



Co-Optimization of
Fuels & Engines

Project ID: FT052

Co-Optimization of Fuels and Engines (Co- Optima): Fuel Kinetics and Simulation Tool Development

McNenly (presenter), Goldsborough,
Grout, Kukkadapu, Pitz, Rahimi,
Wagon, Whitesides, Zhang, and
Zigler

June 20, 2018

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FY18 Vehicle Technologies Office Annual Merit Review

better fuels | better vehicles | sooner

U.S. DEPARTMENT OF
ENERGY

Energy Efficiency &
Renewable Energy

with special thanks to the VTO leadership - Michael Berube, Gurpreet Singh, Kevin Stork, and Michael Weismiller for their guidance and support



Timeline

Project start date: FY16
Project end date: FY18*
Percent complete: 88%

Budget

Funding for FY18: \$1.4M
– VTO funding: \$1.4M
6 tasks at ANL, LLNL,
and NREL
– BETO funding: \$0

* Start and end dates refer to the three-year life cycle of DOE lab-call projects. Co-Optima is proposing a new 3-year cycle to start in FY19.

Barriers

Lack of fundamental knowledge about the fuel kinetics impact on engine performance:

- Dilute Gasoline Combustion
- Clean Diesel Combustion
- Low-Temperature & Multi-mode Combustion

Partners

External Advisory Board:

- USCAR, API, Fuels Inst., Truck & Engines Mfg. Assoc., Adv. Biofuels Inst., Advanced Biofuels Association, and Flint Hills Res.
- EPA, CA Air Resources Board
- Dave Foster (U. Wisc.), Ralph Cavalieri (WSU), John Wall (ret. Cummins)

Stakeholders:

85 individuals representing 46 organizations

Universities:

8 FOA awards at 13 institutions (2017 start)



Three critical technologies on the USDRIVE ACEC Tech Team Roadmap* improve with the foundational research in this project (FT052):

1. Dilute Gasoline Combustion

“The three important combustion challenges are combustion robustness (stochastic, cycle-to-cycle combustion variations, partial burns and misfires), operating lean or EGR-diluted over a wide speed and load range, and controlling engine-out emissions of hydrocarbons (HCs) at light loads and nitrogen oxides (NO_x) at heavy load.”

2. Clean Diesel Combustion

“Inadequate understanding of the fundamentals of the effects of fuel injection, air motion (e.g., swirl, turbulence), thermodynamic state and composition, and combustion chamber geometry on fuel-air mixing, combustion and emission formation processes over the full load range.”

3. Low Temperature Combustion (including multi-mode) - *strong need for chemical kinetic understanding on modeling*

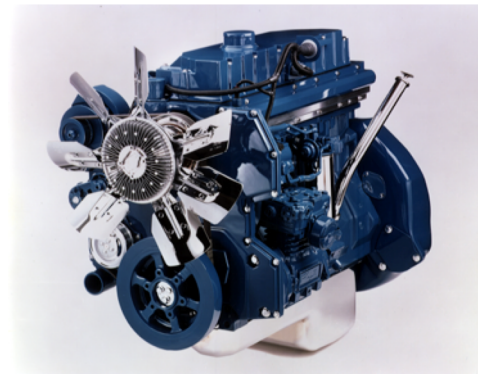
“[Understand] the impact of likely future fuels on LTC and whether LTC can be more fully enabled by fuel specifications different from gasoline and diesel fuel.”

* https://www.energy.gov/sites/prod/files/2018/03/f49/ACEC_TT_Roadmap_2018.pdf



Co-Optimization Hypothesis:

There are engine architectures and strategies that provide higher thermodynamic efficiencies than are available from modern internal combustion engines; new fuels are required to maximize efficiency and operability across a wide speed / load range.



Central Fuel Hypothesis

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



Co-Optima simultaneously pursues engine and fuel development research within this framework to **increase U.S. competitiveness** by enabling more domestic resources to enter the market, which **creates more jobs for Americans.**

The governing hypotheses provide a common connection from the task outcomes to the program goals



From the hypotheses to the bigger picture:

Co-Optima Goals

Determine key fuel properties that enable improved engine efficiency

Provide key science to enable high efficiency combustion modes

Capitalize on unique properties available from bio-blendstocks

Use stakeholder input to guide analysis

Accelerate market penetration of both engines and fuels.

From the tasks to the hypotheses:

Fuel Kinetics and its Simulation Outcomes (FT052)

Measure foundational kinetic properties that impact advanced engine performance

Predict blending behavior for High Performance Fuels and petroleum components

Predict fuel kinetic property impact on engine efficiency and Co-Optimization Hypothesis

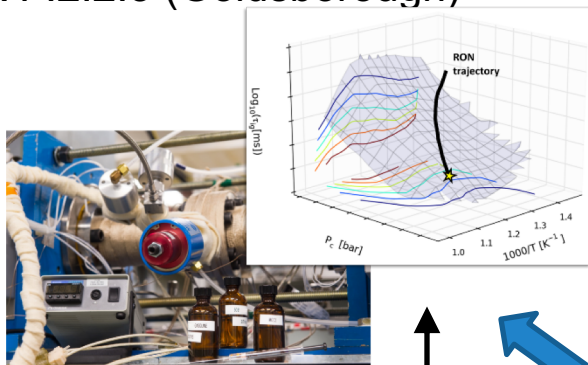
Create a virtual fuel designer to test the Central Fuel Hypothesis

Accelerate the time to solution for all fuel kinetics based analyses

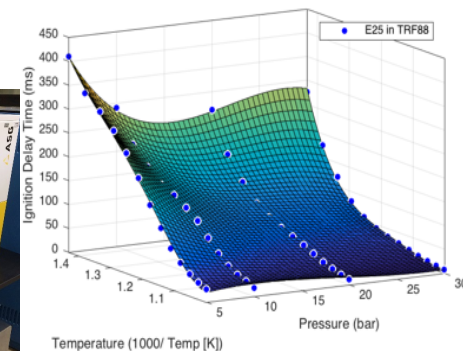
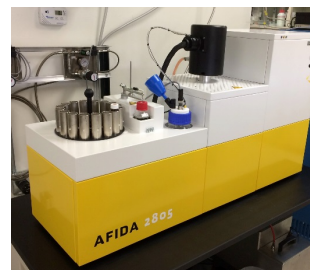
Approach



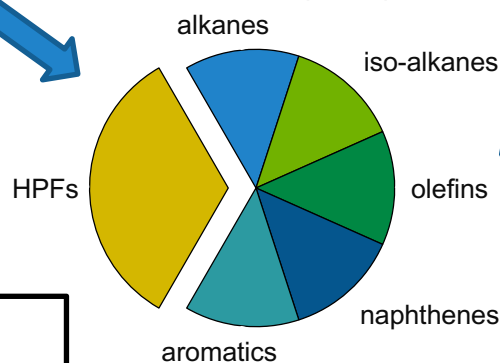
Task F.2.2.3 (Goldsborough)



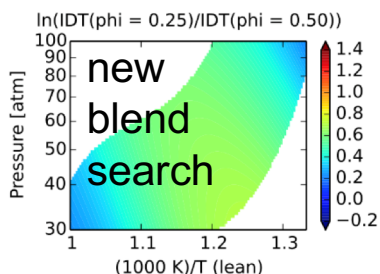
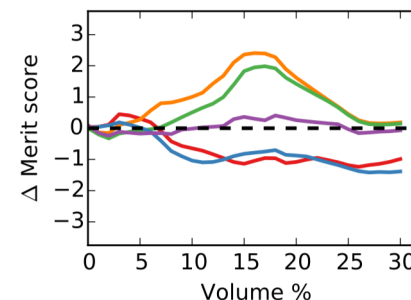
Task F.2.2.1 (Zigler)



Task F.2.2.2 (Pitz)



BOB & Blendstock optimization tools

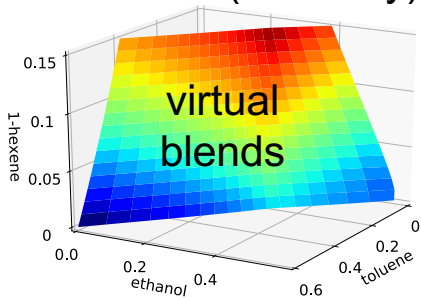


Task G.1.1 (Whitesides/Grout)

