PARTNERSHIP TO ADVANCE COMBUSTION ENGINES

Chemical Kinetic Models for Surrogate Fuels

2021 DOE Vehicle Technologies Office Annual Merit Review Presentation

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Project ID# ace139

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Prepared by LLNL under Contract DE-AC52-07NA27344.
LLNL-PRES-#######

Overview

Timeline

PACE started in Q3 of FY19*

PACE will end in FY23 (~46% complete)

Focus and objectives of individual tasks will be continuously adjusted

Overall PACE workplan discussed in ace138

*Q, FY = Quarter, Fiscal Year. FY20 begins October 1, 2019.

Budget

Lab (PI)	Task(s)	FY20	FY21
ANL (Goldsborough)	A.E.01	$450k	$252k
LLNL (Kukkadapu)	L.M.01.02**		$200k
LLNL (Pitz)	L.M.01.01**	$700k	$425k
LLNL (Whitesides)	L.M.01.05-06**		$150k
SNL (Sjoberg)	S.E.07**	$270k	$270k

**Efforts under these tasks are split across multiple presentations. Please see the reviewer-only slides for the complete PACE budget breakdown.

Barriers***

Poor understanding of and an ability to predictively model and control:

- Knock & low speed pre-ignition (LSPI)
- Dilute combustion
- Cold-start emissions

***Aligned with USDRIVE ACEC Tech Team Priority 1: Dilute gasoline combustion

Partners

PACE is a DOE-funded consortium of five national laboratories working towards a common goal (see ace138)

- Goals and work plan developed considering input from stakeholders including DOE, ACEC Tech Team, CFD code developers and more

Advanced Engine Combustion (AEC) working group

Coordinating Research Council (CRC)

Subcontracts with University of Connecticut, University of Southern California

RD5-87: Co-Optima teams and universities

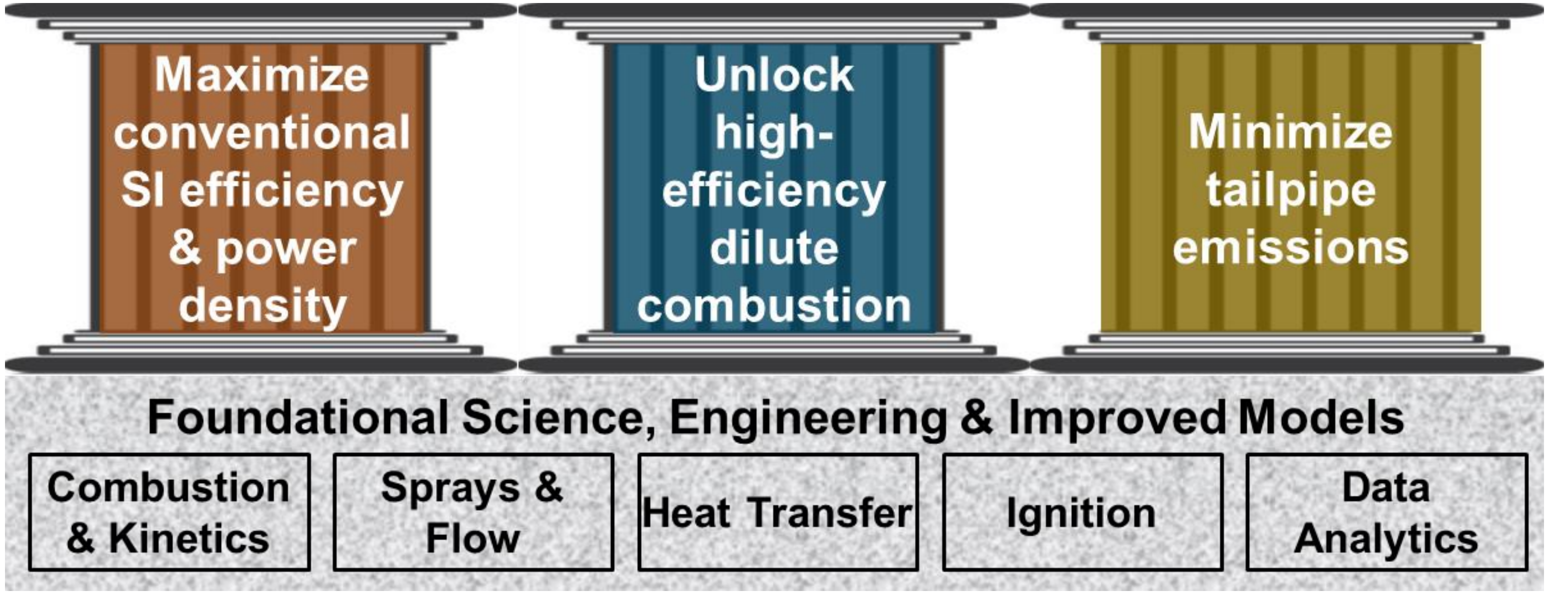
Relevance: Barriers

PACE combines unique experiments with world-class DOE computing and machine learning expertise to speed discovery of knowledge, improve engine design tools, and enable market-competitive powertrain solutions with potential for best-in-class lifecycle emissions

Poor scientific understanding of and/or an ability to predictively model and control:

- **knock response to design changes, low-speed pre-ignition (LSPI), and flame kernel development at high load.**
- **lean and/or dilute combustion burn duration and emissions.**
- **the impact of injection and spark timing on combustion phasing and emissions during cold-start.**

Relevance: Objectives



Quickly turn fundamental science into engineering models that enhance engine design workflows.

Develop and improve a simpler shared gasoline surrogate to enable less challenging analysis and simulations which address technical barriers.

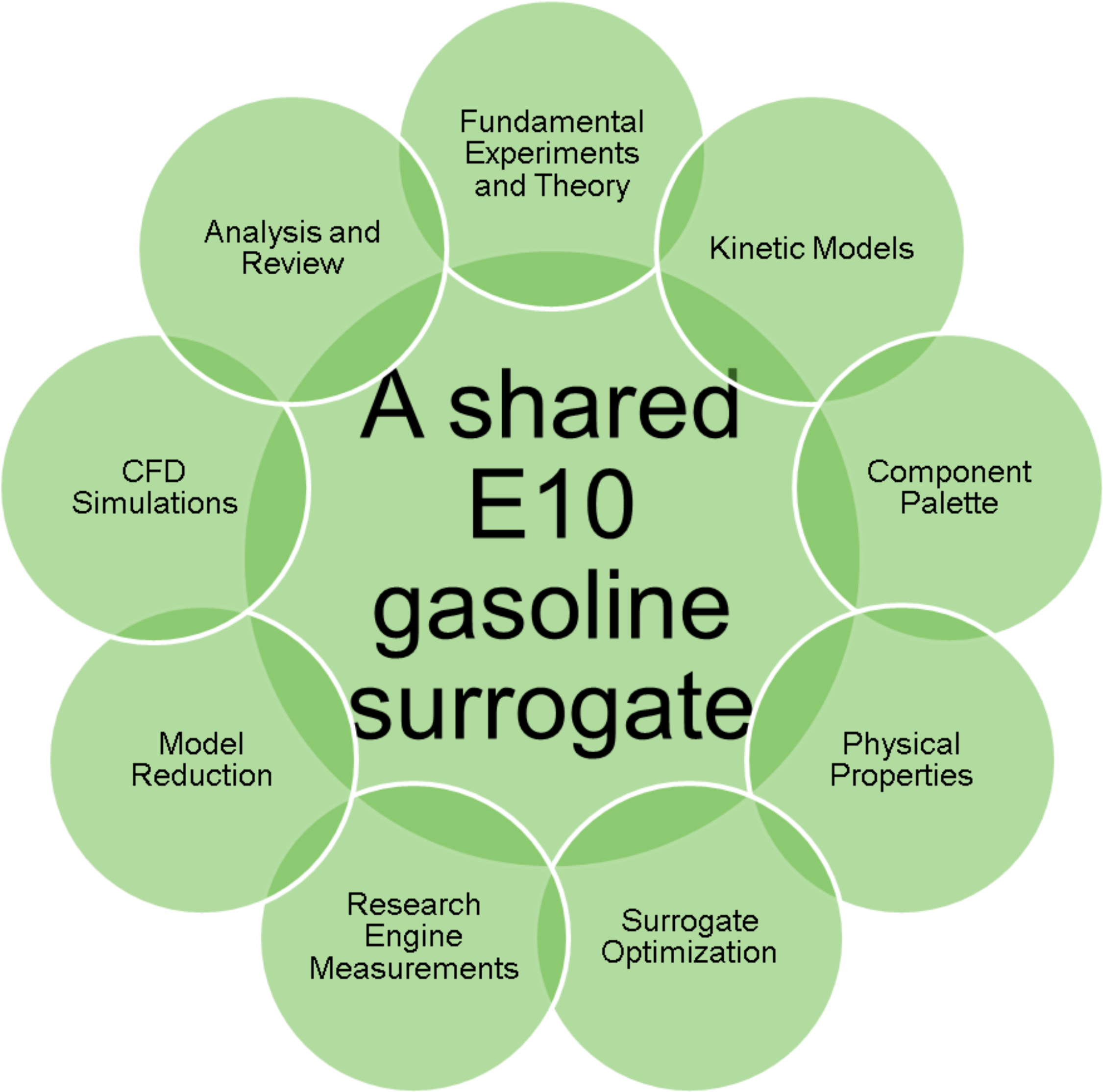
Rapidly deliver a reduced kinetic model of the surrogate for simulations within engine design workflows and tasks leading to PACE major outcomes.

