SAND2020-8186C

Correlating Ignition Properties with Critical Species Concentrations

Zachary Buras, Nils Hansen, Dario Lopez Pintor, Leonid Sheps and Craig Taatjes

Sandia National Laboratories

ACS Fall Meeting

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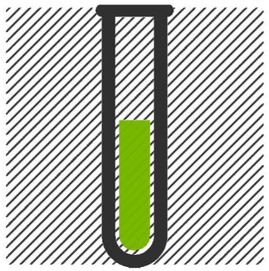
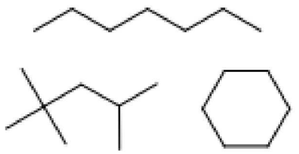
Vision for an Ideal Fuel Screening Platform

Realistic Candidate Fuel



Mix of 100's of Chemical Species

Alkanes



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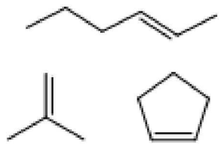
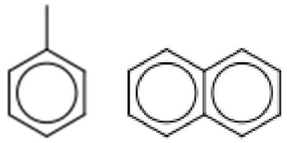
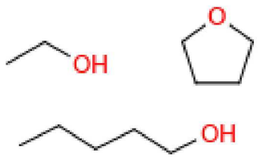


Aromatics



Oxygenates

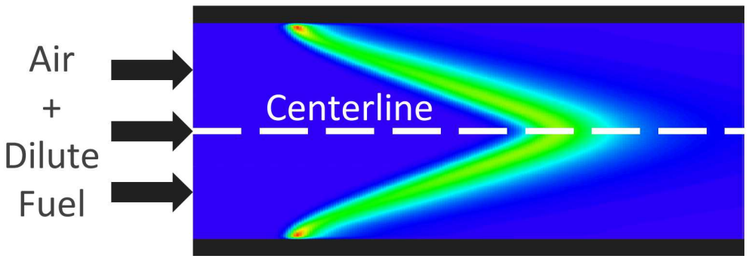


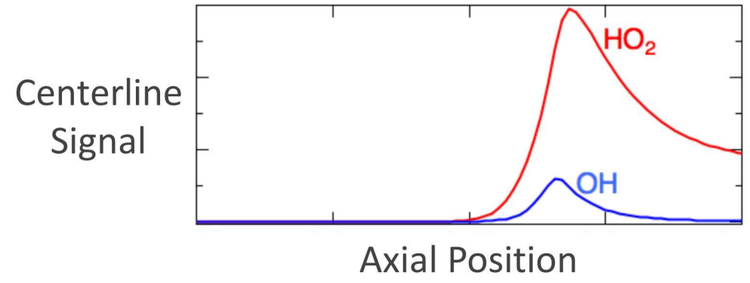
Ideal Screening Platform:

1. General ✓
2. Small Fuel Quantities ✓

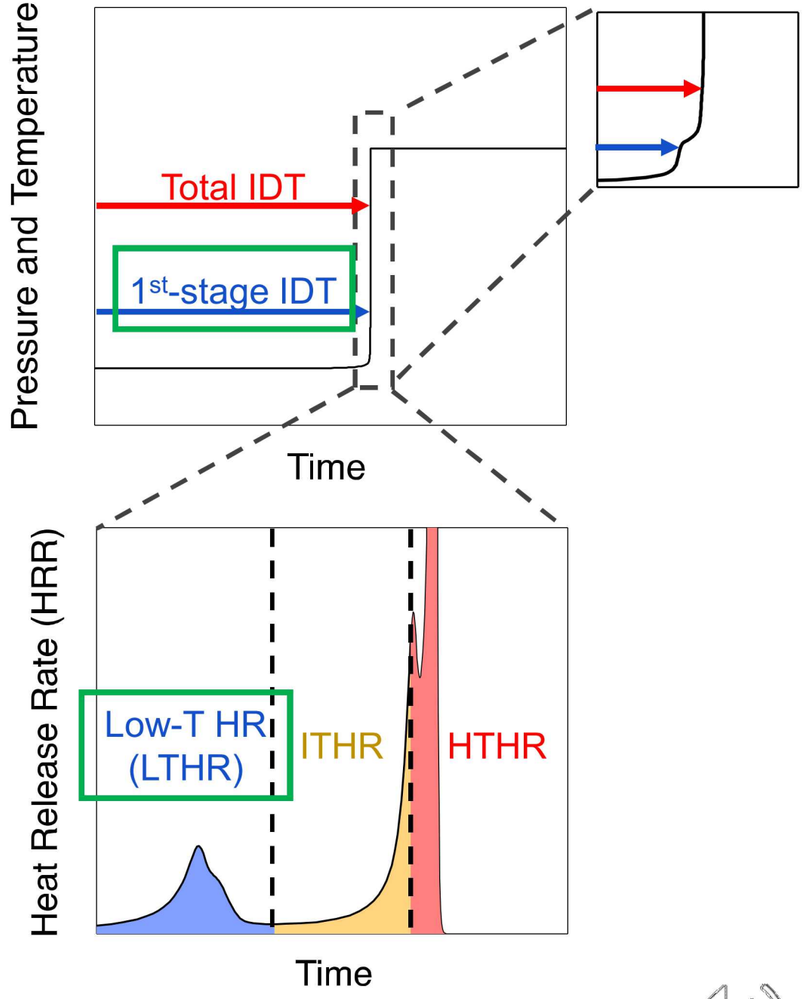
Our Idea:

Measure Universal Oxidation Species
(e.g., OH & HO_2)
in a High-P Flow Reactor





Ignition Properties



Z. Buras, C. Safta, J. Zádor, L. Sheps, Simulated production of OH, HO_2, CH_2O, and CO_2 during dilute fuel oxidation can predict 1st-stage ignition delays, Combust. Flame (2020)

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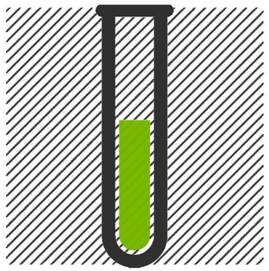

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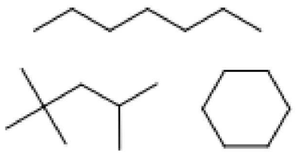

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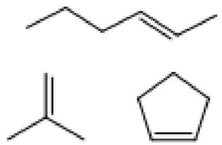

