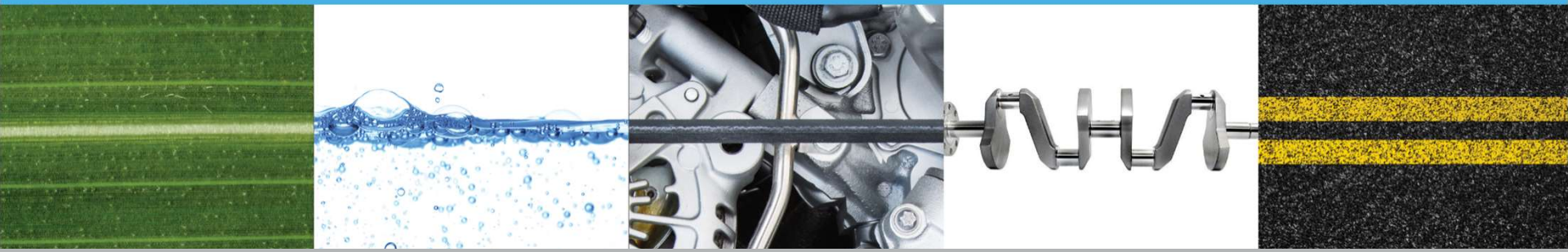
DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Structure – property relationships for bioblendstock identification

CO-OPTIMIZATION OF FUELS & ENGINES

better fuels | better vehicles | sooner

WBS: 3.5.1.5 11
Organizations: PNNL, NREL, ORNL, SNL, LBNL, LANL, INL
Presented by: Vanessa Dagle, PNNL
March 15th, 2021



Project Overview

Goal

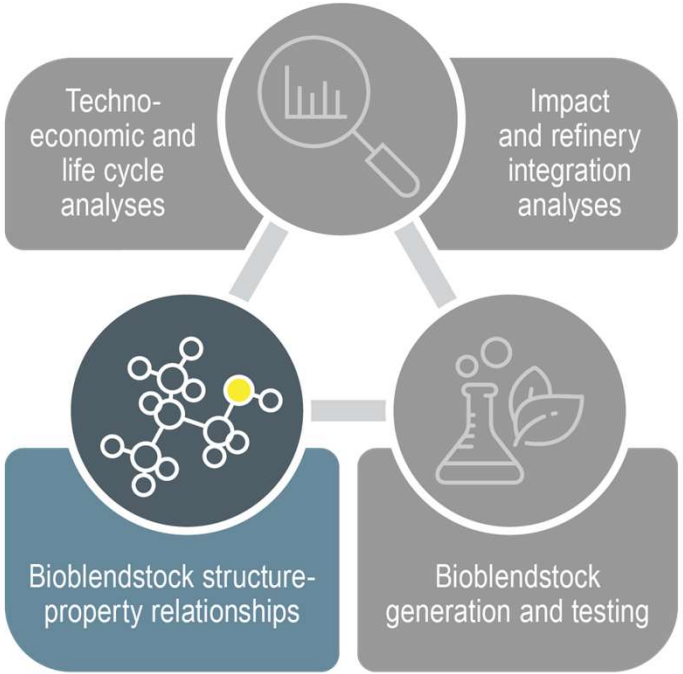
- Identify bioblendstocks with enhanced fuel properties to be evaluated by the broader Co-Optima effort

Approach

- Tie fuel properties to chemical structure to enable bioblendstock selection for the generation-analysis cycle

Relevance

- Identification of performance-advantaged biofuels to increase the bioblendstock value proposition → BETO's goal to accelerate biofuels deployment

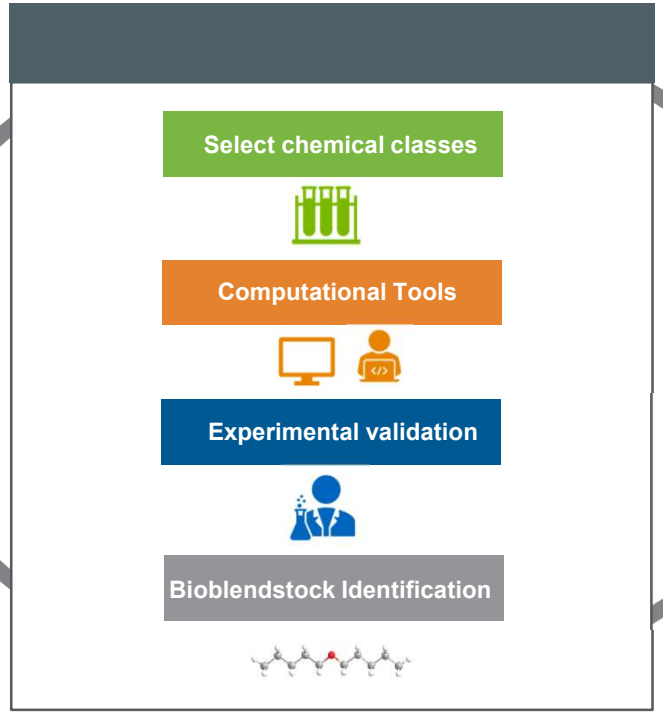


1. Management

SPR Team interfaces with the other Co-Optima teams to advance bioblendstocks

Engine & Fuel Property teams
Inputs to identify relevant fuel properties

Structure-Property Relationships (SPR) assess which blendstocks are promising to target for development & transfer information to **Bioblendstock Generation & Testing**



Bioblendstock Generation & Testing develop conversion pathways, validate **SPR** predictions & provide conversion data to **Analysis**

Analysis conducts TEA/LCA and Refinery integration to inform cost and sustainability metrics

SPR efforts integrated within Co-Optima

1. Management

Comprehensive integration and collaboration across national labs and universities

National Laboratory task leads

HPF Team Lead: Derek Vardon (NREL)