Milestones

Month Year	Description of Milestone or Go/No-Go Decision	Status	Lab
June 2020	A.01.02b: Updated ozone oxidation mechanism.	Completed	LLNL
October 2020	A.01.03: Improved model for PAH and soot predictions.	Completed	LLNL
October 2020	A.01.05: Develop/improve and validate models for 1-2 components.	Completed	LLNL
December 2020	A.E.01: Experimental measurements of two PACE gasoline multi-component surrogates for comparison against RD5-87.	Completed	ANL
December 2020	L.M.01.01: Publish online PACE gasoline detailed kinetic model. Deliver a reduced model for TPRF + ethanol.	Completed	LLNL
March 2021	L.M.01.01: Publish online PACE gasoline reduced kinetic model(s) for a gasoline surrogate.	Completed	LLNL
June 2021	A.01.04: Kinetic model with improved EGR behavior.	On-target	LLNL
September 2021	A.E.01: Experimental measurements of PACE gasoline with EGR constituents.	On-target	ANL
September 2021	L.M.01.01: Improved chemical kinetic model for an RD5-87 surrogate fuel.	On-target	LLNL

Approach

Collaborate to rapidly deliver a shared surrogate fuel and kinetic model(s)



Benefit

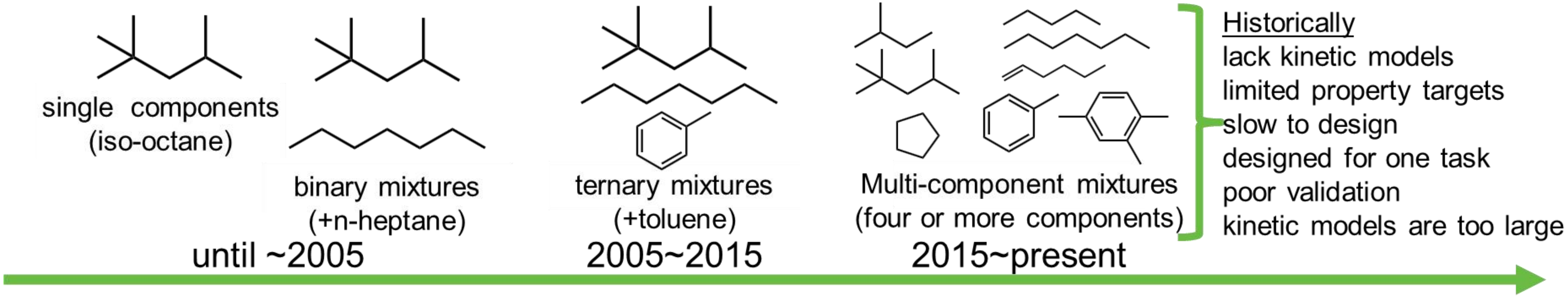
Major outcomes from PACE are informed by cross-cutting analysis of experiments and simulations using a shared surrogate for RD5-87, a complex E10 research gasoline.

Avoid

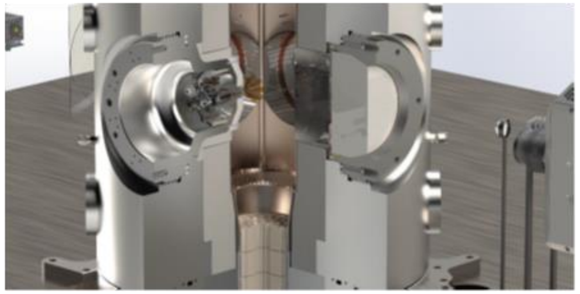
Challenging inter-comparisons of research outcomes.
Simulations and models lacking experimental validation.

Approach

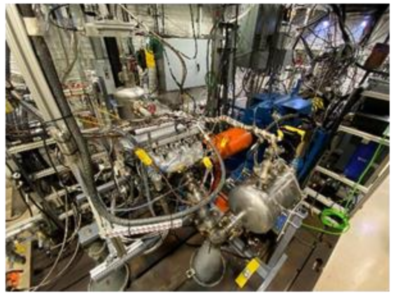
Use the technical expertise and capabilities within PACE to deliver a surrogate fuel and kinetic model(s) for all outcomes



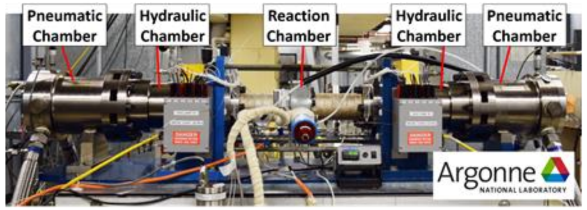
Lawrence Livermore National Laboratory



Sandia National Laboratories



Oak Ridge National Laboratory



Argonne National Laboratory

Members of the surrogate fuel working group include:

Song Cheng	Goutham Kukkadapu	Magnus Sjoberg
Scott Curran	Dario Lopez-Pintor	Jim Szybist
Flavio Dal Forno Chuahy	Matt McNenly	Scott Wagnon
John Dec	Lyle Pickett	Russell Whitesides
Scott Goldsborough	Bill Pitz	Martin Wissink
Nathan Harry	Chiara Saggese	

PACE-20 recommended by surrogate fuel working group as the surrogate fuel until further notice

component	PACE-1	PACE-20
ethanol	0.0940	0.0955
n-pentane		0.1395
iso-pentane	0.0769	
cyclopentane	0.1053	0.1050
1-hexene	0.0661	0.0541
n-heptane	0.1867	0.1153
toluene		0.0919
iso-octane	0.2139	0.2505
1,2,4-trimethylbenzene	0.2573	0.1187
tetralin		0.0295

Compositions are given as liquid volume fractions
Fractional values may not sum to one due to rounding

[1] Measurements from SWRI and Gage (ASTM D2699, D2700, D5291, D4052, D86)
[2] Calculated from DHA (ASTM D6729)

metric	RD5-87(#2A)	PACE-1	PACE-20	EPA Tier III
RON [1]	92.3	91.8	92.1	92.3
MON [1]	84.6	82.3	84.5	84.5
H:C [1]	1.98	1.97	1.97	1.96
density [g/mL] [1]	0.75	0.75	0.74	0.75
PMI [2]	1.68	1.56	1.50	
	D86	**D86**	**D86**	**D86**
T_{10} [C] [1]	57.8	60.4	57.9	52.7
T_{50} [C] [1]	101.3	100.6	89.9	91.2
T_{90} [C] [1]	157.9	165.8	166.0	159.5

The EPA Tier III certification and RD5-87 fuels are complex E10 gasolines.