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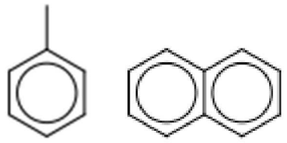

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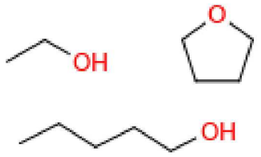

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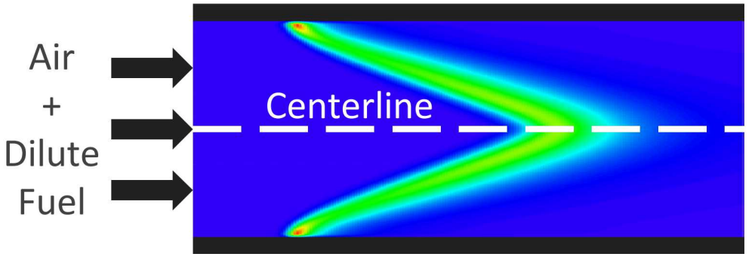
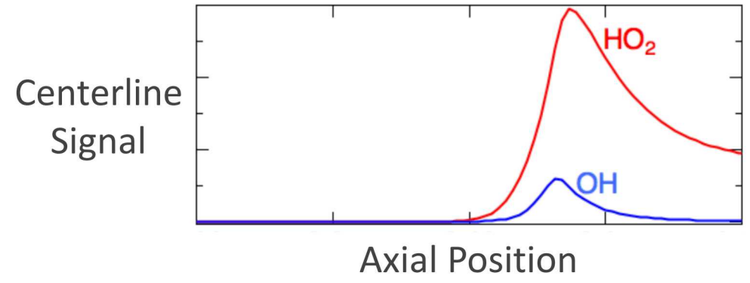
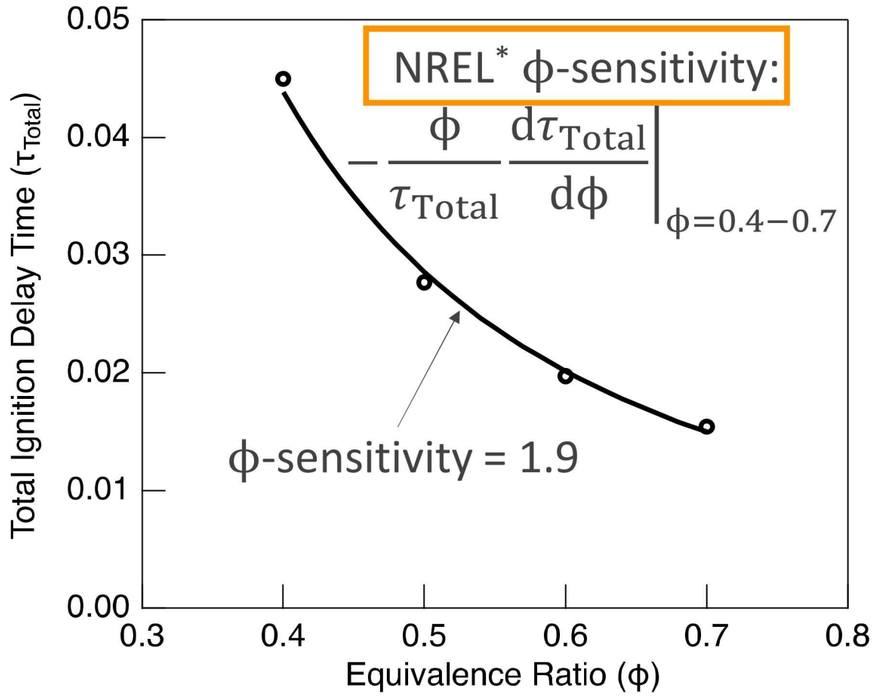




Ignition Properties



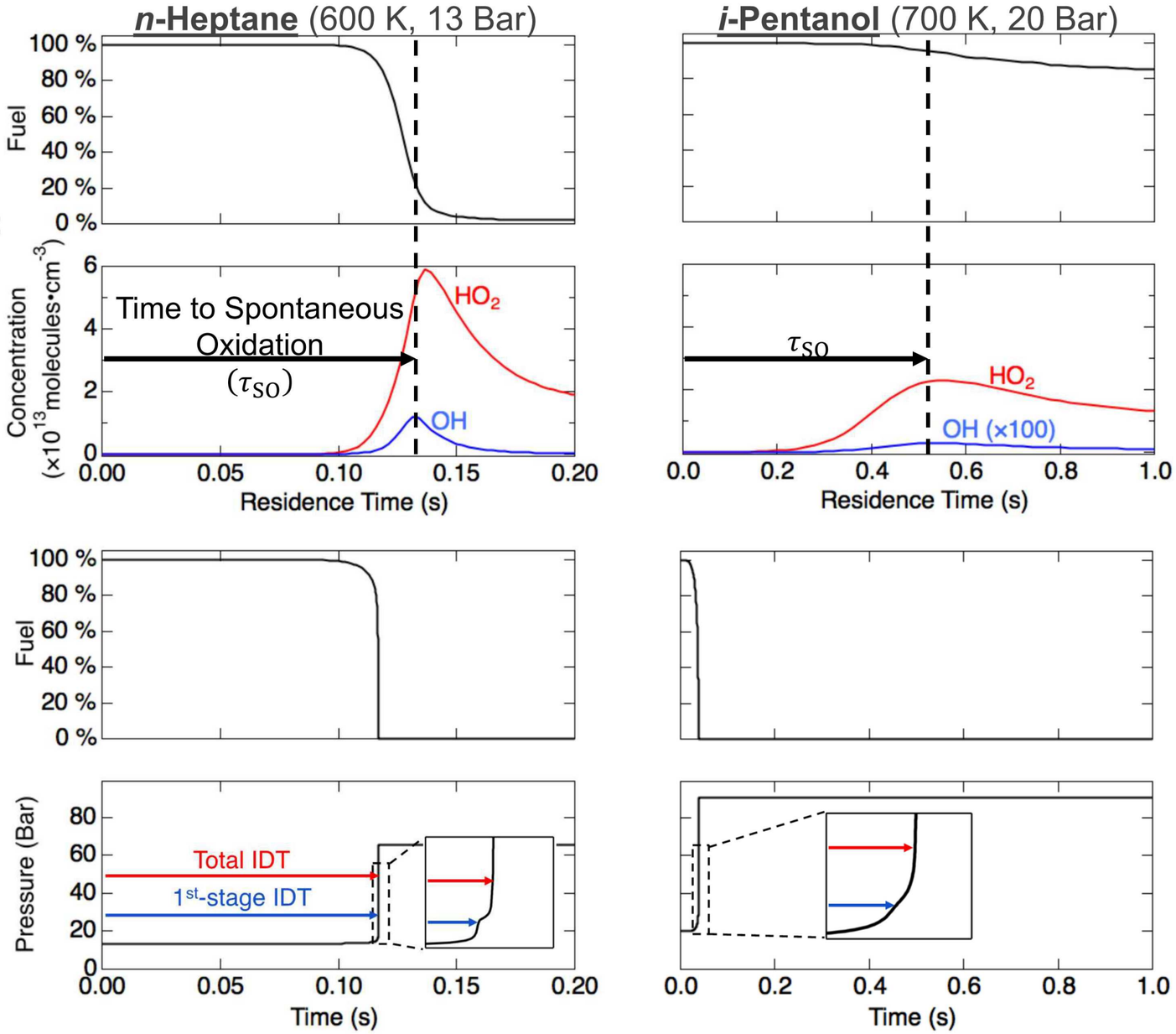
ϕ-sensitivity too complicated to be correlated with OH/HO_2 from dilute fuel measurements alone

