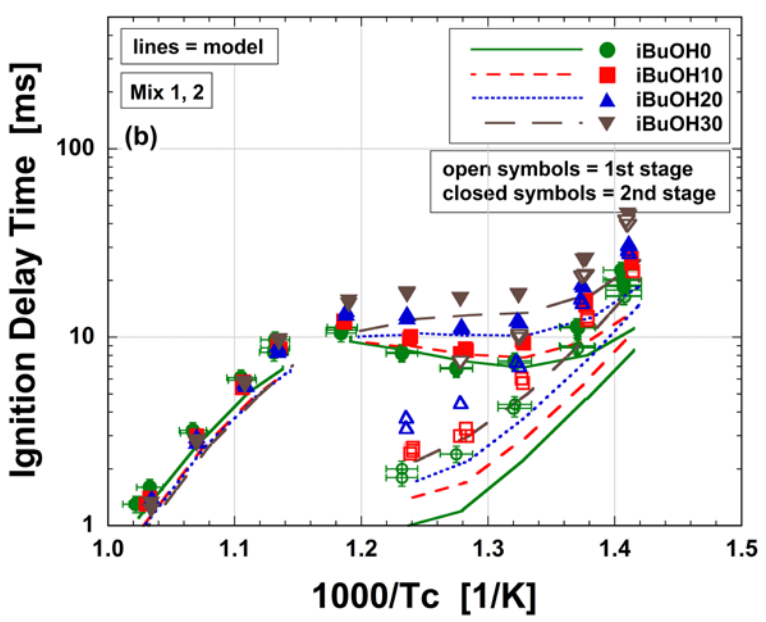
LLNL: Lawrence Livermore National Laboratory
ppm: parts per million
YSI = Yield Sooting Index

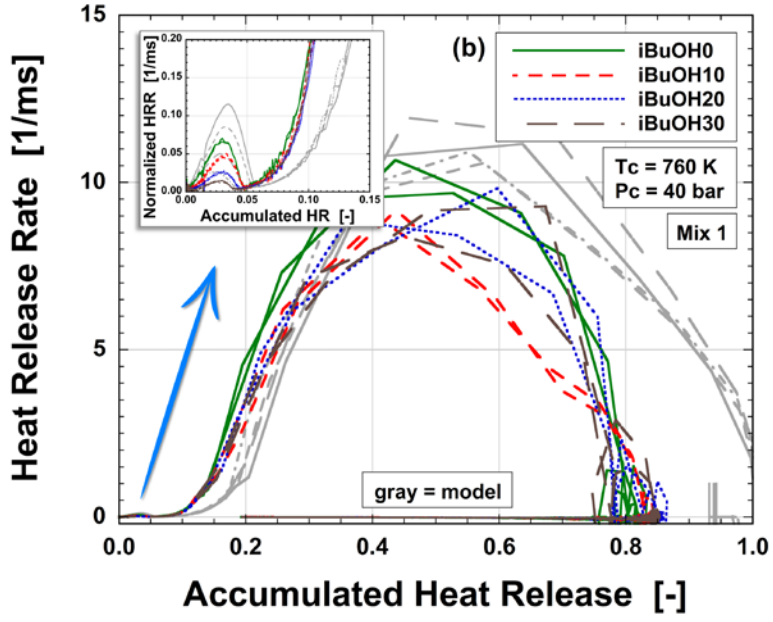
***Impact: A simple yet powerful tool for validating kinetic simulations and soot precursor mechanisms that can be rapidly applied to a wide range of systems***

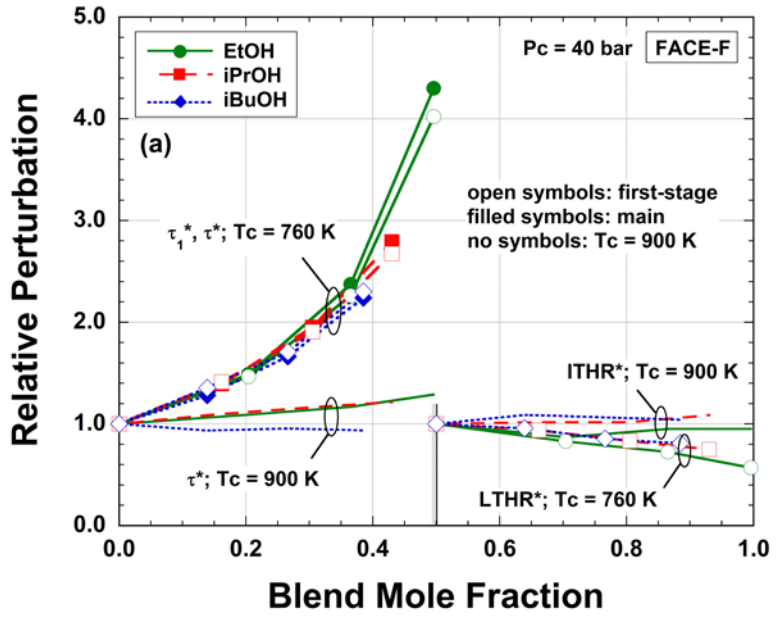
# ANL (Goldsborough) F.2.2.3 Kinetic Mechanism Development

*Accomplishment*

RCM studies identified kinetic interactions of top tier alcohols with petroleum-derived gasoline




- Measurements using ethanol (EtOH), iso-propanol (iPrOH) and iso-butanol (iBuOH) blends into alcohol-free FACE-F can quantify effects on autoignition times, pre-ignition heat release (LTHR, ITHR)
- Critical improvements facilitated in CoOptima kinetic mechanism to better replicate experimental data (IDT, LTHR/ITHR)
- Analysis with model allows kinetic interactions to be discerned, identifying reaction pathways that extend autoignition times, reduce extents of LTHR

***Impact: ANL RCM can replicate engine conditions (T, P, ϕ, EGR and ignition times)***