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Using OH and HO_2 Radicals as Markers of Biofuel Ignition Properties

Combustion Research Facility at Sandia National Laboratories

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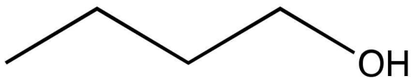
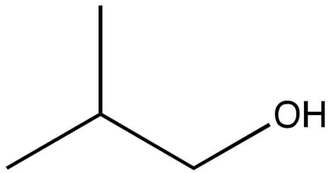
Motivation: Need for Fast Biofuel Screening

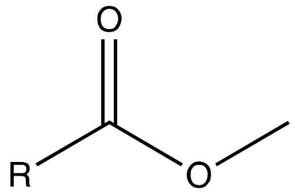
Many Potential Biofuels:*

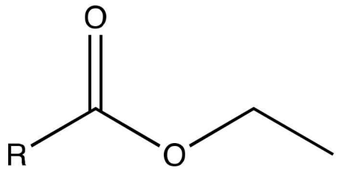
Alcohols



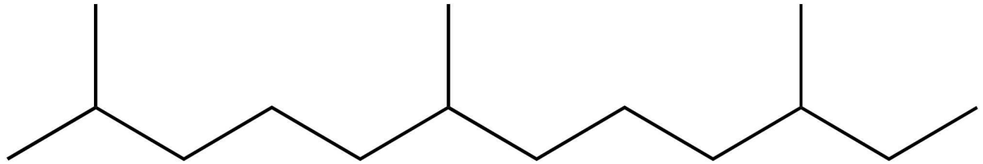


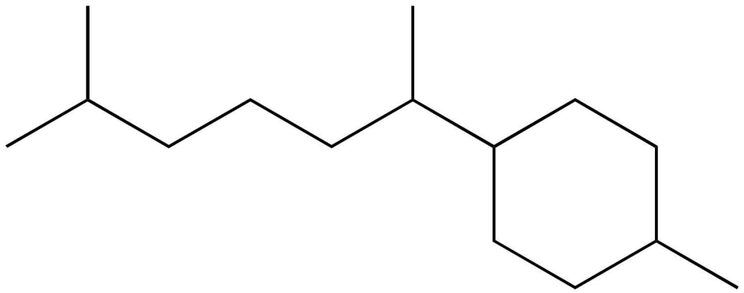
Fatty Acid Esters





Isoprenoids





Or a Mixture!

*Peralta-Yahya, Pamela P., Fuzhong Zhang, Stephen B. del Cardayre, and Jay D. Keasling. "Microbial Engineering for the Production of Advanced Biofuels."*Nature* 488, no. 7411 (August 2012): 320–28.

Motivation: Need for Fast Biofuel Screening

Properties to Screen for:

Physical Properties

Energy Density

Melting Point

Boiling Point

Miscibility with Water

Chemical Properties

Ignition Behavior

Sooting Tendency

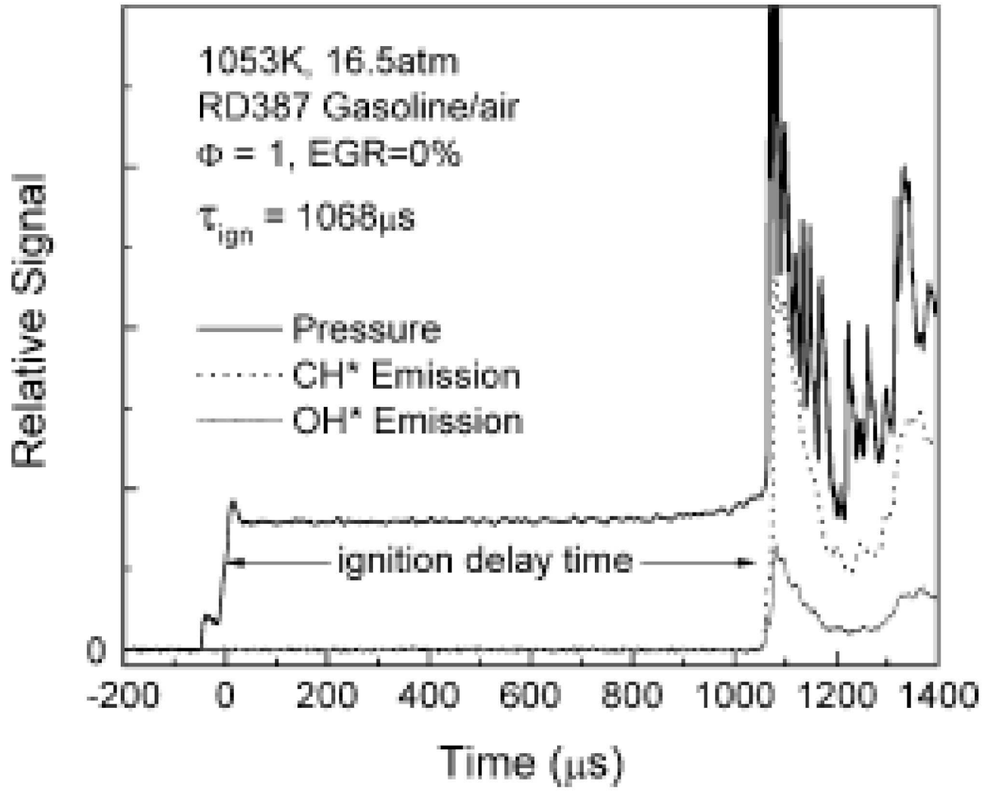
Compatibility with Sealing Material

Economic Properties

Feedstock (Fuel vs. Food)

Cost of Production

Ignition Delay Time (IDT) as Figure-of-Merit



Gauthier, B. M., D. F. Davidson, and R. K. Hanson. "Shock Tube Determination of Ignition Delay Times in Full-Blend and Surrogate Fuel Mixtures." *Combustion and Flame* 139, no. 4 (December 1, 2004): 300–311.

Description:

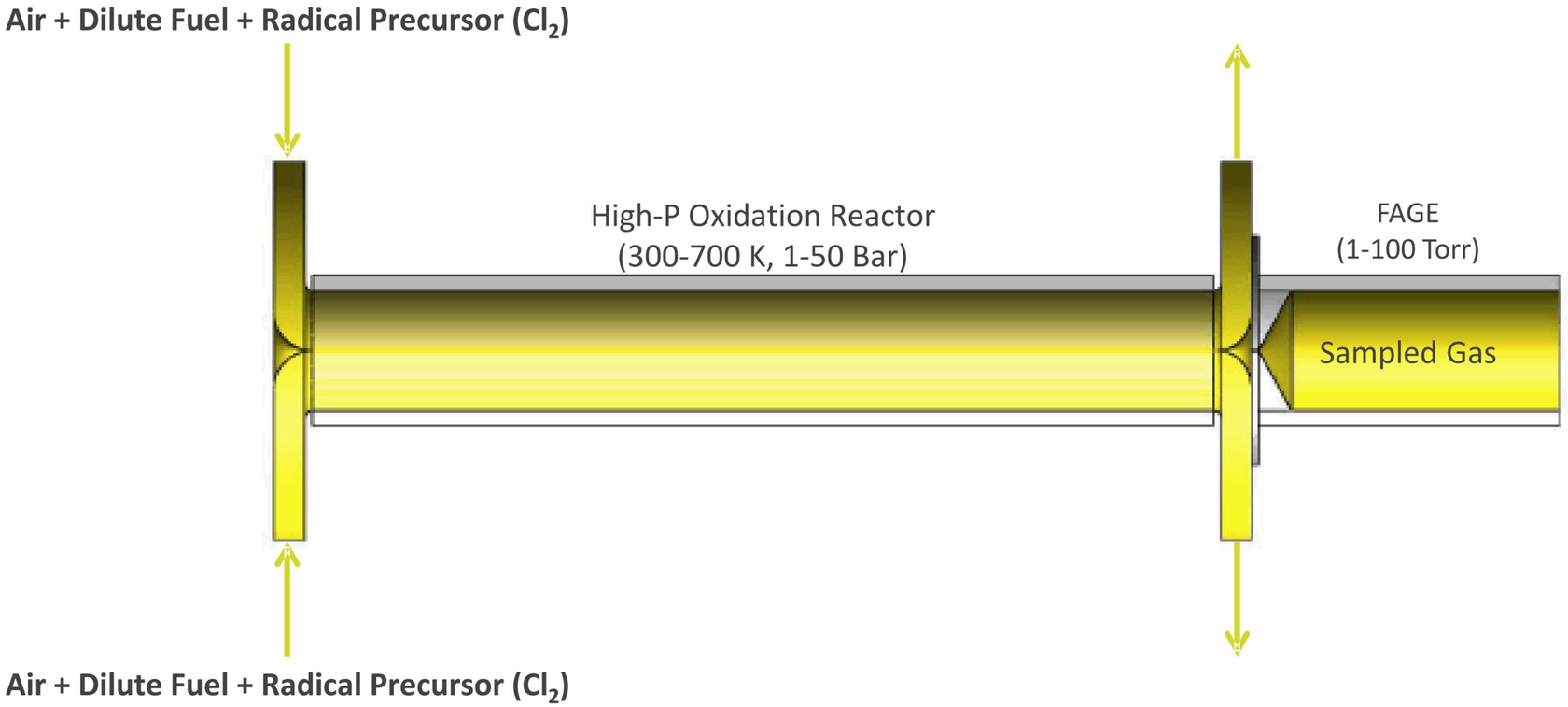
- IDT measured at a fixed, initial T, P and ϕ
- Most commonly measured using shock tubes or rapid compression machines (RCM's)
- Related to Octane Numbers: RON and MON

Drawbacks:

- Substantial quantity of fuel needed
- Difficulty maintaining constant T and P conditions for >100 ms

Idea: Fast Screening Using FAGE*

*__FAGE__ = Fluorescence Assay by Gas Expansion → Used to measure time-resolved OH and HO_2 profiles



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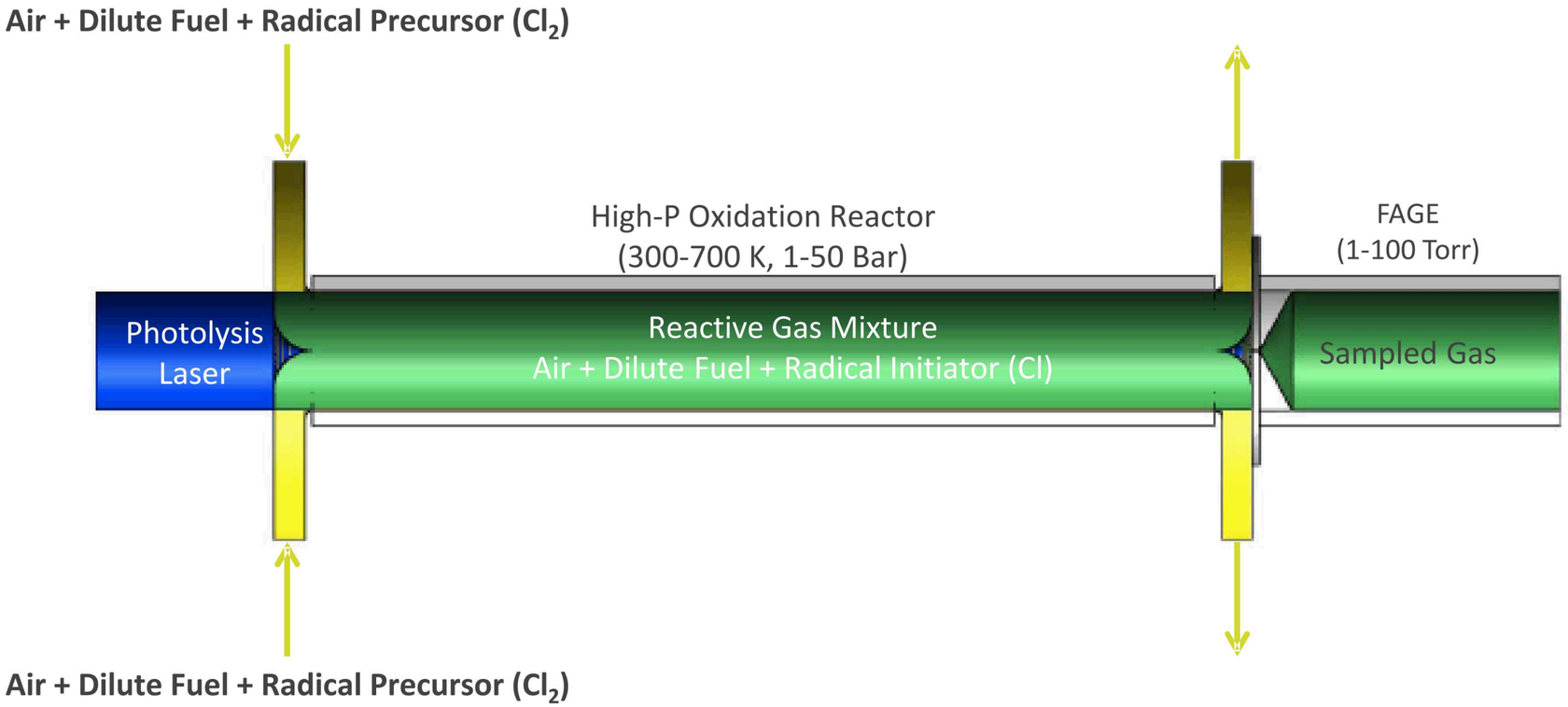


OH = Chain Branching

HO_2 = Chain Terminating

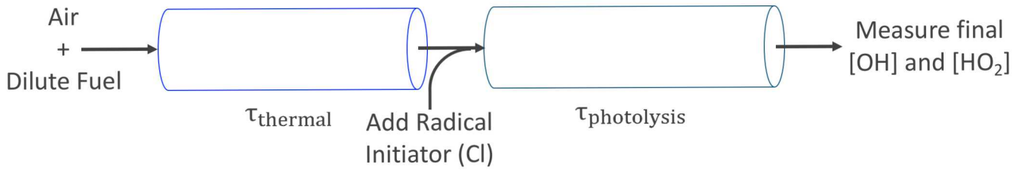
Correlation? → Ignition Properties (IDT, RON, etc.)