- Idaho National Laboratory: Magdalena Ramirez Corredores
- Los Alamos National Laboratory: Andrew Sutton, Cameron Moore, Bill Kubic
- Berkeley Lab: Eric Sundstrom, Taek Soon Lee
- NREL: Derek Vardon, Tom Foust, Dan Ruddy, Seonah Kim, Teresa Alleman, Jon Luecke, Gina Fioroni

HPF Deputy: Vanessa Dagle (PNNL)

- Oak Ridge National Laboratory: Mike Kass, Todd Toops
- Pacific Northwest National Laboratory: Evgueni Polikarpov, Tim Bays, Lelia Cosimbescu, Vanessa Dagle, Karthi Ramasamy, Mike Thorson, Dan Gaspar
- Sandia National Laboratories: Anthe George, Joey Carlson, Ryan Davis, Alexander Landera, Bernard Nguyen, Eric Monroe

University collaborators

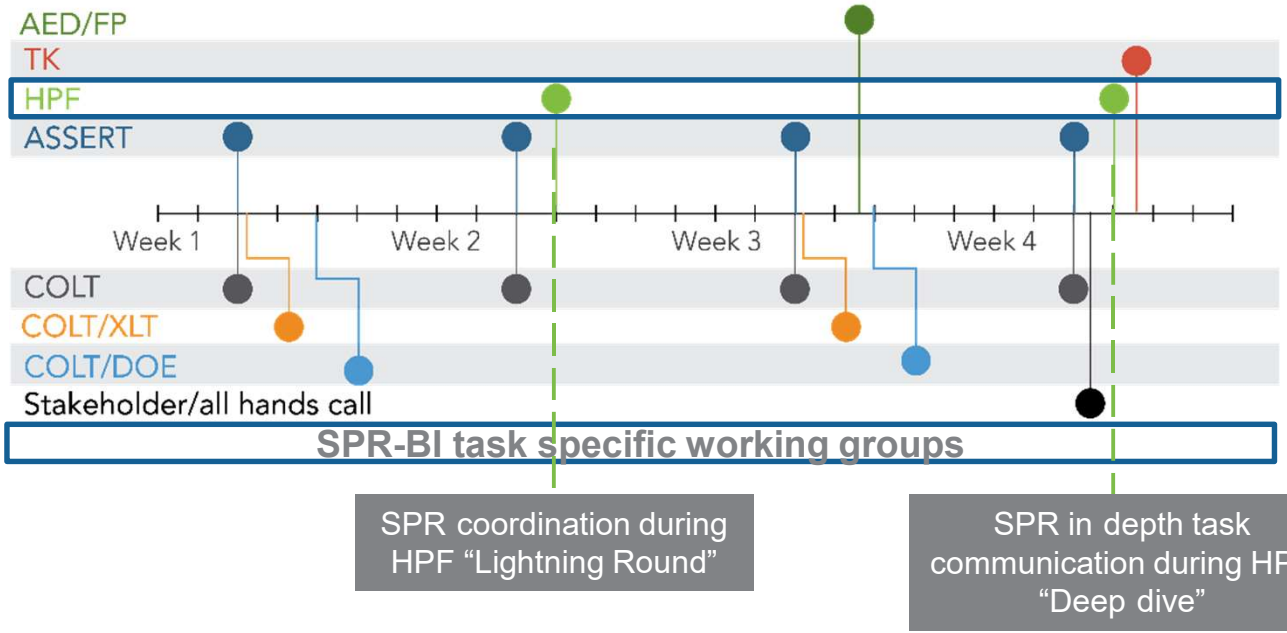
- Yale University: C. McEnally
- University of Central Florida: K. Ahmed
- Cornell University: C. Thomas Avedisian
- University of Alabama: A. Agrawal
- University of Michigan: J. Martz
- Massachusetts Institute of Technology: W. Green
- LSU: I. Schoegl

Experienced researchers from national labs and universities with complementary expertise in fuels and properties

1. Management

Communication & coordination are critical for SPR activities

Regular scheduled meetings



AED = Adv Engine Dev Team

ASSERT = Analysis of Sustainability, Scale, Economics, Risk and Trade Team

FP = Fuel Properties Team

HPF = High Performance Fuels Team

TK = Simulation Toolkit Team

COLT = Co-Optima Leadership Team

XLT = Extended Leadership Team

SPR-BI findings regularly shared with HPF, broader co-Optima & EAB members

1. Management

SPR activities address the major risk factors when evaluating bioblendstock fuel properties

SPR: structure-property-relationship

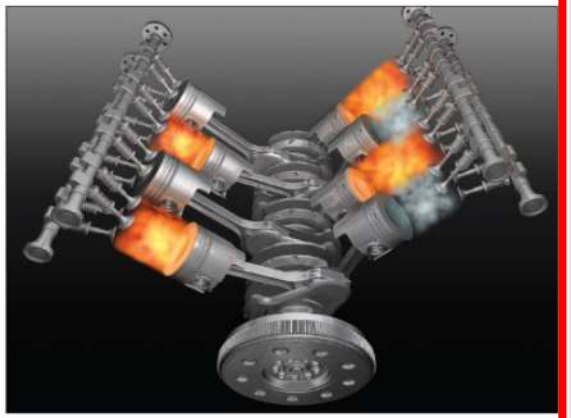
SPR Major Risk Factors	Risk Mitigation Strategy
Time-line for determining relevant fuel properties for light-duty and medium/ heavy-duty incompatible with SPR workflow	Work with Co-Optima Fuel Property and Advanced Engine Development to triage the most critical fuel properties
Computational modeling for single molecules or simple mixtures does not reflect complexity of “real” bioblendstocks	Work with Blendstock Generation & Testing team to apply the latest experimental tools to validate structure-property relationships with neat and blended bioblendstocks

A mitigation strategy is in place to minimize risk impact

2. Approach

Foundational technical questions frame approach

What fuels do engines *really* want?



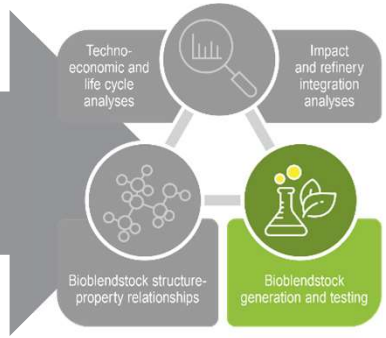
What fuel options work best?

