Co-Optimization of
Fuels & Engines

Co-Optimization of Fuels and Engines (Co- Optima): Topic 7 - Fuel Kinetics and its Simulation

Goldsborough, Grout, Lacaze, McNenly, Pitz, and Zigler

June 6, 2017

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

FY17 Vehicle Technologies Office

Annual Merit Review

better fuels | better vehicles | sooner

Project ID# FT052

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

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

Overview

Timeline

Project start date: FY16
Project end date: FY18*
Percent complete: 53%

Budget

Funding for FY17: $1.88M

- VTO funding: $1.88M
  7 tasks at ANL, LLNL, NREL, and SNL
- BETO funding: $0

***** Start and end dates refer to the three-year life cycle of DOE lab-call projects. Co-Optima is expected to extend past the end of FY18.

Barriers and Challenges

Barrier 1: Predicting the Impact of Fuel Properties

Barrier 2: Efficient, Low-Emissions Engine Knowledge Gap

Challenges:

Schedule for completing R&D and achieving market impact is extremely ambitious.

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)

Relevance

Co-Optima Topic 7 – Fuel Kinetics and its Simulation addresses two main barriers in the VTO Program Plan*:

1. Predicting the Impact of Fuel Properties

   "Inadequate data and predictive tools for fuel property effects on combustion and engine efficiency optimization. Existing data and models for engine efficiency, emissions, and performance based on fuel properties and fuel-enabled engine designs or operating strategies are inadequate."

2. Efficient, Low-Emissions Engine Knowledge Gap

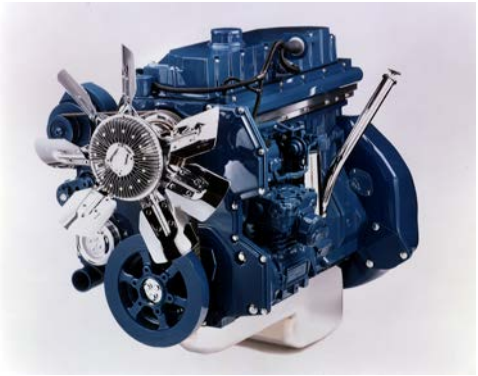
   "Lack of fundamental knowledge of advanced engine combustion regimes. Engine efficiency improvement, engine-out emissions reduction, and minimization of engine technology development risk are inhibited by an inadequate understanding of the fundamentals of … in-cylinder combustion/ emission formation processes over a range of combustion temperature for regimes of interest, as well as by an inadequate capability to accurately simulate these processes."

* https://www1.eere.energy.gov/vehiclesandfuels/pdfs/program/vt_mypp_2011-2015.pdf

The governing hypotheses of Co-Optima organize research tasks to address barriers

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.**

Relevance

From the hypotheses:

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.

To the hypotheses:

Topic 7 Goals

Fuel Kinetics and its Simulation

Measure foundational kinetic properties that impact advanced engine performance

Predict blending behavior for High Performance Fuels and petroleum components

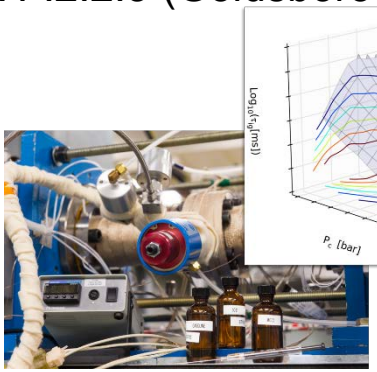
Predict fuel kinetic property impact on engine efficiency and Co-Optimization Hypothesis

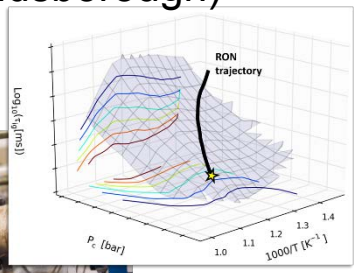
Create a virtual fuel designer to find compositions with identical ignition properties to test the Central Fuel Hypothesis

Accelerate the time to solution for all fuel kinetics based analyses

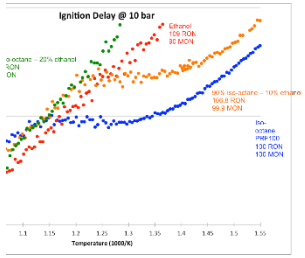
Approach

Task F.2.2.3 (Goldsborough)

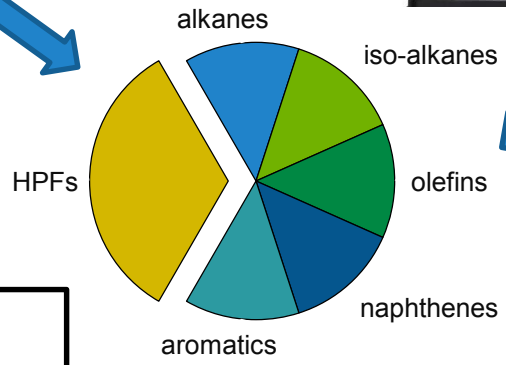


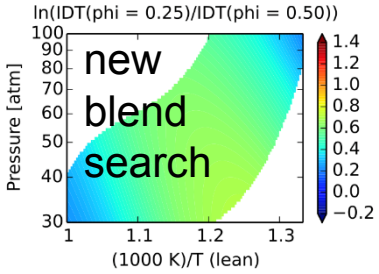


Task F.2.2.1 (Zigler)

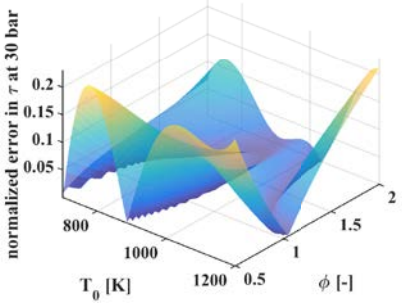


Task F.2.2.2 (Pitz)





Task G.2.4 (Lacaze)



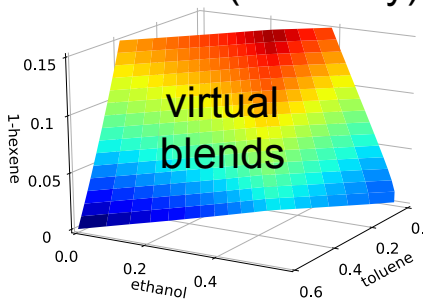
Task G.1.1
(Whitesides/Grout)

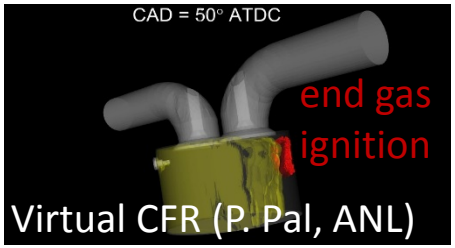
Zero-RK

fast detailed chemistry

faster CFD

Task G.1.2 (McNenly)