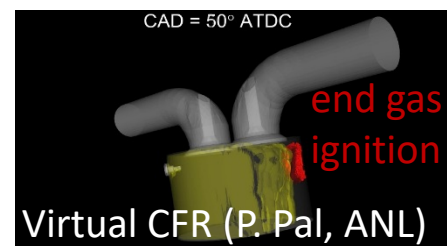
nonlinear octane blending

Zero-RK fast detailed chemistry

Task G.1.2 (McNenly)



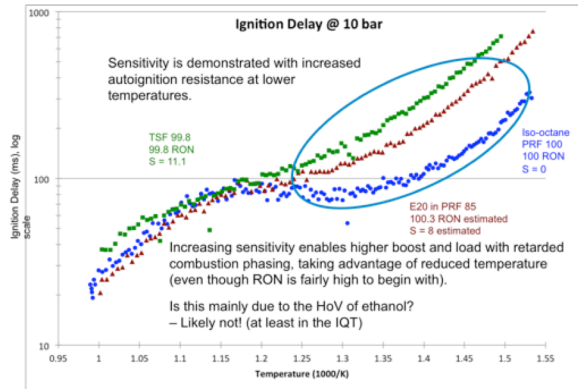
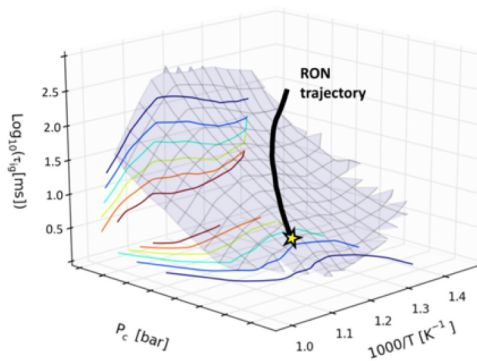
faster CFD



Larger impact of approach



Coupled experiments and simulations deepen the understanding of kinetic-dependent properties needed to analyze light-duty performance
– especially non-linear blending behavior



Fuel	RON	OS	Laminar flame speed [cm/s]
alkylate surrogate	98.9	3.7	45.2
aromatic surrogate	99.0	11.0	43.1
E30 surrogate	96.2	11.1	48.3
kinetics surrogate	91.2	7.1	46.7
w/ 30% ethanol	103.6	12.4	48.4
w/ 30% n-propanol	103.6	11.6	49.1
w/ 30% iso-propanol	102.1	10.4	47.3
w/ 30% 2-butanol	96.2	10.6	47.5
w/ 30% iso-butanol	98.2	11.1	47.1
w/ 30% 2-butanone	97.2	10.2	48.1
w/ 30% diisobutylene	106.4	9.7	45.6
w/ 30% furan mixture	105.6	15.4	50.9

$$\begin{aligned}
 \text{Merit} = & \frac{(RON_{mix} - 91)}{1.6} - K \frac{(S_{mix} - 8)}{1.6} \\
 & + \frac{0.085[ON / kJ / kg] \cdot ((HoV_{mix} / (AFR_{mix} + 1)) - (415[kJ / kg] / (14.0[-] + 1)))}{1.6} \\
 & + \frac{((HoV_{mix} / (AFR_{mix} + 1)) - (415[kJ / kg] / (14.0[-] + 1)))}{15.2} \\
 & + \frac{(S_{mix} - 46[cm / s])}{5.4} \\
 & - H(PMI_{mix} - 1.6)[0.7 + 0.5(PMI_{mix} - 1.4)] \\
 & + 0.008^{\circ}C^{-1}(T_{c,90,conv} - T_{c,90,mix})
 \end{aligned}$$

Milestones



Date	Description of Milestone or Go/No-Go Decision	Status	Lab
Sep 2017	G.1.1: Virtual fuel compositions representing optimized thermo-kinetic performance delivered to HPF for evaluation.	done	LLNL
Dec 2017	G.1.1: Quantify the potential to optimize the BOB and the blendstock performance using a chemical kinetic model for the inputs to the boosted SI merit function.	done	LLNL
Dec 2017	F.2.2.2: Develop a validated kinetic mechanism and surrogate mixture to represent conventional diesel for the heavy-duty engine applications such that HPF blendstocks can be evaluated.	done	LLNL
Mar 2018	G.1.1: Demonstrate how a surrogate composition can be built from mixture flow reactor data. Flow reactor speciation will be used as a target to determine the composition in the “co-optima” mechanism that best matches the experimental data.	done	NREL
Jun 2018	F.2.2.2: Develop/improve and validate kinetic mechanisms for 2-3 high performance fuels for gasoline and/or diesel fuels	on-track	LLNL
Jun 2018	F.2.2.3: Acquire RCM ignition data for priority blendstocks covering a range of blend ratios.	delayed	ANL
Sep 2018	F.2.2.3: Acquire RCM ignition data for secondary blendstocks covering a range of blend ratios.	on-track	ANL

Task budgets



Task	Description	Funds	Lab
F.2.2.1	[Zigler] IQT and AFIDA ignition delay experiments for kinetic mechanism development – blending behavior	\$135K	NREL
F.2.2.2	[Pitz] Kinetic mechanism development	\$800K	LLNL
F.2.2.3	[Goldsborough] RCM experiments for kinetic mechanism development – foundational properties	\$185K	ANL
G.1.1	[McNenly] Virtual properties, reduced mechanism, blending of kinetics properties, and modeling of Fuel Properties	\$175K	LLNL
G.1.1	[Grout] Virtual properties, reduced mechanism, blending of kinetics properties, and modeling of Fuel Properties	\$90K	NREL
G.1.2	[McNenly] Accelerating Co-Optima applications with Zero-RK	\$50K	LLNL

Kinetic models for high-performance fuel and surrogate components developed and improved



Base Gasoline Surrogate Components

n-Alkanes:



iso-Alkanes:



Hexanes
(4 isomers)¹

2-Methylhexane



Cycloalkanes:

Cyclopentane

Aromatics

Toluene^{1,2}

o-Xylene^{1,2}

p-Xylene^{1,2}

Ethylbenzene

1,3,5-Trimethylbenzene^{1,2}

1,2,4-Trimethylbenzene^{1,2}

Alkenes

1-hexene

2-Hexene

3-Hexene

Diisobutylene (2 Isomers)¹

High performance fuels

Alcohols

Methanol

Ethanol

Propanol (2 isomers)

Butanol (4 isomers)

Pentanol (3 isomers)

Esters

Methyl Acetate^{1,2}

Ethyl Acetate^{1,2}

Methyl Butanoate¹

Furans

2-Methyl Furan

2,5-Dimethyl Furan

Others

Acetone

2-Butanone

Anisole¹

Cyclopentanone^{1,2}

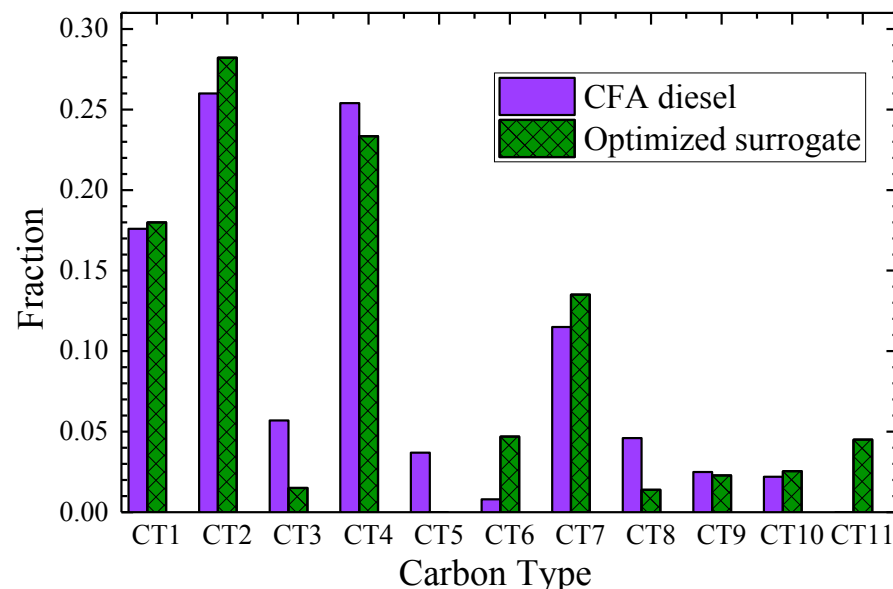
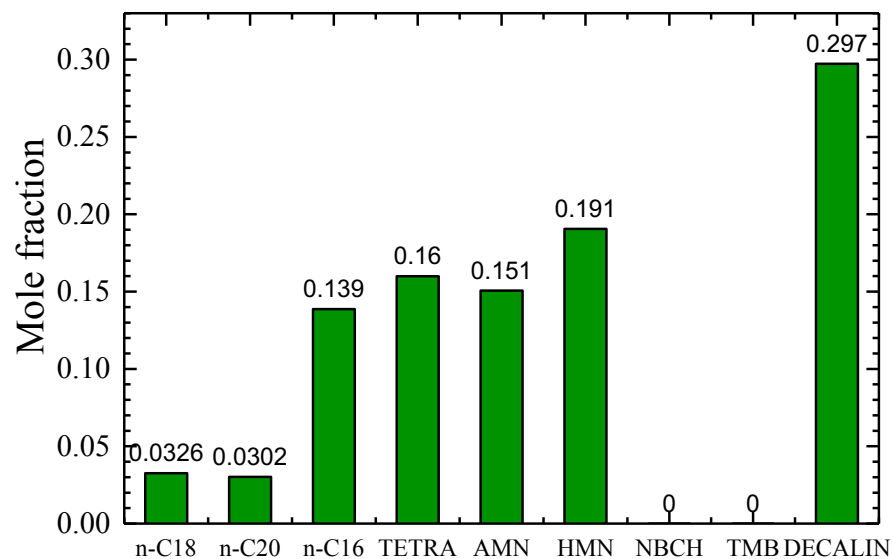
Current model size:
2,840 species
12,236 reactions