*R. Messerly, et al., Towards quantitative prediction of ignition-delay-time sensitivity on fuel-to-air equivalence ratio, Combust. Flame (2020).

Simulations of Expected OH/HO_2 Profiles

Flow Reactor Simulations:
(~1 Torr of Fuel, $\phi \approx 0.001$)

Ignition Simulations:
($\Phi = 1.0$)



For *n*-heptane:

- $\tau_{SO} \approx 1^{st}$-Stage IDT
- Peak $[OH] \approx 10^{13}\ cm^{-3}$

For *i*-pentanol:

- $\tau_{SO} \gg 1^{st}$-Stage IDT
- Peak $[OH] \approx 10^{10}\ cm^{-3}$

Is this a general trend among all fuels?

- To answer, simulated ~14k perturbed mechanisms for a diversity of fuels from 600-700 K and 10-40 bar

Perturbing Mechanisms to Generate Dataset

”Real” Fuels with Validated Chemical Mechanisms

Class	Fuel
Alkanes	Pentane isomers
	n-Heptane
	i-Octane
	Cyclohexane
	Methylcyclohexane
Alkenes/Aromatics	Butene isomers
	Hexene isomers
	Butylbenzene
Oxygenates	1-Butanol
	i-Pentanol
	Dimethyl Ether (DME)
	Dimothoxy Methane (DMM)
	Tetrahydrofuran (THF)
	Methyl Decanoate
Blends	Binary/Ternary/Quaternary Blends of n-Heptane/i-Octane/Ethanol/Toluene

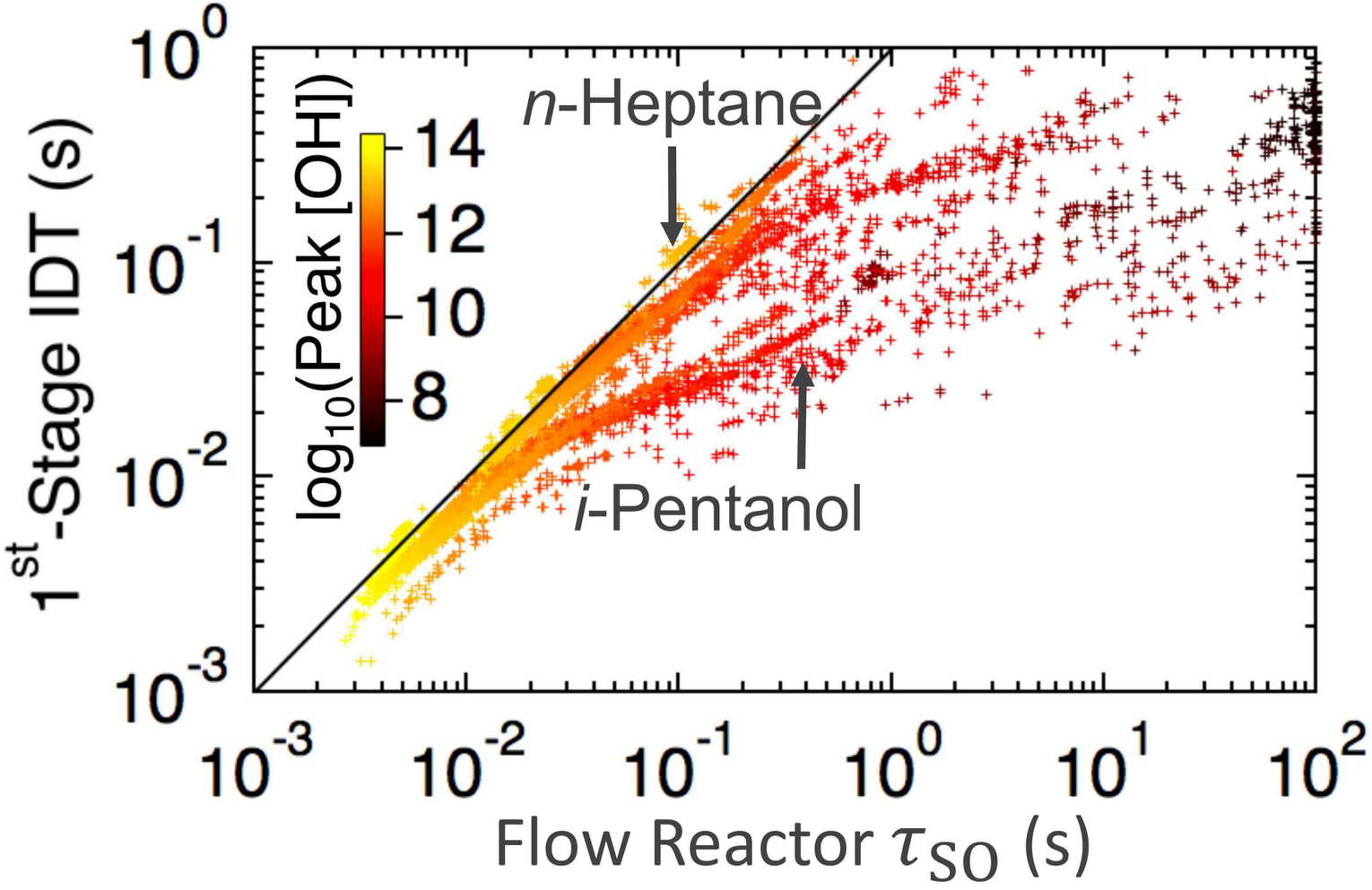
”Hypothetical” Fuels with Perturbed Chemical Mechanisms