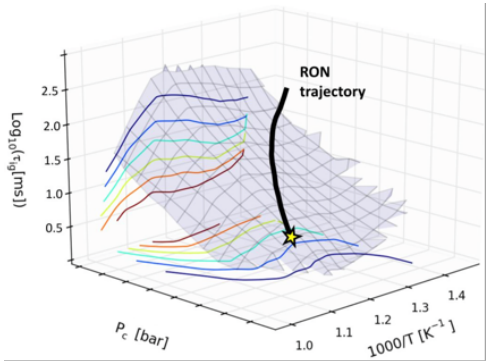


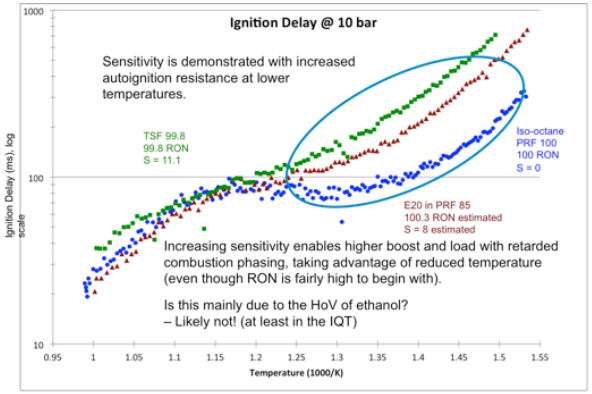
nonlinear octane blending

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

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

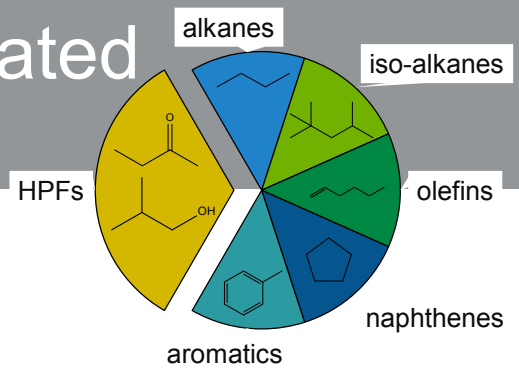
$$Merit = \frac{(RON_{mix} - 91)}{1.6} - K\frac{(S_{mix} - 8)}{1.6} + \frac{0.085[ON/kJ/kg]\cdot((HoV_{mix}/(AFR_{mix}+1)) - (415[kJ/kg]/(14.0[-]+1)))}{1.6} + \frac{((HoV_{mix}/(AFR_{mix}+1)) - (415[kJ/kg]/(14.0[-]+1)))}{15.2} + \frac{(S_{mix} - 46[cm/s])}{5.4} - H\left(PMI_{mix} - 1.6\right)\left[0.7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

Milestones and task budgets

Date	Description of Milestone or Go/No-Go Decision	Status	Lab
Mar 2017	Predict blend behavior for high-performance blend-stocks in base fuels at light-duty engine conditions and compare to ethanol blend behavior [Task F.2.2]	done	LLNL
Sep 2017	Virtual fuel compositions representing optimized thermo-kinetic performance delivered to HPF for evaluation [Task G.1.1]	on-track	LLNL

Task	Description	Funds	Lab
F.2.2.1	IQT and AFIDA ignition delay experiments for kinetic mechanism development – blending behavior	$250K	NREL
F.2.2.2	Kinetic mechanism development	$500K	LLNL
F.2.2.3	RCM experiments for kinetic mechanism development – foundational properties	$250K	ANL
G.1.1	Modeling impact of fuel composition changes on chemistry	$200K	LLNL
G.1.1	Creating simulation inputs for virtual property exploration	$210K	NREL
G.1.2	Accelerating Co-Optima applications with Zero-RK	$195K	LLNL
G.2.4	Chemical model optimization for extreme reduction	$270K	SNL

Developed, assembled, and validated gasoline surrogate + HPFs model



High Performance Fuels (HPFs):

alcohols
methanol[1]
ethanol
n-propanol
iso-propanol (2-propanol)
n-butanol[2]
2-butanol[2]
iso-butanol (2-methyl-1-propanol)[2]

esters
methyl acetate (developed)
ethyl acetate (developed)
Methyl butanoate (improved)

ketones
butanone

furans
2-methylfuran
2,5-dimethylfuran

Validations enabled by Zero-RK (e.g. +20,000 simulations of validation targets in 15 min.)

RON, OS, flame speed:

Key terms in Merit Function:

At various levels of readiness, most predictions of neat compound RON and OS to ≤~3 octane units

Blending predictions are favorable but vary, ≤~3 octane units on RON

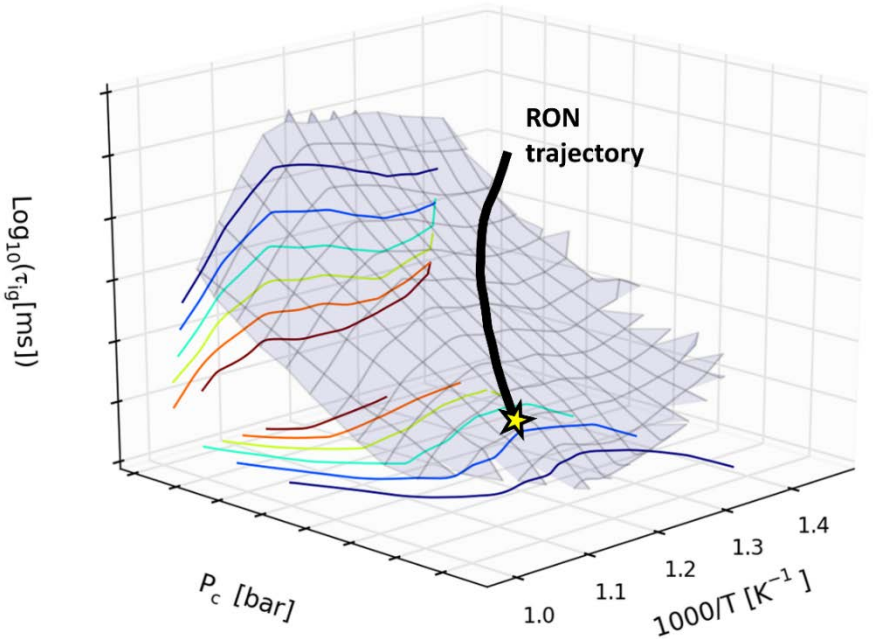
Flame speeds predicted for 7 HPFs

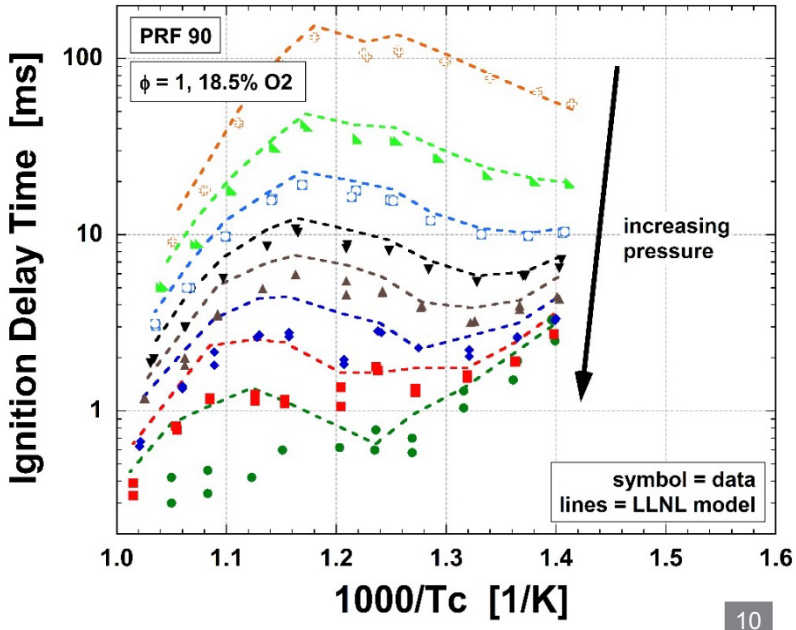
other classes
anisole (developed)
di-iso-butylene (trimethyl-pentene)(improved)

[1]Component models not labeled were taken from the literature
[2]Previously developed at LLNL

Significantly improved pressure dependence in kinetic model with FY17 ANL RCM campaign