Modeling Approach

Shock Tube/RCM

Physical Model

High-P FAGE Reactor



$\tau_{thermal} + \tau_{photolysis} = \tau_{total}$

Vary $0 \leq \tau_{photolysis} \leq \tau_{total}$

\+ **Chemical Mechanism**

"Real" Fuels = *Alkanes* (Linear, Branched and Cyclic), *Alcohols* (Linear and Branched), *Aromatics*, *Alkenes* (Linear), *Ethers* (Linear and Cyclic) and *Esters*

+

"Hypothetical" fuels = "Real" fuels with the most sensitive reactions in the mechanism perturbed by a factor of two

Chemical Mechanisms

Fuel	Class	Authors	Reference
n-Heptane	Linear Alkane	LLNL	1
n-Heptane	Linear Alkane	NUIG	2
i-Octane	Branched Alkane	LLNL	3
Cyclohexane	Cyclic Alkane	LLNL	4
1-Hexene	Linear Alkene	Co-Optima	5
2-Hexene	Linear Alkene	Co-Optima	5
Butylbenzene	Aromatic	LLNL	6
1-Butanol	Linear Alcohol	LLNL	7
i-Pentanol	Branched Alcohol	KAUST	8
Dimethyl Ether (DME)	Ether	LLNL	9
Tetrahydrofuran (THF)	Cyclic Ether	CNRS	10
Methyl Decanoate	Ester	LLNL	11
Binary, Ternary and Quaternary Blends of Heptane/Octane/Toluene/Ethanol	Blend	Co-Optima	5

[1]Mehl, Marco, William J. Pitz, Charles K. Westbrook, and Henry J. Curran. “Kinetic Modeling of Gasoline Surrogate Components and Mixtures under Engine Conditions.” *Proceedings of the Combustion Institute*33, no. 1 (January 1, 2011): 193–200.

[2]Zhang, Kuiwen, Colin Banyon, John Bugler, Henry J. Curran, Anne Rodriguez, Olivier Herbinet, Frédérique Battin-Leclerc, Christine B’Chir, and Karl Alexander Heufer. “An Updated Experimental and Kinetic Modeling Study of N-Heptane Oxidation.” *Combustion and Flame*172 (October 1, 2016): 116–35.

[3]Curran, H. J., P. Gaffuri, W. J. Pitz, and C. K. Westbrook. “A Comprehensive Modeling Study of Iso-Octane Oxidation.”*Combustion and Flame*129, no. 3 (May 1, 2002): 253–80.

[4]Silke, Emma J., William J. Pitz, Charles K. Westbrook, and Marc Ribaucour. “Detailed Chemical Kinetic Modeling of Cyclohexane Oxidation†.”*The Journal of Physical Chemistry A*111, no. 19 (May 1, 2007): 3761–75.

[5]Mehl, Marco, Kuiwen Zhang, Scott Wagnon, Goutham Kukkadapu, Charles K. Westbrook, William J. Pitz, Yinjia Zhang, et al. “A Comprehensive Detailed Kinetic Mechanism for the Simulation of Transportation Fuels.” In *10th US National Combustion Meeting*. Lawrence Livermore National Laboratory, 2017.

[6]Nakamura, Hisashi, Daniel Darcy, Marco Mehl, Colin J. Tobin, Wayne K. Metcalfe, William J. Pitz, Charles K. Westbrook, and Henry J. Curran. “An Experimental and Modeling Study of Shock Tube and Rapid Compression Machine Ignition of N-Butylbenzene/Air Mixtures.” *Combustion and Flame*161, no. 1 (January 1, 2014): 49–64.

[7]Sarathy, S. Mani, Stijn Vranckx, Kenji Yasunaga, Marco Mehl, Patrick Oßwald, Wayne K. Metcalfe, Charles K. Westbrook, et al. “A Comprehensive Chemical Kinetic Combustion Model for the Four Butanol Isomers.” *Combustion and Flame*159, no. 6 (June 1, 2012): 2028–55.

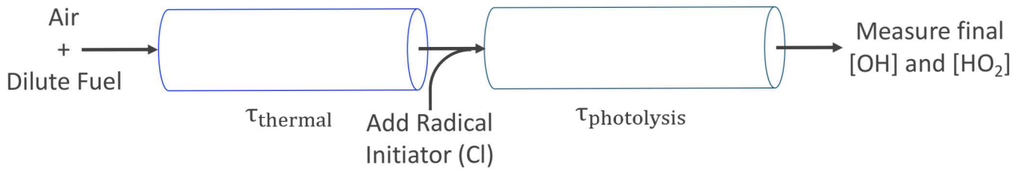
[8]Mani Sarathy, S., Sungwoo Park, Bryan W. Weber, Weijing Wang, Peter S. Veloo, Alexander C. Davis, Casimir Togbe, et al. “A Comprehensive Experimental and Modeling Study of Iso-Pentanol Combustion.”*Combustion and Flame*160, no. 12 (December 1, 2013): 2712–28.

[9]Kaiser, E. W., T. J. Wallington, M. D. Hurley, J. Platz, H. J. Curran, W. J. Pitz, and C. K. Westbrook. “Experimental and Modeling Study of Premixed Atmospheric-Pressure Dimethyl Ether−Air Flames.”*The Journal of Physical Chemistry A*104, no. 35 (September 1, 2000): 8194–8206.

[10]Fenard, Yann, Adrià Gil, Guillaume Vanhove, Hans-Heinrich Carstensen, Kevin M. Van Geem, Phillip R. Westmoreland, Olivier Herbinet, and Frédérique Battin-Leclerc. “A Model of Tetrahydrofuran Low-Temperature Oxidation Based on Theoretically Calculated Rate Constants.” *Combustion and Flame*191 (May 1, 2018): 252–69.

[11]Herbinet, Olivier, William J. Pitz, and Charles K. Westbrook. “Detailed Chemical Kinetic Mechanism for the Oxidation of Biodiesel Fuels Blend Surrogate.”*Combustion and Flame*157, no. 5 (May 1, 2010): 893–908.

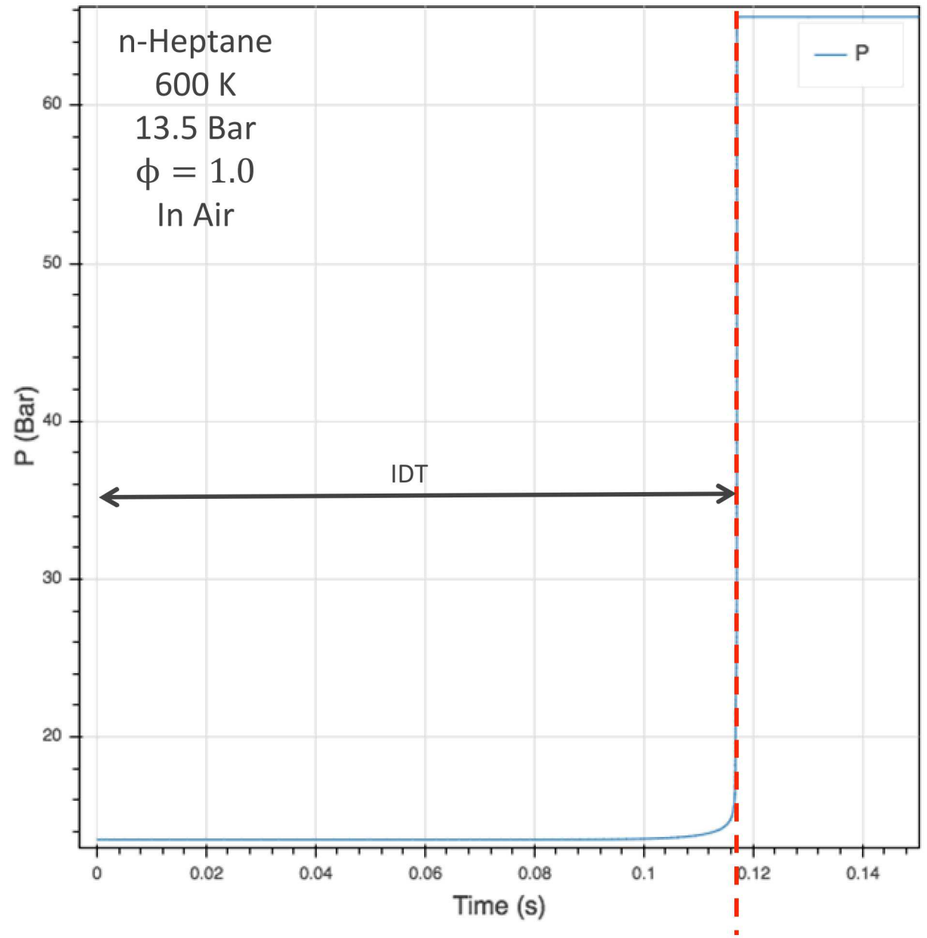
Modeling Approach

	Shock Tube/RCM	High-P FAGE Reactor
Physical Model		 $\tau_{thermal} + \tau_{photolysis} = \tau_{total}$ Vary $0 \leq \tau_{photolysis} \leq \tau_{total}$
+ **Chemical Mechanism**	**"Real" Fuels** = *Alkanes* (Linear, Branched and Cyclic), *Alcohols* (Linear and Branched), *Aromatics*, *Alkenes* (Linear), *Ethers* (Linear and Cyclic) and *Esters* + **"Hypothetical" fuels** = "Real" fuels with the most sensitive reactions in the mechanism perturbed by a factor of two	
+ **Other Effects**	None	Wall Reactions (k_{wall} = 10 s^{-1}) + Detection Limit ([OH] = 1e6 cm^{-3}) + Finite Time Resolution (100 µs) + FAGE Interference from β-hydroxyalkylperoxy radicals*

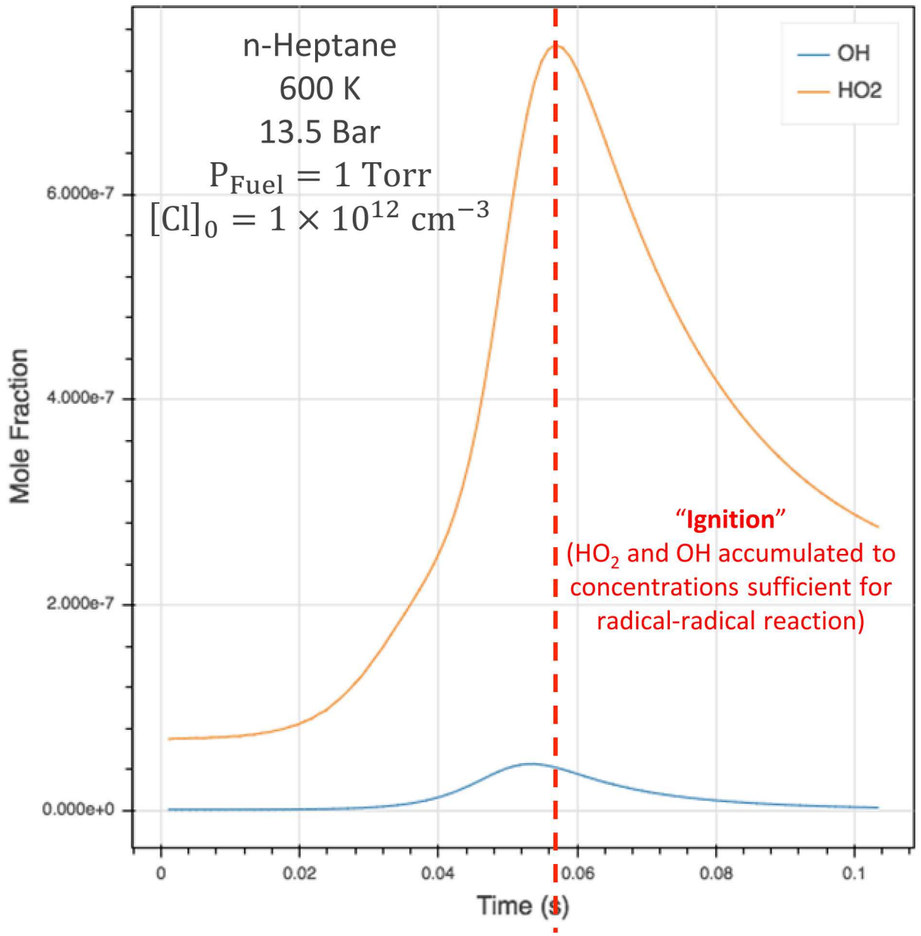
*Whalley, L. K., M. A. Blitz, M. Desservettaz, P. W. Seakins, and D. E. Heard. "Reporting the Sensitivity of Laser-Induced Fluorescence Instruments Used for HO2 Detection to an Interference from RO2 Radicals and Introducing a Novel Approach That Enables HO2 and Certain RO2 Types to Be Selectively Measured."*Atmos. Meas. Tech.*6, no. 12 (December 9, 2013): 3425–40.