What will work in the real world?

2. Approach

SPR workflow leads to fuel bioblendstock determination

Computational methods → **Preferred Functional groups** → **Experimental methods**



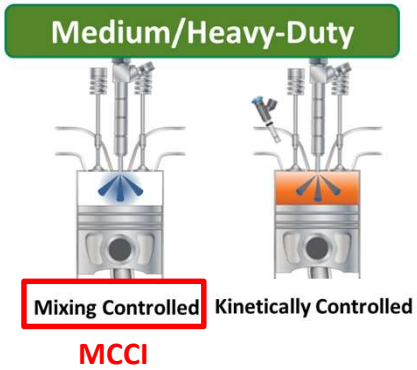
- High throughput tools developed to measure fuel properties of **many chemical classes**
- Computer based structure fuel properties relationship determined

- Experimental measurements of candidates from **selected functional groups**
- Validate structure fuel property relationships
- Select preferred bioblendstock candidates for generation at scale for testing

Computational methods used to quickly screen candidates
Experimental methods validate screening

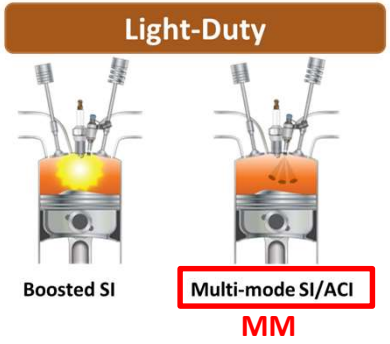
2. Approach

SPR address both light-duty and medium/heavy-duty combustion modes



Performance:
CN, Sooting,
Flash point, LHV

Operability:
$M_{p,}$ η, solubility, stability



Performance:
RON, MON, S, phi sensitivity,
HoV, Sooting

Operability:
P_{vap}, B_p, $M_{p,}$ η, σ, stability

Light Duty: moved from SI to MM

Medium/Heavy Duty: Accelerated MCCI effort

2. Approach

Critical success factors and barriers to overcome

SPR Success Factors

Discover underlying science that links properties to chemical structure

Define combustion-appropriate blendstock candidates for further evaluation by Co-optima

SPR Barriers to overcome

Relevant properties for advanced combustion approaches not fully defined

Computational tools developed for single components, simple mixtures reduce their reliability

SPR key activities

Regularly engage with engine and fuel properties teams to (re)define most relevant fuel properties

Experimental tools validate SPR for complex mixtures

Developed tools to predict mixture properties

SPR integrated approach and workflow (computational + experimental validation) reduce barriers to success

2. Approach

Well-defined milestones

SPR Demonstrated Ability

- **SPR** completed 7 milestones in FY20 related to Light Duty and Medium/ Heavy Duty bioblendstocks
- **SPR** identified blendstocks scaled up by **Blendstock Generation & Testing**

Selected FY20 Milestone

- Report on the Top 11 most promising MCCI bio-blendstocks identified by Co-Optima, including fuel properties, production information, and techno-economics, incorporating new information generated during FY20

Progress measurable with milestones in place

3. Impact

SPR connects with stakeholders and the broader BETO and VTO programs

VTO Program Interactions

- Advanced Combustion
- Fuel Effects
- Aftertreatment
- Modeling

BETO Program Interactions

- Analysis
- Sustainability
- Feedstocks
- Conversion
- Scale-Up

Co-Optima

- Techno-economic and life cycle analysis
- Impacts analysis
- Bioblendstock generation and testing
- Structure-property relationships

Inputs and requirements

- Industry (biofuels, energy companies, OEMs)
- EAB
- Regulatory (EPA, CARB)
- Other stakeholders
- Co-Optima Fuel Properties, Toolkit and Adv Engine Dev

Data and Outputs

- Fuel Property Database
- SPR tools
- Techno-economic and lifecycle analysis outputs
- Performance-advantaged bioblendstock candidate lists

3. Impact

SPR tools and outcomes shared and leveraged outside Co-Optima

SPR contributes to new market opportunities

- ✓ **Identify new performance-advantage biofuels** with potential to increase vehicle engine efficiency, improve fuel economy, and reduce emissions.

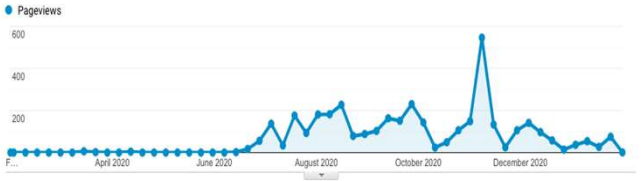
- ✓ **SPR outcomes leveraged by industrials**:
  2 new CRADA* projects with industrials in FY20
  - " 100+ RON Gasoline Blendstock for High Efficiency, Low Emission Engines" in collaboration with LanzaTech
  - "Renewable Octane Hyperboosting Blendstock for High-efficiency Co-optimized Engines" in collaboration with Visolis

SPR tools made publicly available

- ✓ **Software for CN, RON, MON**:
  https://www.github.com/sandialabs/FeatureCreature

- ✓ **Sooting web app**:
  https://ysipred.herokuapp.com

3716 page views since June 2020



- ✓ **NMR tool**:
  web page under development

3. Impact

SPR impacts community with technical handoffs, engagement and results dissemination

Technical Handoff	Stakeholder Engagement	Disseminating Results
✓ Identified 7 blendstocks that meet MCCI Tier 1 fuel properties criteria	✓ Attend Co-Optima bi-annual External Advisory Board meetings	✓ Published 10 papers that incorporate SPR
✓ Identified 20 blendstocks with RON >98 and S >8	✓ Conduct quarterly meetings with Cummins to share & receive feedback	✓ Produced software and webs apps for predicting cetane & sooting fuel properties
✓ Blendstocks scaled up and tested by **Blendstock Generation & Testing** team and evaluated by the **broader co-optima effort**.	✓ Arrange bi-annual presentations with industry experts for High Performance Fuels Team	✓ Scheduled upcoming Co-Capstone webinars and regular ACS Conference symposium