- Acquired new RCM data for PRF60-100 blends, covering range of conditions relevant to light duty engine operation and CFR octane rating tests
- Validated recent updates to LLNL gasoline surrogate model (foundational chemistry, and alkane sub-mechanisms)

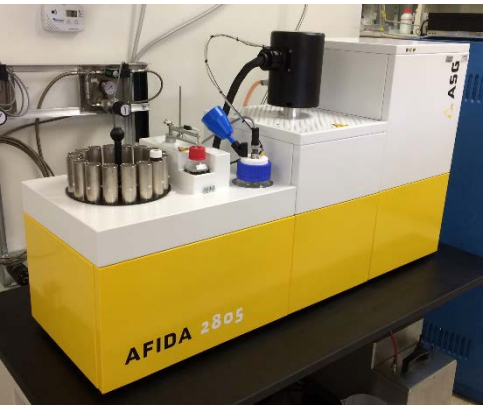




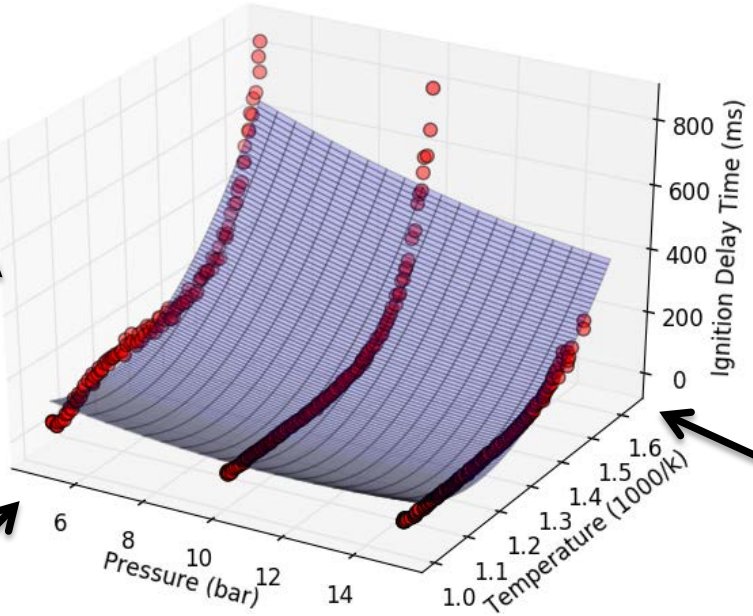
NREL's rapid measurement of blending behavior aids gasoline surrogate mechanism design

Parametric (T, P, √, $|_{O2}$) ignition delay studies

Ignition Quality Tester (IQT)



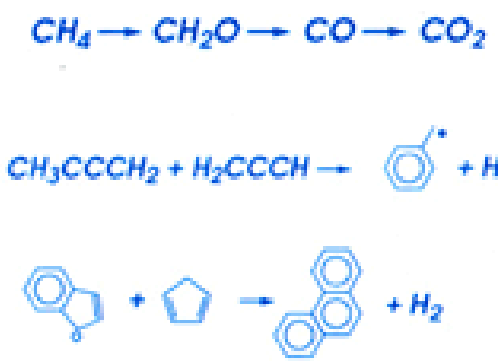
Advanced Fuel Ignition Delay Analyzer (AFIDA)



Simulations for mechanism development & validation

Gasoline surrogate TRF blends (iso-octane, n-heptane, toluene) with varying levels:

- ethanol
- p-cresol
- anisole
- other light duty engine candidates that passed Tier I & II screening

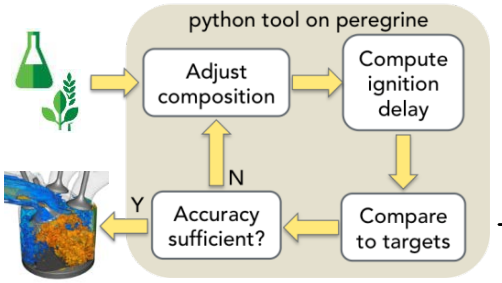


Accomplishment – F.2.2.1 Zigler ($250K)

Detailed kinetics simulation produces non-linear octane blending model for co-optimizer

Kinetics simulation provides more accurate interpolation for the Scenario Co-Optimizer than simple linear blending

1. Match BOB:



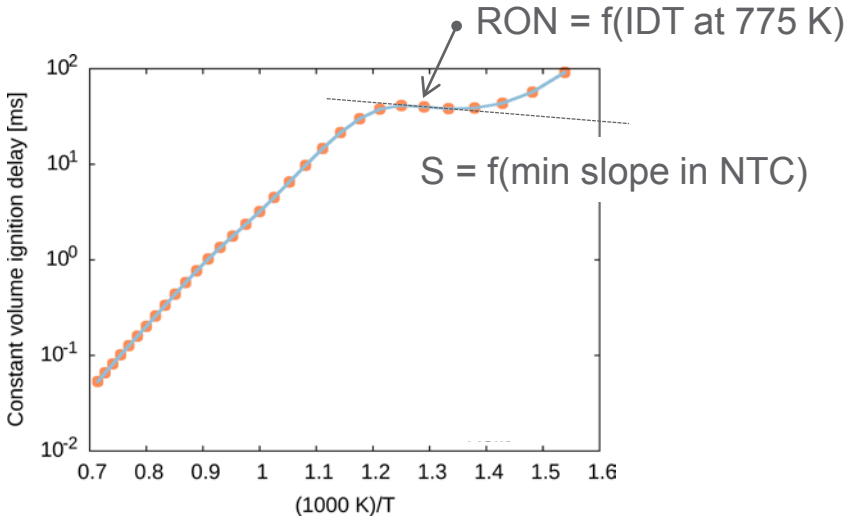
RON
S
Distillation
H/C
PIONA

2. Select oxygenate composition:

Pass Tier I & II screening (McCormick)

ethanol	*2-butanone*
2-butanol	methanol
isobutanol	methoxybenzene
diisobutylene	2,5-dimethylfuran
iso-proponal	2-methylfuran
n-proponal	methyl acetate
2-methyl-1-butanol	ethyl acetate

3. Compute constant volume IDT
   approx. 5 seconds on 16 cores; ORNL Tasmanian version trained for interpolation in milliseconds

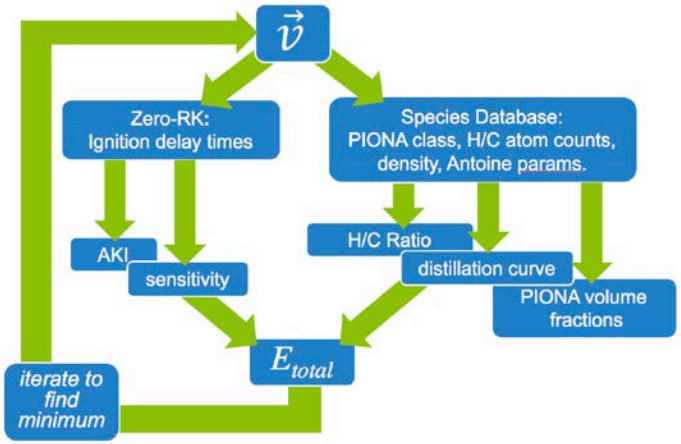


4. Compute model RON and S from Mehl correlation
5. Evaluate Merit Function in the Scenario Co-Optimizer

Accomplishment – G.1.1 McNenly ($200K)