Modeling Approach

Shock Tube/RCM



High-P FAGE Reactor

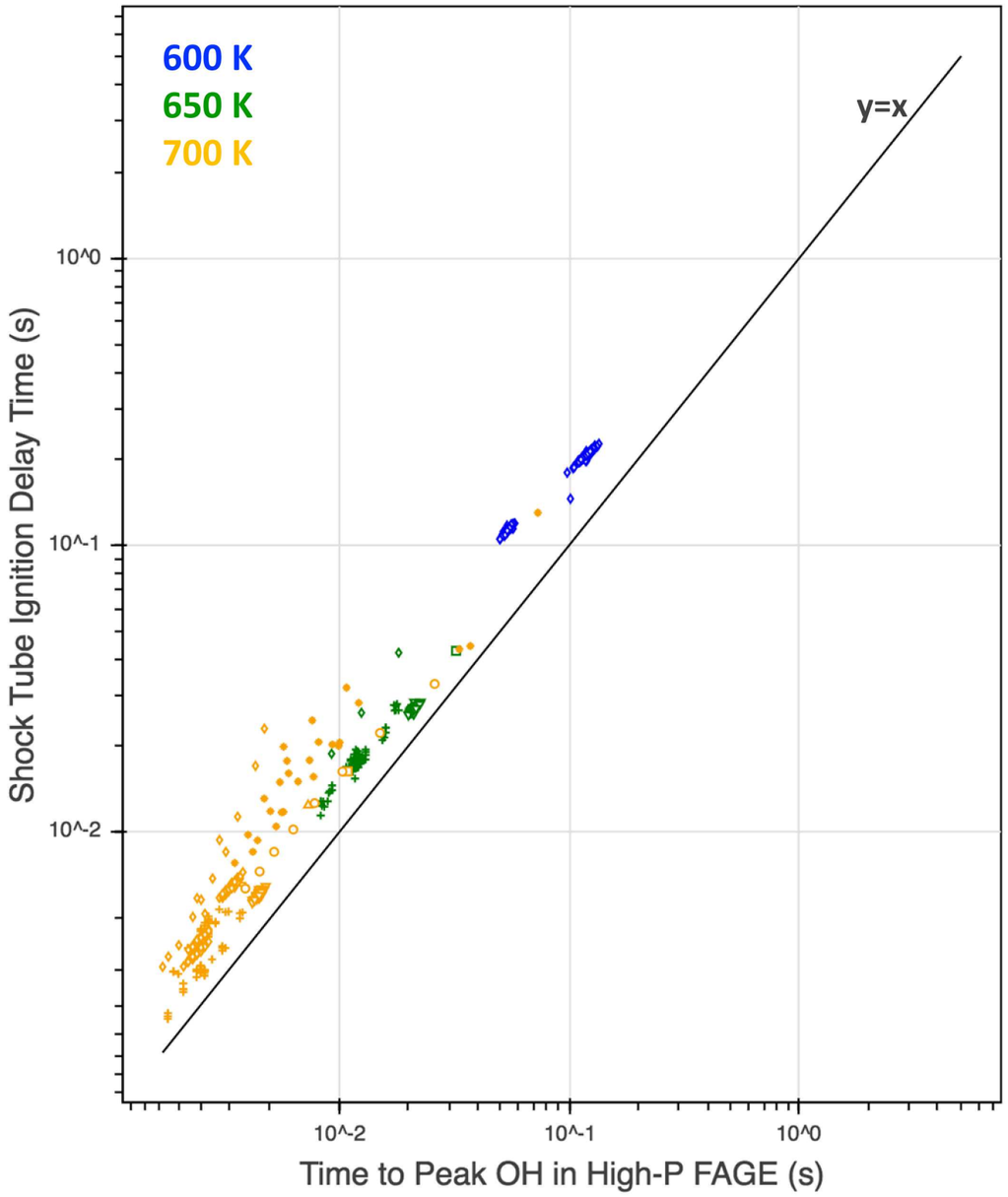


Possible correlation between IDT and time to peak OH/HO_2?

Results: 1st Order Correlation with IDT

"Well-Behaved" Fuels:

- n-Heptane
- i-Octane
- 1-Hexene
- Methyl Decanoate
- DME
- PRF and TPRF Blends



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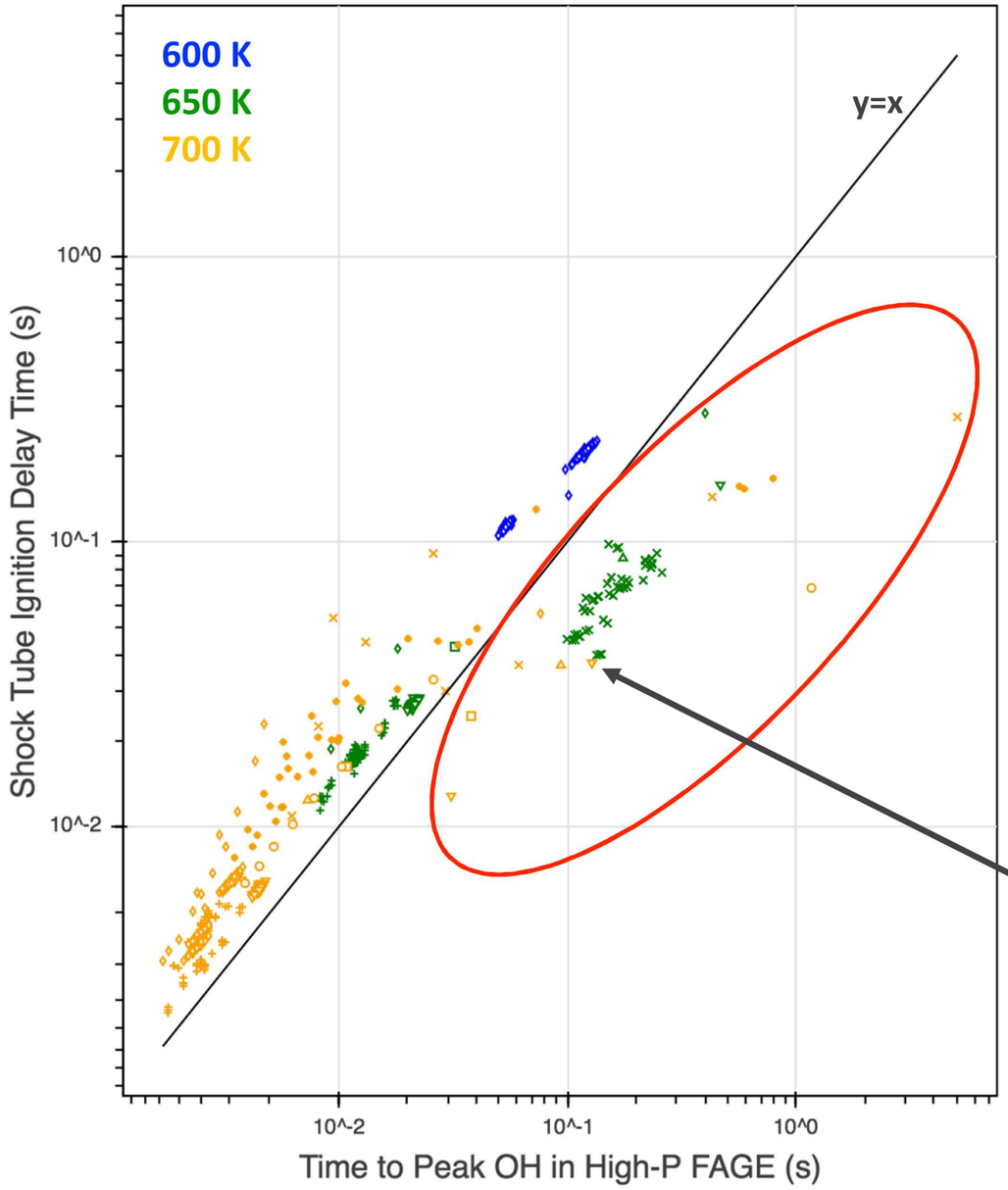
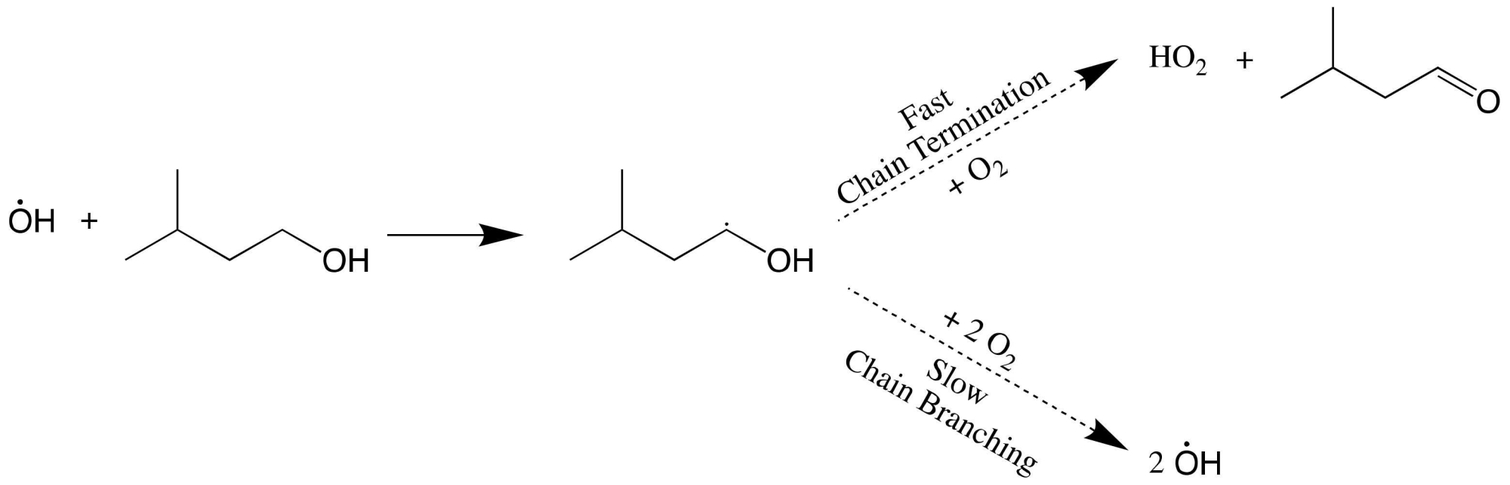


"Outlier" Fuels:

- i-Pentanol
- Butanol
- 2-Hexene
- Cyclohexane
- THF
- Butylbenzene
- Ethanol-containing Blends

Examine i-Pentanol more closely

Explaining an Example Outlier: Pentanol



Apply QSSA and Solve ODE's

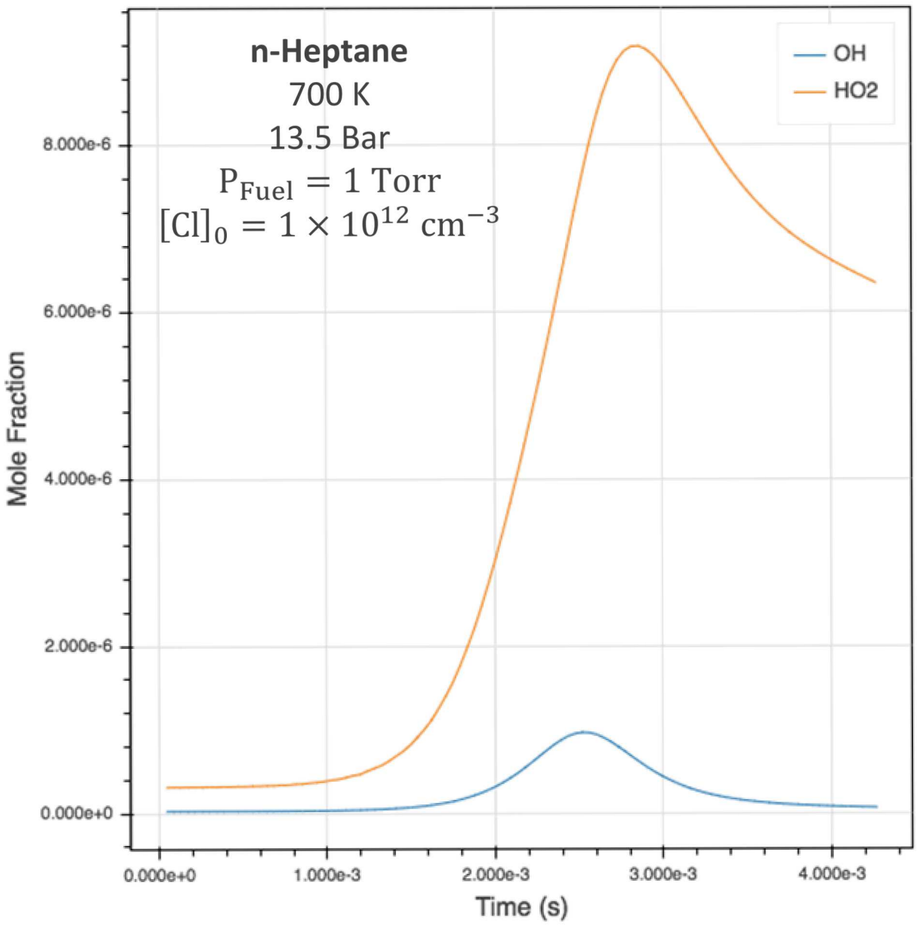
$[OH] \text{ and } [HO_2] \propto e^{k'[\text{Fuel}]t}$

Ignition is dependent on [Fuel] → Dilute fuel conditions not equivalent to $\phi \approx 1$ conditions