4. Progress and Outcomes

Tools developed by SPR widely used to estimate candidate fuel properties

Predictive and SPR tools developed prior to FY2019

- FeatureCreature software to visualize structural contributions to CN
- Machine learning to map molecular structure- sooting relationship
- Reid Vapor Pressure prediction
- NMR-based blending models to predict RON
- Machine learning framework to rapidly classify molecules by RON, MON, S, CN, melting point, threshold sooting index

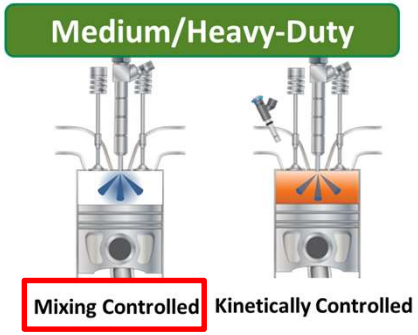
New tools since FY2019

- Theoretical method to predict for phi-sensitivity
- Machine learning for laminar flame speed
- Cloud point and gel point prediction tools

Previous work on SPR tools utilized to screen candidate blendstocks

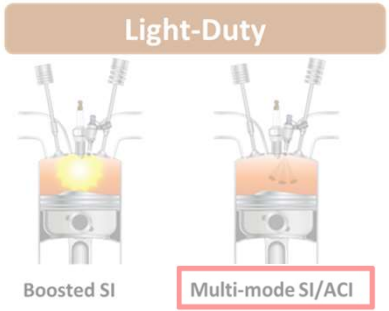
New predictive SPR tools relevant to MM and MCCI combustion

4. Progress and Outcomes – MCCI



Performance:
CN, Sooting, Flash point, LHV

Operability:
M_p, η, solubility, stability



Performance:
RON, MON, S, phi sensitivity, HoV, Sooting

Operability:
P_{vap}, B_p, M_p, η, σ, stability

4. Progress and outcomes

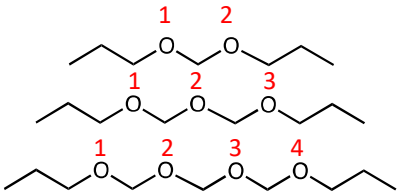
Structure impacts on CN used to identify promising blendstocks for MCCI

Progress

- **Innovation**: software visualizes how structural differences impact cetane numbers
- **Experimental validation**: Strong focus on selected oxygenated compounds (mainly ethers)
  > 50 compounds tested
- **Multiple structure-CN relationships** experimentally validated or established
- **37 blendstocks identified with CN > 40**

Key findings

- **Increase of alkyl chain length** results in CN increase for n and iso-ethers, dioxolanes, myrcenes
- **Increase of C chain length** leads to higher CN for n and iso-ethers, dioxolanes, myrcenes
- **Higher number of**  leads to higher CN for POMEs



CN: 84

CN: 107

CN: 126

Outcome: CN prediction tool complemented by experimental measurements have led to identification of 37 blendstocks with CN > 40 for MCCI combustion mode

4. Progress and outcomes – MCCI

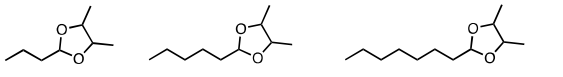
Molecular structure impacts on sooting used to identify promising

Progress

- **Innovation**: machine learning links sooting tendency to molecular structure
- **Tool heavily used** since FY19 to identify promising functional groups
- **Experimental validation** for 8 functional groups and > 40 compounds (long chain alcohols, (poly)-ethers, branched cyclohexanes, iso-alkanes, dioxolanes, oxetanes, ketones, esters)
- **25 blendstocks identified with YSI <100**

Key findings

- **Increase of alkyl or C chain length** typically results in YSI increase
- **Addition of O to C_xH_y** compounds typically results in lower YSI
- **Increase of**  in POMEs leads to a very slight decrease of YSI



YSI			
Predicted	39	52	65
Measured	37	49	63

Outcome: Sooting predictive tool complemented by YSI experimental measurements have led to identification of 25 compounds with YSI < 100 for MCCI combustion mode

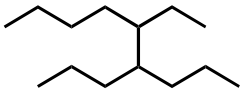
4. Progress and outcomes – MCCI

Seven new blendstocks identified through structure-property relationships

MCCI Tier 1 Fuel Property Criteria

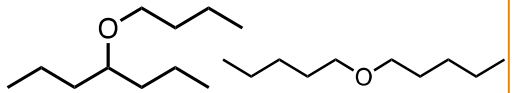
Property	Limit
Boiling point or distillation curve	<338°C
Flashpoint	> 52°C
Melting point (pure compound) or cloud point (mixtures)	< 0°C
Solubility in water	< 20 g/L
Toxicity: OSHA category 1 or 2 for acute toxicity, carcinogenicity and reproductive toxicity excluded	
Autoignition metric (CN)	≥ 40
Corrosion (ASTM D3672)	TAN < 0.3 mg KOH/ g

Alkane



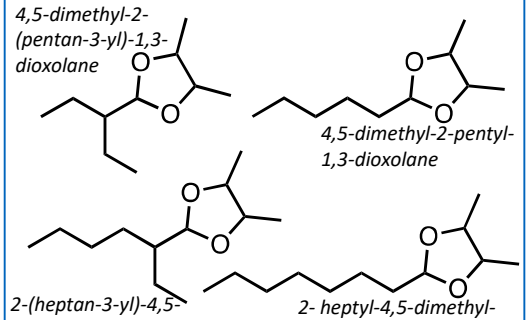
5-ethyl-4-propylnonane

Ethers



4-butoxyheptane *Dipentylether*

Dioxolanes



4,5-dimethyl-2-(pentan-3-yl)-1,3-dioxolane

4,5-dimethyl-2-pentyl-1,3-dioxolane

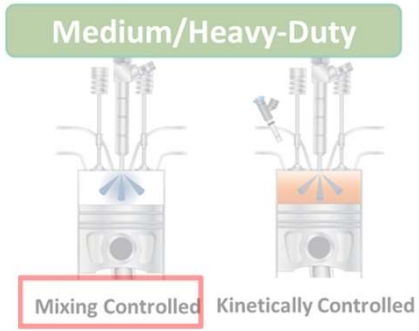
2-(heptan-3-yl)-4,5-dimethyl-1,3-dioxolane