Virtual fuels created to test the Central Fuel Hypothesis in CFD

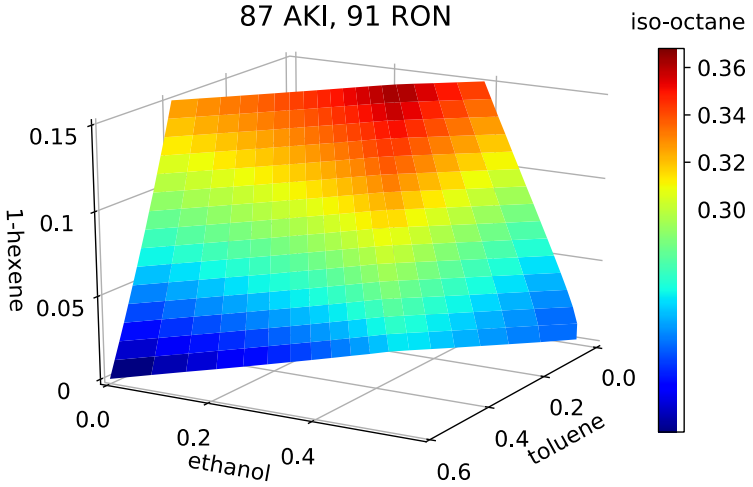
Surrogate Co-Optimizer (FY16):



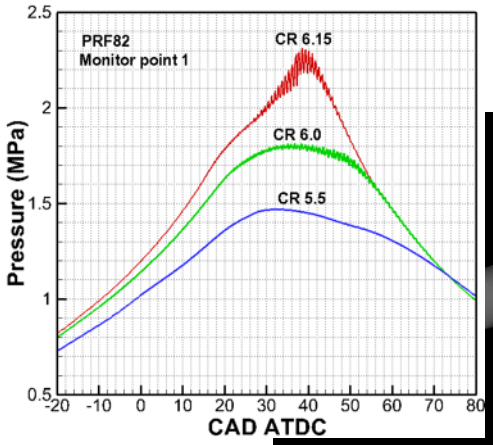
Central Fuel Hypothesis (CFH) Testing:

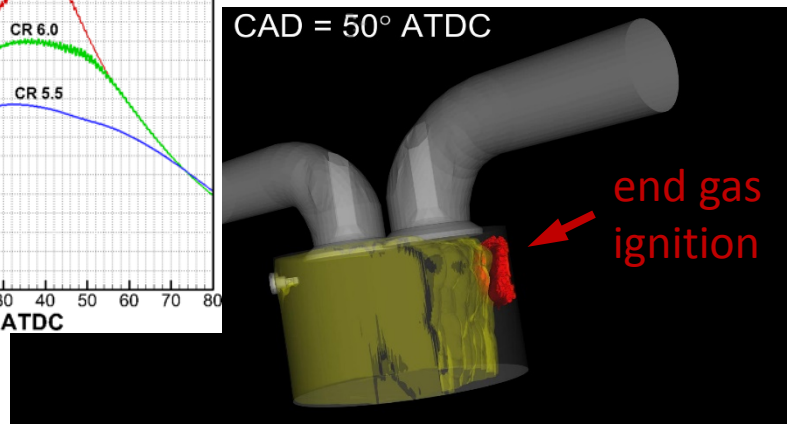
1. created matched 4-component TRF + ethanol surrogates (RON, S, flame speed, and HoV)
2. validate(d) fuel performance in CFR simulation at RON and MON conditions
3. test if the CFH holds or breaks down under boosted (beyond RON) conditions

Ex. 5-component surrogates at matched model octane rating



Virtual CFR (P. Pal, ANL)

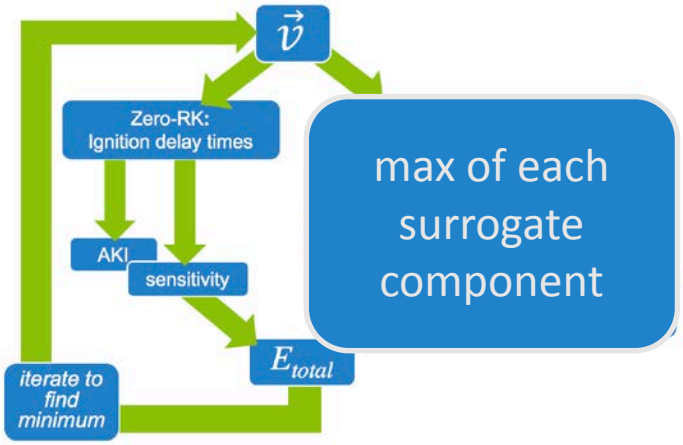




Accomplishment – G.1.1 McNenly ($200K), Grout ($210K)

Virtual fuels created to test the Central Fuel Hypothesis in CFD

Surrogate Co-Optimizer (FY16):



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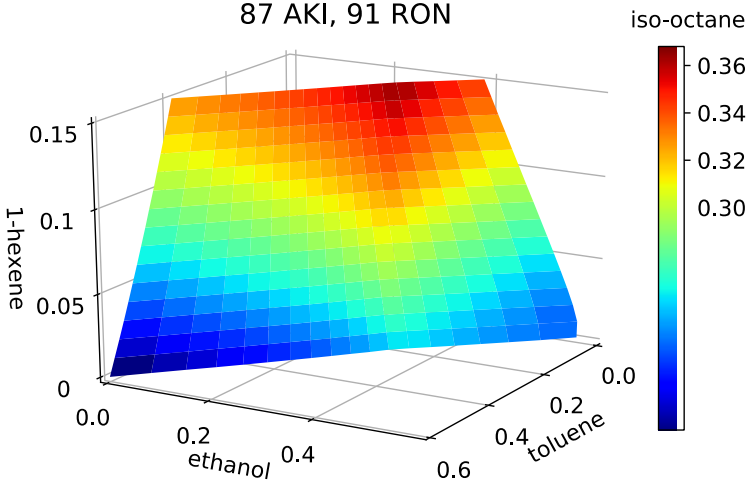
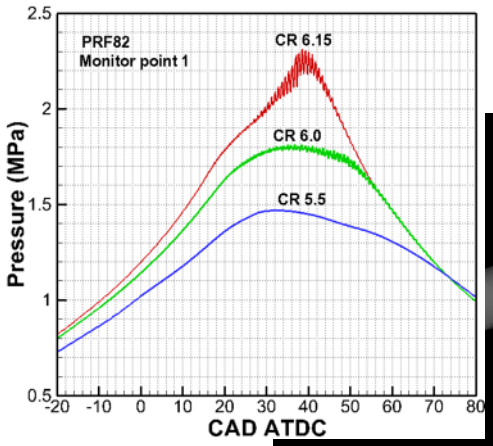
Ex. 5-component surrogates at matched model octane rating





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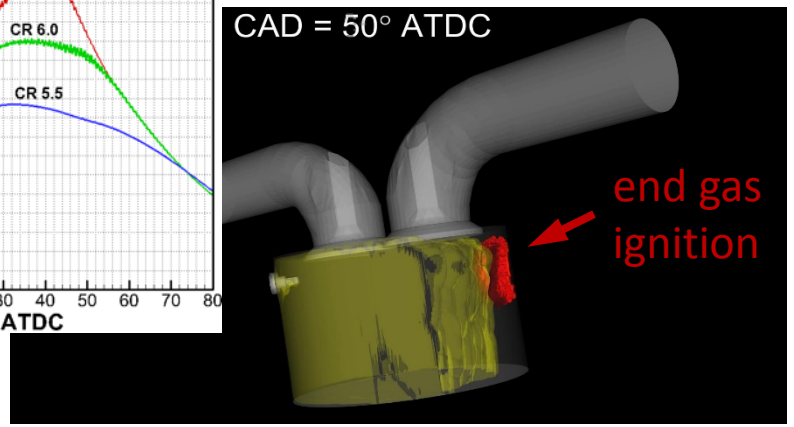