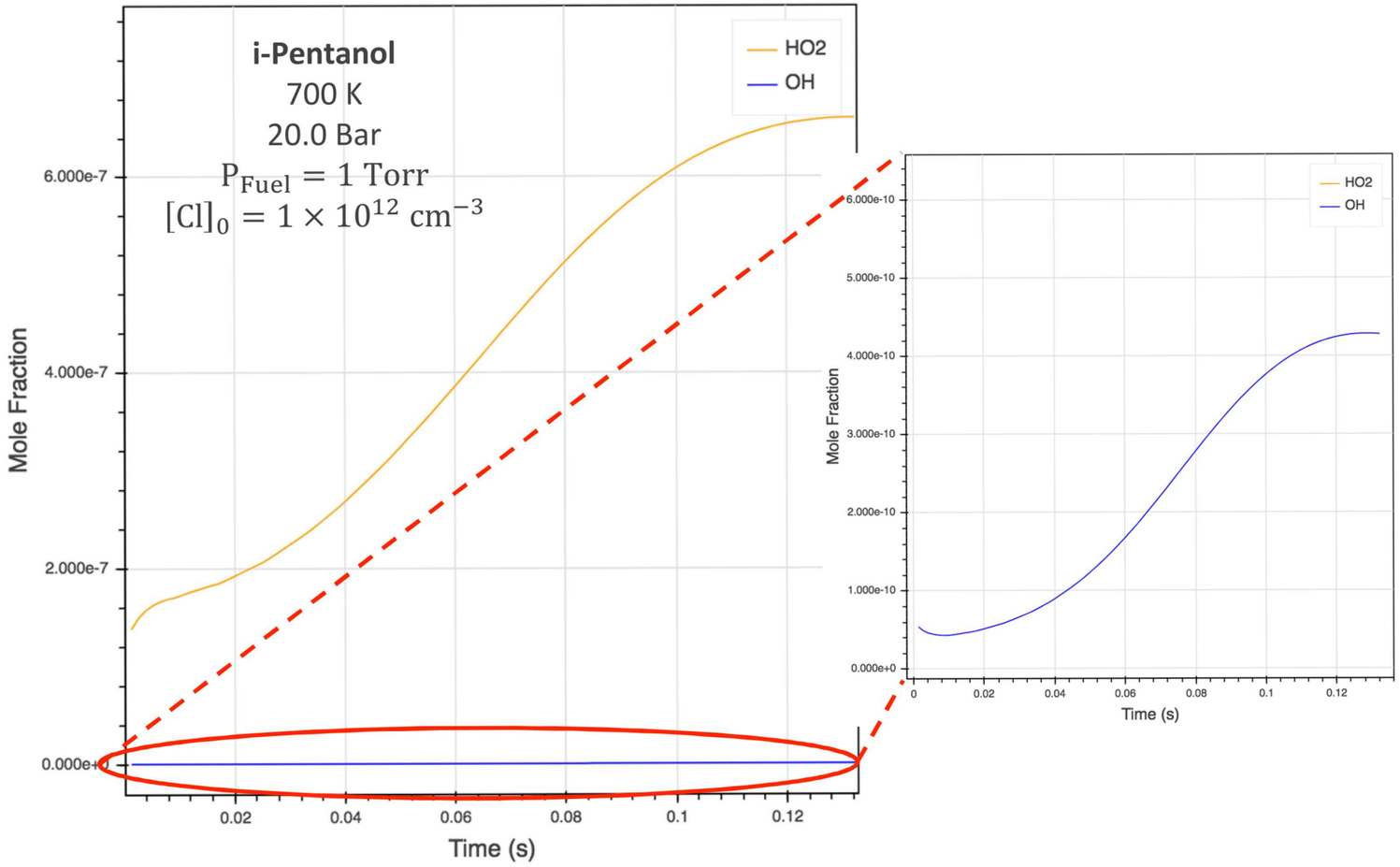
Other outlier fuels exhibit similar [Fuel] dependence, although mechanistic cause is not investigated

Explaining an Example Outlier: Pentanol

"Well-Behaved" Fuel



"Outlier" Fuel



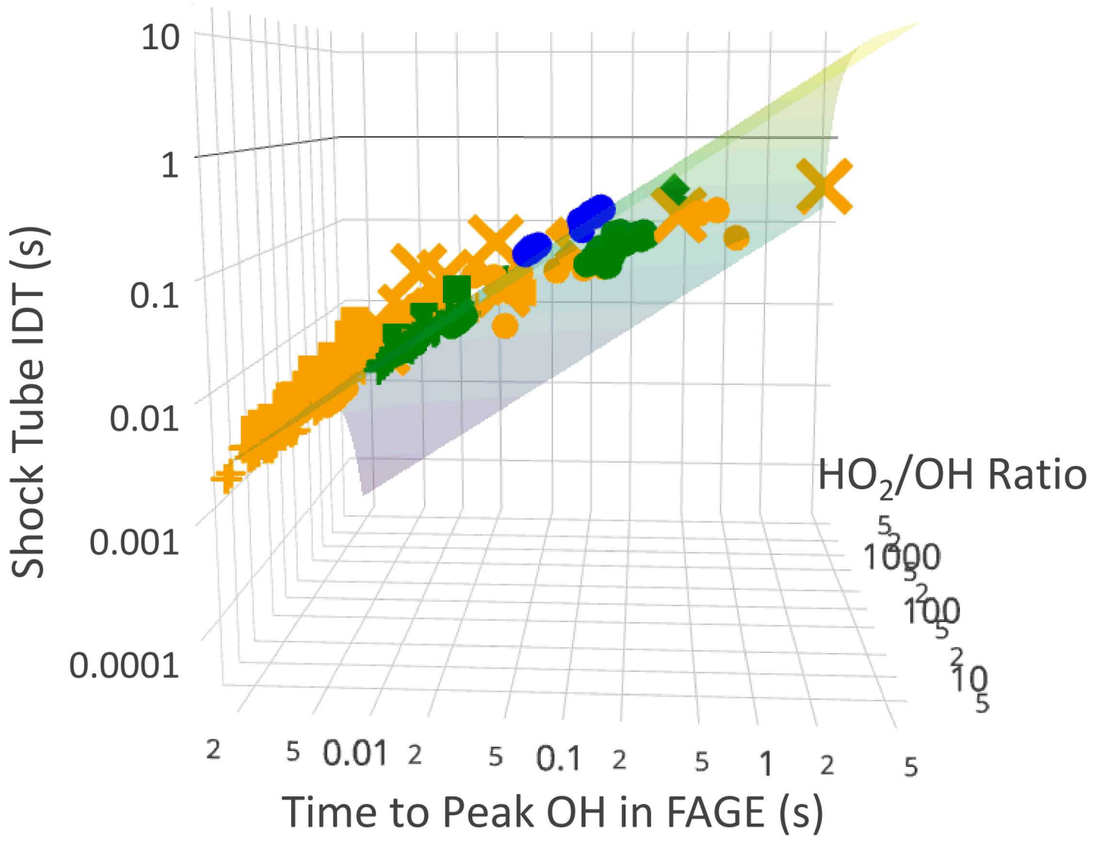
Outlier Fuels exhibit a larger HO_2/OH Ratio!

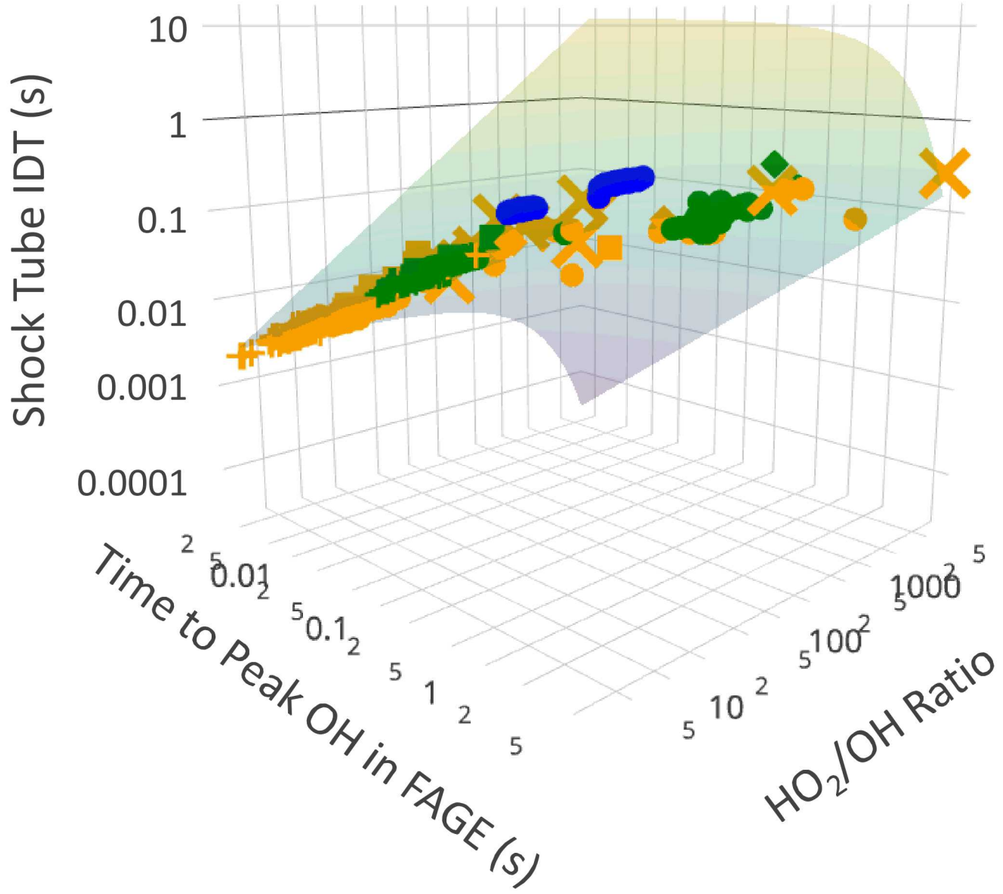
Results: HO_2/OH ratio as 2nd Order Correction

Shock Tube

$\phi = 1.0$

600 K
650 K
700 K



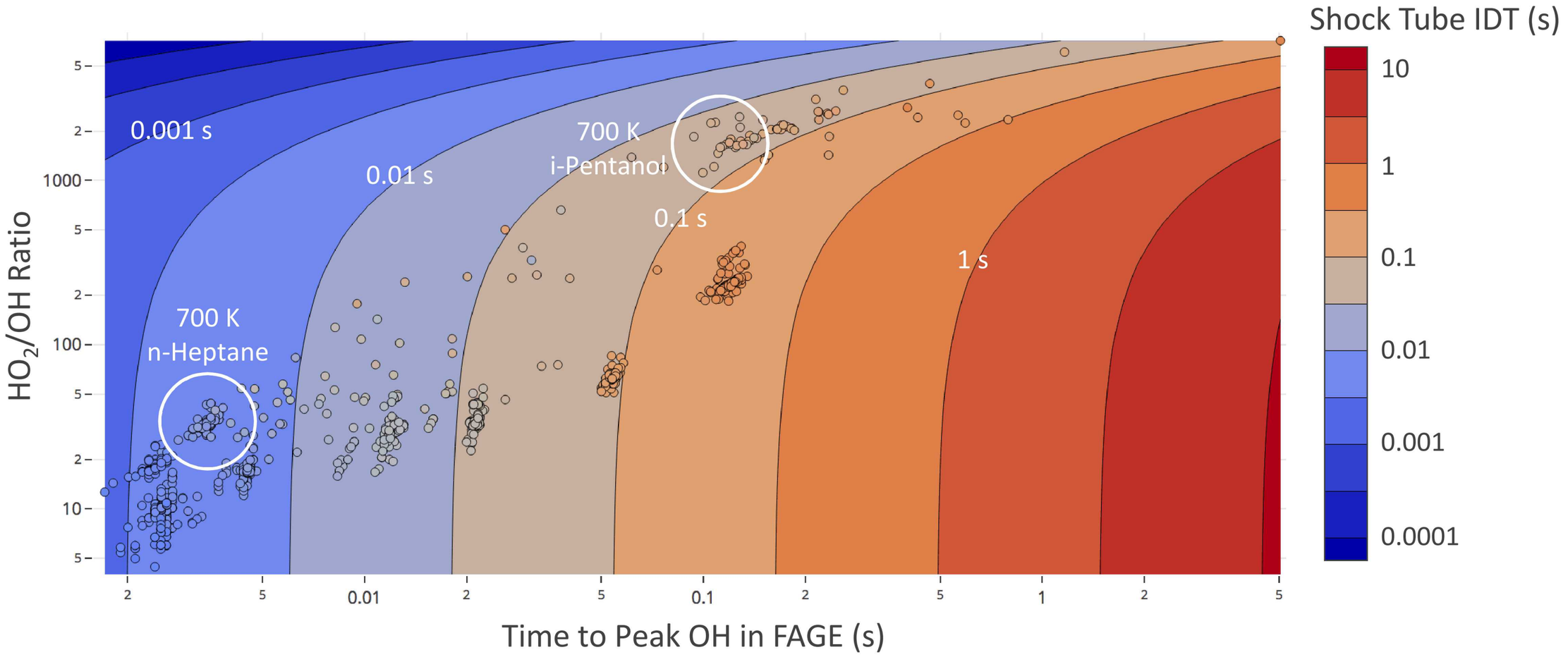


$$\text{Shock Tube IDT} = \mathbf{f}(\text{Time to Peak OH}, HO_2/\text{OH Ratio})$$

17% Error for 1063 simulations

Results: HO_2/OH ratio as 2nd Order Correction

Shock Tube
$\phi = 1.0$

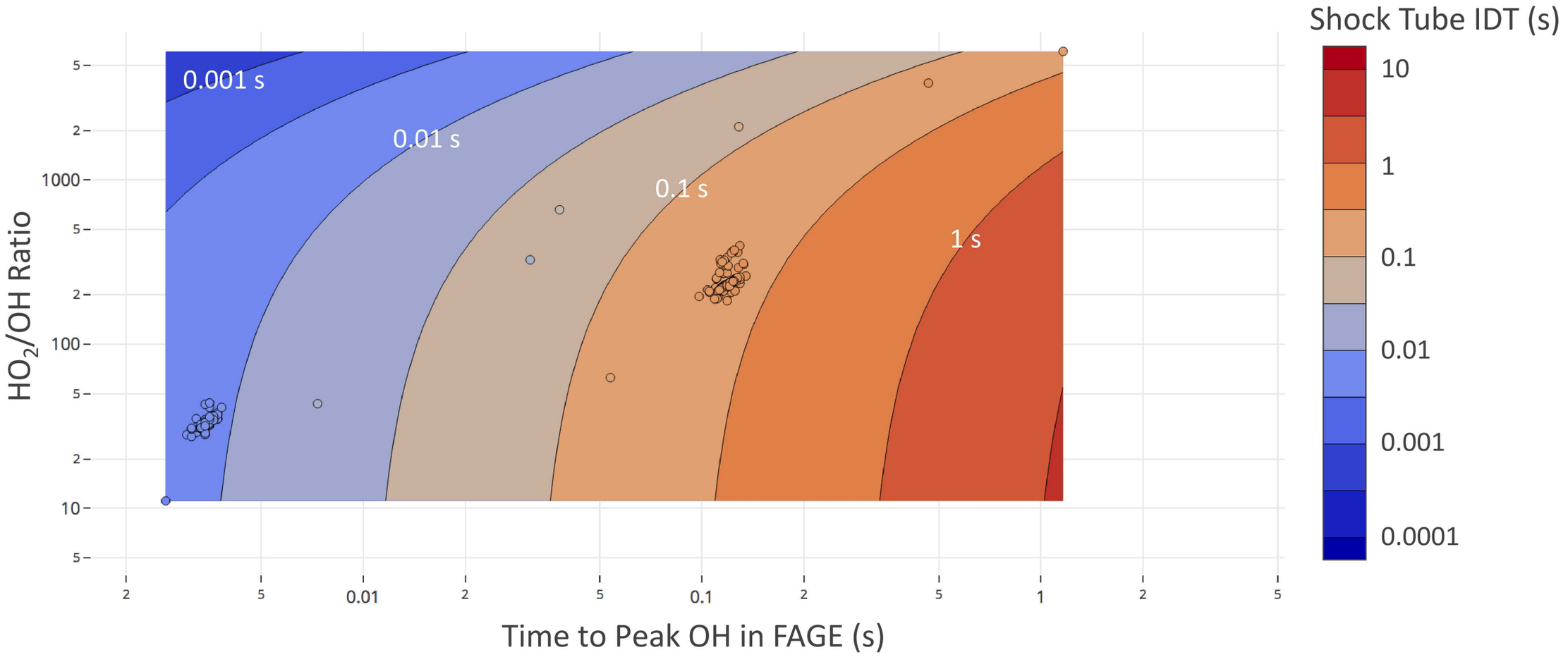


$$\text{Shock Tube IDT} = \mathbf{f}(\text{Time to Peak OH}, HO_2/\text{OH Ratio})$$