PACE-1 was recommended as the surrogate fuel for FY20.

Argonne National Laboratory
Lawrence Livermore National Laboratory
Oak Ridge National Laboratory
Sandia National Laboratories

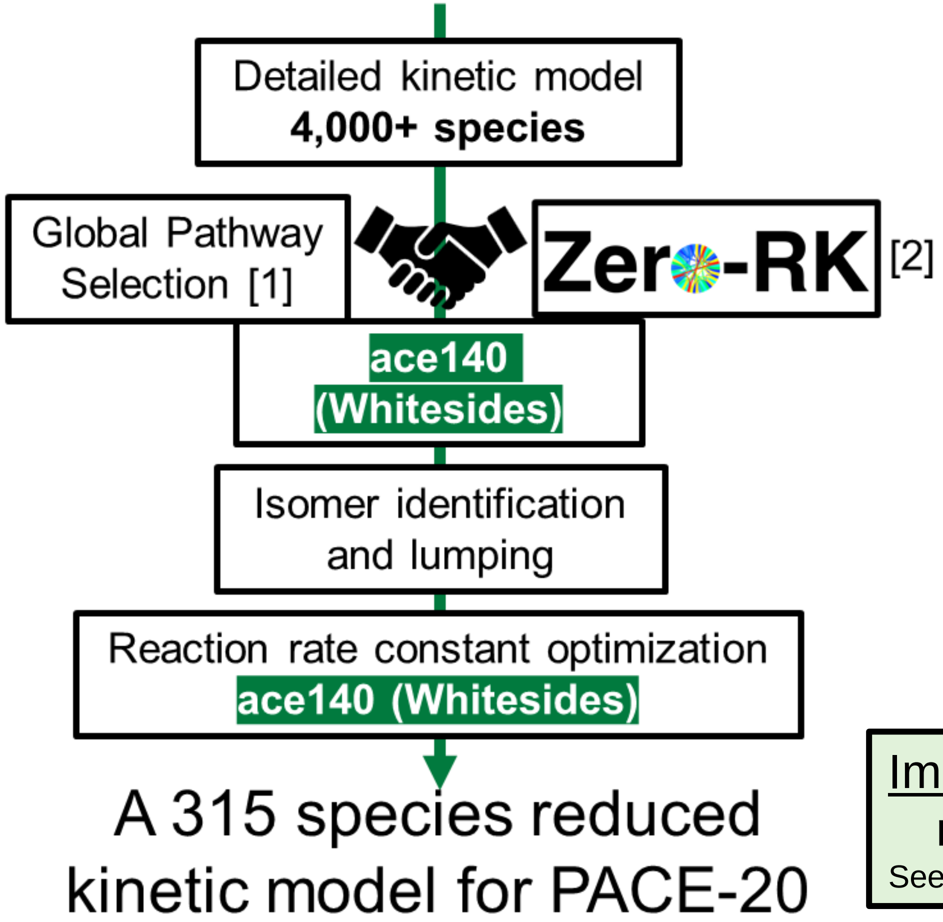
Impact: A single E10 gasoline surrogate fuel may acceptably match ignition delay time, laminar burning velocity, spray behavior, soot volume fraction, engine data, and more aiding analysis and modeling of complex gasoline.
See also **ace143 (Powell)**, **ace144 (Pickett)**, **ace167 (Torelli)**, **ace168 (Manin)**

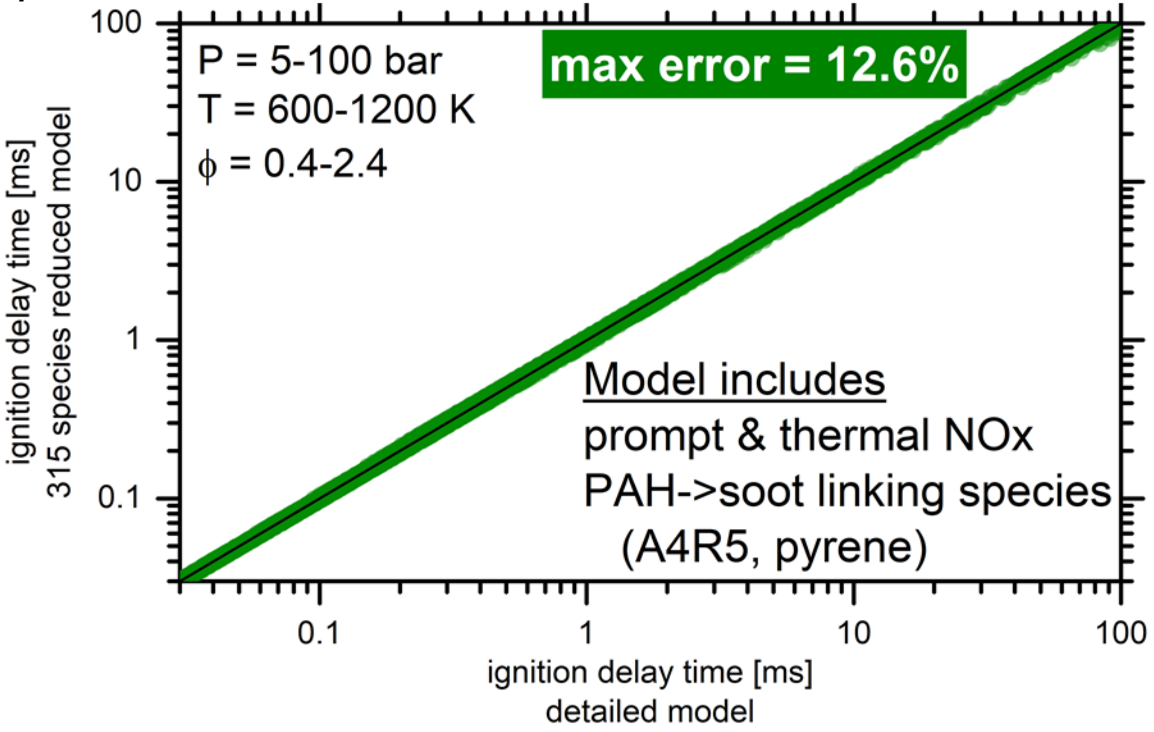
RON/MON = research/motor octane number
SWRI = Southwest Research Institute
PMI = particulate matter index
$T_{\#\#}$ = temperature at ##% liq.vol. recovered

An improved detailed kinetic model for surrogate fuels and a reduced kinetic model for PACE-20 are available

Release of an improved detailed kinetic model to consortium members after simulating **5,500+ ignition delay times** and **1,100+ laminar flame speeds** including PACE-20 neat components and their mixtures.