1. Sensitive Reaction ch3och2o2<=>ch2och2o2h A-factor Multiplied by 0.5 ×
2. Sensitive Reaction ch3och2o2<=>ch2och2o2h A-factor Multiplied by 2.0 ×
3. Sensitive Reaction ho2ch2ocho<=>och2ocho+oh A-factor Multiplied by 0.5 ×
4. Sensitive Reaction ho2ch2ocho<=>och2ocho+oh A-factor Multiplied by 2.0 ×
5. Sensitive Reaction o2ch2och2o2h<=>ho2ch2ocho+oh A-factor Multiplied by 0.5 ×
6. Sensitive Reaction o2ch2och2o2h<=>ho2ch2ocho+oh A-factor Multiplied by 2.0 ×
7. Sensitive Reaction ho2+oh<=>h2o+o2 A-factor Multiplied by 0.5 ×
8. Sensitive Reaction ho2+oh<=>h2o+o2 A-factor Multiplied by 2.0 ×

~10 Validated Chemical Mechanisms → **~14,000** Hypothetical Fuel Mechanisms

Z. Buras, C. Safta, J. Zádor, L. Sheps, Simulated production of OH, HO_2, CH_2O, and CO_2 during dilute fuel oxidation can predict 1st-stage ignition delays, Combust. Flame (2020)

Qualitative Trend between τ_{SO} and 1st-Stage IDT



Why are some fuels affected by dilution (e.g., *i*-pentanol) and others are not (e.g., *n*-heptane)?

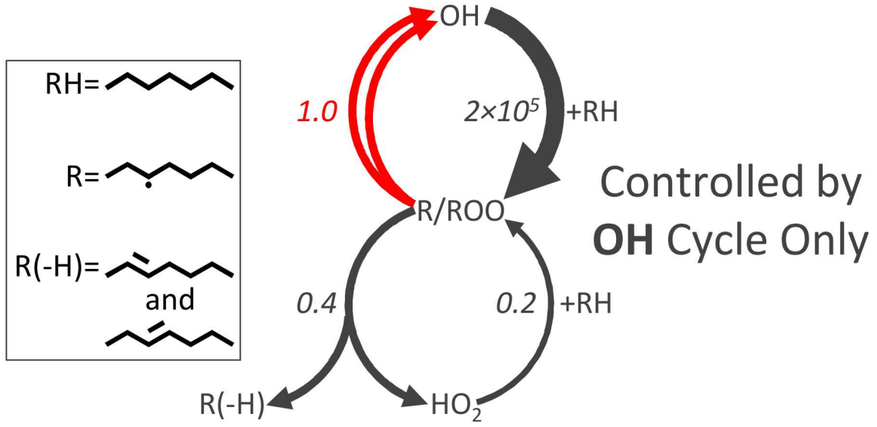
Z. Buras, C. Safta, J. Zádor, L. Sheps, Simulated production of OH, HO_2, CH_2O, and CO_2 during dilute fuel oxidation can predict 1st-stage ignition delays, Combust. Flame (2020)

Mechanistic Effect of Fuel Dilution

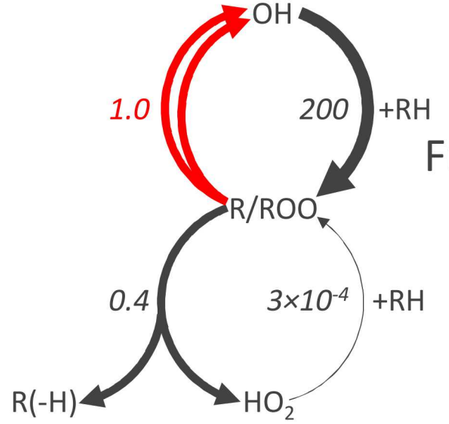
$\phi = 1.0$ in air:

$\phi \approx 0.001$
([Fuel] ≈ 1 Torr):