17% Error for 1063 simulations

Results: Dependence on Equivalence Ratio (ϕ)

Shock Tube
$\phi = 0.5$

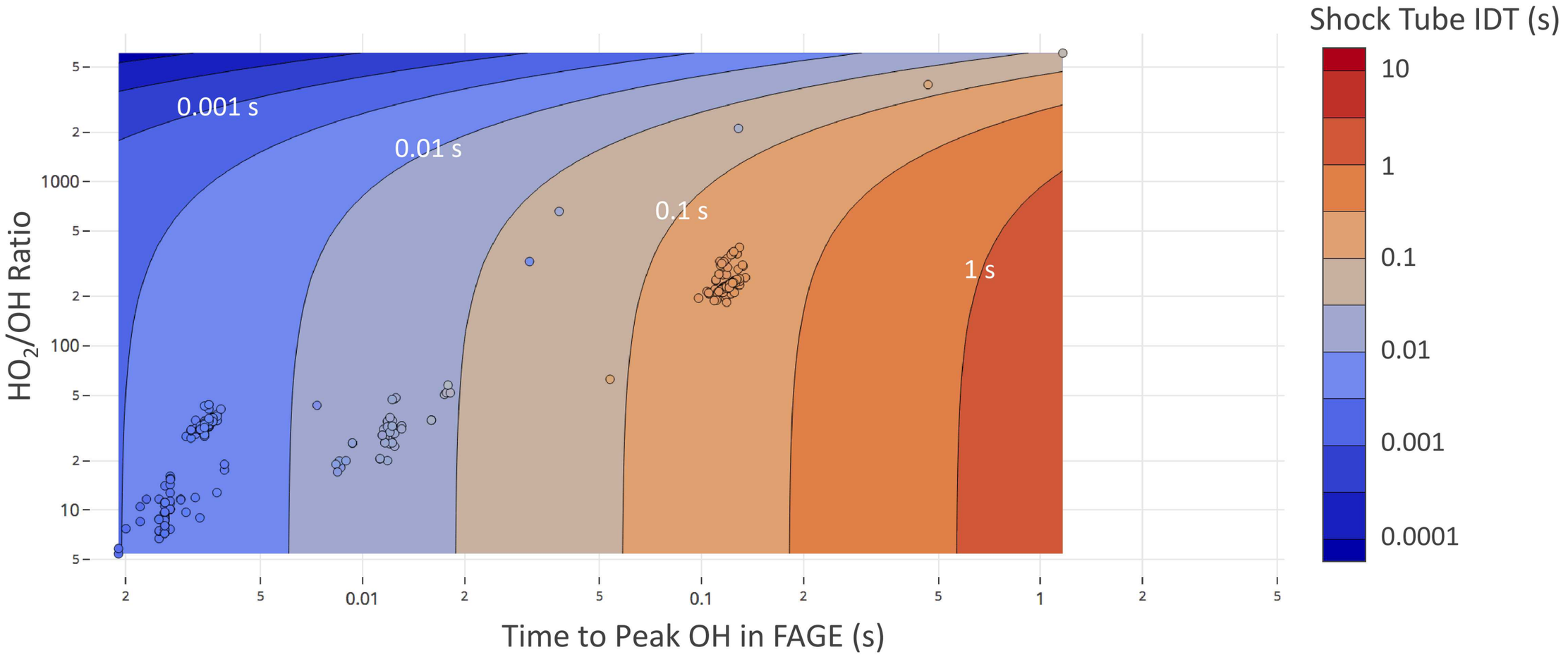


$$\text{Shock Tube IDT} = \mathbf{f}(\text{Time to Peak OH}, \text{HO}_2/\text{OH Ratio})$$

3% Error for 224 simulations

Results: Dependence on Equivalence Ratio (ϕ)

Shock Tube
$\phi = 2.0$



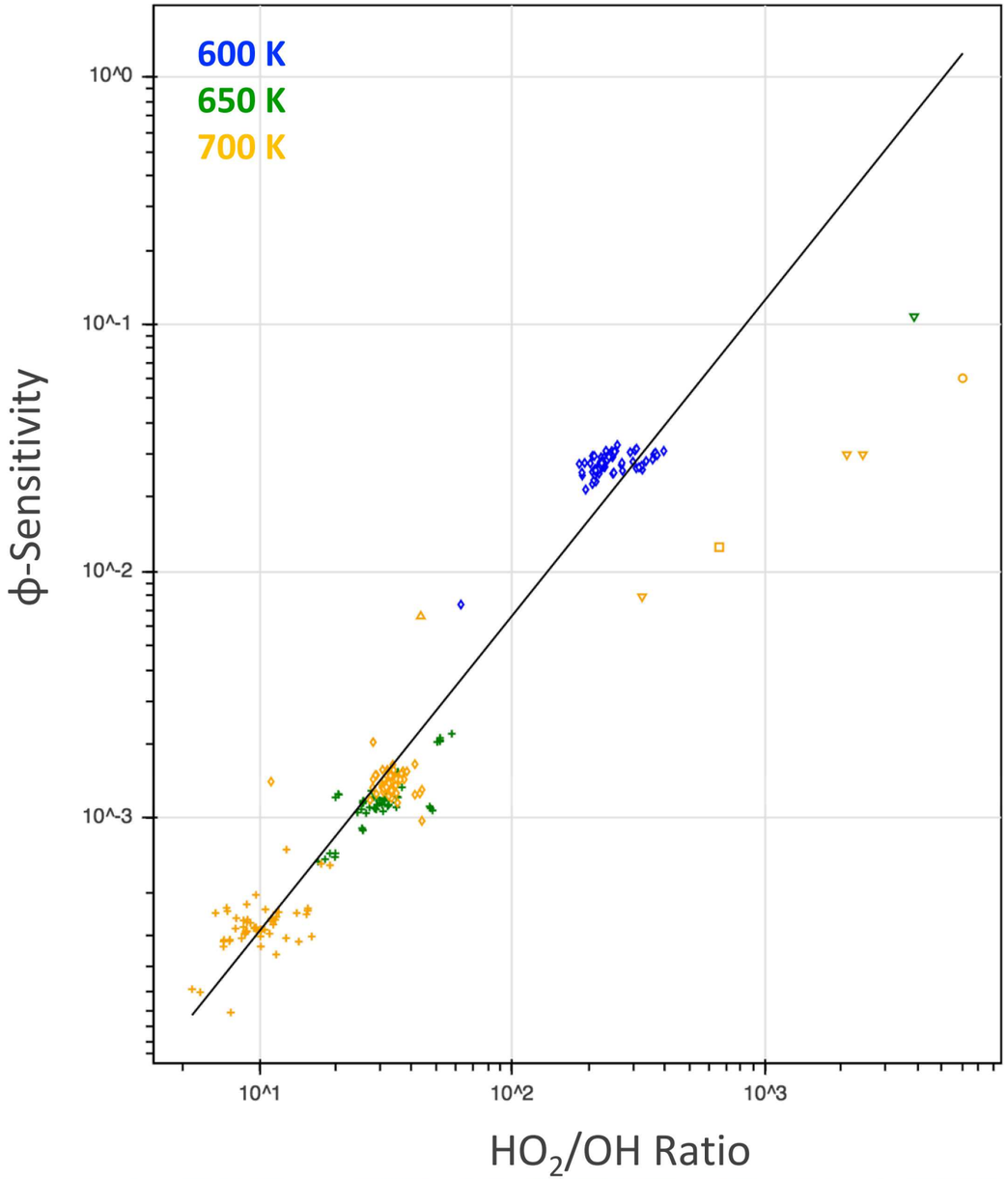
$$\text{Shock Tube IDT} = \mathbf{f}(\text{Time to Peak OH}, \text{HO}_2/\text{OH Ratio})$$

10% Error for 338 simulations

Results: Dependence on Equivalence Ratio (ϕ)

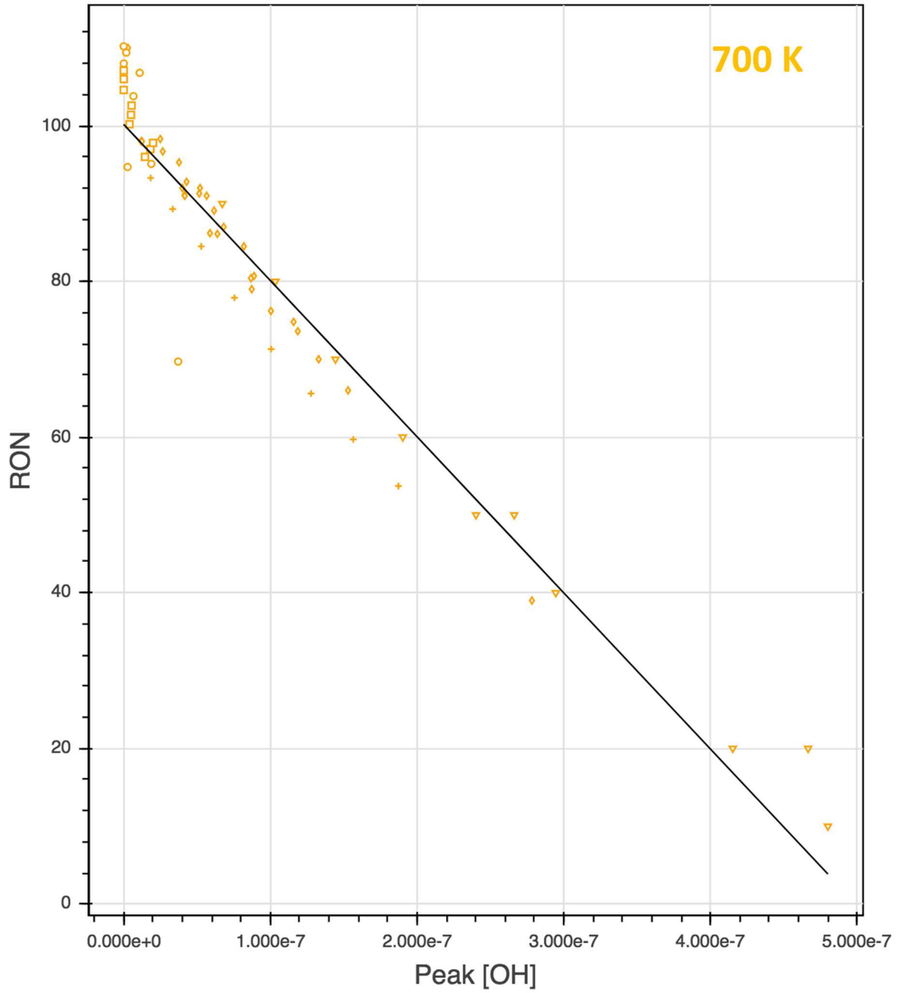
$$\phi\text{-Sensitivity} = \left.\frac{d(IDT)}{d(\phi)}\right|_{\phi=1.0} \propto HO_2/OH$$

Future engines might employ fuel-lean conditions (ϕ<1.0), therefore dependence of fuel ignition on ϕ is important to know

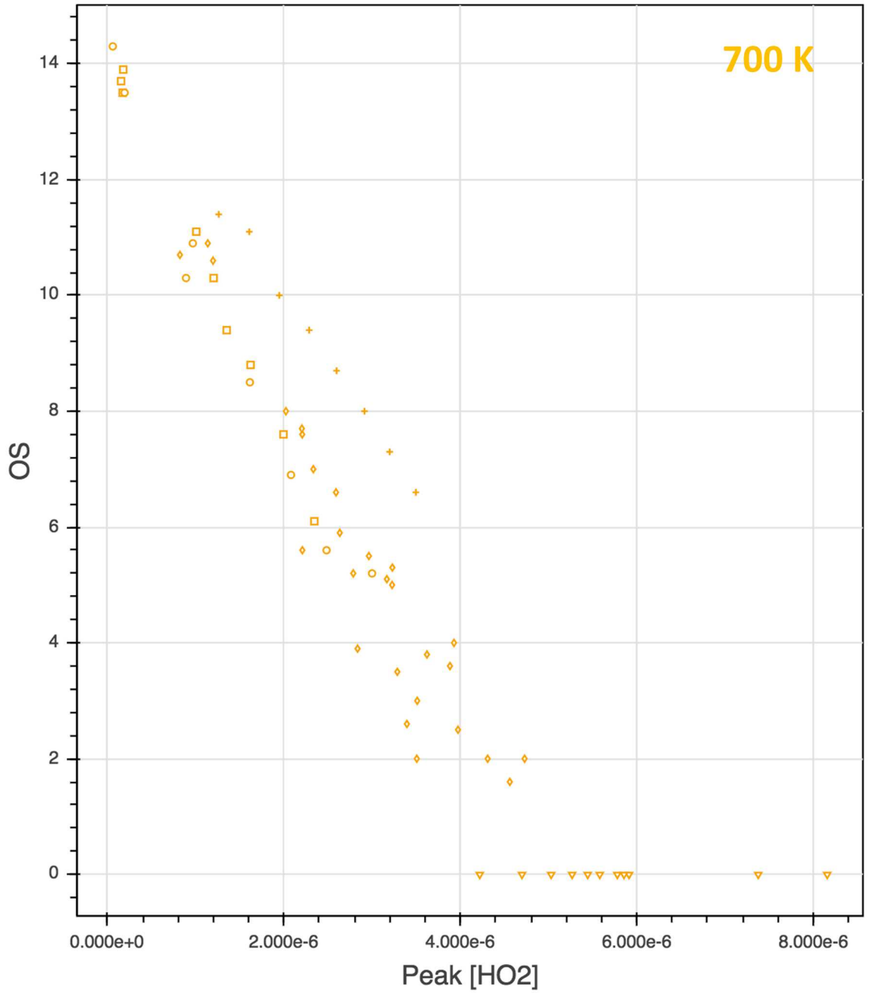


Results: Possible Correlations with Octane Numbers

Only considered fuel blends with known RON, MON and OS:



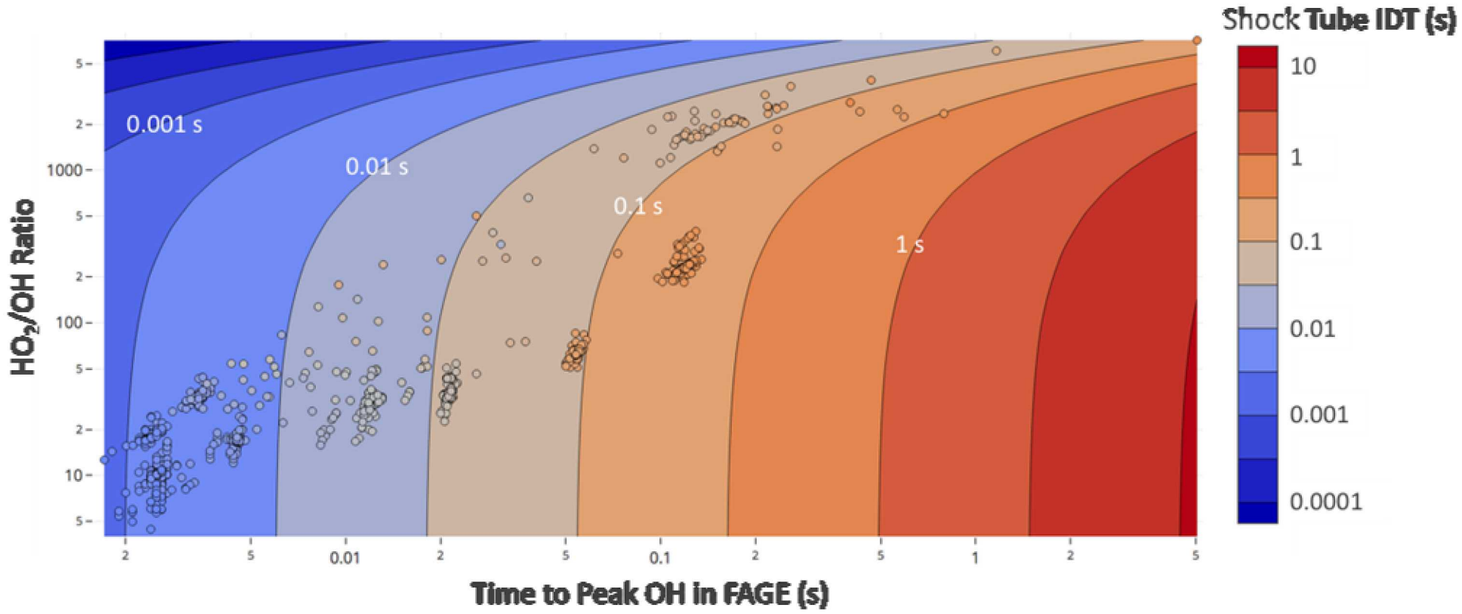
$$\mathrm{RON} \propto [\mathrm{OH}]$$



$$\mathrm{OS} = (\mathrm{RON} - \mathrm{MON}) \propto [\mathrm{HO_2}]$$

Conclusions

- Simulations predict that for ”well-behaved” fuels like n-Heptane, IDT can be measured directly with proposed High-Pressure FAGE Reactor
- However, ignition of ”outlier” fuels such as i-Pentanol are dependent on [Fuel], complicating comparisons between ultra-lean and stoichiometric fuel conditions
  - HO_2/OH Ratio can be used as a correction term for outliers
- Two-term correlation between IDT and High-P FAGE simulations predicted to be accurate within 20% for a wide range of fuel classes from 600-700 K
- Outlier fuels with higher HO_2/OH ratio are predicted to have more ϕ-sensitive ignition



Acknowledgments

This work is supported by Sandia National Laboratories under the Laboratory-Directed Research and Development (LDRD) program. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

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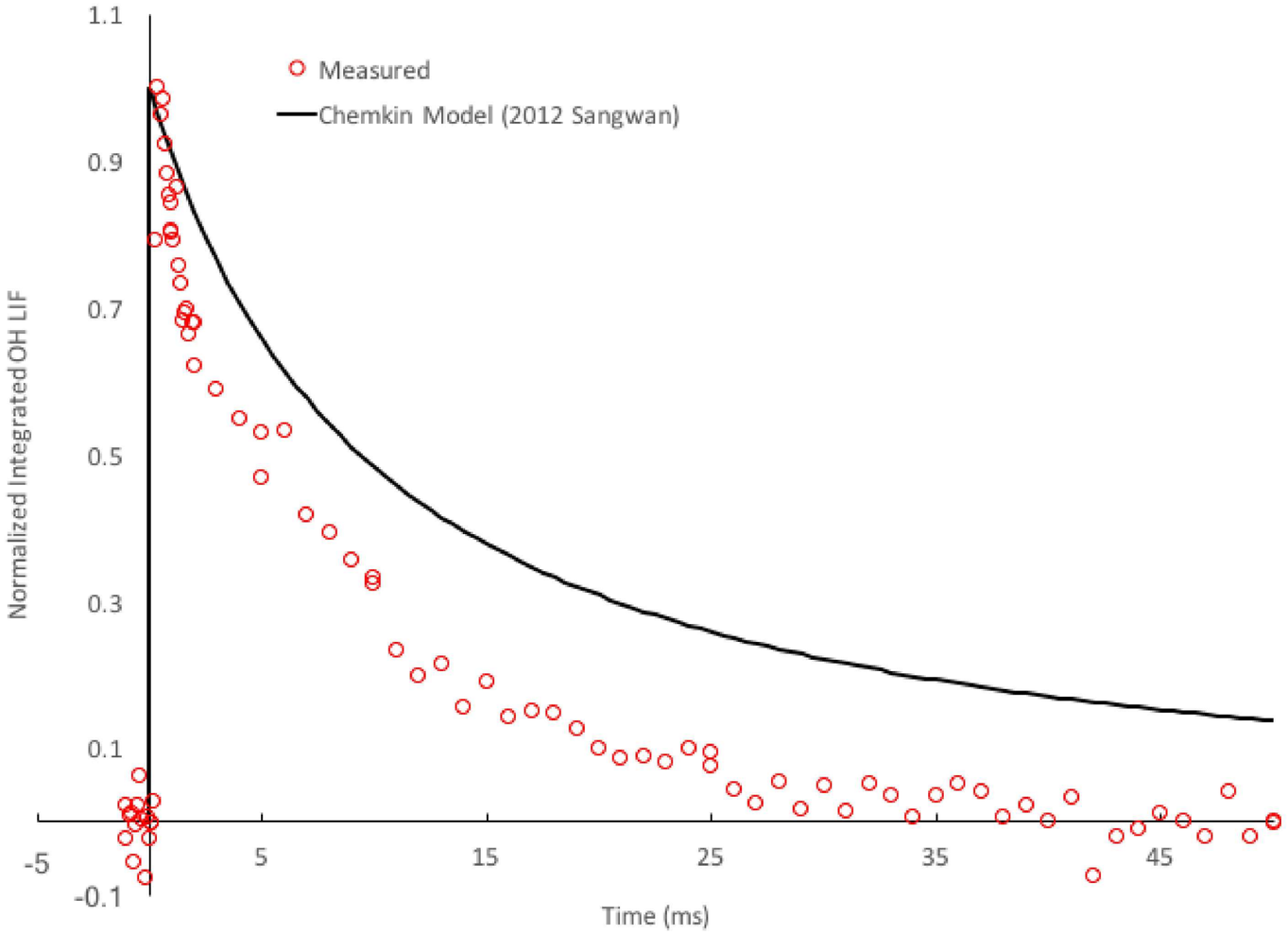
Back Up

Experimental Results



Important Reactions:

$$N_2O \xrightarrow{193\ nm} O(^1D) + NO$$

$$O(^1D) + H_2O \rightarrow 2OH$$

$$OH + OH \rightarrow H_2O_2$$

Conditions:

$$T = 300\ K$$

$$P = 1\ atm$$

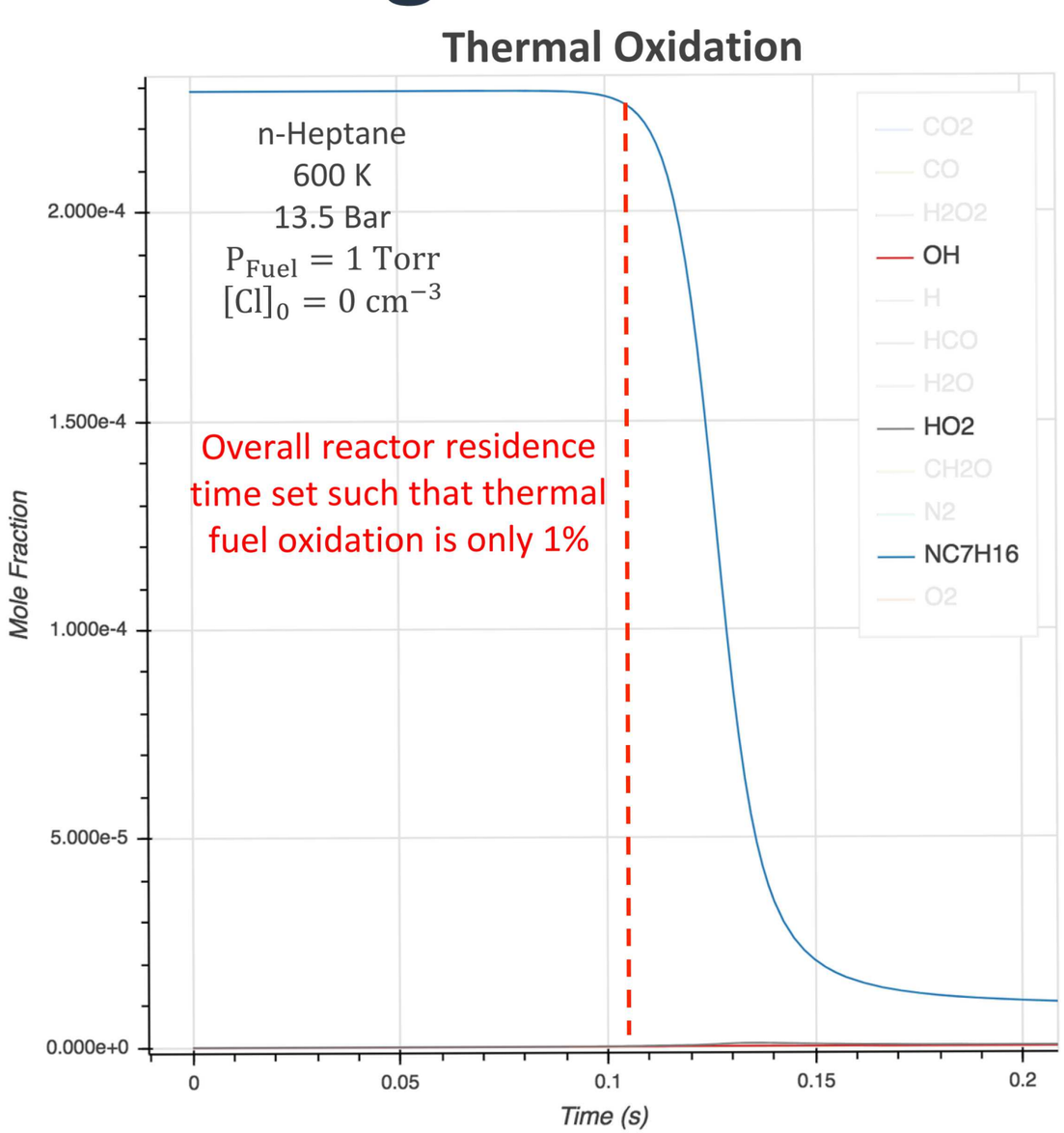
$$[N_2O] = cm^{-3}$$

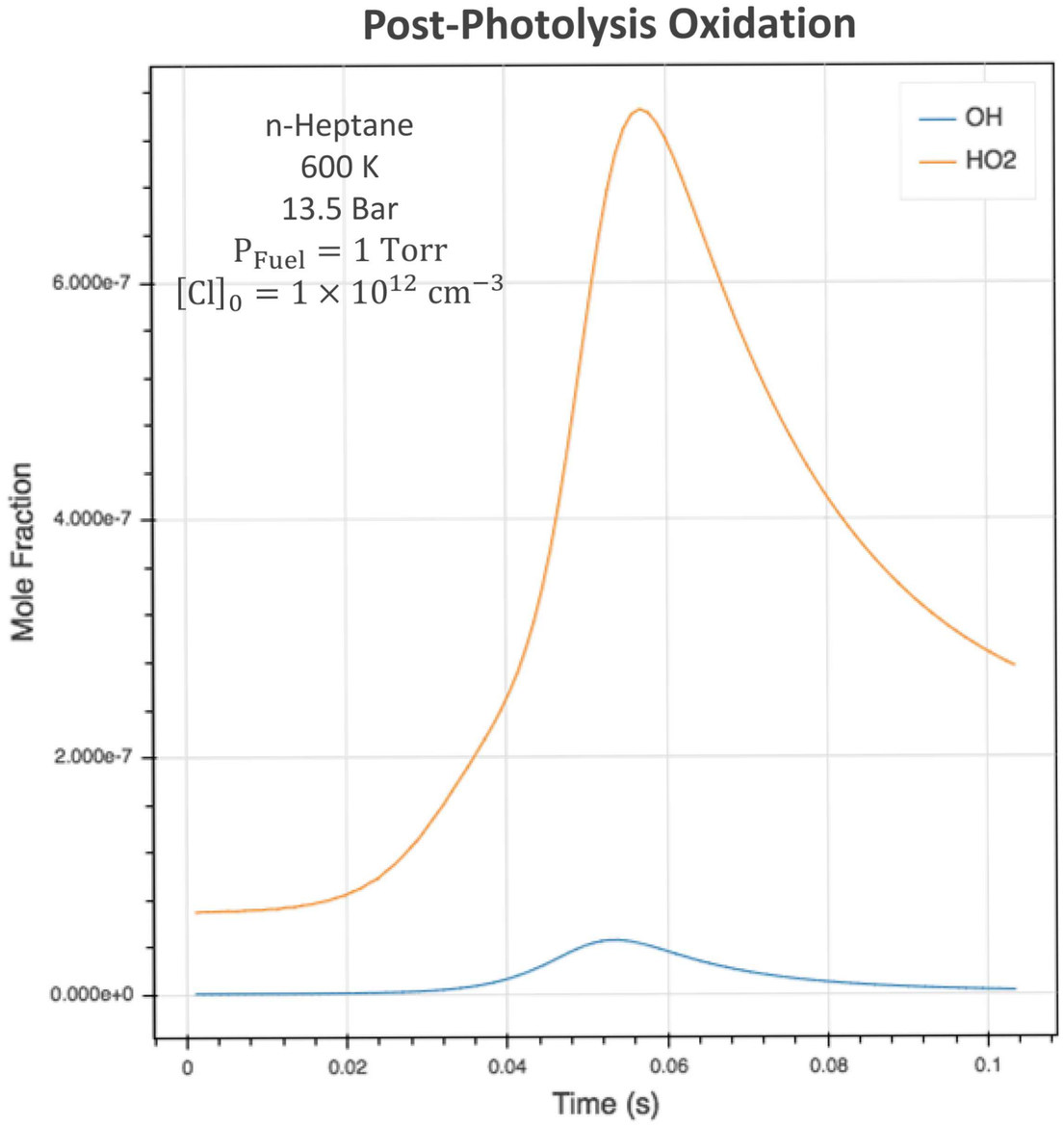
$$[H_2O] = cm^{-3}$$

$$[O(^1D)]_0 = cm^{-3}$$

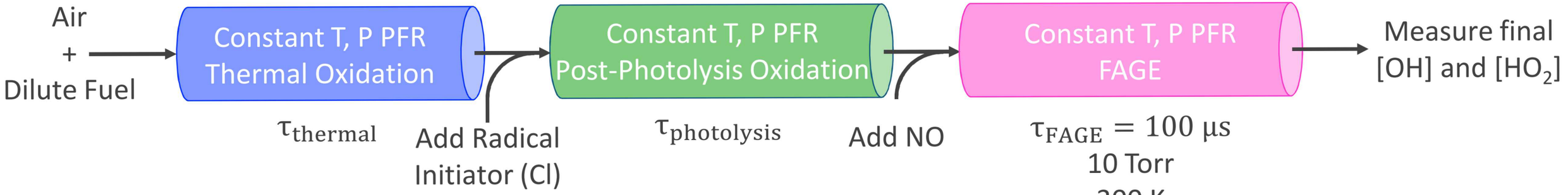
Sangwan, Manuvesh, Evgeni N. Chesnokov, and Lev N. Krasnoperov. “Reaction OH + OH Studied over the 298–834 K Temperature and 1 - 100 Bar Pressure Ranges.”*The Journal of Physical Chemistry A*116, no. 24 (June 21, 2012): 6282–94.

Modeling Thermal Oxidation





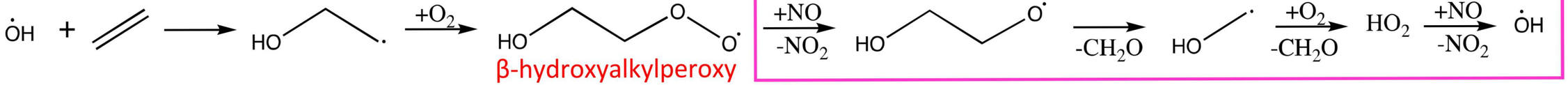
Modeling β-hydroxyalkylperoxy Radical Interference



$$\tau_{thermal} + \tau_{photolysis} = \tau_{total}$$

Vary $0 \leq \tau_{photolysis} \leq \tau_{total}$

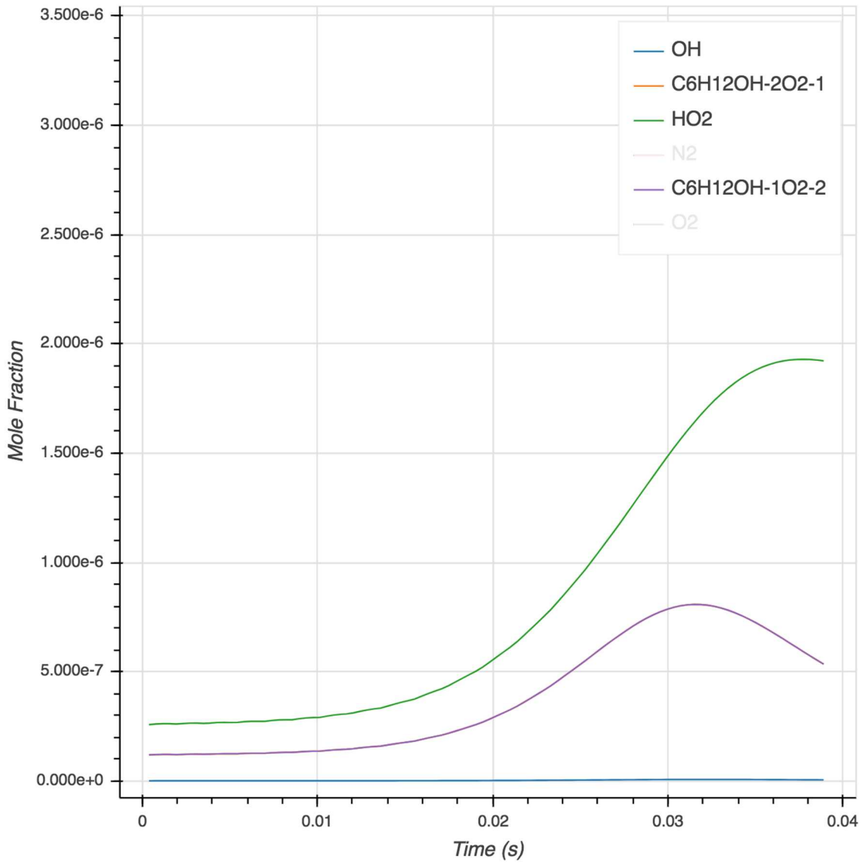
FAGE Reactions*



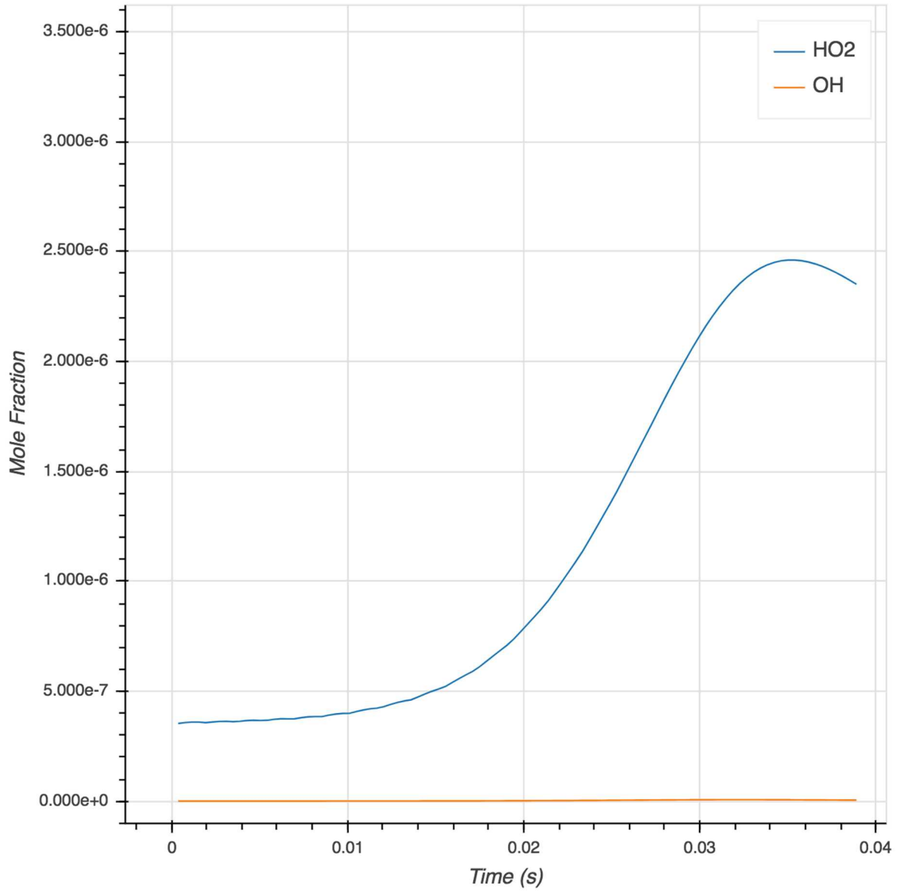
*Rates from NIST Kinetics Database

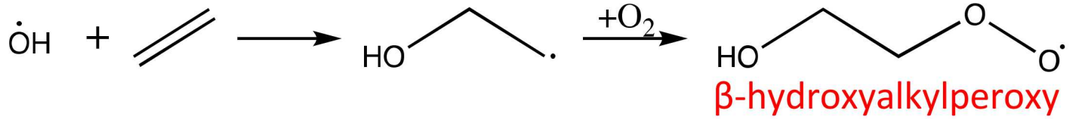
Modeling β-hydroxyalkylperoxy Radical Interference