Accomplishment – G.1.1 McNenly ($200K), Grout ($210K)

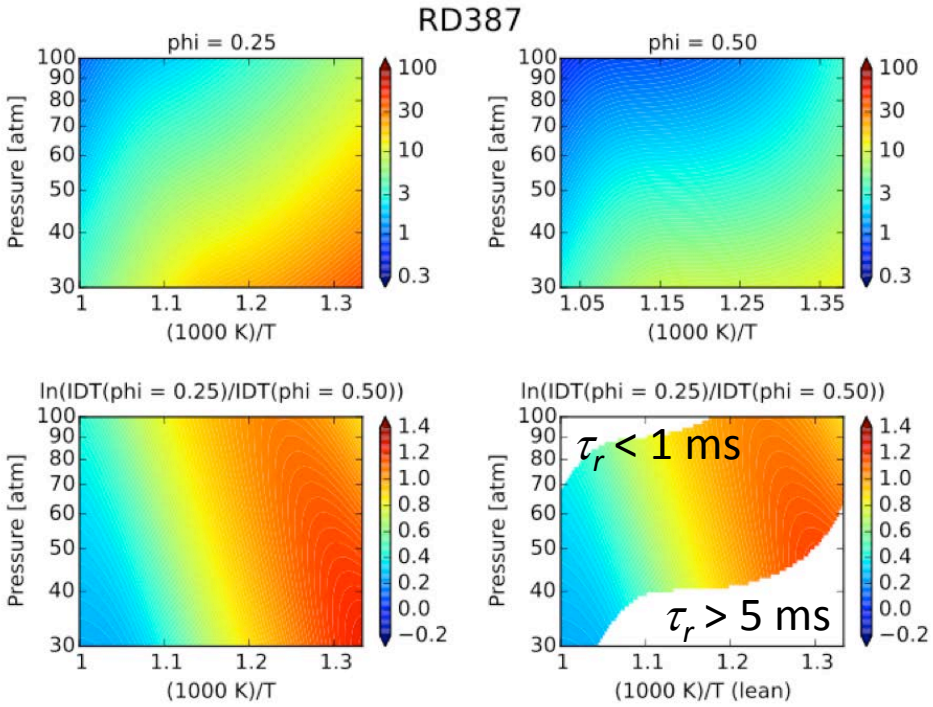
Created a searchable phi-sensitivity metric for partially stratified charge compression ignition

Need a computable phi-sensitivity metric to search for a virtual fuel with an optimal blend composition:

- measure the ratio of the lean τ_l and rich τ_r ignition delay times
- evaluate for a wide range of potential pressures and temperatures, 30 - 100 atm and 750 – 1000 K
- use the integral as a balance of the maximum value and extent
- limit integration to usable ignition delays (1 – 5 ms)
- use log *p* and 1000/*T* as coordinates to reduce the number of evaluations per integral

Next steps:

- search +1M combinations of the 28 surrogate components for RON > 95, max Φ, and max octane sensitivity
- validate in Dec's engine at SNL*



*reproduces ethanol blending trends**

RD387	Φ = 0.60
+ 10% ethanol	Φ = 0.23
+ 20% ethanol	Φ = 0.09

Accomplishment – G.1.2 McNenly ($195K)

Extreme mechanism reduction accelerates parametric analysis with simulation

Goal: 100X speed up of piston engine simulations

- Derive extremely reduced chemical mechanisms using Bayesian inference

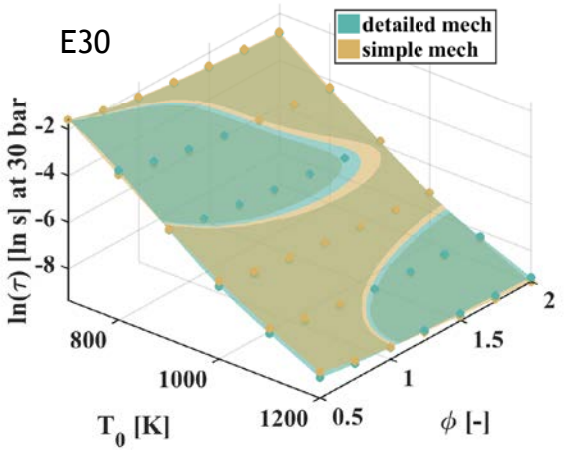
$$p(\boldsymbol{\alpha}|\ln \boldsymbol{\tau}^d) \propto p(\ln \boldsymbol{\tau}^d|\boldsymbol{\alpha})p(\boldsymbol{\alpha})$$

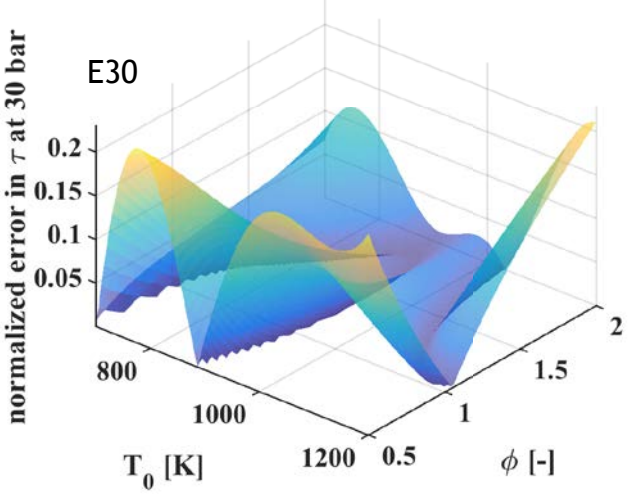
ignition delay

global reaction parameters

$$C_mH_n + \left(\frac{m}{2} + \frac{n}{4}\right) O_2 \rightarrow mCO + \frac{n}{2}H_2O$$

$$CO + \frac{1}{2}O_2 \leftrightarrow CO_2$$





- Decrease cost of chemistry while capturing chemical quantities of interest (e.g. ignition delay τ^d) for different fuel blends

- Quickly generate simple chemical mechanisms to match new experimental measurements of biofuels (detailed mech. not needed)

Response to reviewers

1. "… more collaboration with industry and universities would be helpful in the long run."

   Response: Highlights and deep-dives are discussed on monthly stakeholder calls. Chemical kinetic models and engine simulations are shared with OEM collaborators. Eight university FOA's were awarded so that there will be more collaboration with academia.

2. "… there has to be a step taken beyond research octane number (RON) and cetane number (CN). The reviewer offered that more details about fuel chemistry are probably best studied using a combination of detailed kinetic modeling, surrogate fuels, and refinery-based blended fuels."

   Response: Research in model discovery is proposed to help automate the merit function development for advanced compression ignition light-duty and medium & heavy-duty. The automated framework should allow for rapid testing of extra parameters and uncover missing multi-property correlations. Another benefit is that uncertainty quantification will be easier to implement to provide "error bars" around merit function sensitivity coefficients and engine performance outputs.

Response to reviewers

3. “[The] approach follows a logical progression for defining key fuel properties and parameters, screening candidate fuels according to those properties as well as some other key characteristics, and testing performance of the identified fuels in laboratory combustion experiments, along with kinetic modeling followed by engine testing. The reviewer noted that in order to do this, new test methods such as heat of vaporization and auto-ignition quality from small samples are to be developed. The reviewer said promising approaches to those have been described.”