¹Improved ²Accepted for Int. Sym. Combustion

Developed fuel surrogate mixtures and kinetic models to represent diesel fuels

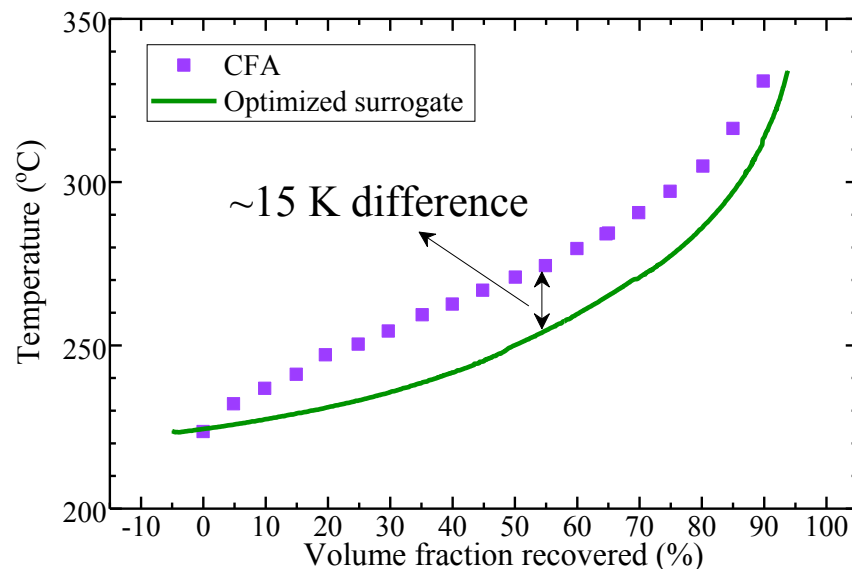


optimized diesel surrogate

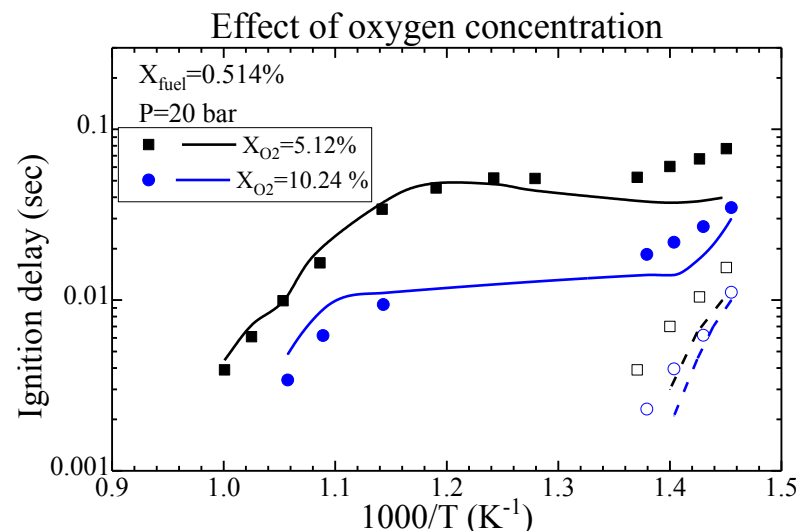
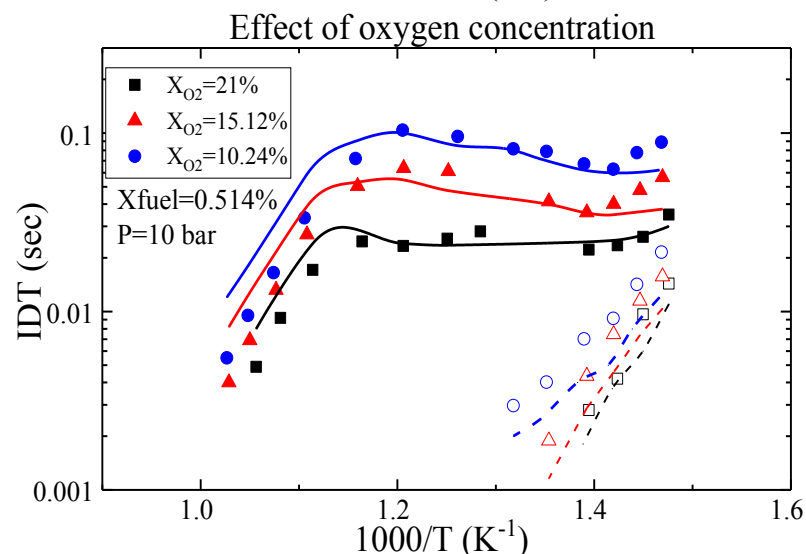
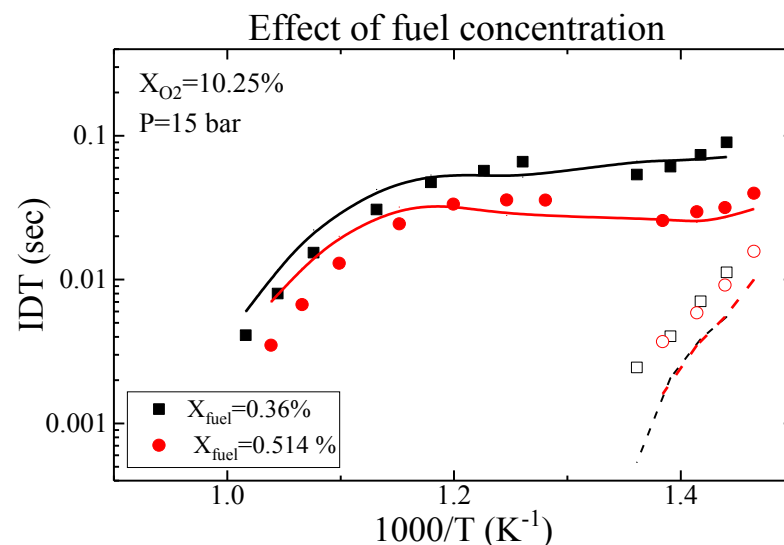
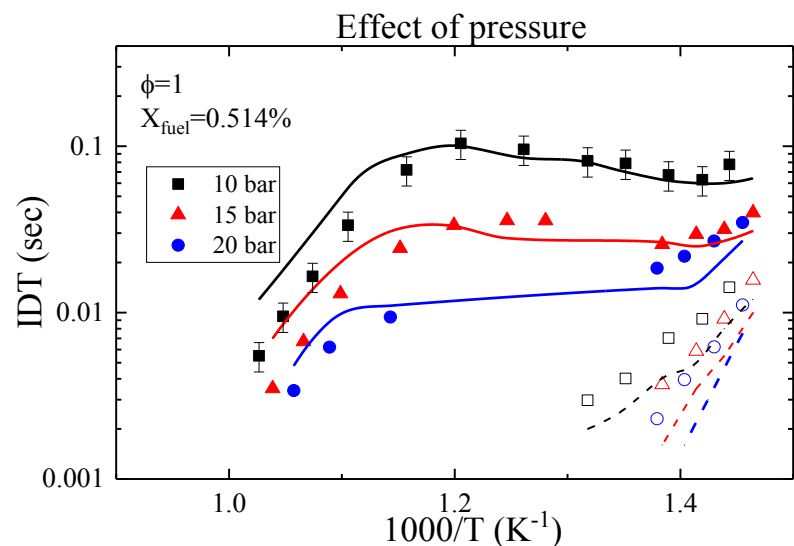