n-Heptane Autoignition

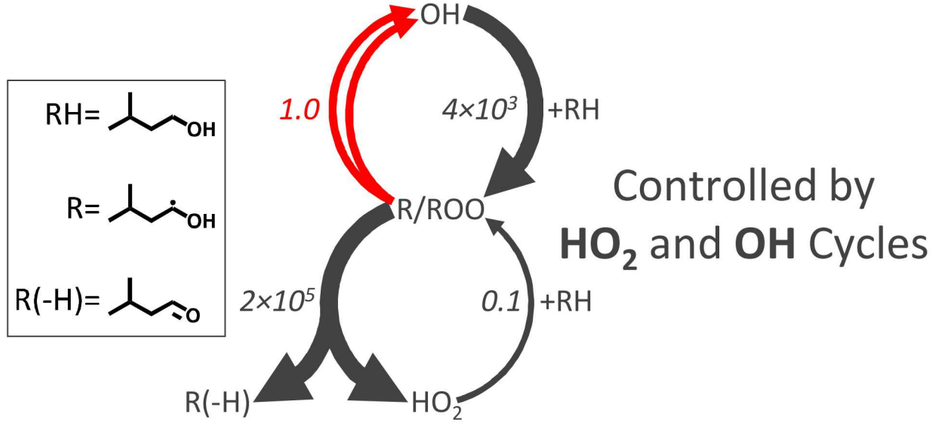


Controlled by **OH** Cycle Only

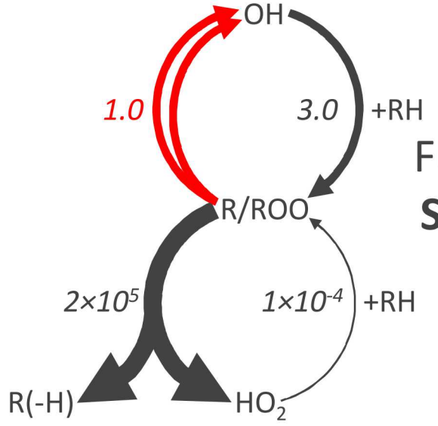


Fuel Dilution Has **No Effect** on Ignition Time

i-Pentanol Autoignition



Controlled by **HO_2** and **OH** Cycles

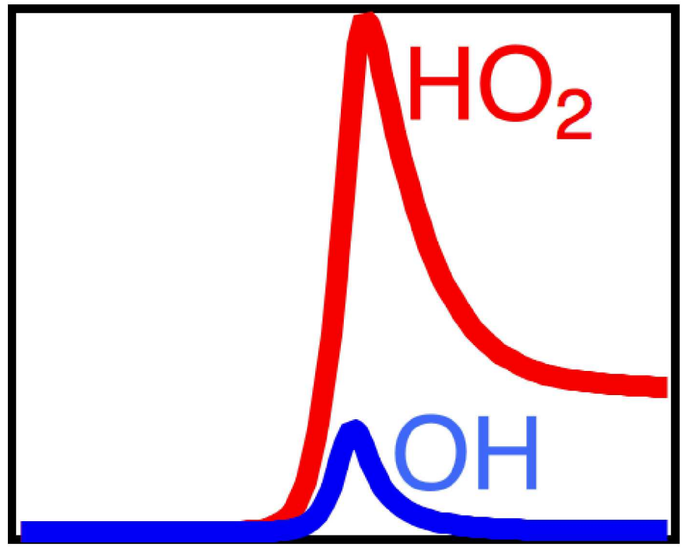


Fuel Dilution Has **Strong Effect** on Ignition Time

Z. Buras, C. Safta, J. Zádor, L. Sheps, Simulated production of OH, HO_2, CH_2O, and CO_2 during dilute fuel oxidation can predict 1st-stage ignition delays, Combust. Flame (2020)

Correlation from Polynomial Chaos Expansion (PCE) with Regularization

Inputs $(\underline{x})$



Flow Reactor Residence Time

$$\underline{x} = \begin{bmatrix} \tau_{SO} \\ \text{Max OH} \\ \text{Max } HO_2 \\ \text{Max OH Slope} \\ \text{Max } HO_2 \text{ Slope} \\ T \\ P \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \\ x_7 \end{bmatrix}$$

Fitting Function $\left(\underline{w} \cdot \underline{f}(\underline{x})\right)$

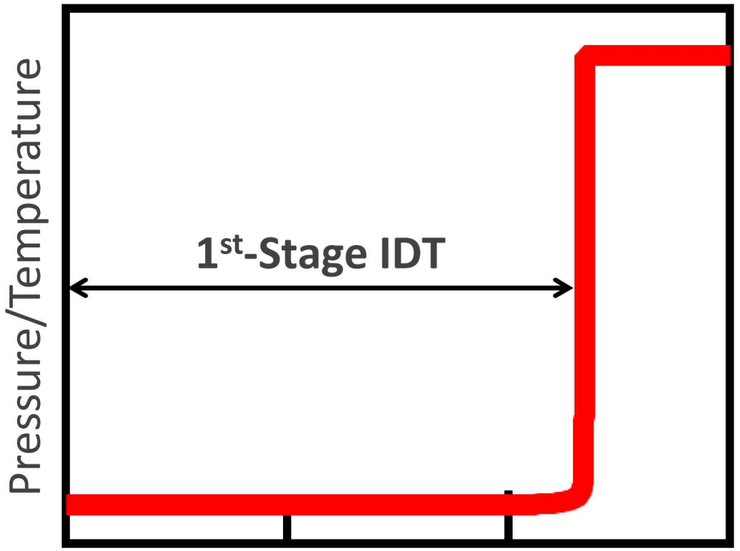
Fitting weights:

$$\underline{w} = \begin{bmatrix} w_1 \\ w_2 \\ w_3 \\ w_4 \\ w_5 \\ \dots \\ w_{35} \\ w_{36} \end{bmatrix}$$

Polynomial Order ≤ 2:

$$\underline{f}(\underline{x}) = \begin{bmatrix} 1 \\ x_1 \\ x_1^2 \\ x_1 x_2 \\ x_1 x_3 \\ \dots \\ x_6 x_7 \\ x_7^2 \end{bmatrix}$$

Target (y)



Objective Function (L)

$$L = \left|y - \underline{w} \cdot \underline{f}(\underline{x})\right| + \lambda \left|\underline{w}\right|_1$$

$y = 1^{st}$-Stage IDT
or
$y =$ LTHR
or
$y = \phi$-Sensitivity

Value that is minimized in order to fit a **parsimonious** function to data

Difference between polynomial fit and data

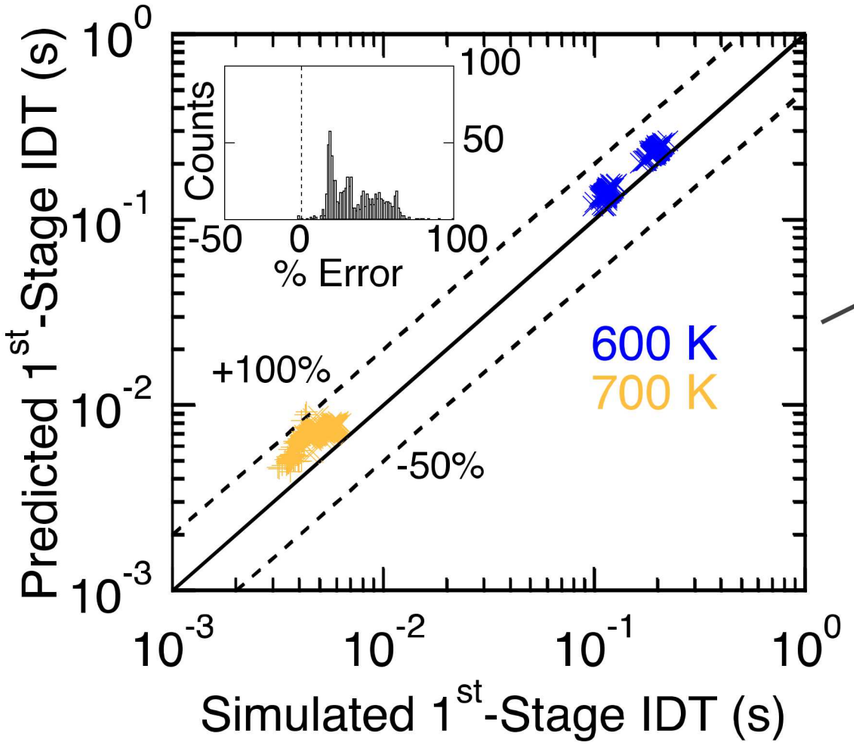
Regularization term to prevent overfitting (λ is adjustable parameter)