   Response: Colleagues at NREL have developed bench-scale techniques to quantify HoV, including as a function of boiling fraction. Engine experiments separating HoV from RON and S for high temperature and knock conditions were conducted, and these experiments are being integrated with CVCC-based parametric ignition delay studies. The Microliter Fuel Ignition Tester experiments conducted by Prof. Schoegl will continue at LSU under the University FOA. Unfortunately, the research at ANL to develop a smaller scale, higher throughput rapid compression machine was delayed due to budget cuts.

Collaboration and coordination

Within the Co-Optima program

- Four labs (ANL, LLNL, NREL, SNL) coordinating on Topic 7 (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

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
- ANL - Chevron collaboration through FOA (FY15-FY17)
- NREL - Colorado School of Mines, IQT analysis and simulation
- LLNL - Convergent Sciences Inc., chemistry solver development

Remaining challenges and barriers

- Increasing the accuracy of real fuel models to co-optimize fuels and engines
- Validating chemical kinetic models over wider pressure ranges, 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*
- Searching for optimal fuel surrogate blends for expected engine performance
- Identifying the dependency between critical chemical pathways and functional groups and engine performance
- Discovering missing properties and multi-property correlations in new merit functions
- Automating the extremely reduced mechanism creation procedure to handle a wider range of blends

Proposed future work*

ANL
- Conduct RCM tests with the blending BOBs and gasoline surrogate blendstocks.

LLNL
- Develop and improve HPF component models for light, medium and heavy duty engines and incorporate them into improved gasoline and diesel surrogate models.
- Create Zero-RK accelerated, kinetics-based engine impact analysis tools (e.g., multi-zone, and stochastic reactor models).
- Complete reaction rate sensitivity and pathway analysis to find relationships to more complex engine metrics (e.g., phi-sensitivity metric, intermediate heat release along engine trajectory, and late combustion phasing stability).

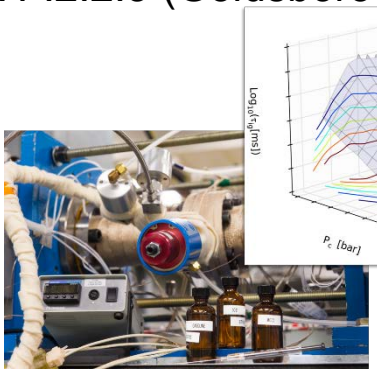
NREL
- Continue development of AFIDA-based capability to provide ignition delay and heat release data feedback for kinetic mechanism development; and link constant volume experimental measurements to engine performance.

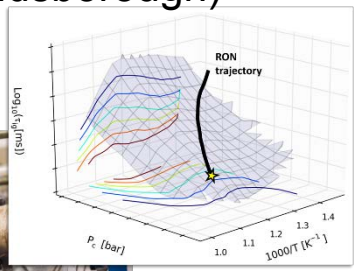
SNL
- Simulate fuel property impact on spray-based charge preparation

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

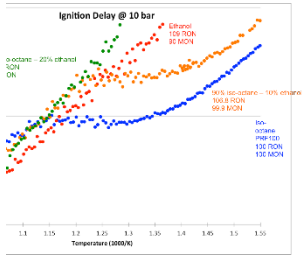
Advances in chemical kinetics research deepen the understanding of fuel impacts on engines

Task F.2.2.3 (Goldsborough)

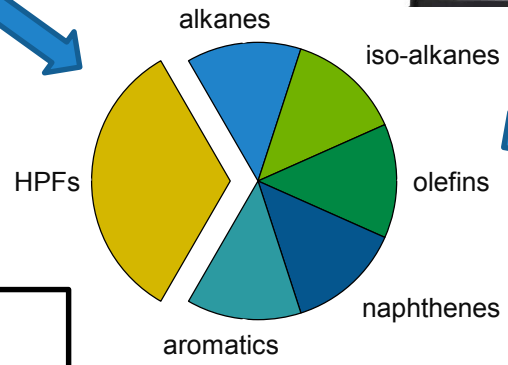


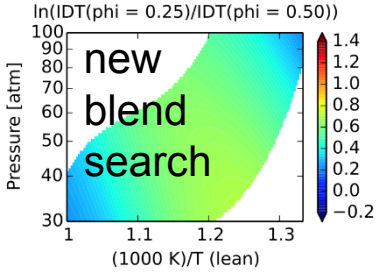


Task F.2.2.1 (Zigler)

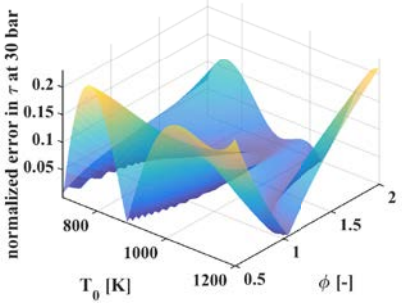


Task F.2.2.2 (Pitz)





Task G.2.4 (Lacaze)



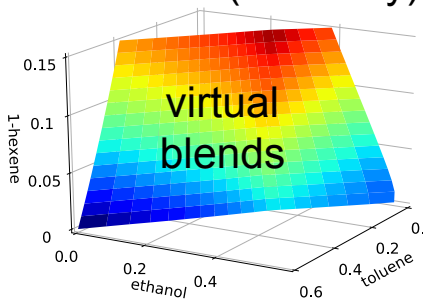
Task G.1.1
(Whitesides/Grout)

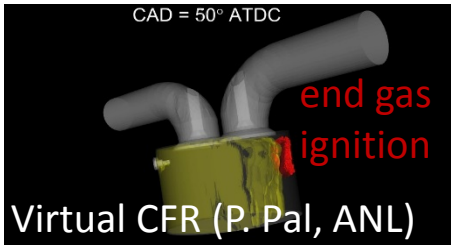
Zero-RK

fast detailed chemistry

faster CFD

Task G.1.2 (McNenly)





nonlinear octane blending

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

Technical backup slides

Task F.2.2.1 Backup
B. Zigler, NREL, $250K

NREL kinetics experiments, connections to mechanism development

Parametric (T, P, Φ, χ_{O_2}) ignition delay studies

Ignition Quality Tester (IQT)

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 ~ 10x that of IQT.

Task F.2.2.2 Backup
W. Pitz, LLNL, $500K

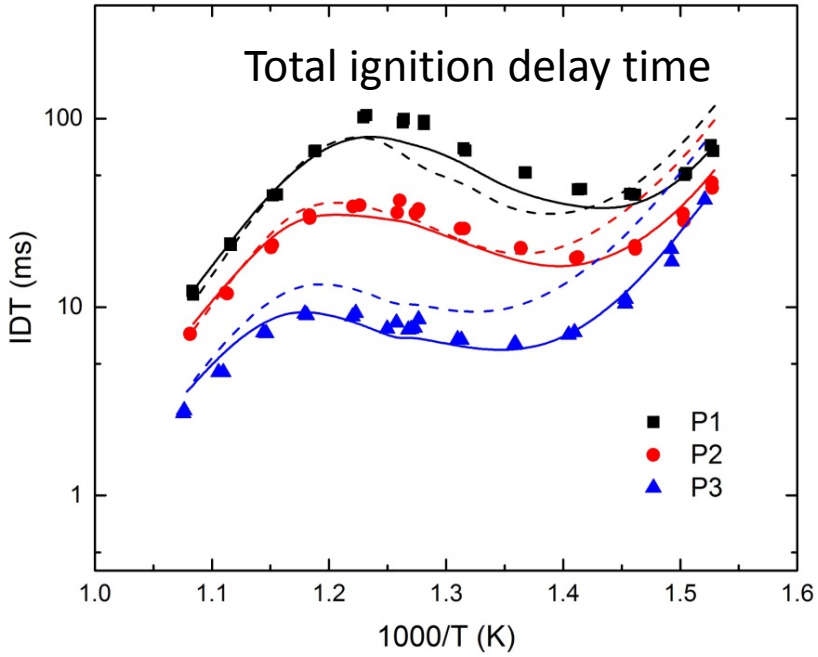
Improved iso-octane sub-mechanism developed