Lawrence Livermore National Laboratory





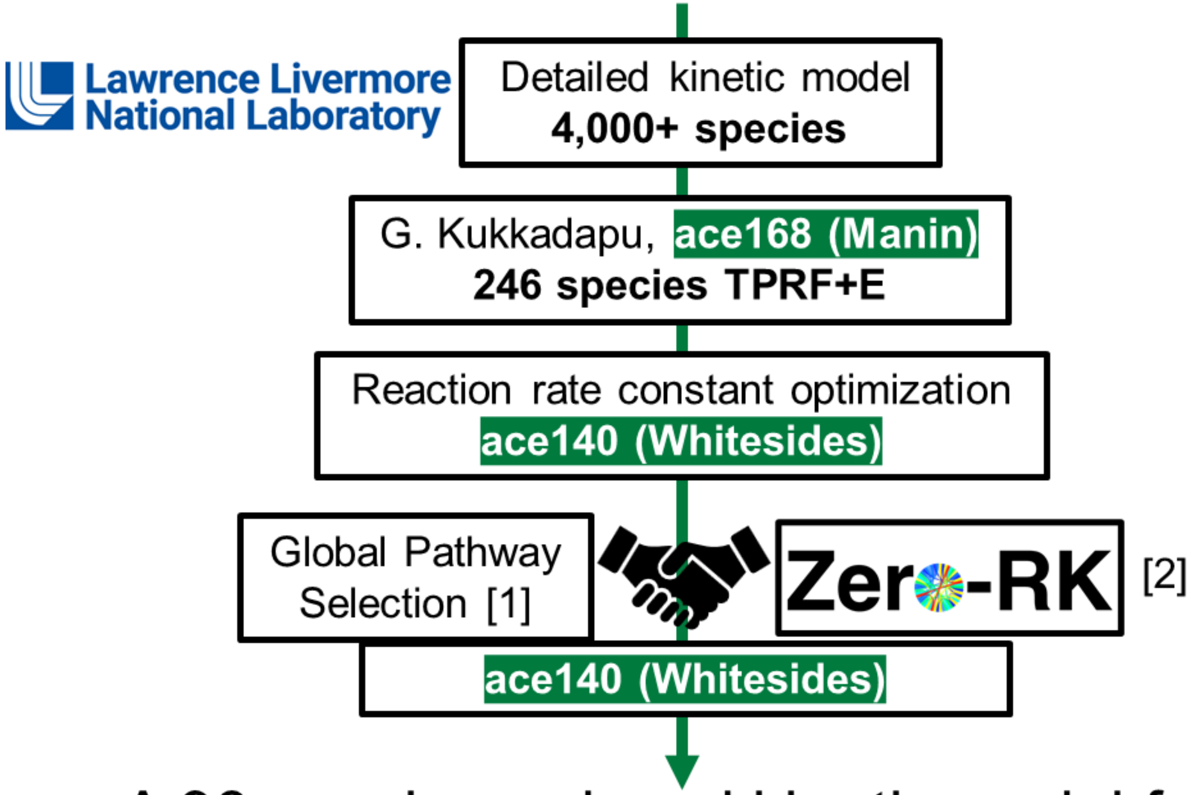
Impact: A robust, accurate, and computationally cheaper kinetic model is available for use in engine simulations.

See also ace142 (Scarcelli), ace145 (Edwards), ace146 (Ameen), ace167 (Torelli)

[1] Gao et al. Combust. Flame 167 (2016) 238-247 http://dx.doi.org/10.1016/j.combustflame.2016.02.007

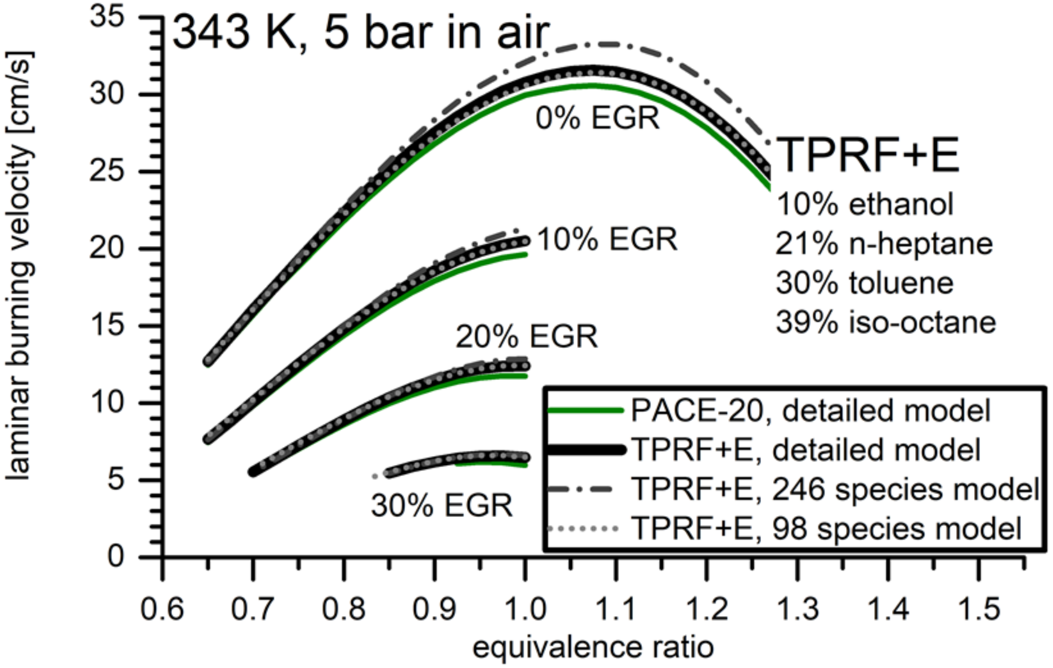
[2] M. McNenly, R. Whitesides, S. Lapointe et al. https://github.com/LLNL/zero-rk

Two TPRF+E10 reduced kinetic models are available for direct numerical simulations



A 98 species reduced kinetic model for TPRF+E10

Verified for
- ✓ autoignition, ace140 (Whitesides)
- ✓ polycyclic aromatic hydrocarbons, ace168 (Manin)
- ✓ laminar burning velocities



<u>Impact</u>: Computationally demanding simulations can use a simpler surrogate fuel, and therefore a smaller kinetic model, to study flame kernel development and near wall interactions.
See also **ace140 (Whitesides)**, **ace141 (Ekoto)**, **ace142 (Scarcelli)**, **ace143 (Powell)**, **ace146 (Ameen)**, **ace168 (Manin)**

[1] Gao et al. Combust. Flame 167 (2016) 238-247 http://dx.doi.org/10.1016/j.combustflame.2016.02.007
[2] M. McNenly, R. Whitesides, S. Lapointe et al. https://github.com/LLNL/zero-rk

Lean autoignition timing and heat release of RD5-87 is well reproduced by PACE-20