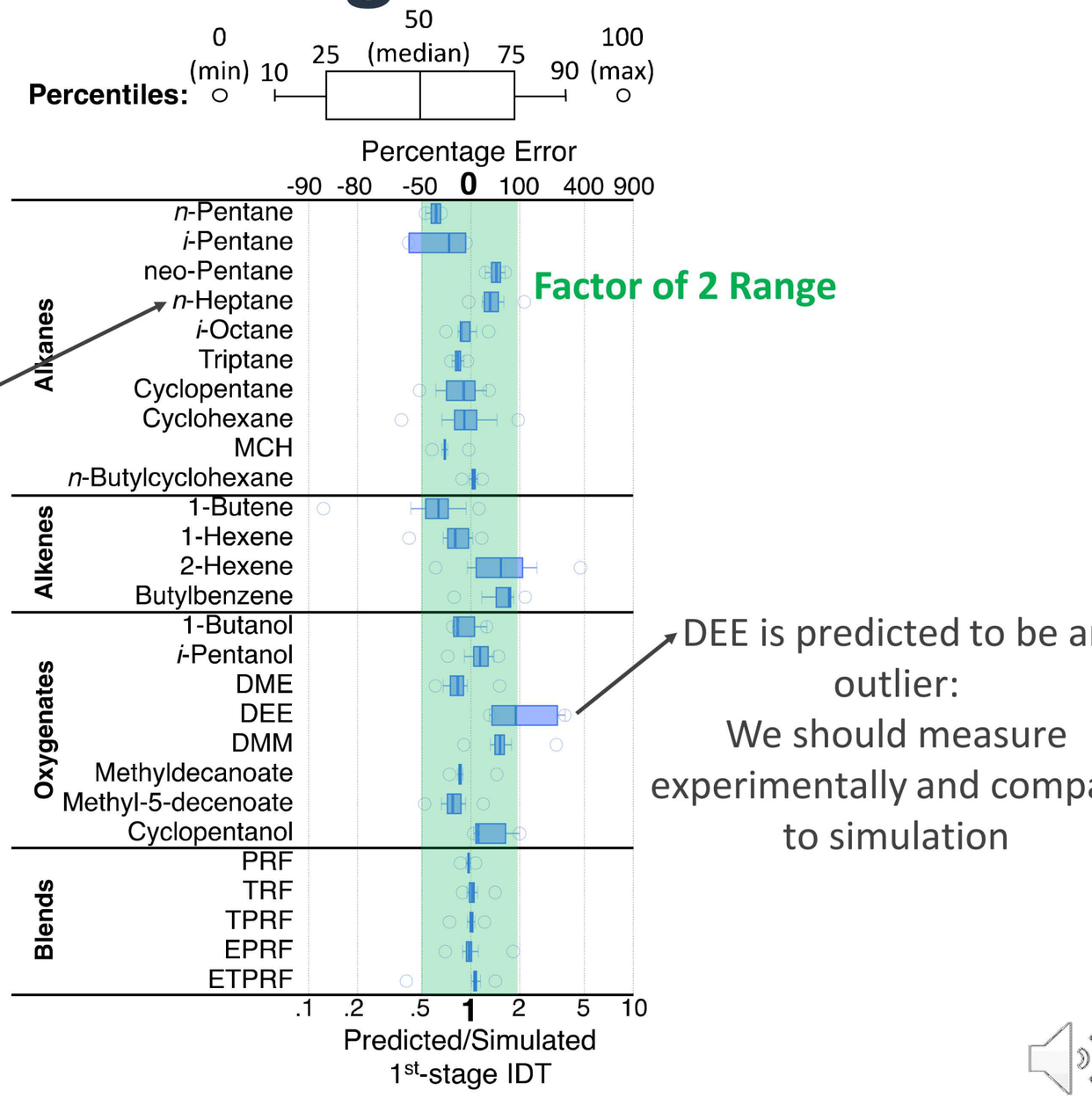
Leave-One-Fuel-Out Tests: 1st-Stage IDT

For Example:

Train on All ~13k Simulations Except *n*-Heptane

Test on ~1k *n*-Heptane Simulations





Factor of 2 Range

DEE is predicted to be an outlier:
We should measure experimentally and compare to simulation