High-P Reactor Profiles



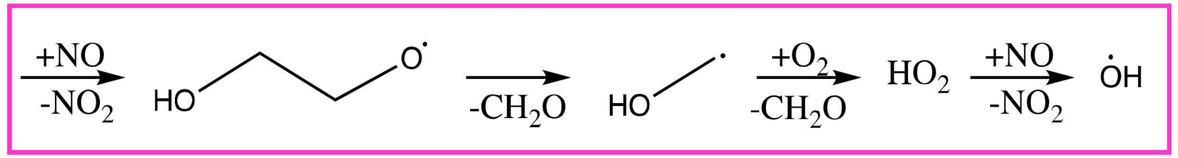
FAGE Profiles



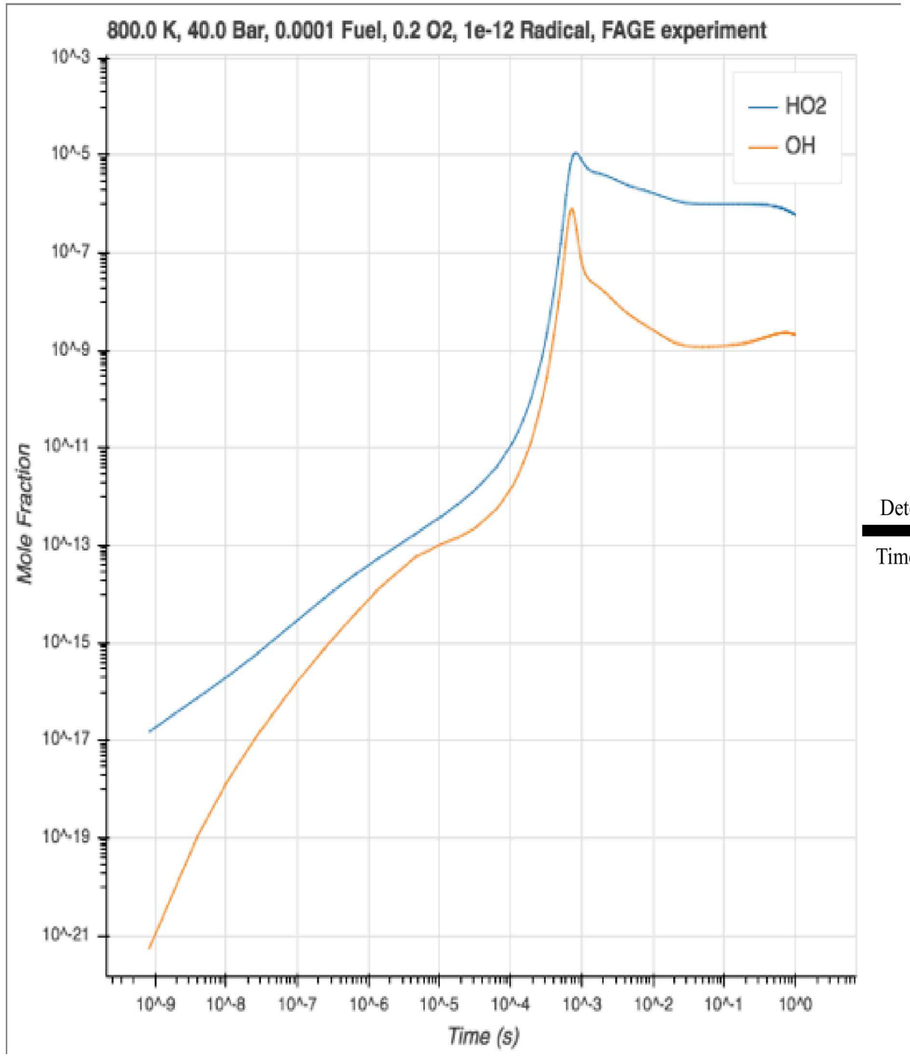


β-hydroxyalkylperoxy

FAGE Reactions*

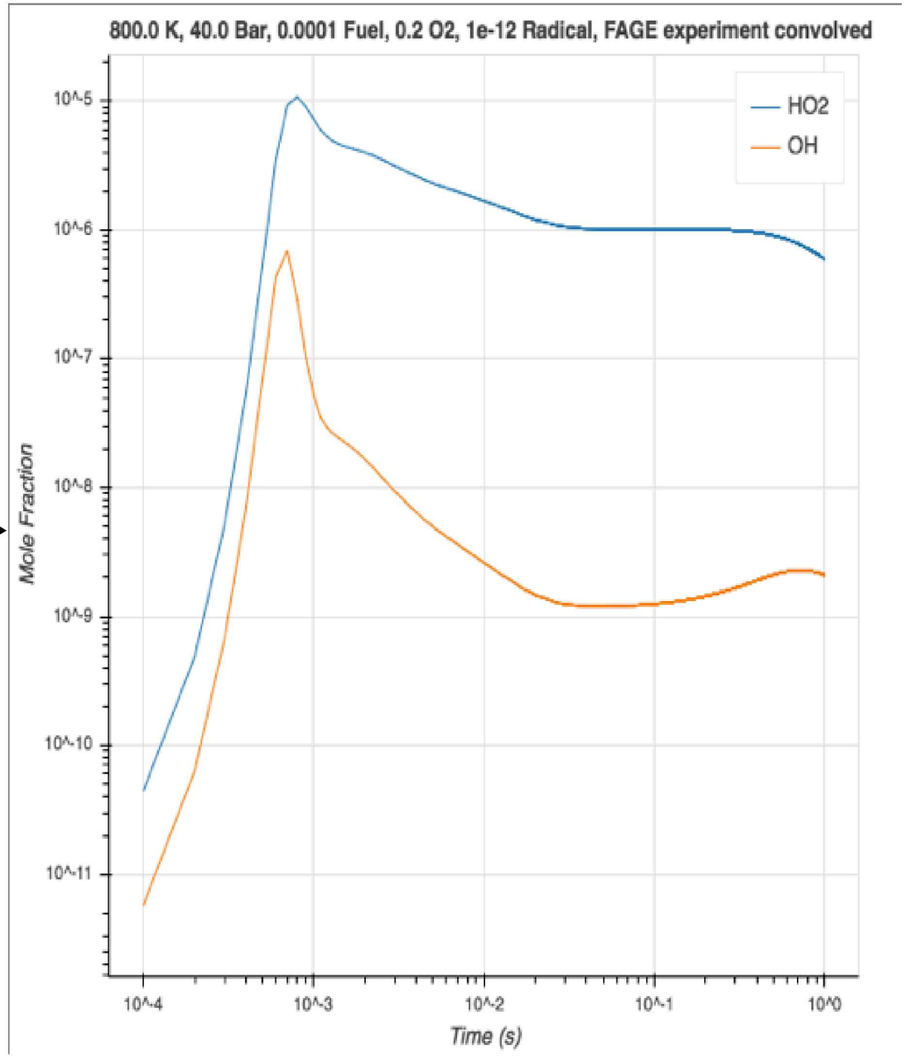


Modeling Detection Limit and Time Resolution

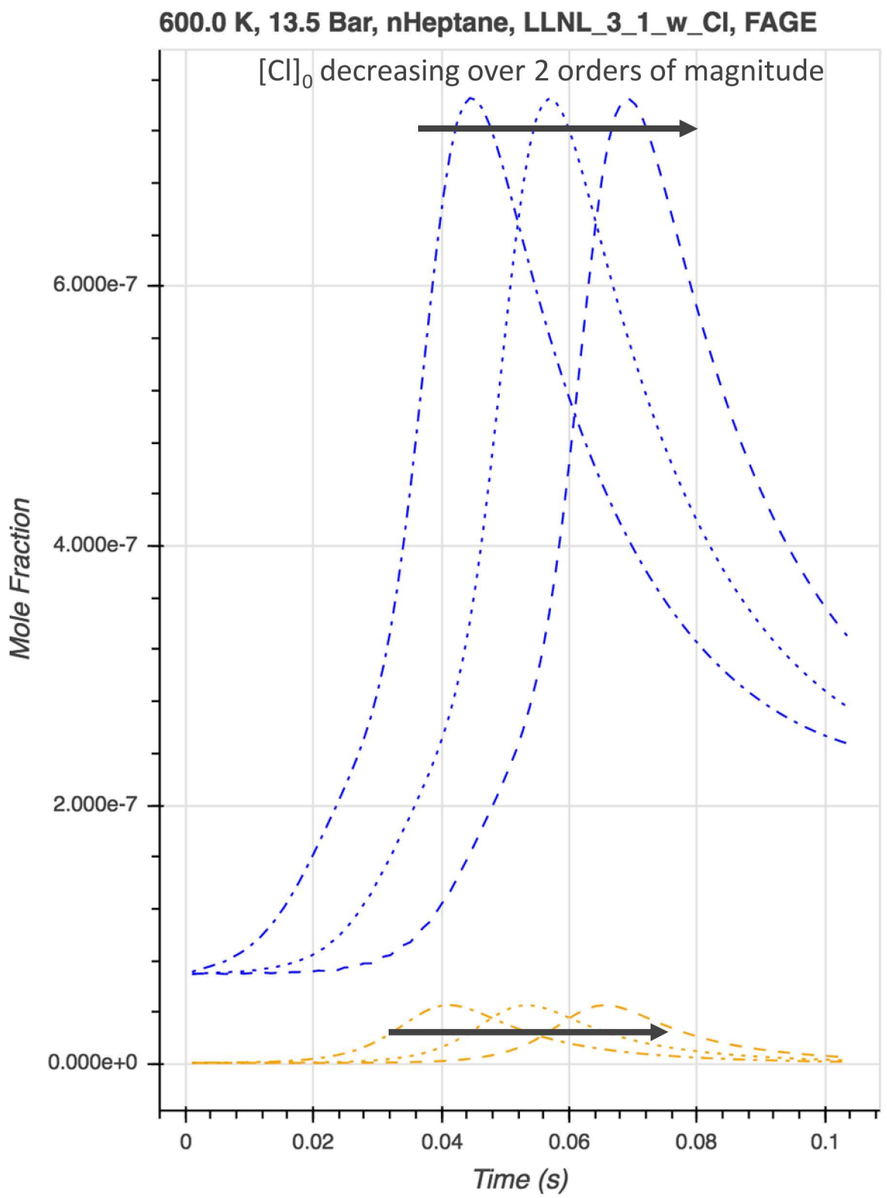


Detection Limit = 1e-12

Time Resolution= 100 µs



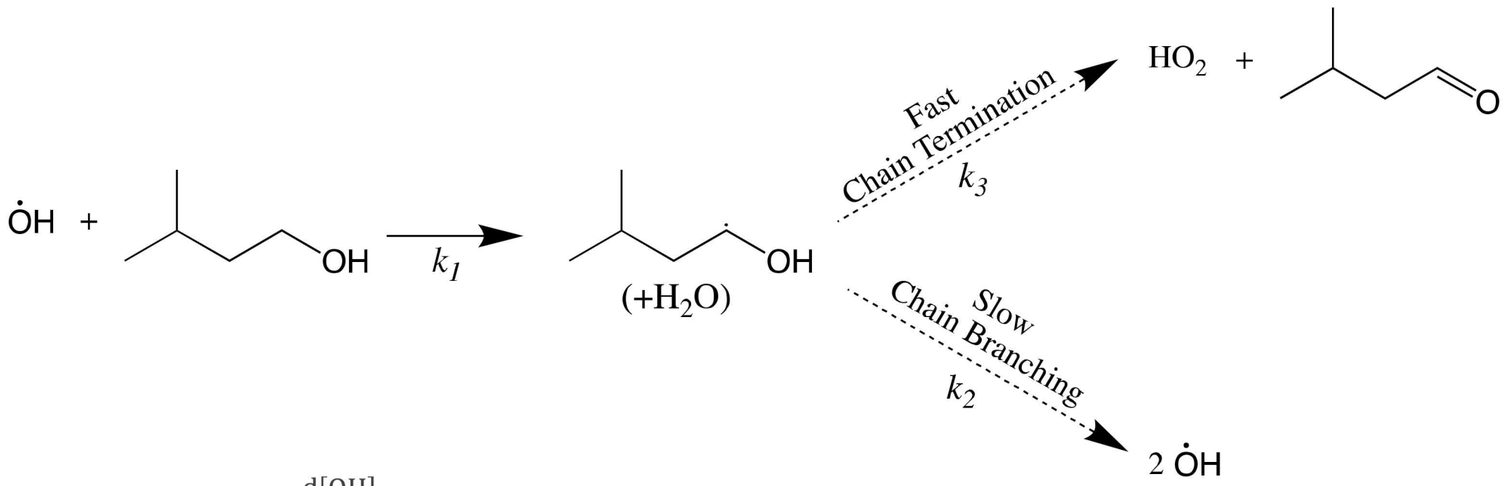
Sensitivity of Results to $[Cl]_0$



Identifying Sensitive Reactions

Sensitive Reaction	Sensitivity For:			Overall Sensitivity Rank
	Temperature (Shock Tube)	*HO_2 (FAGE)*	*OH (FAGE)*	
ch3och2o2<=>ch2och2o2h	1.0	1.0	1.0	3.0
ho2ch2ocho<=>och2ocho+oh	0.47	0.84	0.69	1.99
o2ch2och2o2h<=>ho2ch2ocho+oh	0.1	0.18	0.16	0.45
ho2+oh<=>h2o+o2	-	-0.26	-0.19	0.44

Solving Simple Pentanol Ignition Model



$$\frac{\mathrm{d[OH]}}{\mathrm{dt}} = -k_1[\mathrm{RH}][\mathrm{OH}] + 2k_2[\mathrm{R}]$$

$$\frac{\mathrm{d[R]}}{\mathrm{dt}} = k_1[\mathrm{RH}][\mathrm{OH}] - k_2[\mathrm{R}] - k_3[\mathrm{R}] \approx 0 \text{ (QSSA)}$$

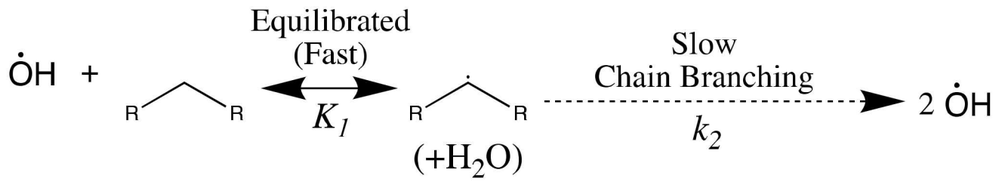
$$\frac{\mathrm{d[HO_2]}}{\mathrm{dt}} = k_3[\mathrm{R}]$$

$$\frac{[\mathrm{OH}]}{[\mathrm{OH}]_0} = \mathrm{e}^{\left(\frac{k_2-k_3}{k_2+k_3}\right)k_1[\mathrm{RH}]t} = \mathrm{e}^{k[\mathrm{RH}]t}$$

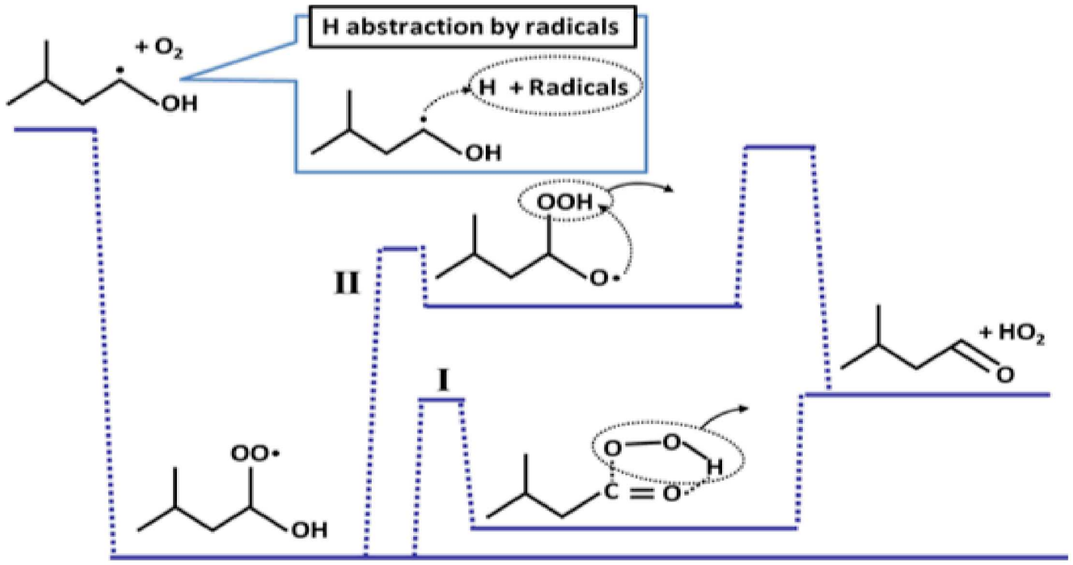
$$\frac{[\mathrm{HO_2}]}{[\mathrm{OH}]_0} = \left(\frac{k_3}{k_2-k_3}\right)[\mathrm{e}^{\left(\frac{k_2-k_3}{k_2+k_3}\right)k_1[\mathrm{RH}]t} - 1] = \mathrm{A}[\mathrm{e}^{k[\mathrm{RH}]t} - 1]$$

$$\tau_{"ignition"} = \frac{\ln\left(\frac{[\mathrm{OH}]_{\mathrm{critical}}}{[\mathrm{OH}]_0}\right)}{k[\mathrm{RH}]}$$

Solving Simple Alkane Ignition Model



Concerted HO_2 Elimination in Pentanol Oxidation



Tsujimura, Taku, William J. Pitz, Fiona Gillespie, Henry J. Curran, Bryan W. Weber, Yu Zhang, and Chih-Jen Sung. “Development of Isopentanol Reaction Mechanism Reproducing Autoignition Character at High and Low Temperatures.” *Energy&Fuels*26, no. 8 (August 16, 2012): 4871–86.