Argonne NATIONAL LABORATORY

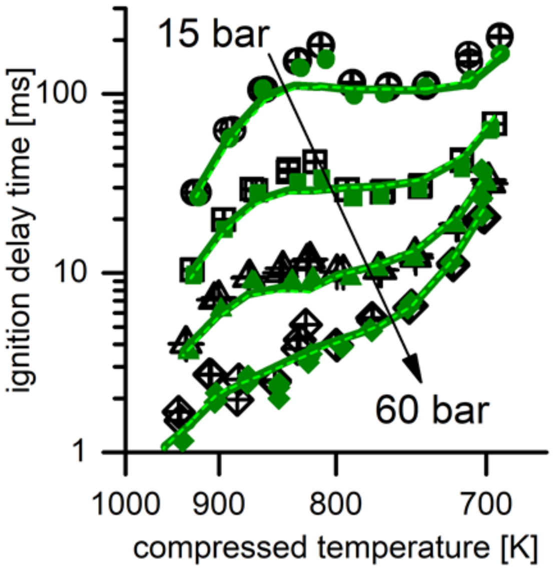
Lawrence Livermore National Laboratory

$\Phi = 0.4$, 21% O_2

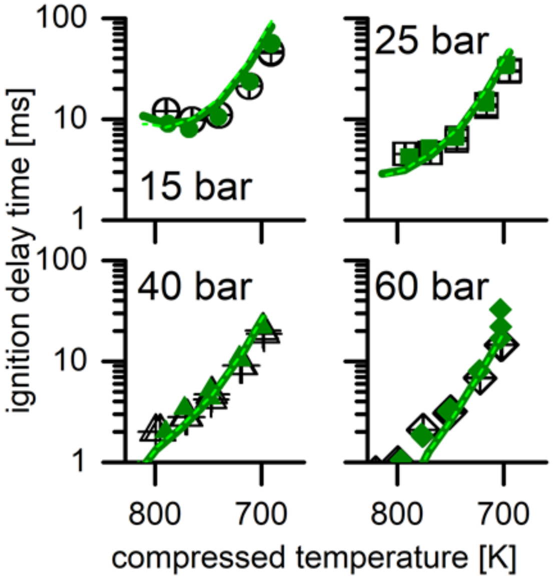
open symbols = RD5-87, measurement
closed symbols = PACE-20, measurement

solid line = PACE-20, detailed kinetic model
dashed line = PACE-20, 315 species kinetic model

overall ignition timing



1st stage ignition timing



Characterization of stoichiometric dilute autoignition relevant to engine operation with exhaust gas recirculation underway in ANL rapid compression machine

The experiments are coordinated with an upcoming Szybist engine study in task O.E.02, see also **ace147 (Splitter)**

Additional measurements taken in the ANL rapid compression machine of PRF88.4, PACE-1, PACE-8 surrogate fuels (not shown)

Pressure histories were analyzed for all experiments to characterize heat release rates (not shown)

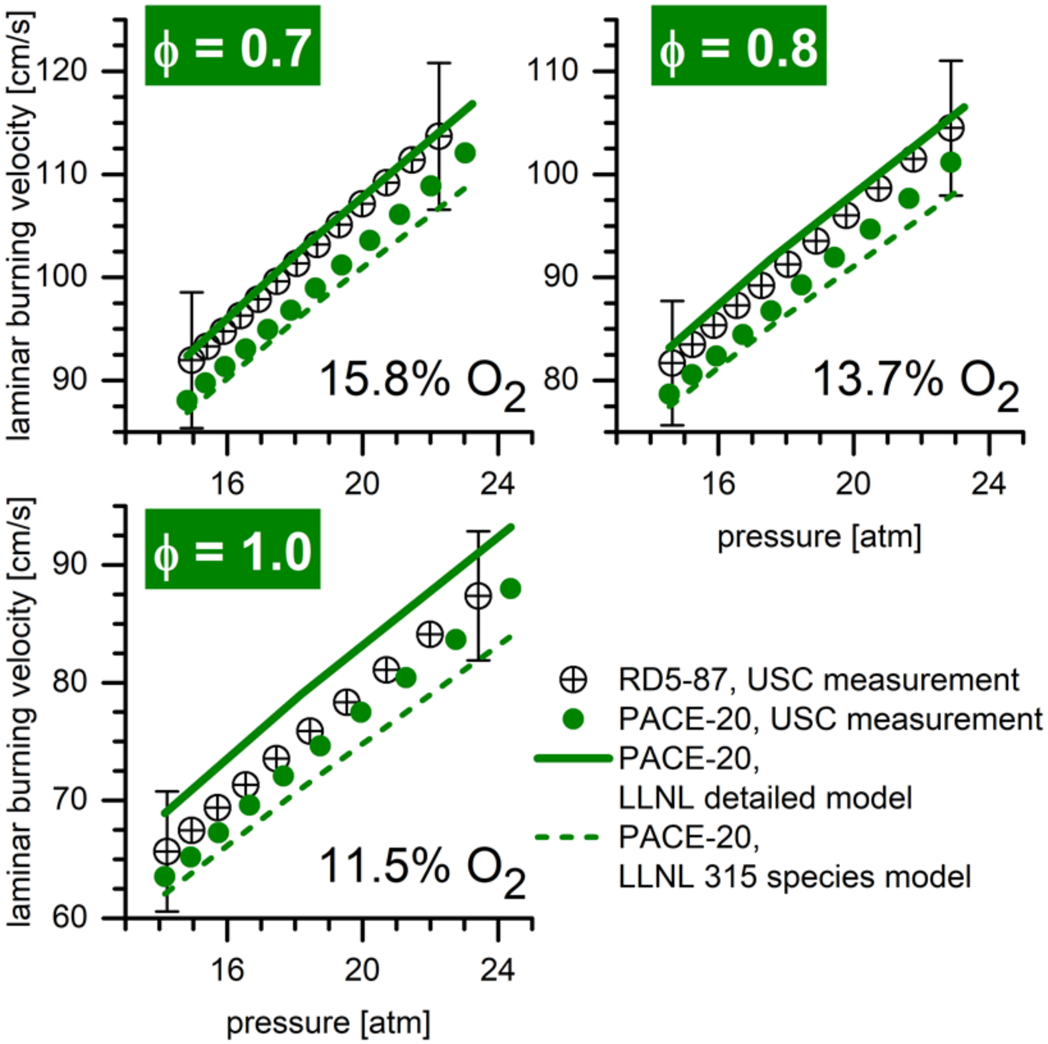
Impact: Surrogate fuels, such as PACE-20, are better characterized and kinetic models can be validated for lean autoignition timing and heat release.

Elevated temperature & pressure burning velocities of surrogate fuels match RD5-87 well

Anguo Hu, Ashkan Movaghar, Robert Lawson, and Prof. F. Egolfopoulos under subcontract to LLNL (Pitz)

- Laminar burning velocities of RD5-87 and two surrogate fuels were measured in premixed counterflow (not shown) and constant volume chamber configurations
- Both surrogate fuels, PACE-1* (not shown) and PACE-20, were found to acceptably match the laminar burning velocities of RD5-87
- Simulations of PACE-20 with the LLNL detailed kinetic model show largely acceptable agreement to the data, but are typically faster than the measurements