Property	CFA	optimized surrogate
DCN	43.7	44.04
H/C ratio	1.782	1.71
Density	0.848	0.845

CFA data taken from CRC Project AVFL-18, (Energy Fuels, 26 (6) (2012) 3284–3303)



Diesel fuel-surrogate kinetic model captures behavior of a commercial diesel tested in the UCONN RCM

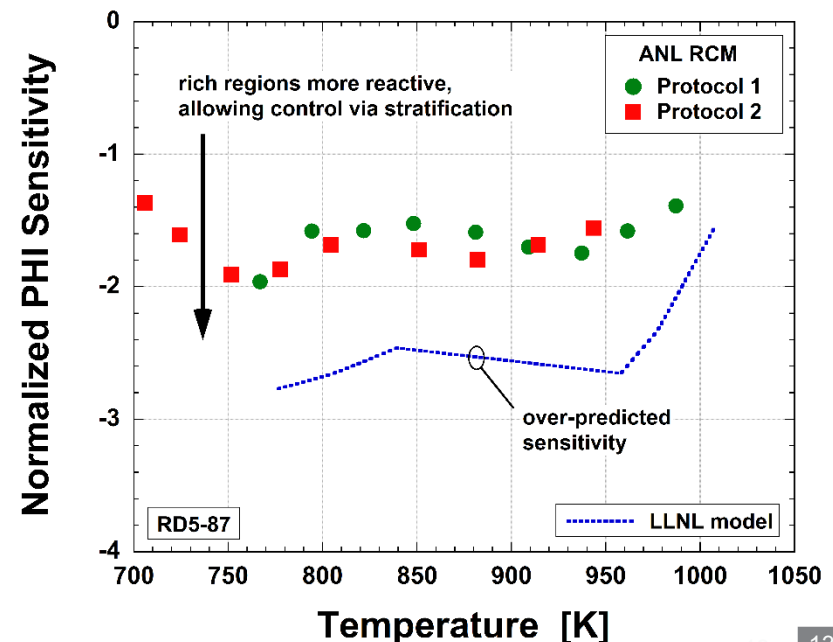
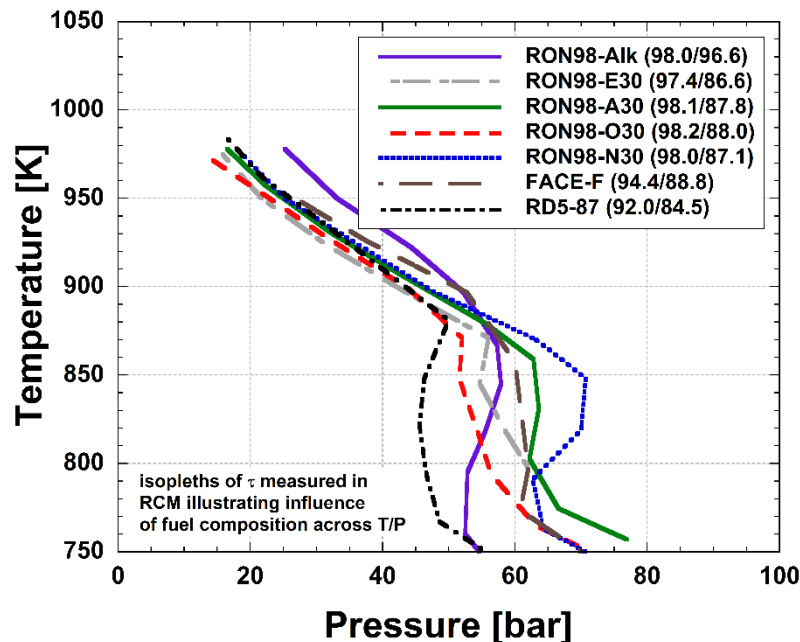


The commercial diesel fuel CFA is from Coordinating Research Council Project AVFL-18

Identified fuel chemistry influence on autoignition behavior with FY18 ANL RCM campaign



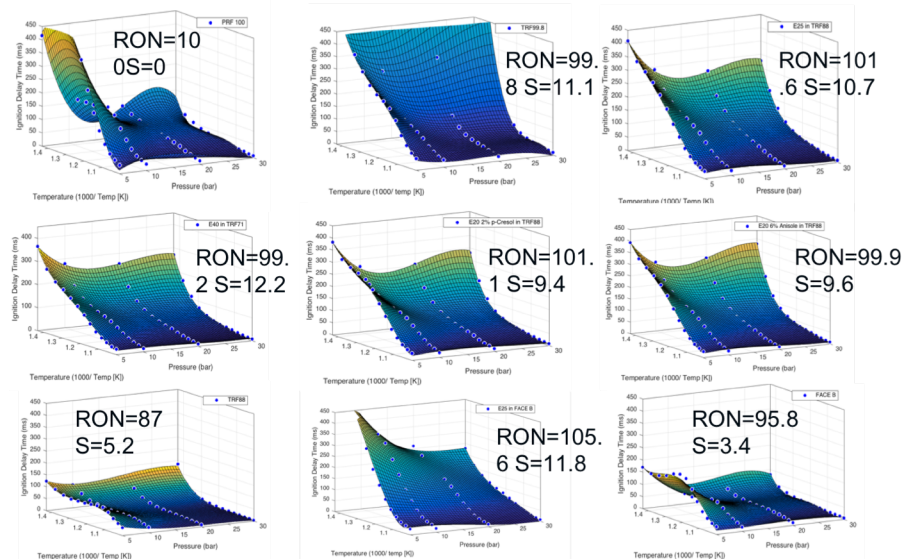
- Acquired new RCM data for Core Fuels and HPF alcohols, covering range of conditions relevant to light duty engine operation
- Quantified ϕ -sensitivity predicted by LLNL model (using $(\frac{1}{\tau} \frac{\partial \tau}{\partial \phi})$), and compared to experimentally-measured ϕ -sensitivity of full-boiling range gasoline



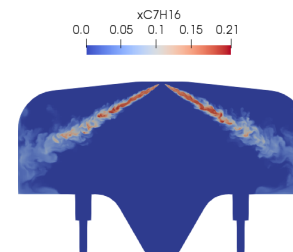
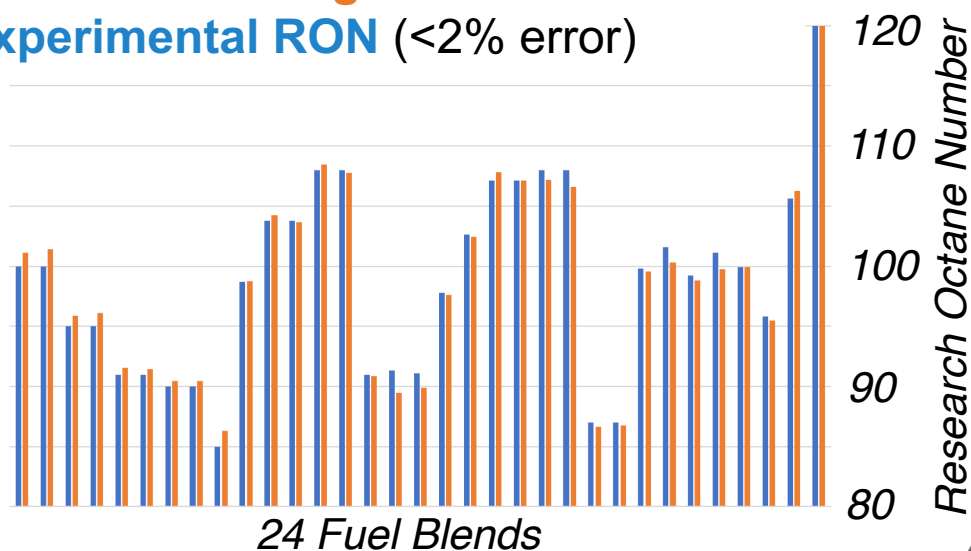
NREL's rapid measurement of blending behavior aids SI and ACI fuel surrogate mechanism design



Parametric (T, p, ϕ, χ_{O_2}) ignition delay maps



AFIDA characterization and CFD simulations (link to G.1.1) for mechanism development and validation



Accomplishment – F.2.2.1 Zigler, NREL (\$135K)

Search with realistic fuel models found potential blends to extend the PCCI operating range



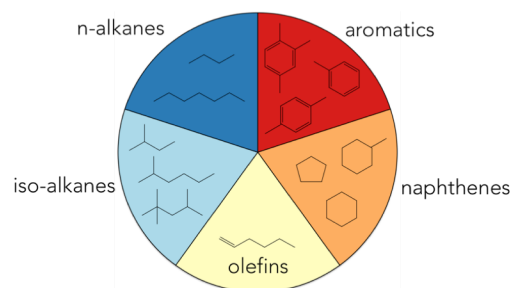
What fuel chemistry do PCCI engines want?