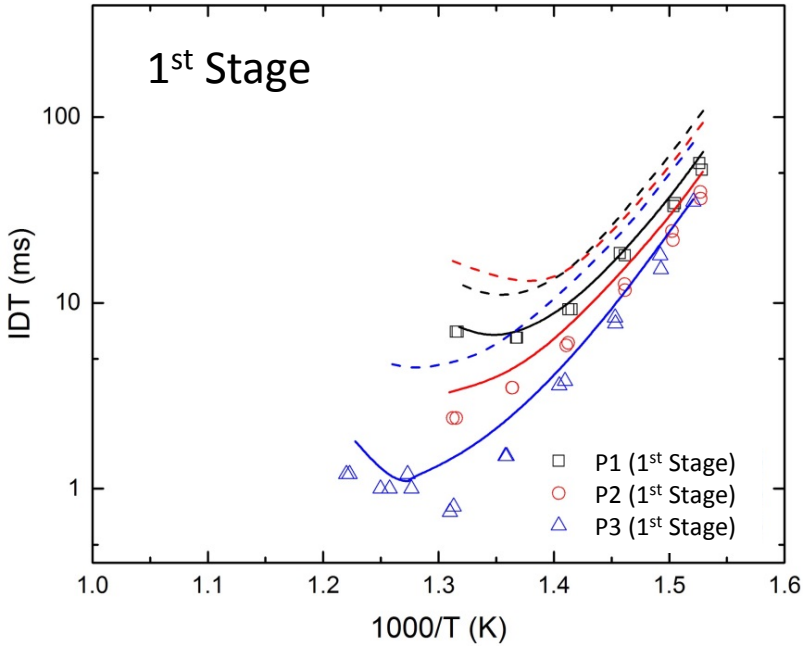
- iso-octane (improved in FY16 &17)
- improve prediction of
  - pressure dependence
  - first-stage ignition

Comparison with previous mechanism (Phi = 1.0 in air)

Experimental data from ANL RCM

Argonne NATIONAL LABORATORY



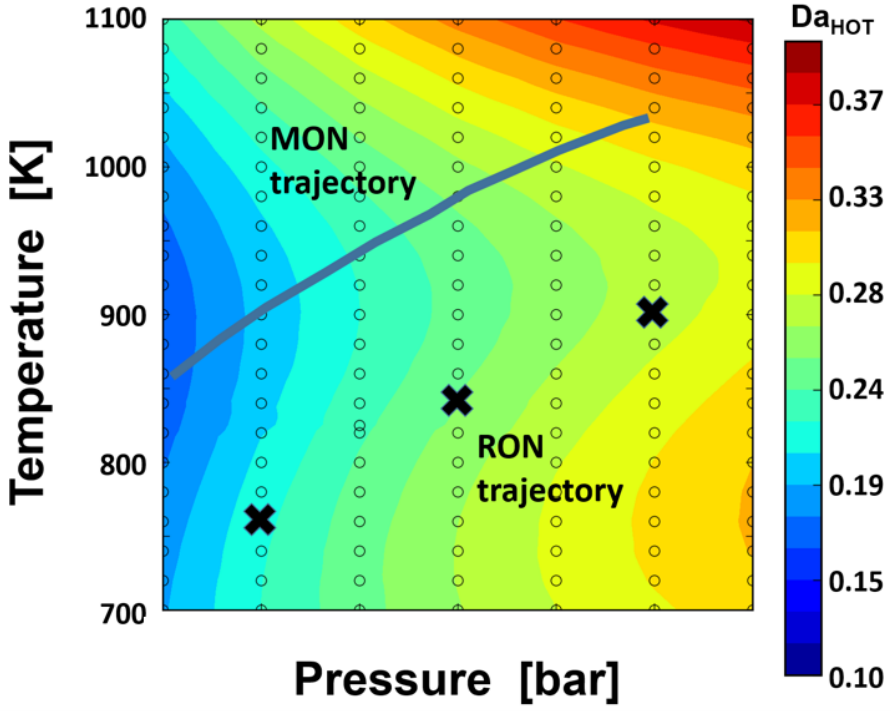


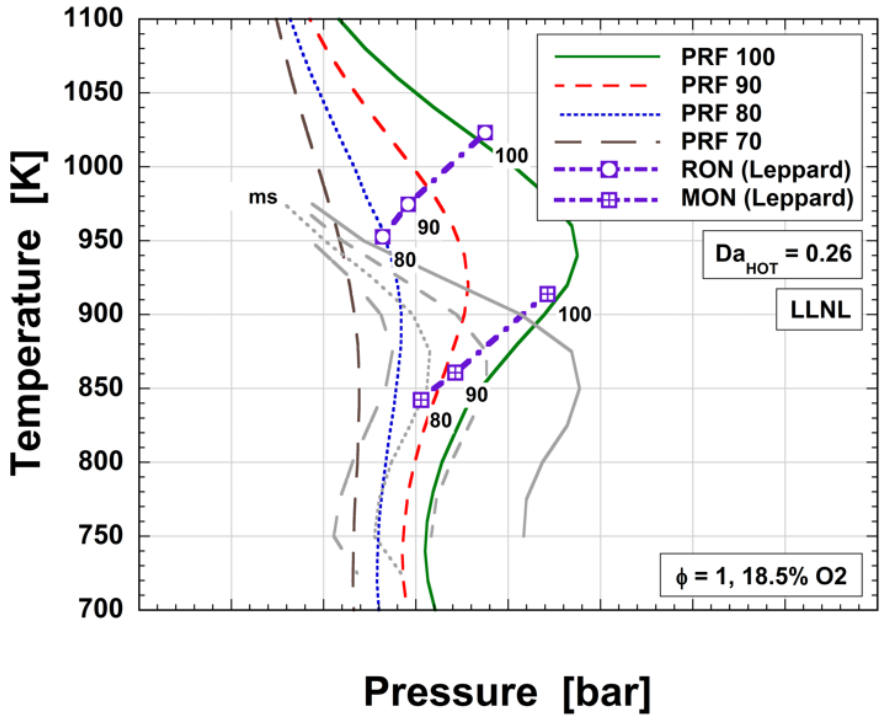
Task F.2.2.3 Backup
S. Goldsborough, ANL, $250K

New RCM data, kinetic modeling, and analysis at light-duty conditions highlight relationships between auto-ignition timing / knock onset, and rates of chemical heat release / knock intensity

- Results indicate importance of fundamentally understanding how fuel composition (petro-/bio-) affects these auto-ignition properties

$$Da_{HOT} = \frac{\text{energy deposition (heat release) rate}}{\text{gas dynamic (transport) rate}} = \frac{(\dot{q}_{chem}/c_v T)_{max}}{a_0/r_{HOT}}$$