2- heptyl-4,5-dimethyl-1,3-dioxolane

Outcomes:

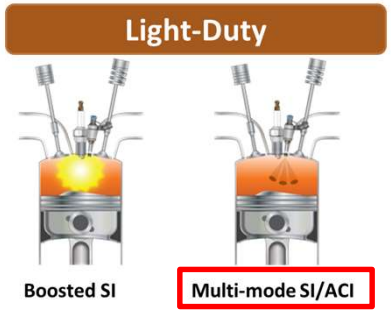
- Combined computational and experimental structure-property relationships contributed to identification of 7 blendstocks meeting MCCI Tier 1 fuel property criteria
- 7 more promising classes identified; experimental validation in progress

4. Progress and Outcomes – MM



Performance:
CN, Sooting, Flash point, LHV

Operability:
M_p, η, solubility, stability



Performance:
RON, MON, S, phi-sensitivity, HoV, Sooting

Operability:
P_{vap}, B_p, M_p, η, σ, stability

4. Progress and Outcomes

SPRs developed for blends to improve for RON and S

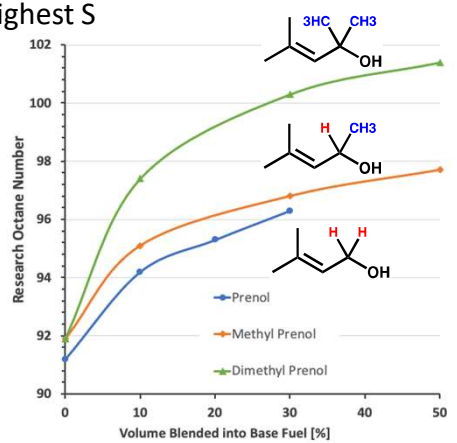
Progress

- **Innovation**: a software that visualizes how structural differences impact RON and MON
- NMR model predicts RON for blends : a newly developed web page under completion
- **Experimental validation: Strong focus on blends and mixtures**
  5 functional groups (Olefins blends, alcohols blends, olefinic alcohols blends, esters, ketone blend)
- **> 20 blendstocks with RON >98, S* >8**

S* = RON - MON

Key findings

- **Mixtures of alcohols trend:**
  RON: C_3-C_7 odd numbers alcohols > C_2-C_8 even numbers
  S: C_3-C_7 odd numbers alcohols < C_2-C_8 even numbers
- **Olefinic esters**: Structures with internal C=C bonds and > 1 C=C bond present highest S
- **Olefinic alcohols**: Replacing weakest C-H bonds on prenol with CH_3 groups leads to increased RON



Outcome: Combined computational and experimental SPR tools led to identification of > 20 blendstocks with RON > 98 and S >8

4. Progress and Outcomes

Structure-φ-sensitivity relationship for MM combustion

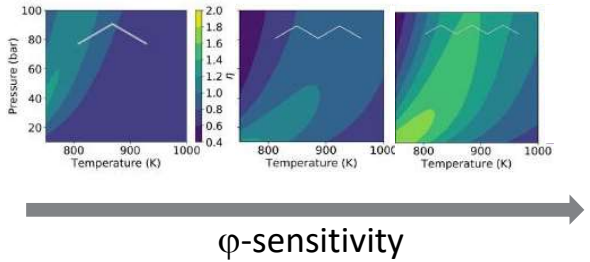
New: SPR Tool for φ-sensitivity

- **φ-sensitivity** is a change in ignition delay time in respect to a change in fuel-to-air ratio
- **State-of-the-art**: φ-sensitivity measured in engines requiring large volume of fuel. Inadequate for new blendstock identification
- **Innovation:** Use kinetic simulations
- **Evaluated 7 functional groups**: n-alkanes, iso-alkanes, ketones, ethers, esters, cyclics

Key findings

- C chain length
- degree of branching
- position of alkyl group
- location of O

Direct impact on φ-sensitivity



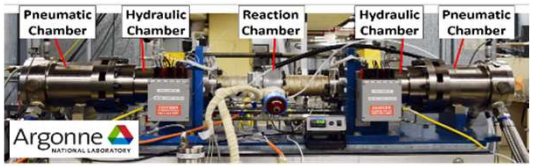
Outcome: Novel kinetic simulations tool enables to predict the structure- φ-sensitivity relationship

4. Progress and Outcomes

Structure-φ-sensitivity relationship for MM combustion

New: SPR Tool for φ-sensitivity

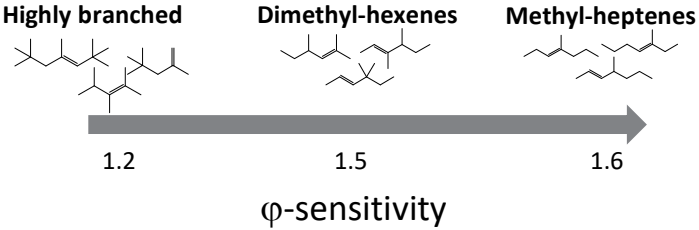
- **Innovation:** Rapid compression machine test that requires only few ml.
  In collaboration with VTO program



- **Iso-olefins blendstocks for MM**:
  High RON & S, but little know for φ-sensitivity
- **Leverage theoretical studies**: iso-alkanes φ-sensitivity increases with decrease of branching

Key findings

- **φ-sensitivity of complex iso-olefins mixtures** increases when the degree of branching decreases



