High Pressure Ignition Chemistry of Alternative Fuels

Bryan W. Weber

Prepared for Ph.D. Defense

June 19, 2014

UCONN COMBUSTION DIAGNOSTICS LABORATORY

Combustion drives the energy economy

- Combustion is predicted to remain the dominant energy conversion process for many years into the future
- The combustion of fossil fuels has been implicated in a number of harmful effects on human health, the environment, and the economy
- Two solutions have been proposed:
  - Better engines
  - Better fuels

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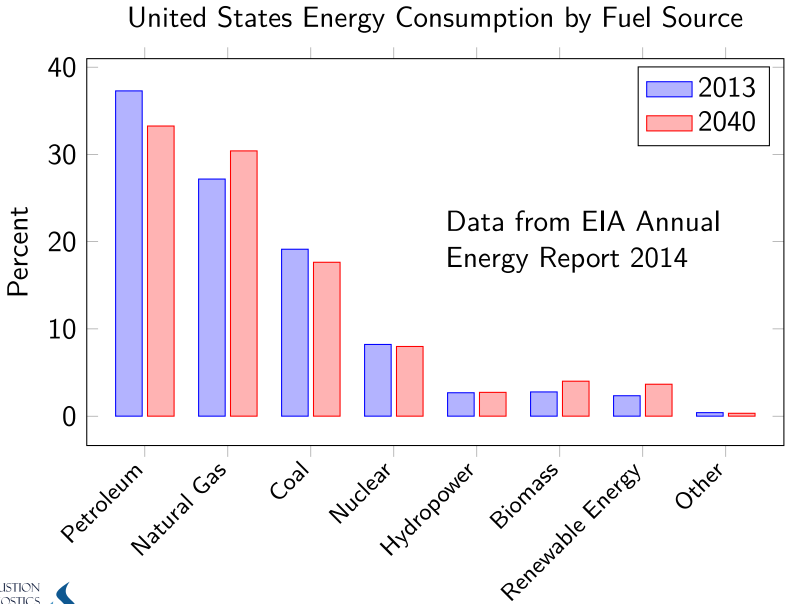

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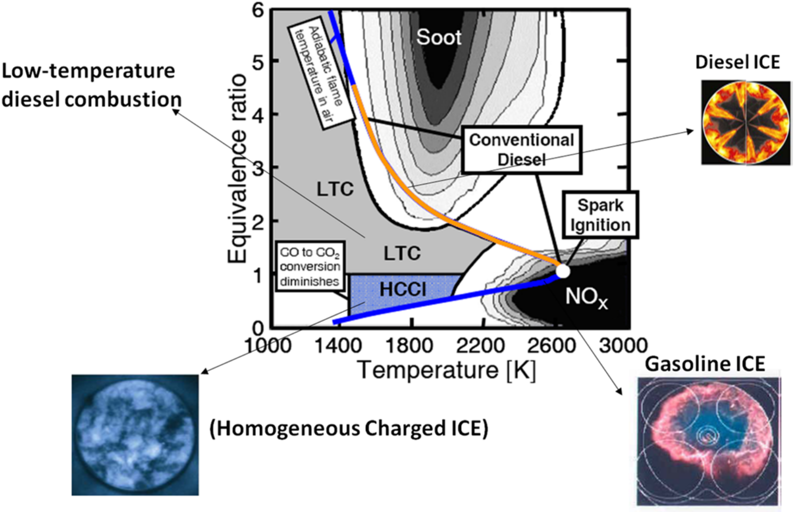
Better engines have higher efficiency and lower emissions



Reproduced in part from J.E. Dec, Proc. Combust. Inst. 32 (2009) 2727–2742

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Better fuels have lower emissions and reduce dependence on fossil fuels

- Better fuels help move us away from traditional fuel sources

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Methylcyclohexane is a major component in stepping-stone fuels