For partially stratified charge compression ignition [J. Dec, 2017 All-Hands Meeting]:

1. Large change in ignition delay time as stratified mixture becomes richer
= High "phi-sensitivity"
2. Small change in ignition delay time as pressure increases
= High octane sensitivity

How do we construct a search?

Co-Optima Surrogate [Pitz, Mehl, Wagnon, Zhang, Kukkadapu]:

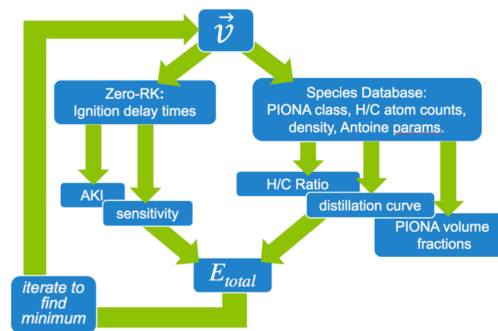


+ 12 more oxygenates

ethanol
2-butanol
isobutanol
diisobutylene
iso-propanol
n-propanol
2-methyl-1-butanol
2-butanone

Pass Tier I & II screening
(McCormick)

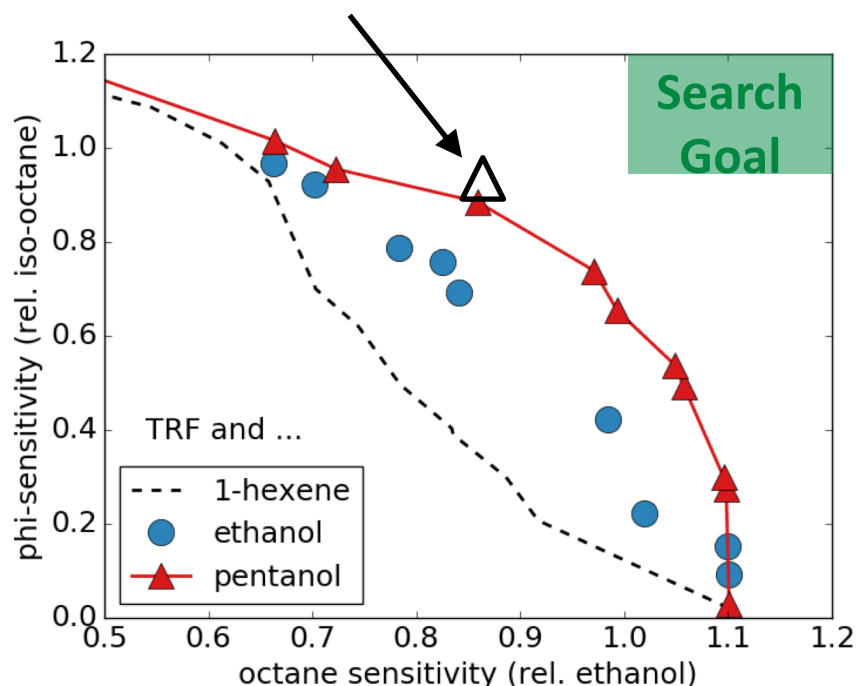
Surrogate Blend Optimizer [Whitesides]:



Search with realistic fuel models found potential blends to extend the PCCI operating range



Current best with latest mechanism,
n-pentanol + 7 hydrocarbons: 87% of
 $S(\text{ethanol})$, and 93% $\text{Big-}\Phi(\text{iso-octane})$



Results:

- Created a candidate phi-sensitivity metric based with FP & AED team input.
- Searched over 150,000 blends.
- Found n-pentanol to be the best blendstock (so far) to maximize both octane sensitivity and phi-sensitivity.

Next Steps:

- propose blends for PCCI validation that are optimized over an engine-specific p, T range
- develop chemistry model metrics for ACI operation of Sjoberg/Vuilleumier engine

Created five virtual BOBs with a model RON of 90.3 +/- 0.1 and model MON of 84.7 +/- 0.1



Composition constraints (by vol.)

- total *pentanes* less than 20%
- total *olefins* less than 25%
- total *naphthenes* less than 25%
- total *aromatics* less than 50%
- *n-pentane* less than 15%
- *iso-pentane* less than 15%
- *n-heptane* less than 25%



NREL 4-component BOB

55% iso-octane (by vol.)
25% toluene
15% n-heptane
5% 1-hexene

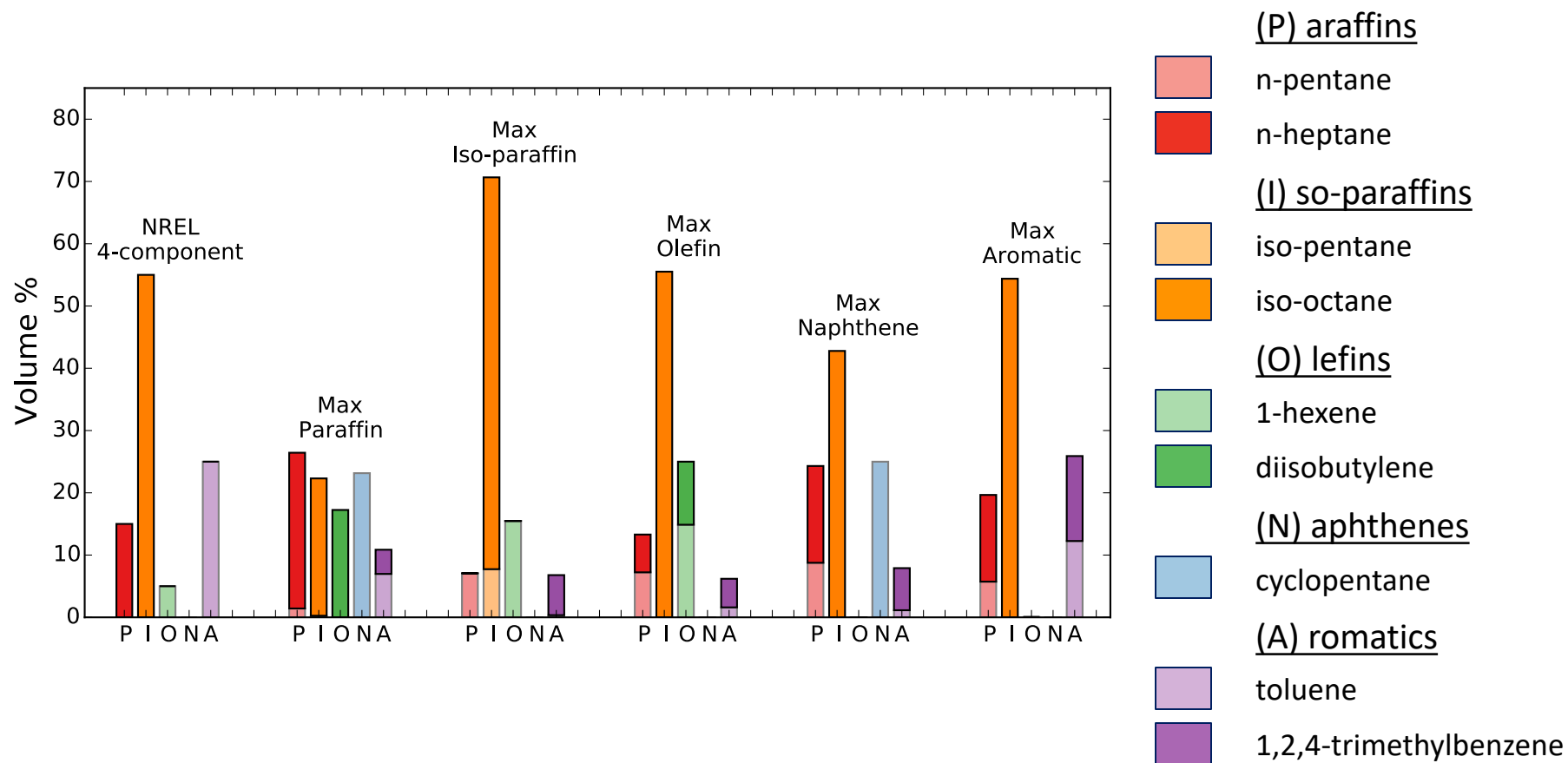
ASTM ratings*:


RON 90.3

MON 84.7

* McCormick, R., Fioroni, G., Fouts, L., Christensen, E. et al., "Selection Criteria and Screening of Potential Biomass-Derived Streams as Fuel Blendstocks for Advanced Spark-Ignition Engines," *SAE Int. J. Fuels Lubr.* 10(2):442-460, 2017, <https://doi.org/10.4271/2017-01-0868>. (SAE Paper No. 2017-01-0868)

Created five virtual BOBs with a model RON of 90.3 +/- 0.1 and model MON of 84.7 +/- 0.1



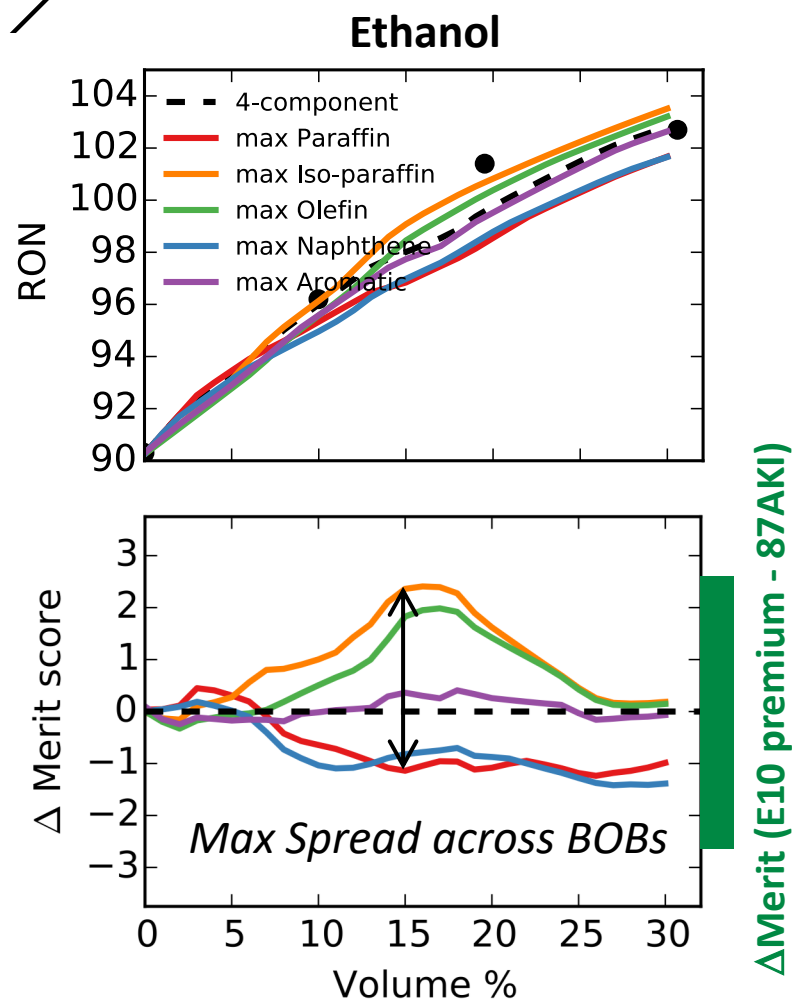
The model-based variation in the BOB merit scores is ~50% of the net gain switching from 87 AKI to E10 premium 

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



NREL 4-component BOB

55% iso-octane (by vol.)
25% toluene
15% n-heptane
5% 1-hexene



Response to reviewers



1. “The reviewer questioned how the authors will determine if the model properties match the engine results, and asked for evidence that the simplified kinetic model and fuel set matches the engine output for a fully formulated fuel that is multi component.”

Response: Experimental validation of the multi-component surrogate formulations are planned in FY18 and FY19 (if funding is available) to test the optimized BOB performance and the extended operating range for partially-stratified advanced compression ignition engines (Dec and Sjoberg engines).

2. “The reviewer indicated, however, that much of the actual approach to developing the model is difficult to understand from the presentation and slides.”

Response: It is challenging to delve into the chemical kinetic model development, and cover all the applications of the model in Co-Optima and its broader impact on the VTO goals. For this review, the talk focuses more on the Co-Optima applications and the broader impacts. The details of the models are left for publications listed in the Reviewer-Only section. The PIs in this talk contributed to six papers accepted for presentation at the 37th International Combustion Symposium in Dublin this summer. Also, a deeper discussion of the model development was presented to the Advanced Engine Combustion Working Group on Jan. 29 - Feb. 1, 2018 by Wagnon, Kang, Rockstroh, Whiteside, and McNenly.



3. “... put more effort toward developing a computational fluid dynamics (CFD) model for the Advanced Fuel Ignition Delay Analyzer. The reviewer added that the ignition quality tester (IQT) uses an obsolete injector and the spray model is not very well studied, and was not very confident of using IQT to validate fuel combustion kinetics.”

Response: NREL is currently developing a CFD model of the AFIDA (slide 14), which will be used to evaluate reduced mechanisms against experimental data. To support CFD model development, NREL has extensively mapped temperature distribution within the AFIDA for a range of set T, P points. Majority of the work has shifted to parametric ignition kinetics studies with AFIDA, and the IQT is used on a very limited basis (see recent paper published with U. Michigan comparing IQT data with RCM data to quantify physical-chemical property interactions).

4. “The reviewer pointed out that there are many places where researchers are looking at ignition delay/quality and kinetics, ... The reviewer postulated that perhaps there is room for more extensive collaboration.”

Response: Pitz’s team at LLNL maintains a large collaboration with researchers performing fundamental kinetic experiments including significant interactions with NUIG and KAUST. NREL hosted Prof. Boehman (U. Michigan) for a sabbatical to collaborate on the AFIDA system. More interactions are sought for cetane number measurements as the diesel mechanism development continues.



Within the Co-Optima program

- Four labs (ANL, LLNL, NREL) coordinate on FT052 (Fuel Kinetics and Simulations) with results impacting the Scenario Co-Optimizer, Merit Function and the Central Fuel Hypothesis.
- Bi-weekly 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
- Recent FOA awards to 8 projects at 13 universities includes four groups with which LLNL mentors or collaborates:
 - Prof. Green's group, MIT: *ab initio* calculations of key low temperature reactions for inclusion in kinetic models of HPFs
 - Prof. Vasu's group, Univ. Central Florida: Shock tube measurements of intermediates species from HPFs
 - Prof. Xuan's group, Penn. St. Univ: YSI predictions of soot using Co-Optima HPFs fuel kinetic models
 - Prof. Schoegl's group, Louisiana St. Univ.: micro-scale flow reactor to estimate fuel properties with microliters sample volumes



Beyond Co-Optima

- Coordinating Research Council (AVFL-18a, AVFL-20, AVFL-30/31, and the FACE working group)
- AEC working group semi-annual project reviews with industry MOU partners
- NREL
 - Univ. Michigan: development of the correlation of IQT to RCM studies, and faculty sabbatical hosting for surrogate development.
 - Univ. Colorado: M.S. thesis project to study gasoline surrogate blends in the AFIDA.
- LLNL
 - Nat. Univ. Ireland Galway [Curran]: development of base mechanism; and shock tube and RCM experiments on fuels for kinetic model validation.
 - King Abdullah Univ. Sci. Tech. [Sarathy]: mechanism development; and shock tube, RCM, and JSR experiments on fuels for kinetic model validation.

Remaining challenges and barriers



- Increasing the accuracy of real fuel models to co-optimize fuels & engines
- Validating chemical kinetic models over wider pressure ranges, equivalence ratios, EGR dilution levels, and blending – *need lots of data*
- Producing experimental kinetic data for a large number of blendstocks and blending levels in a short time frame with very small sample volumes – *need small volume, high throughput ignition testing methods*
- Identifying the dependency between critical chemical pathways and functional groups and engine performance
- Searching for optimal fuel surrogate blends for expected engine performance, including multi-mode combustion strategies
- Establishing error bars on kinetic simulation results such that fuel-engine comparisons have a confidence percentage.
- Creating a framework to fairly compare the benefits of different mixed-mode strategies and fuel combinations.