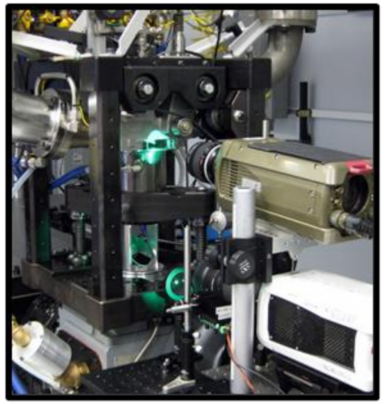
*PACE-1 w/ 2.5% liq.vol. tetralin

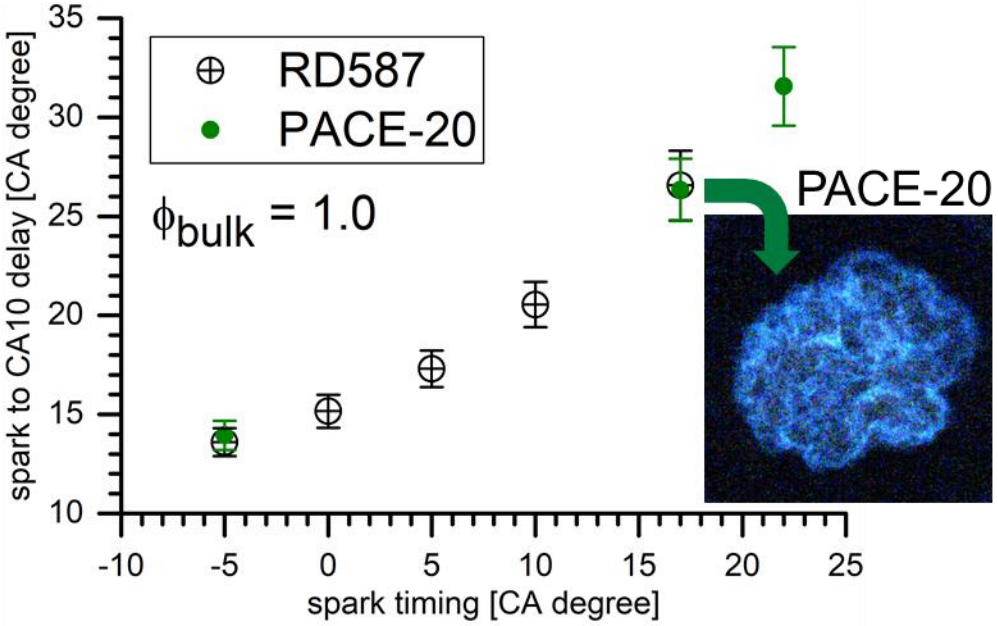


Impact: See next slide.

Experimental burning velocities of PACE-20 surrogate fuel matches RD5-87 well in an engine

Sandia National Laboratories





Is good agreement of laminar burning velocities in fundamental measurements indicative of good agreement in a turbulent engine environment for RD5-87 and a surrogate fuel?

CA10 = crank angle at 10% burn duration

- Sandia engine operated with $T_{coolant}$ = 20°C, focusing on the first fired cycle in a simulated cold-start Fire1-Skip4 scheme
- The PACE-20 surrogate fuel reproduces spark to CA10 delay of RD5-87 well under cold-start conditions
  - 200-cycle average falls within ±1 standard deviation (not shown)
  - Pressure traces are nearly indistinguishable (not shown)
- PACE-20 data transferred to Argonne for cold-start ignition modeling validation, see also **ace142 (Scarcelli)**

<u>Impact</u>: PACE-20 is an acceptable surrogate fuel for analysis and modeling of complex E10 gasoline flame kernel development, propagation.

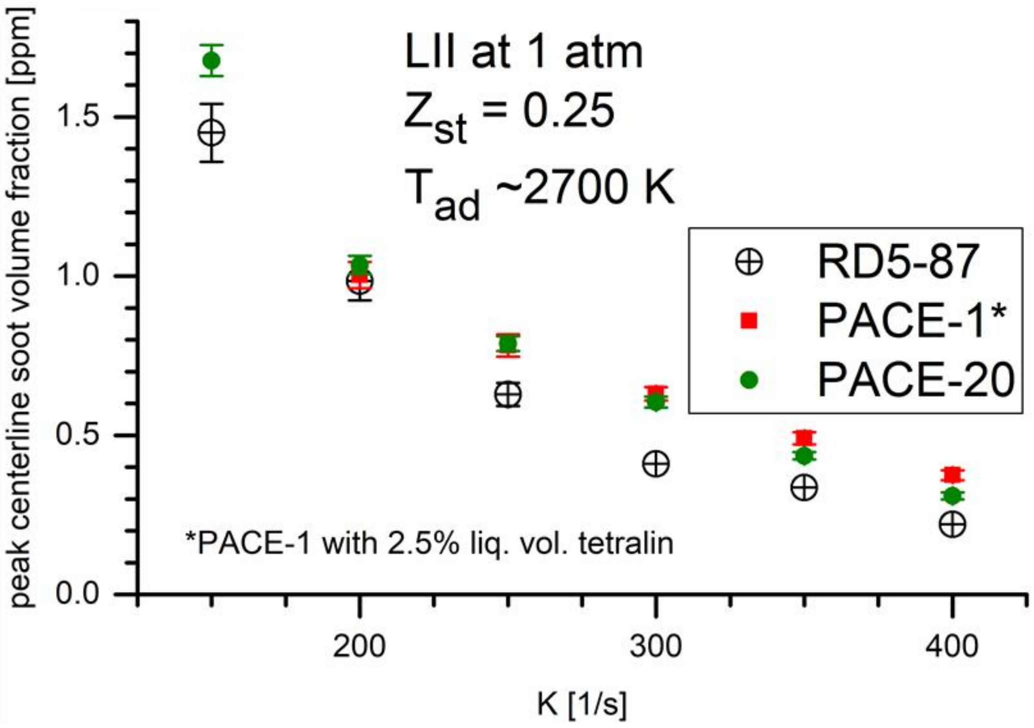
PACE-20 surrogate fuel reproduces well smoke point and soot volume fraction measurements of RD5-87

UCONN
UNIVERSITY OF CONNECTICUT
Lawrence Livermore National Laboratory

Ruozhou Fang and Prof. C.J. Sung under subcontract to LLNL (Pitz)

ASTM D1322 smoke point measurements
Lower values indicate a higher smoke producing tendency

Soot volume fraction measurements in non-premixed counterflow flames via laser-induced incandescence (LII) calibrated by light extinction (not shown)



Additional studies planned including planar laser-induced fluorescence (PLIF) of OH, particle imaging velocimetry (PIV)

Z_{st} = Stoichiometric mixture fraction
T_{ad} = Adiabatic flame temperature

Impact: Increased confidence that PACE-20 is well suited for analysis and simulations of engine-out emissions. See also **ace140 (Whitesides)**, **ace168 (Manin)**

Response to previous year reviewers' comments

"The reviewer called this a fantastic approach and really liked the quick organization of a surrogate working group to develop a common fuel for PACE."

"This is a solid approach to a central element bridging the experimental measurements and simulations that are a key output of the program."

ID #	PI	Approach	Technical Accomplishments	Collaborations	Future Research	Weighted Average	Relevant to DOE objectives	Sufficiency of Resources
ace139	Wagnon	3.70	3.60	3.80	3.30	3.61	100% Yes	80% Sufficient 20% Excessive

Reviewer 2: "… there should be a declining need for a similar effort moving forward."
Reviewer 4: "… question the extent of the validation effort."
Reviewer 5: "… take issue with the idea that behaviors are 'well validated,'…"

Response FY20 focused on an initial definition of a surrogate fuel and early characterization efforts. Some properties of the surrogate fuel, such as MON, were modified for FY21 based on FY20 results. Additional surrogate fuel characterization studies are presented in several FY21 talks. This characterization effort may continue as needed if the major outcomes of PACE are potentially negatively impacted.

Reviewer 3: "… continue to pursue changes to get better soot match…"
Reviewer 4: "… additional experiments should be conducted for model validation, such as flame speed and ignition delay (ID)…"

Response We agree and subcontracts were specifically established with the University of Connecticut and the University of Southern California to fill gaps in fundamental soot and flame measurements. Additional measurements of ignition delay times continue to be carried out in the Argonne National Laboratory rapid compression machine.

Collaboration and coordination with other institutions

PACE is a collaborative project of multiple National Laboratories that combines unique experiments with world-class DOE computing and machine learning expertise to speed discovery of knowledge, improve engine design tools, and enable market-competitive powertrain solutions with potential for best-in-class lifecycle emissions.