Leave-One-Fuel-Out Tests: LTHR

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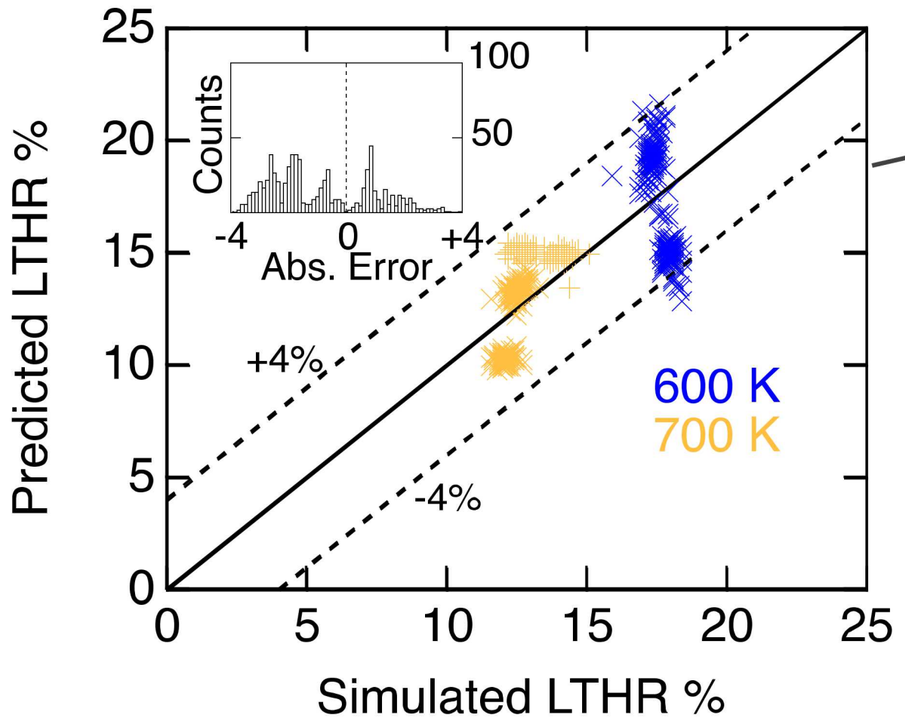
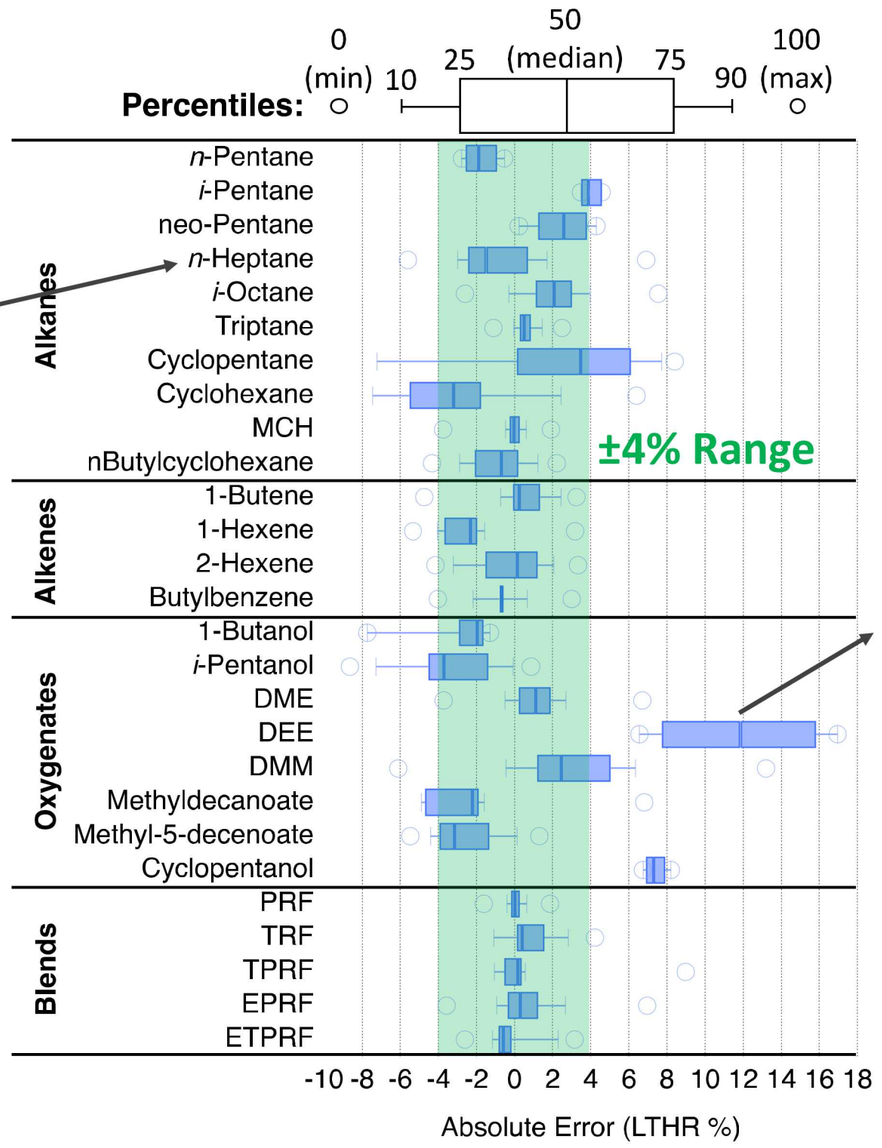
Test on ~1k *n*-Heptane Simulations:





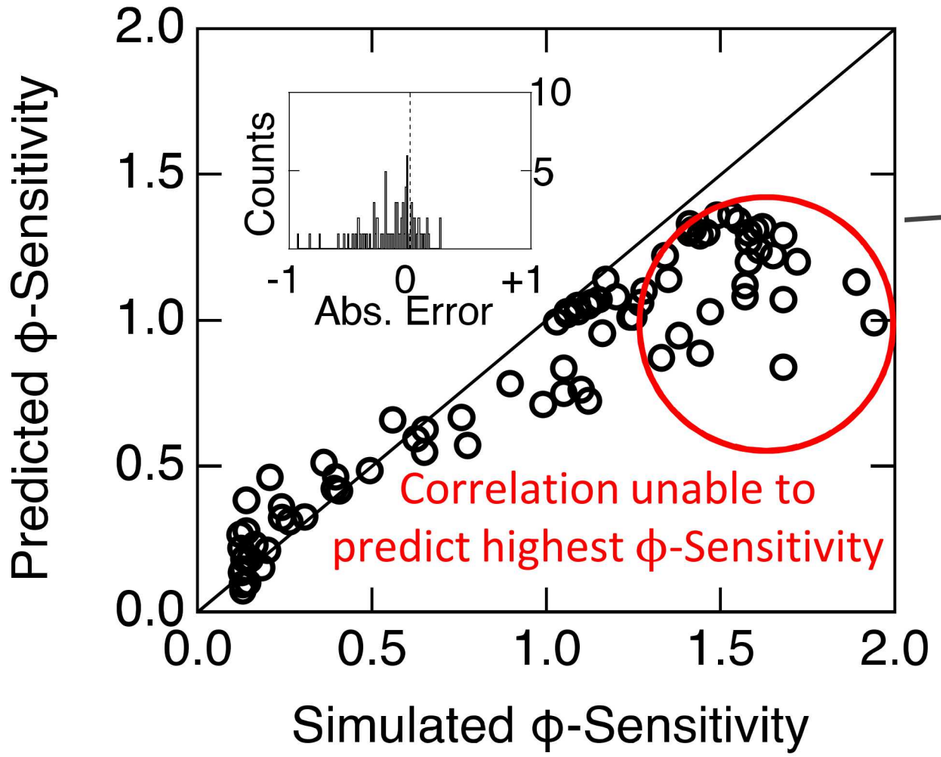
DEE is predicted to be an outlier:
We should measure experimentally and compare to simulation