Proposed future work*



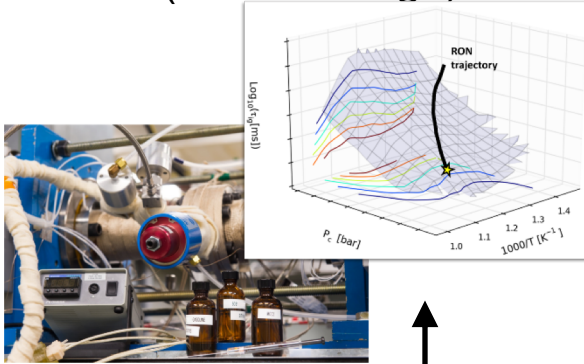
- ANL
 - Conduct RCM tests with the blending BOBs and gasoline surrogate blendstocks.
 - Automate LTHR and ITHR quantification in kinetic models for experimental comparison.
- ANL/
LLNL
 - Quantify uncertainty in the chemical kinetic models and propagate the uncertainty through kinetics based analyses to establish a confidence percentage on the model-based conclusions.
- LLNL
 - Develop new kinetic models, update existing models, and incorporate literature data for new HPFs for multi-mode, kinetically-controlled advanced compression ignition (ACI), and mixing-controlled compression-ignition.
 - Validate kinetic mechanisms for higher EGR beyond RON and MON conditions, and low equivalence ratios for ACI strategies.
 - Develop and add additional cycloalkane components to the gasoline + HPFs mechanism and update their reactions to better represent gasoline base fuels (e.g. methylcyclohexane and cyclohexane).
 - Create Zero-RK accelerated, kinetics-based engine models to analyze fuel impact on performance (e.g., multi-zone, and stochastic reactor models).
 - Apply multi-level optimization algorithms to the engine models to move beyond static control trends and allow for a more informative comparison of fuel-engine combinations.
- NREL
 - Continue development of AFIDA-based capability to provide ignition delay and heat release data feedback for kinetic mechanism development, including CFD simulations; and link constant volume experiments to engine performance.

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

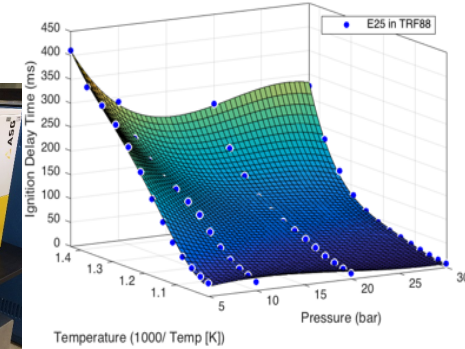
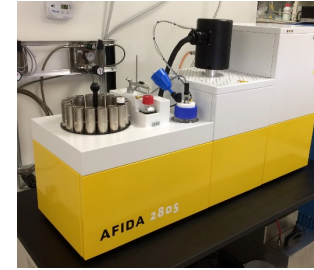
Advances in chemical kinetics research deepen the understanding of fuel impacts on engines



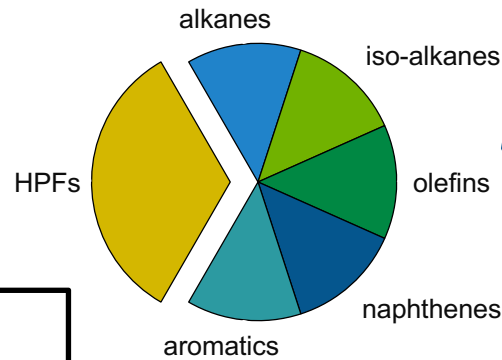
Task F.2.2.3 (Goldsborough)



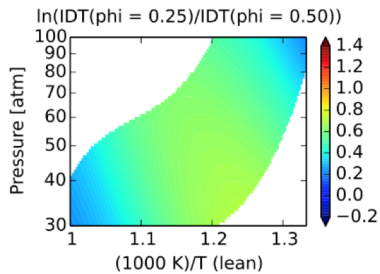
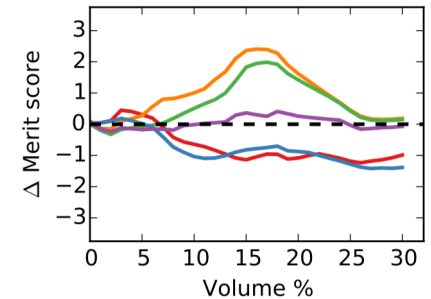
Task F.2.2.1 (Zigler)



Task F.2.2.2 (Pitz)



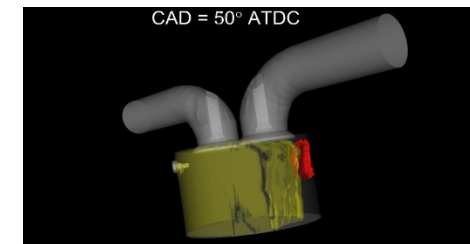
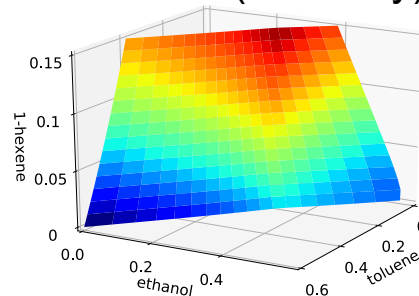
BOB & Blendstock optimization tools



Task G.1.1
(Whitesides/Grout)

nonlinear octane
blending

fast detailed chemistry
Task G.1.2 (McNenly)

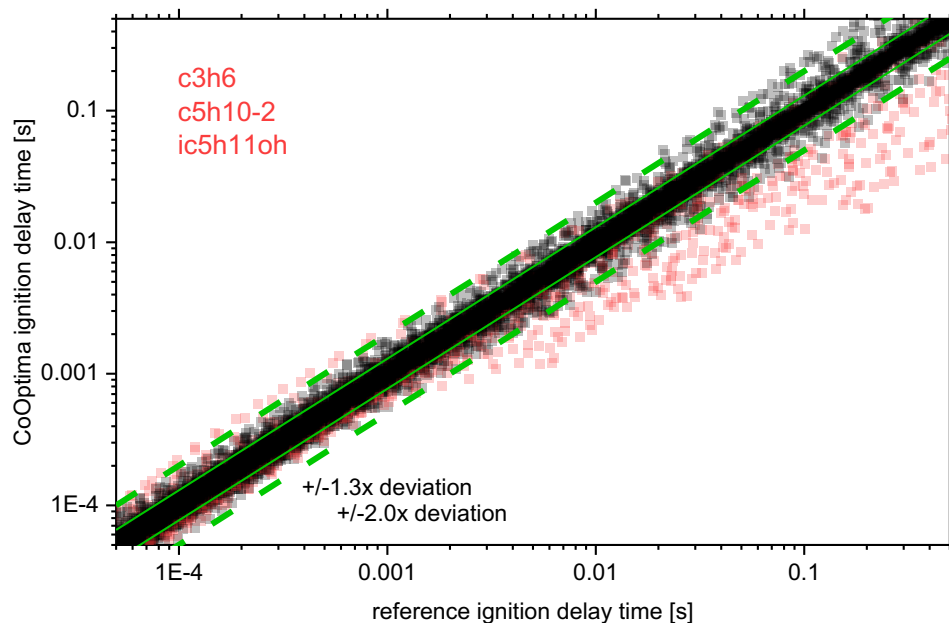
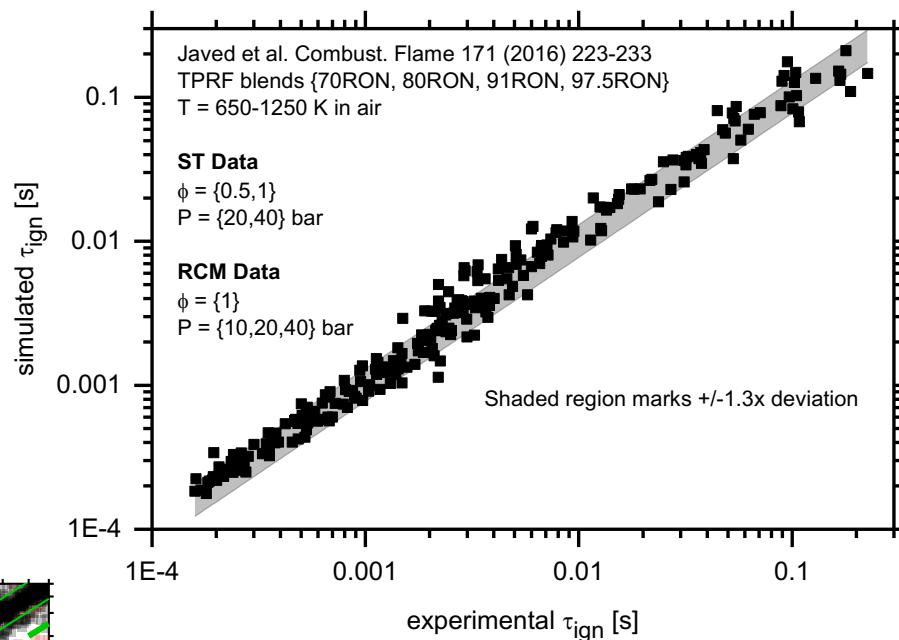
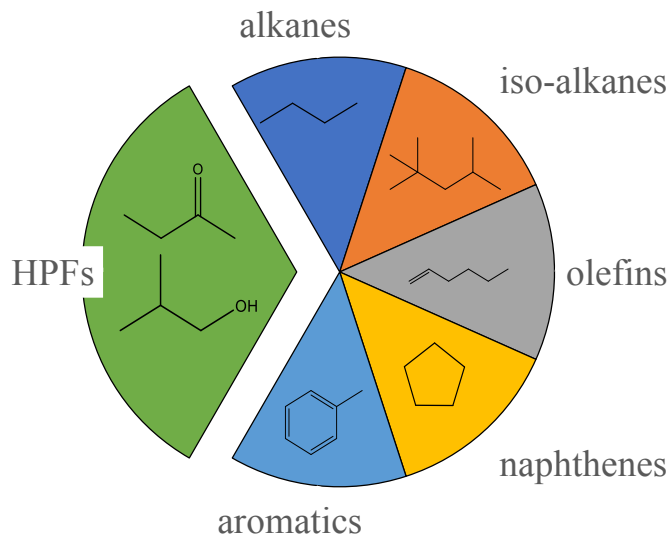