Four national laboratories in PACE

Goldsborough, Scarcelli (ANL); Kukkadapu, Lapointe, McNenly, Pitz, Wagnon, Whitesides (LLNL); Edwards, Szybist (ORNL); Chen, Ekoto, Hansen, Manin, Nguyen, Pickett, Sjoberg (SNL)

University collaborators

King Abdullah University of Science and Technology -> Experiments; calculations
National University of Ireland – Galway -> Experiments; modeling; calculations

Two university subcontracts by LLNL

University of Connecticut -> Soot volume fraction and smoke point measurements of RD5-87, surrogate fuels
University of Southern California -> Laminar burning velocity measurements of RD5-87, surrogate fuels

Industry

Advanced Engine Working Group
Coordinating Research Council
General Motors
Computational Chemistry Consortium

Coordination

Monthly team meetings
Quarterly leadership planning meetings
Annual all-hands meeting

Remaining challenges and barriers

We don’t know how sensitive the major outcomes are to the surrogate fuel and kinetic model

More experimental data for analysis and kinetic model validation are needed

More analytical techniques and modeling tools are needed that lead to robust and accurate chemistry

Small kinetic models are needed that lack numerical stiffness and are accurate

*Note: PACE-wide barriers discussed in ace138 (McNenly)

Proposed future research*

Surrogate fuel: Work across the consortium teams to characterize RD5-87 and the surrogate fuel, PACE-20, and improve the surrogate fuel if necessary.

Measure autoignition, burning velocities, heat release, and stable species of binary and multi-component mixtures including ethanol and EGR constituents in the ANL rapid compression machine, other fundamental devices, and engines.

Use this experimental data to improve the predicted behavior of binary and multicomponent blends in the chemical kinetic model. Validate/improve gasoline surrogate model behavior under dilute conditions (EGR). Improve NOx submodel including NO interaction reactions with gasoline surrogate components. Validate/improve the kinetic model for cold-start emissions (hydrocarbons, NOx, PAH/soot).

Use new analytical and computational approaches to rapidly establish and implement more accurate models of the important surrogate fuel chemistry. Perform quantum chemistry calculations of rate constants for new gasoline/ethanol interacting reactions. Apply machine learning algorithms to check and estimate kinetic model parameters such as rate constants, thermodynamic properties, and transport properties.

Work with the LLNL numerics team to quickly reduce kinetic models to deliver to PACE members and industry. Develop smaller reduced kinetic models while retaining accuracy.

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

Summary

Relevance Quickly turn fundamental science into engineering models that enhance engine design workflows.

Approach Collaborate to rapidly develop and improve gasoline surrogate fuels and practical kinetic models based on experimental data from the ANL rapid compression machine, engines, and other devices.

Technical Accomplishments and Progress

- Multiple PIs/tasks contributed to defining an improved shared surrogate fuel, PACE-20, as well as characterization tests. PACE-20 is recommended for all tasks and major outcomes.
- Reduced kinetic models for PACE-20 and TPRF+E10 suitable for engine simulations are available. Released improved detailed gasoline surrogate model to consortium members.
- New measurements of autoignition timing, laminar burning velocities, and soot for surrogate fuels and complex RD5-87.

Collaborations and Coordination with Other Institutions

More than 15 partners across industry, academia, and national laboratories.

Proposed Future Research*

- Rapidly refine the PACE gasoline surrogate fuel to meet the needs of remaining major outcomes.
- Acquire novel measurements in the ANL rapid compression machine and engine platforms.
- Improve the detailed kinetic model to simulate lean-dilute (EGR) combustion, cold-start emissions.
- Develop, improve, and deliver “right-sized” reduced kinetic models that capture autoignition, flame development, and emissions species for use in PACE and industry.

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

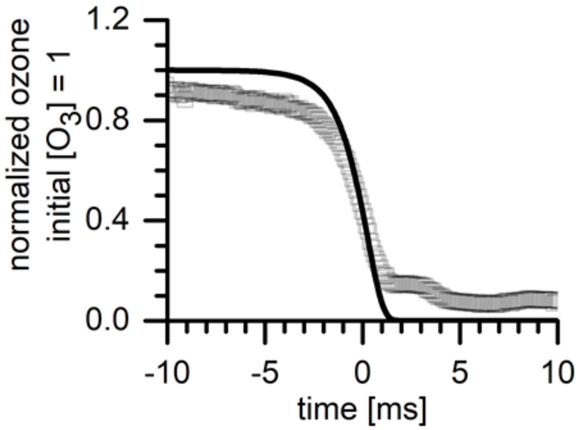
Technical Back-up Slides

A kinetic model for ozone and surrogate fuels is available for simulations of plasma assisted ignition

Orleans rapid compression machine measurements

500 ppm iso-octane
in air, 21% O_2
ozone = 90 ppm

symbols = Orleans measurements
lines = LLNL kinetic model



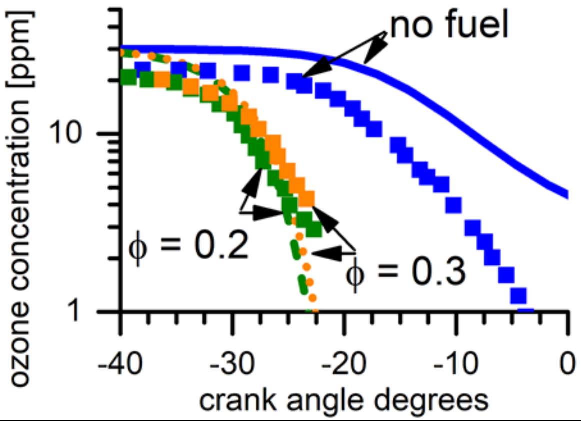
SNL single cylinder engine measurements (Ekoto)

N. Seignour, I. Ekoto, I., F. Foucher, B. Moreau SAE Technical Paper 2019 No. 2019-01-2254 https://doi.org/10.4271/2019-01-2254

Sandia National Laboratories

fuel = iso-octane
ozone = 30 ppm

symbols = SNL measurements
lines = LLNL kinetic model



Ozone can significantly promote ignition for lean-dilute mixtures and is generated by low temperature plasma discharge ignition systems, see also **ace141 (Ekoto)**

Important ozone chemistry was identified after a review of several literature models [1-6] and incorporated into the LLNL kinetic model (not all reactions shown)

$$O_3(+M)=O_2+O(+M)\ [1]$$

$$O_3+C_2H_4=\text{products}\ [2]$$

The kinetic model was validated against speciation from rapid compression machines, flow reactors, and jet stirred reactors for small hydrocarbons, neat surrogate fuel components, and the third-body effects of CO_2 and H_2O (not shown)

Previous SNL engine measurements of ozone were simulated using the homogenous charge compression ignition module of CHEMKIN with the Woschni correlation for wall heat transfer

[1] Y. Song & F. Foucher Fuel 276 (2020) 118009
[2] A. C. Rousso et al. J.Phys.Chem. A 122 (2018) 8674-8685
[3] T. Ombrello et al. Combust. Flame 157 (2010) 1906-1915
[4] J.-B. Masurier et al. Proc. Combust. Inst. 35 (2015) 3125-3132
[5] H. Zhao et al. Combust. Flame. 173 (2016) 187-194
[6] W. Sun et al. Prog. Energy Combust. Sci. 73 (2019) 1-25

Impact: Simulations of advanced ignition systems using surrogate fuels are more accurate, incorporating an ozone and fuel interaction model to capture ignition promotion of lean-dilute mixtures.