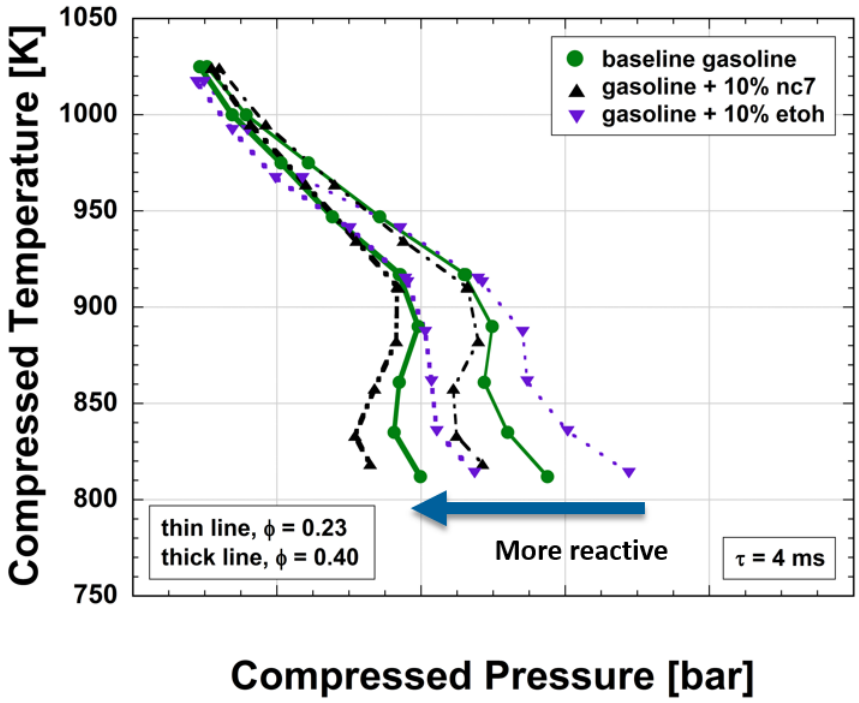


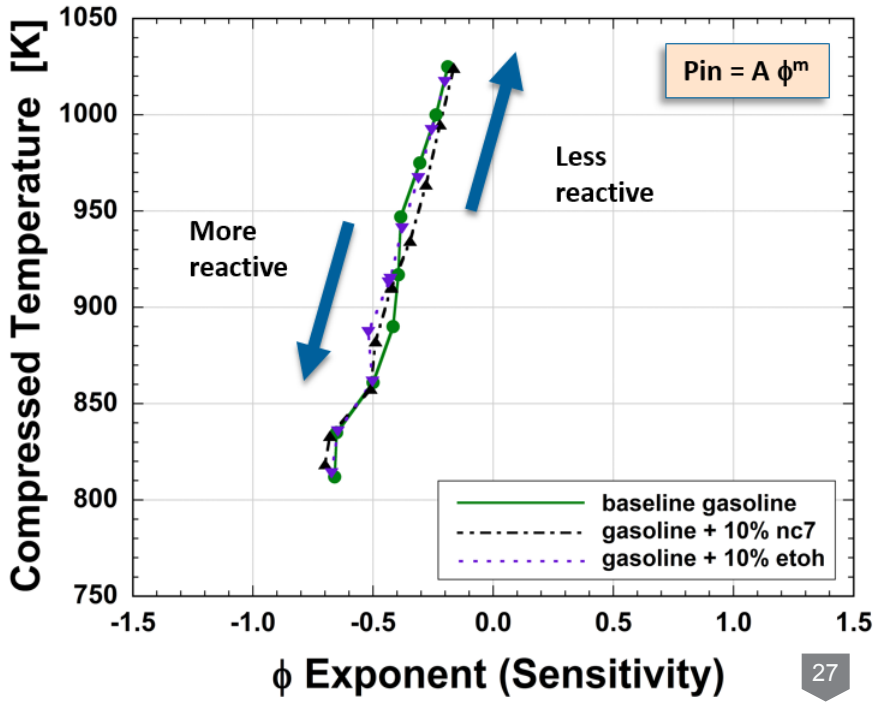


Task F.2.2.3 Backup
S. Goldsborough, ANL, $250K

In adjacent FOA project RCM data combined with ACI and medium & heavy duty engine experiments to better understand / quantify fuel stratification and ϕ-sensitivity of refinery-based blended fuels

- Power-law functionality utilized to highlight temperature dependence of ϕ-sensitivity for range of fuel blends, indicating influence of engine operating regime towards exploiting fuel stratification effects





Task G.2.4 Backup
G. Lacaze, SNL, $270K

Bayesian inference to parameterize extremely reduced mechanisms

1. Obtain reference data (e.g. ignition delay) using detailed mechanism or experiments over relevant range of P, T and phi
2. Expert knowledge: derive a n-step (n<10) mechanism based on literature and experience
3. Build surrogate (Polynomial Chaos Expansion) of the chemical model: Chemkin-like simulations used to find the surface response of the mechanism in parameter space
4. Use Bayes' Rule and surrogate to find best chemical parameters of optimized mechanism

Impact: help simulation team to shorten simulation cycles and increase scope of parametric investigations

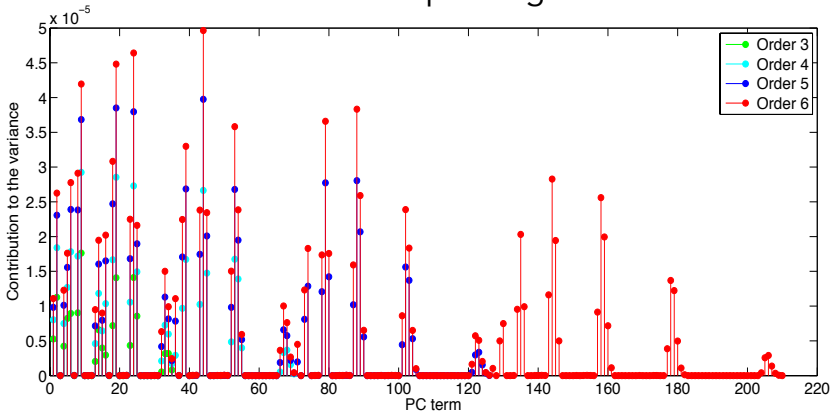
3-step mech. for E30:

$$GASO + 17/2\ O_2 \Leftrightarrow 8CO + 9H_2O$$

$$C_2H_5OH + 2\ O_2 \Leftrightarrow 2\ CO + 3\ H_2O$$

$$CO + 1/2\ O_2 \Leftrightarrow CO_2$$

Active coefficients depending on PCE order



These optimized chemistries run 100x faster than detailed mechanisms with only a 10-15% normalized error

Acronym list

AED	Advanced Engine Development Team
ACI	Advanced Compression Ignition
ANL	Argonne National Laboratory
AOP	Annual Operating Plan
ASSERT	Analysis of Sustainability, Scale, Economics, Risk and Trade Team
BETO	Bioenergy Technologies Office
BOB	Blendstock for oxygenated blending
COLT	Co-Optima Leadership Team
CI	Compression Ignition (combustion)
EAB	External Advisory Council
EERE	Energy Efficiency and Renewable Energy Office
FE	Fossil Energy (content)
FP	Fuel Properties Team
FOA	Funding Opportunity Announcement
GHG	Greenhouse gas
HOV	Heat of Vaporization
HPF	High Performance Fuels Team
INL	Idaho National Laboratory
IP	Intellectual Property
LANL	Los Alamos National Laboratory
LBNL	Lawrence Berkeley National Laboratory
LLNL	Lawrence Livermore National Laboratory
LCA	Lifecycle Analysis
MT	Market Transformation Team
NREL	National Renewable Energy Laboratory
ORNL	Oak Ridge National Laboratory
POC	Point of Contact
PNNL	Pacific Northwest National Laboratory
R&D	Research and Development
RON	Research Octane Number
SI	Spark Ignition (combustion)
SOT	State of Technology
SNL	Sandia National Laboratory
TEA	Techno-economic analysis
TK	Toolkit and Simulation Team
TRL	Technology Readiness Level
VTO	Vehicle Technologies Office