- **Blendstock scaled up under Blendstock Generation & Testing** & engine tested
- **New Co-Optima CRADA project** will leverage these findings

Outcome: Experimentally demonstrated increase of φ-sensitivity with decrease of iso-olefins degree of branching

4. Progress and Outcomes

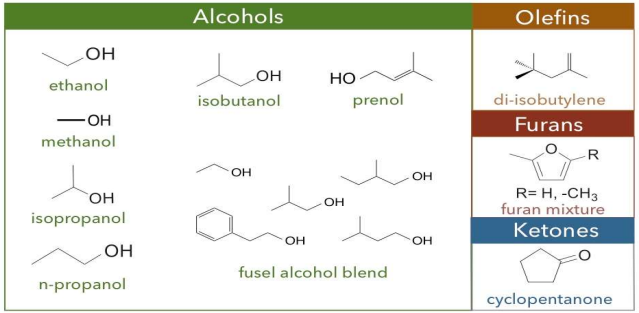
SPR contributed to achievement of Co-Optima goals over the past 6 years

Light Duty

- 10% fuel economy gain over 2015 baseline

✓ Developed merit function to determine what properties and to what level properties impact engine efficiency and fuel economy
→ RON and S are the most critical properties

✓ Merit function and SPR helped to identify 10 bioblendstocks with potential to increase engine efficiency by 10%



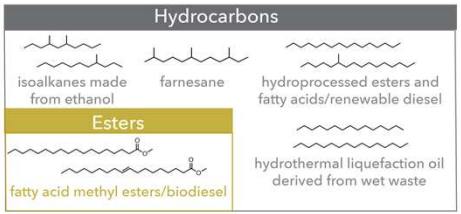
Merit function value ≥E10 premium (RON =98) when blended at ≤ 30% level

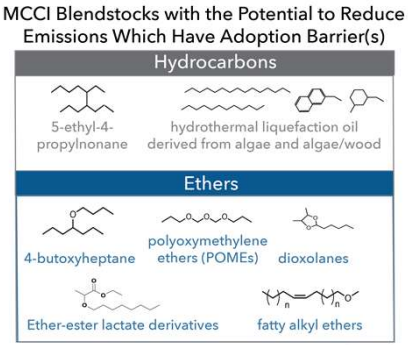
Medium- and Heavy-Duty

- Lower-cost path to reduced engine-out criteria emissions
- Up to 4% fuel economy gain

✓ Developed SPR tools for CN and sooting tendency
→ Utilized SPR tools to quickly screen many candidates and identified preferred blendstocks.

✓ LCA indicates all top 11 blendstocks have the potential to reduce GHG emissions by at least 60% relative to petroleum diesel





Summary for SPR effort

Management	• Integrated team effort with stakeholders from other Co-optima teams provide inputs and/ or outputs. • Collaboration between national laboratories & universities • Regular communication and coordination with HPF, broader Co-optima and EAB members • Mitigation strategy based on integrated team effort, communication and collaboration is in place to minimize risks
Approach	• Determine key properties for a given combustion mode with inputs from AED and FP teams. • Define suite of chemistries and functional groups • Computational tools utilized to screen many chemicals and establish SPR • Identify preferred functional groups for experimental validation of the SPR • Identify blendstock to be evaluated in generation/ testing- analysis cycle
Impact	• Enhanced bioblendstocks value proposition by identifying bioblendstocks that maximize engine performance, energy efficiency, and minimize environmental impacts
Technical Progress	• SPR computational and predictive tools developed in FY19 and prior have been heavily used to identify preferential functional groups for experimental validation of the structure-property relationship (SPR) • Experimental validation of SPR conduced for > 80 blendstocks • A new web app for fuel property prediction of complex blends using NMR • A new high-throughput computational tool for phi-sensitivity-structure relationship.
Outcome	• Over the last 2 years SPR contributed to identification of: - 7 blendstocks that meet all Tier 1 MCCI criteria - > 20 blendstocks with RON >98 and S > 8 for MM

Acronyms

BOB	Blendstock for oxygenated blending
Boosted SI	Boosted spark ignition for light-duty vehicles
Bp	Boiling point
bRON	Research octane number for a blend of gasoline and bioblendstock
CN	Cetane number
DCN	Derived cetane number based on ignition delay measurements
HoV	Heat of vaporization
KC	Kinetically controlled ignition for heavy-duty vehicles
LHV	Lower heating value
MCCI	Mixing controlled compression ignition for heavy-duty vehicles
Mp	Melting point
MON	Motor octane number
MM	Multi-mode ignition for light-duty vehicles
RON	Research octane number
RVP	Reid vapor pressure
S	Octane sensitivity, defined as RON minus MON
SPR	Structure-property relationships
YSI	Yield sooting index
η	Viscosity
σ	Surface tension

Quad Chart Overview

Timeline

- Phase 1: October 1, 2015 to September 30, 2018
- Phase 2: October 1, 2019 to September 30, 2021

	FY20	Active Project
DOE Funding	$3,820,000	$12,025,000

Partner Labs

- ANL, INL, LANL, LBNL, LLNL, NREL, ORNL, PNNL, SNL

Barriers addressed

19ADO-E: Co-development of Fuels and Engines

19At-D: Identifying New Market Opportunities for Bioenergy and Bioproducts

Project Goal

Identify bioblendstocks with enhanced fuel properties to be evaluated by the broader Co-Optima effort

End of Project Milestone

Identify low carbon fuel-engine combinations that increase fuel economy by 35% (light duty) or 4% (heavy duty) over a 2015 baseline, with reduced emissions

Funding Mechanism

AOP

Past Reviewers' Comments and responses

Given the importance of biodegradability and low toxicity for these blendstocks for which sustainability and improved environmental performance will be critical, it makes sense to evaluate these blendstock elements as an early screening; these should be part of the Tier 1 screening rather than waiting until Tier 3.