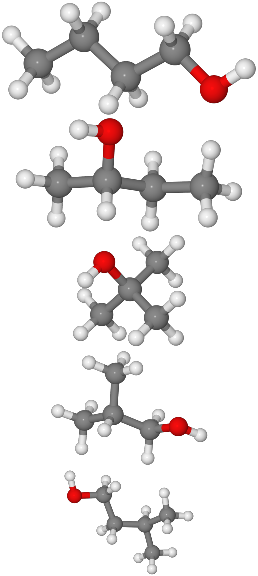
- Methylcyclohexane (MCH) is an important component of fuels produced from alternative petroleum sources, such as shale oil
- Models of real transportation fuels are difficult to construct and use due to the chemical complexity of the fuels
- Surrogate models use a limited number of components to represent the chemical and physical properties of the real fuel
- MCH is a component in many surrogate transportation fuel formulations

Better fuels have lower emissions and reduce dependence on fossil fuels

- Better fuels help move us away from traditional fuel sources
- Better fuels help reduce total emissions

Bio-alcohol fuels can be sustainably produced to reduce well-to-wheel emissions

- Ethanol is a very common biofuel in use today
- Alcohols with more carbon atoms have higher energy density
- Butanol and pentanol can be produced from bio-based and waste sources
- Butanol is the smallest alcohol with each type of C-O bond



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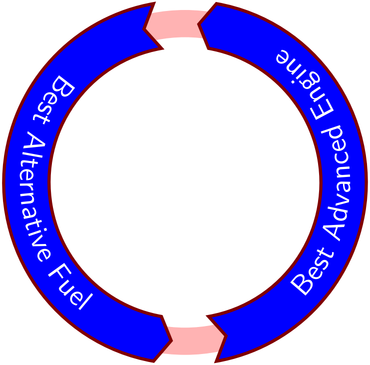
We need both solutions to make substantial progress

- Selecting the "best" alternative fuel requires knowledge of the "best" engine, which depends on which alternative fuel is selected...
- Testing every fuel in every engine is prohibitively expensive and time consuming



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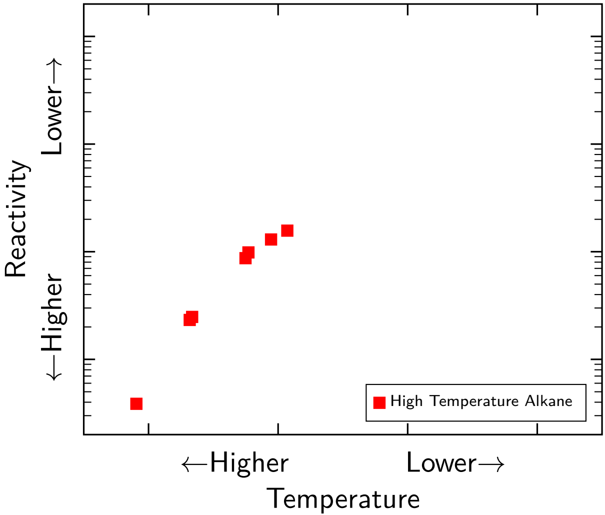
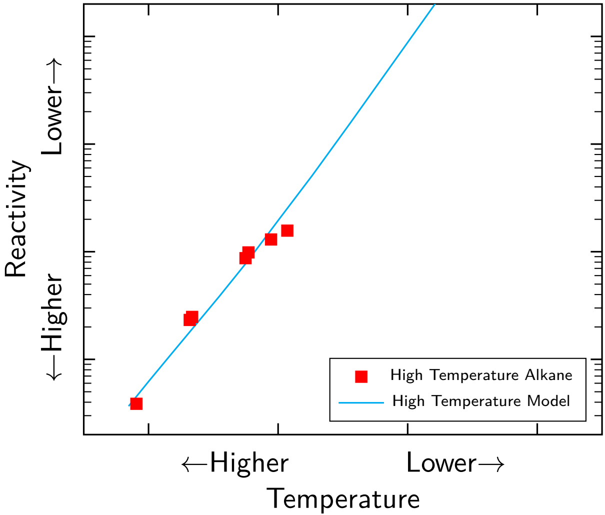
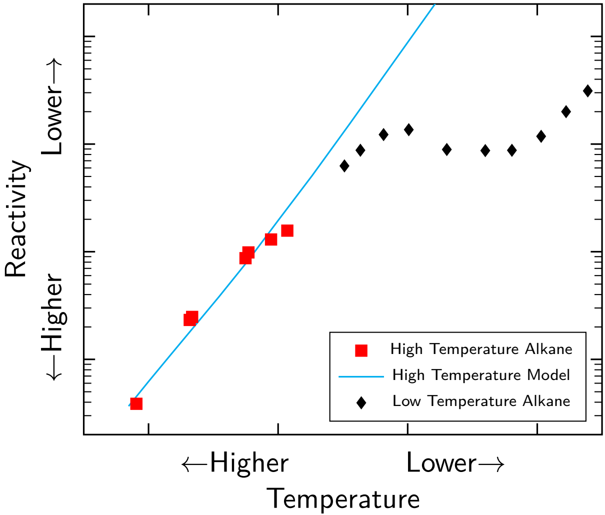
- Computer-aided design can be employed to create fuel-flexible engines if the fuel models are predictive under LTC conditions