Improved kinetic model captures formation of polycyclic aromatic hydrocarbons (PAH) from TPRF surrogate fuels

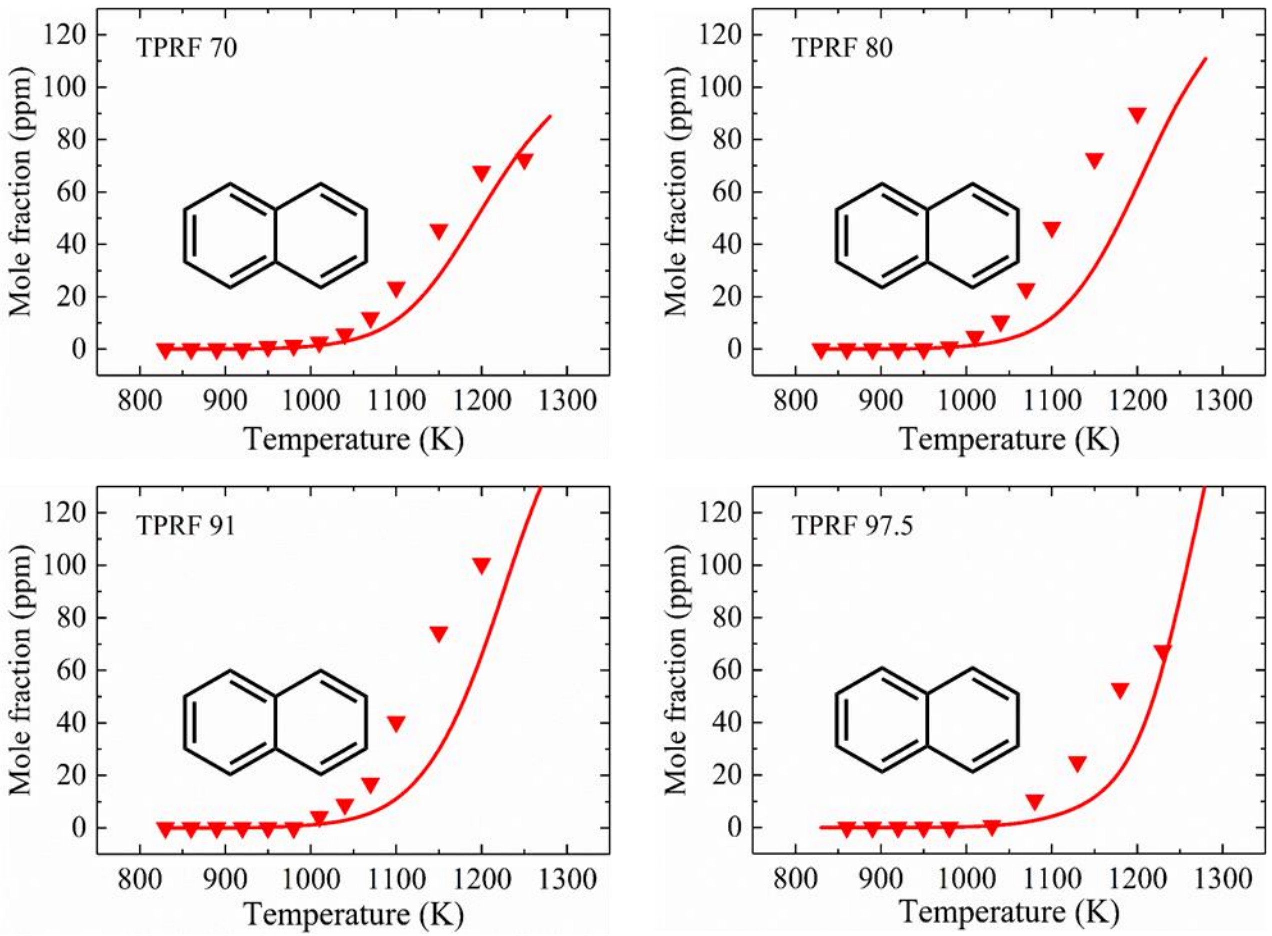
Lawrence Livermore National Laboratory

Jet stirred reactor pyrolysis measurements from C. Shao et al. Combust. Flame 219 (2020) 312-326
https://doi.org/10.1016/j.combustflame.2020.06.001

	n-heptane [mol.frac.]	toluene [mol.frac.]	iso-octane [mol.frac.]	RON
TPRF70	0.35	0.29.	0.37	70
TPRF80	0.27	0.40	0.33	80
TPRF91	0.17	0.54	0.29	91
TPRF97.5	0.15	0.78	0.08	97.5

Measurements of naphthalene, and additional soot precursors (not shown), are well captured by the kinetic model

Additional efforts to improve kinetic models for PAH formation from PACE-20 components trimethylbenzene and tetralin are shown in **ace168 (Manin)**



symbols = KAUST measurements lines = LLNL kinetic model

Impact: Kinetic models for common components in surrogate fuels, like PACE-20, are well validated for formation of soot precursors.

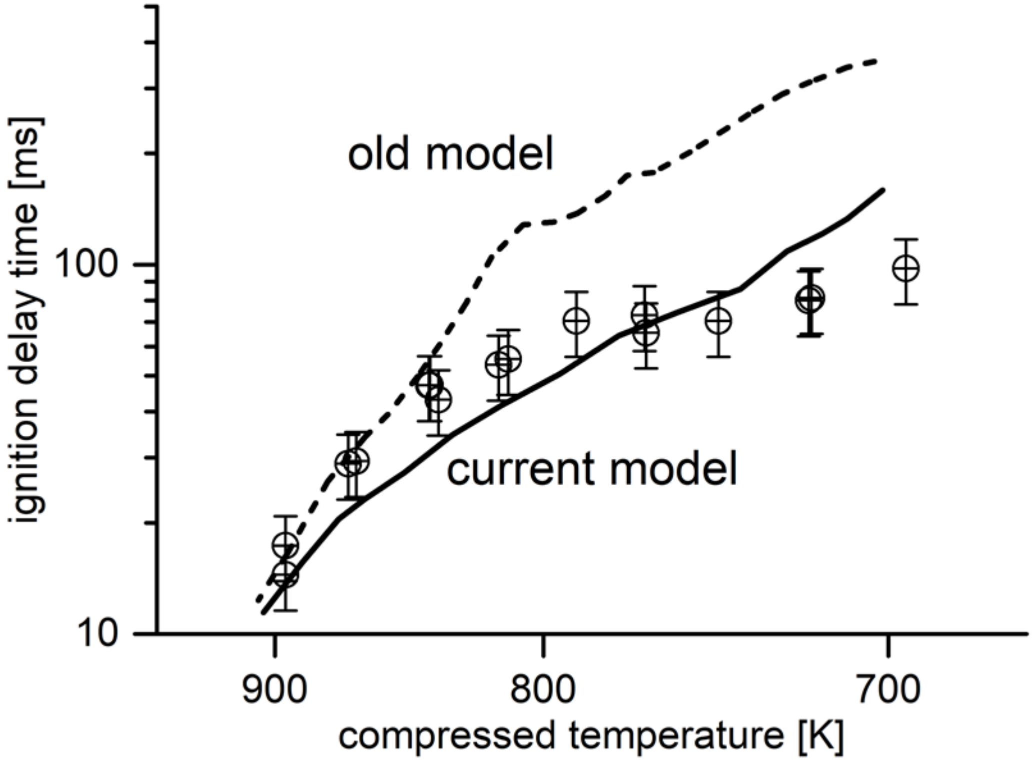
Improved kinetic model for trimethylbenzene ignition

Lawrence Livermore National Laboratory

Measurements of ignition delay times in the National University Ireland Galway rapid compression machine

neat 1,2,4-trimethylbenzene,
a component of the surrogate fuel PACE-20
Φ = 1
T = 650-900 K
P = 30 bar
O_2 = 21%

Two-stage ignition was recorded, which is indicative of low temperature chemistry **not previously reported in literature**, and is better captured by the current model



Additional kinetic model improvements for 1,2,4-trimethylbenzene focused on pyrolysis and polycyclic aromatic hydrocarbon formation are presented in **ace168 (Manin)**

Impact: Ignition and combustion of surrogate fuels that include significant levels of 1,2,4-trimethylbenzene, like PACE-20, are more accurately simulated.