- Toxicity and biodegradation have been incorporated to the Tier 1 fuel property criteria table
- Activities dedicated to toxicity and biodegradation are being conducted under a task entitled "Toxicology and biodegradability assessment of bioblendstocks"

The team could consider engagement at ASTM to enable use of these predictive models to facilitate new fuel qualification under the ASTM Committee D.02

- A task under Co-optima to facilitate participation in ASTM D.02 has continued for several years; the task lead is aware of the prediction work and can raise it as appropriate

Publications FY19-21

- **Development of robust models for the prediction of Reid vapor pressure (RVP) in fuel blends and their application to oxygenated biofuels using the SAFT-γ approach** - A. Landera, N. Mac Dowell, A. George. Fuel. 2021. https://doi.org/10.1016/j.fuel.2020.118624
- **Investigation of structural effects of aromatic compounds on sooting tendency with mechanistic insight into ethylphenol isomers** - Kim, Y., Etz, B. D., St. John, P., Fioroni, G. M., Messerly, R., Vyas, S., Beekley, B. P., Guo, F., McEnally, C. S., Pfefferle, L. D., McCormick, R. L., Kim, S.. Proceedings of the Combustion Institute. 2020. doi.org/10.1016/j.proci.2020.06.321
- **Production and fuel properties of iso-olefins with controlled molecular structure and obtained from butene oligomerization** - V. L. Dagle, J. S. Lopez, A. Cooper, J. Luecke, M. Swita, R. A.Dagle, D. Gaspar. Fuel. 2020. https://doi.org/10.1016/j.fuel.2020.118147
- **Combined Experimental/Numerical Study of the Soot Formation Process in a Gasoline Direct-Injection Spray in the Presence of Laser-Induced Plasma Ignition** – F. Tagliante, H. Sim, L. Pickett, T. Nguyen, and S. Skeen. WCX SAE World Congress Experience, 2020. https://doi.org/10.4271/2020-01-0291
- **Co-Optimization of Fuels & Engines: FY19 Year in Review** – R. Wagner, 2020. https://www.energy.gov/eere/bioenergy/downloads/co-optima-fy-2019-year-review
- **Methodology for the Development of Empirical Models Relating ^{13}C NMR Spectral Features to Fuel Properties** – A. Heredia-Langner, J.R. Cort, K. Grubel, M.J. O'Hagan, K.H. Jarman, J.C. Linehan, K.O. Albrecht, E. Polikarpov, D.L. King, T.D. Smurthwaite, and J.T. Bays. Energy & Fuels, 34(10):12556–12572, 2020. https://doi.org/10.1021/acs.energyfuels.0c00883

Publications FY19-21

- **Performance-Advantaged Ether Diesel Bioblendstock by A Priori Design** – N.A. Huq, X. Huo, G.R. Hafenstine, S.M. Tifft, J. Stunkel, E.D. Christensen, G.M. Fioroni, L. Fouts, R.L. McCormick, P.A. Cherry, C.S. McEnally, L.D. Pfefferle, M.R. Wiatrowski, P.T. Benavides, M.J. Biddy, R.M. Connatser, M.D. Kass, T.L. Alleman, P. St. John, S. Kim, and D.R. Vardon. Proceedings of the National Academy of Sciences of the United States of America, 116(52):26421–26430, 2019. https://doi.org/10.1073/pnas.1911107116
- **Sooting Tendencies of Furans and Their Derivatives as Potential Biofuels** – J. Zhu, B.D. Etz, B. Hu, H. Kwon, Y. Xuan, P. St. John, S. Kim, L.D. Pfefferle, and C. McEnally. Abstracts of Papers of the American Chemical Society, 2020. https://www.morressier.com/article/sooting-tendencies-furans-derivatives-potential-biofuels/5e735fe2cde2b641284a9e93
- **Towards Quantitative Prediction of Ignition-Delay-Time Sensitivity on Fuel-to-Air Equivalence Ratio** – R. Messerly, P. St. John, M. Rahimi, B.T. Zigler, J. Luecke, N. Huq, B. Etz, T. Foust, R.L. McCormick, and S. Kim. Combustion and Flame, 214:103–115, 2020. https://doi.org/10.1016/j.combustflame.2019.12.019
- **Discovery of novel octane hyperboosting phenomenon in prenol/gasoline blends –** E. Monroe; J. Gladden; K. O. Albrecht; J. T. Bays; R. L. McCormick; R. W Davis; A. George. https://doi.org/10.1016/j.fuel.2018.11.046
- **Measuring and Predicting the Vapor Pressure of Gasoline Containing Oxygenates** – D.J. Gaspar, S.D. Phillips, E. Polikarpov, K.O. Albrecht, S.B. Jones, A. George, A. Landera, D.M. Santosa, D.T. Howe, A.G. Baldwin, and J.T. Bays. Fuel, 243:630-644, 2019. https://doi.org/10.1016/j.fuel.2019.01.137

Additional slides

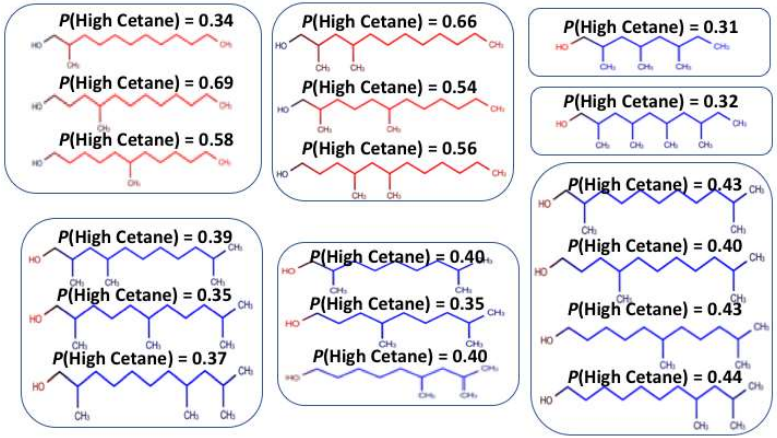
Software for RON, MON, CN

Software visualizes how structural differences impact fuel properties

- Provided a basis for visually evaluating model performance relative to known functional groups
- Focused on properties RON, MON, CN