Reactivity
←Higher
Lower→
High Temperature Alkane
←Higher
Lower→
Temperature



High Temperature Alkane
High Temperature Model
←Higher
Lower→
Temperature
Reactivity
←Higher
Lower→



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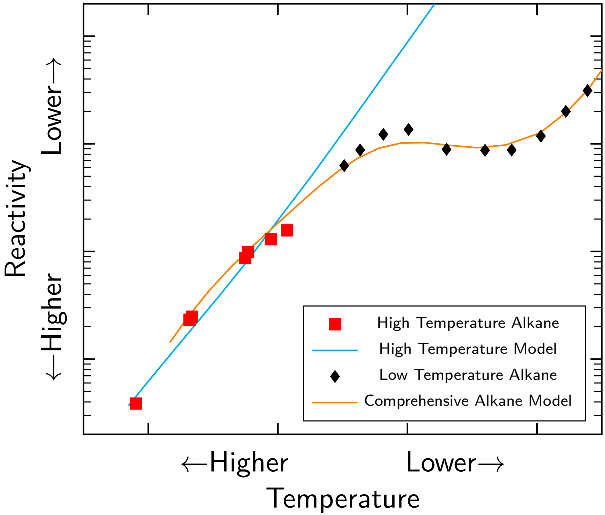

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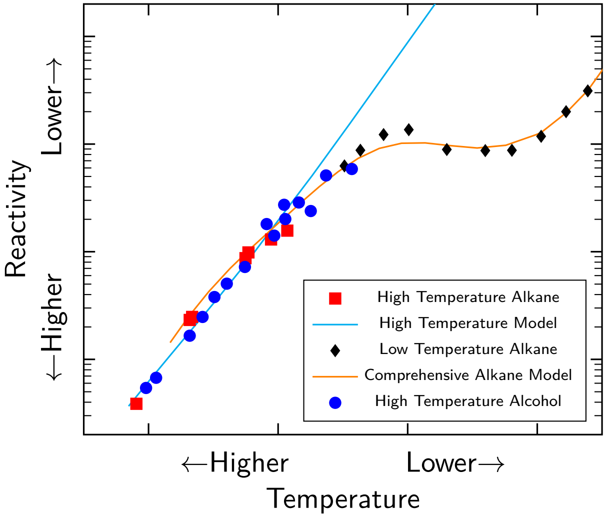
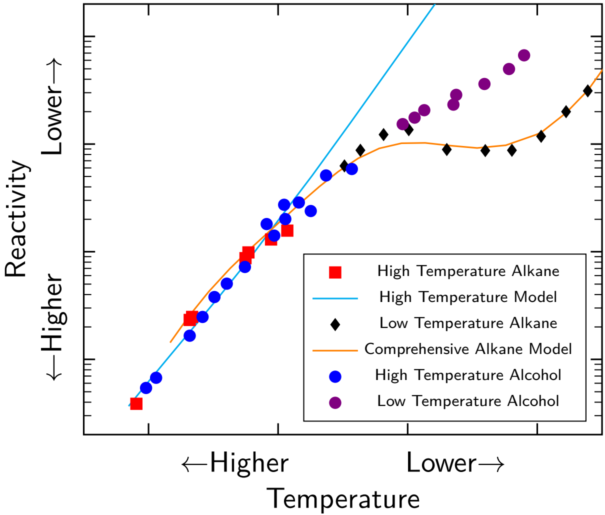