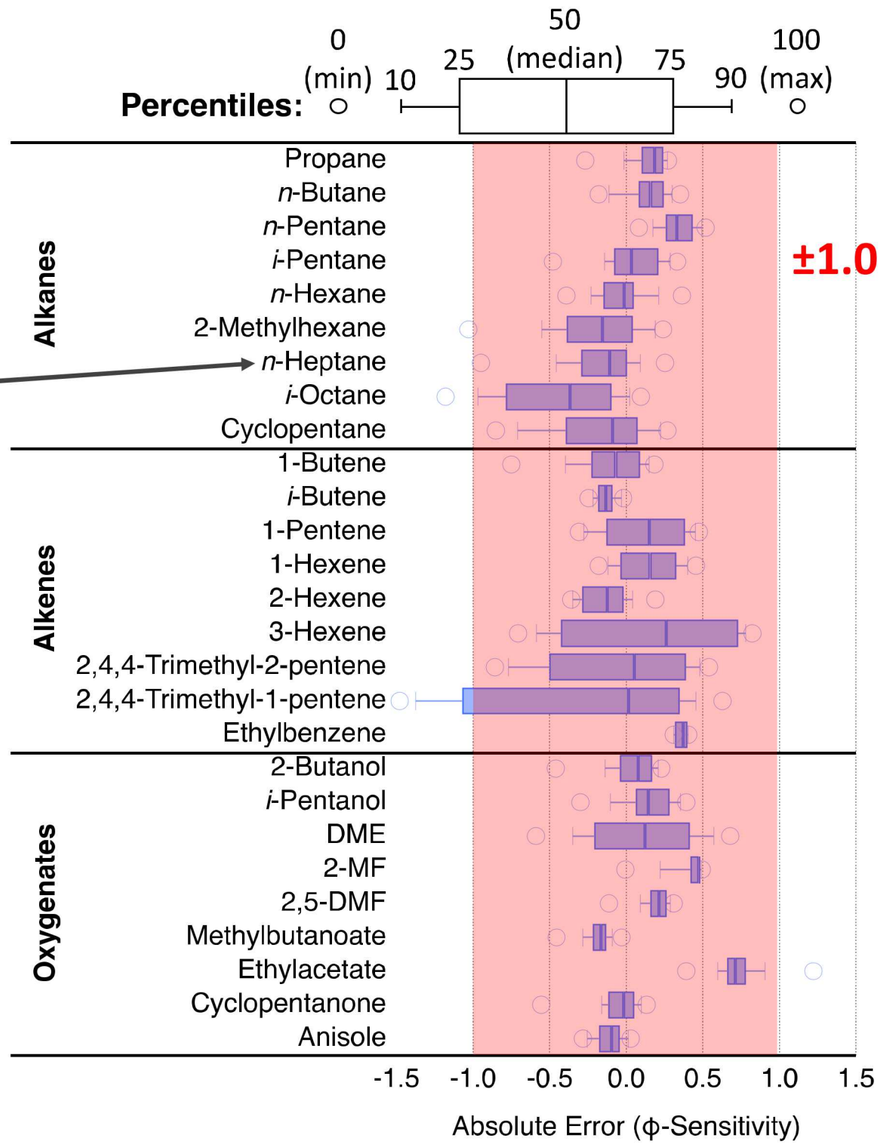
Leave-One-Fuel-Out Tests: ϕ-sensitivity

For Example (smaller dataset):

Train on All ~1.8k Simulations Except *n*-Heptane

Test on ~80 *n*-Heptane Simulations:





Conclusions

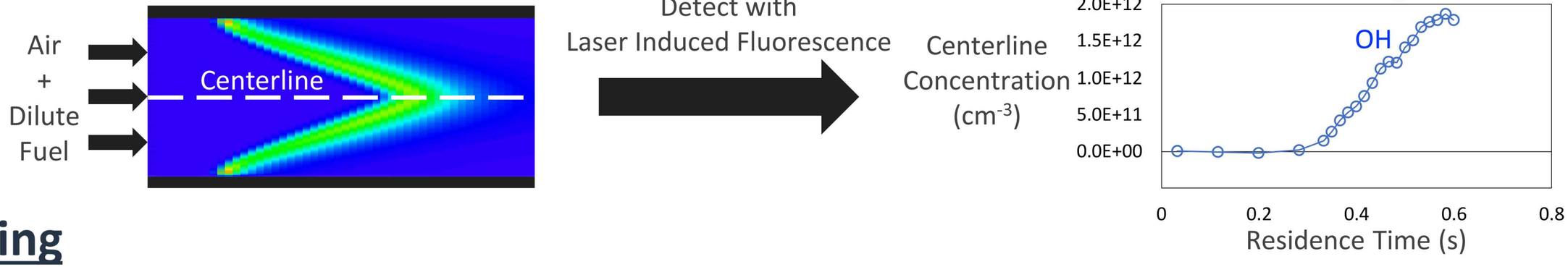
Used PCE to find correlations between OH/HO_2 profiles simulated in a high-P flow reactor with dilute fuel and:

1. 1^{st}-Stage IDT → Correlation predicts values within a factor of 2
2. LTHR % → Correlation predicts absolute values within 4%
3. ϕ-Sensitivity → Correlation does not predict (interesting) high values

   → A different experiment that can measure intermediate-T chemistry might be more suitable

Next Steps

Experimental measurements of OH currently being conducted in a new, high-P (up to 100 bar) laminar flow reactor:



HO_2 In Progress…

Funding

This research was conducted as part of the Laboratory-Directed Research and Development (LDRD) program and the Co-Optimization of Fuels and Engines (Co-Optima) initiative sponsored by the US Department of Energy Office of Energy Efficiency and Renewable Energy and Bioenergy Technologies and Vehicle Technologies Offices. Co-Optima is a collaborative project of multiple national laboratories initiated to simultaneously accelerate the introduction of affordable, scalable, and sustainable biofuels and high-efficiency, low-emission vehicle engines. Special thanks to the Vehicle Technologies Office program managers Kevin Stork, Gurpreet Singh, Leo Breton, and Mike Weismiller, as well as the Bioenergy Technology Office Program manager Alicia Lindauer.

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