Nearly all blendstocks being considered by Co-optima have been evaluated

- 1000s of molecules evaluated to understand impact of structure on RON MON CN



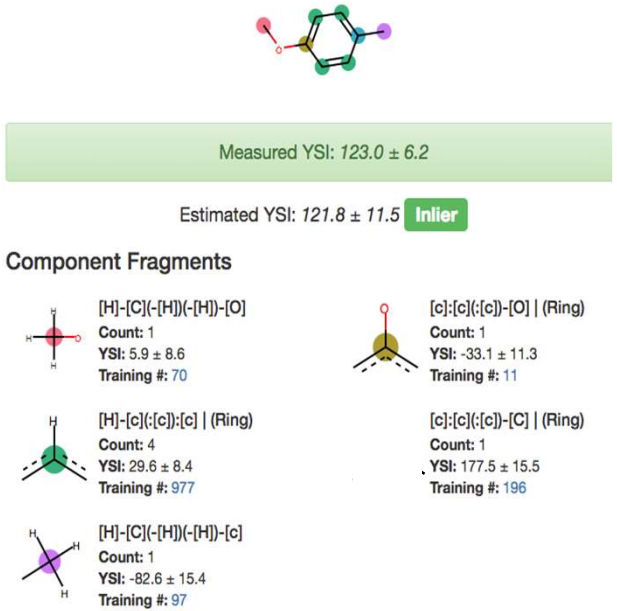
Sooting tool

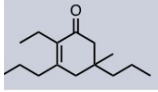
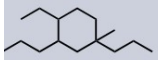
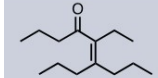
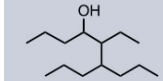
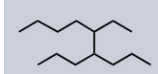
Sooting tool maps relationship between molecular structure and sooting properties

- Machine learning using molecular structure and experimentally YSI (Yield Sooting Index) values for ~500 species
- Allows screening of a wide range of chemical functionality for blendstocks that resist soot formation

Fuel design explores chemical space where we lack existing measurements

- Provides detailed information per each carbon type to design low sooting fuel candidates

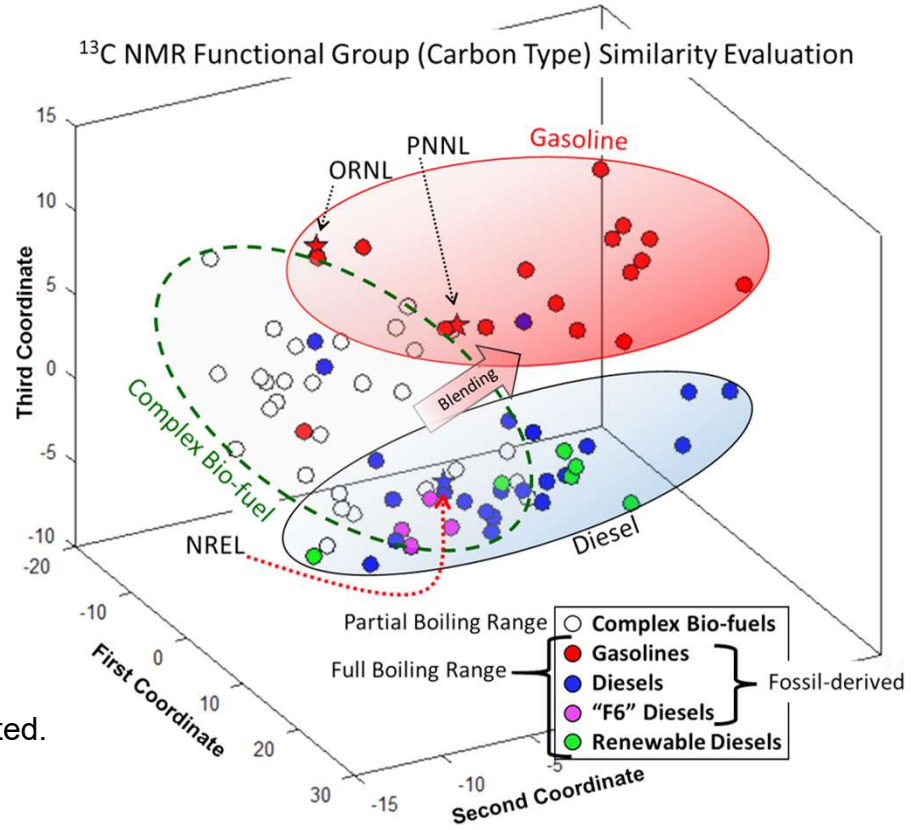


Structure	CN	YSI
	16	**165**
	39	**105**
	36	**95**
	40	**90**
	49	**91**

PI: Kim & St. John, NREL

13C NMR tool for RON of complex blends

- NMR-based Fuel Classification Model
  - ~200 µL NMR samples enable characterization of fuel & blendstock properties
  - Library data sets include gasoline, diesel, renewables (HTL, ETJ, ETD, algae…), Co-optima Core Fuels, BOBs, etc.
  - Proximity of user sample to fuels in library shows similarity of carbon type composition
  - Model compares 27 functional groups (carbon types) for 72 (shown) and >100 (not shown) complex fuels
  - Property predictions include DCN, Simulated Distillation (T10, T50, T90), and RVP.
  - Identifies key carbon-type differences between sample and library fuel sets, enabling users to understand origins of property differences
- Next
  - Web page for outlier assessment is nearly completed.
  - Confidence factors and further implementation of property predictions.



Lab PI: Bays PNNL

Quantifying ϕ-sensitivity

$$\tau(T,P,\phi) = C(T,P)\phi^{-\eta(T,P)}$$

Intuitive definition:

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

$$\frac{d\tau}{d\phi}\bigg|_{T,P} = -C\eta\phi^{-\eta-1}$$

τ-Normalized definition:

$$-\frac{1}{\tau}\frac{d\tau}{d\phi}\bigg|_{T,P} = \eta\phi^{-1}$$

Log-log definition:

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