$$RON(a + b) \neq \alpha RON(a) + \beta RON(b)$$

Technical backup slides



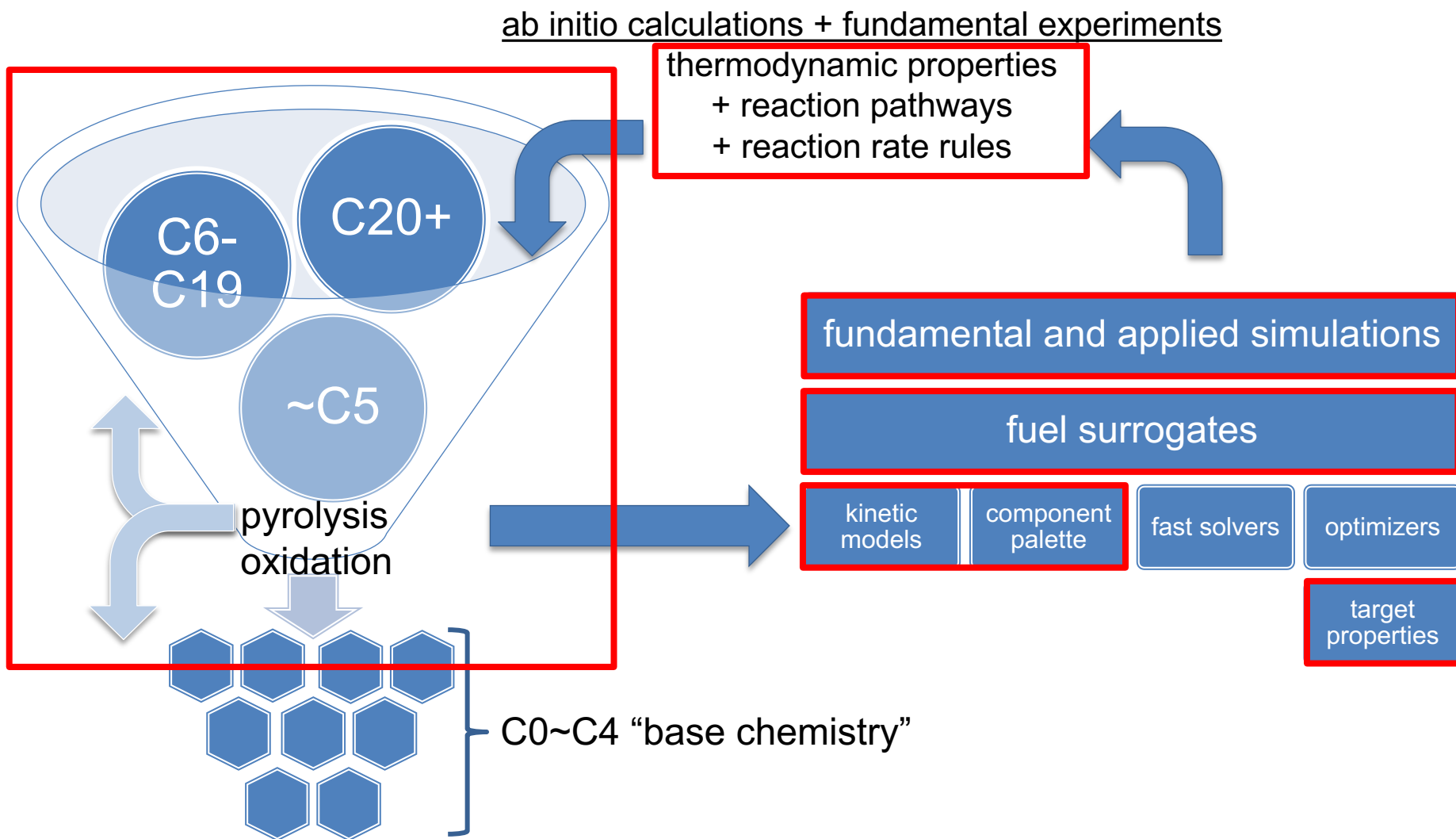
Leveraging LLNL HPC to build the Co-Optima mechanism with high performance fuels (HPFs)



Develop or include literature kinetic mechanisms into a single framework

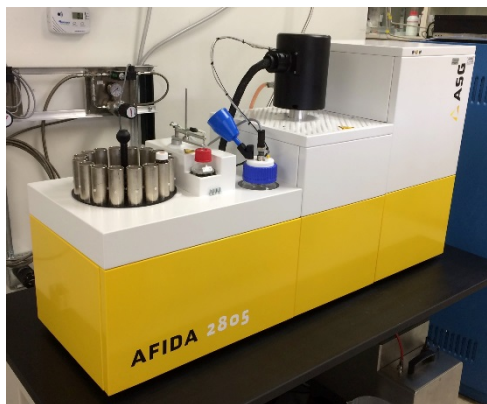
Using HPC + fast solvers developed at LLNL (McNenly and Whitesides), simulation validations are ~ 100 - $1,000x$ faster

Development of kinetic and fuel surrogate models

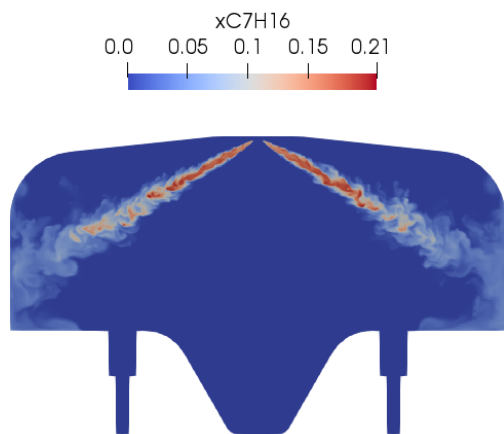




NREL kinetics experiments, connections to mechanism development
Parametric (T, p, ϕ, χ_{O_2}) ignition delay studies



Advanced Fuel Ignition
Delay Analyzer (AFIDA)



NREL added a new capability with an AFIDA in late FY16 (internally funded). Improvements with the AFIDA include:

- A piezoelectric injector with up to 1200 bar injection pressure, significantly reducing spray physics effects in relation to overall ignition delay time.
- Improved capability to study full boiling range gasoline blends, many of which could not be studied in the IQT.
- Up to 50 bar, 1000 K initial conditions.
- Improved repeatability and pressure transducer signal, helping characterize low temperature heat release.
- Experimental throughput $\sim 10\times$ that of IQT.
- Development of new AFIDA CFD simulation to evaluate mechanisms against experimental data.