←Higher
Reactivity
Lower→
High Temperature Alkane
High Temperature Model
Low Temperature Alkane
Comprehensive Alkane Model
High Temperature Alcohol
←Higher
Lower→
Temperature



Reactivity
←Higher
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Temperature
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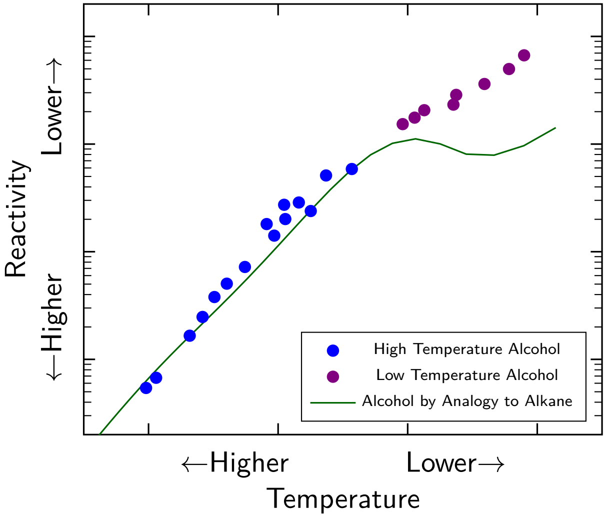

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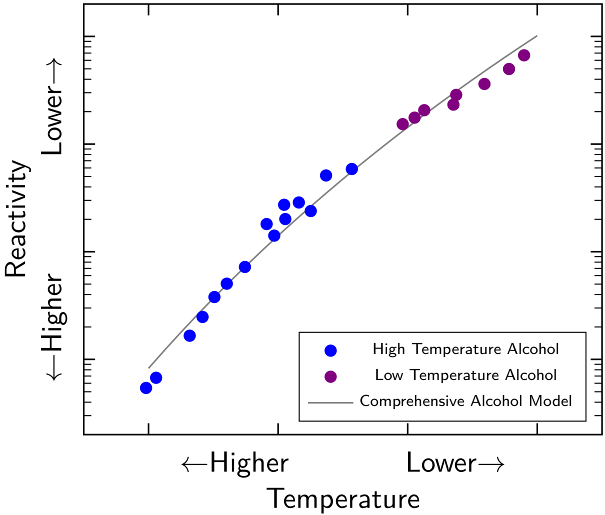
High Temperature Alcohol
Low Temperature Alcohol
Comprehensive Alcohol Model
←Higher Reactivity Lower→
←Higher Lower→
Temperature

How can we understand the effect of better fuels on better engines?

- We need to know the physical properties
  - Density
  - Viscosity
  - ...
- We need to know the combustion properties
  - Heat of combustion
  - Reactivity
  - Pollutant Production
  - ...

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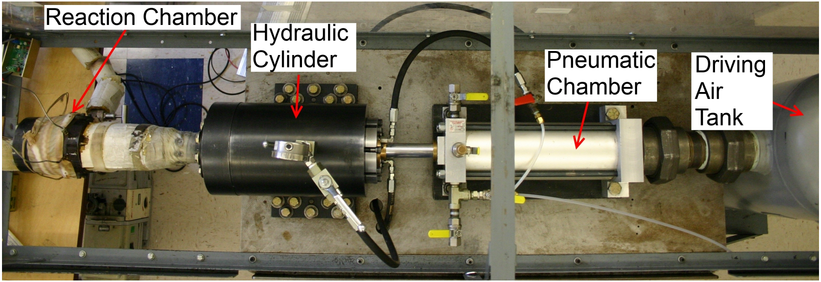
  - Pollutant Production $\leftarrow$ Detailed reaction pathways
  - ...

Experimental Methods

Rapid Compression Machine



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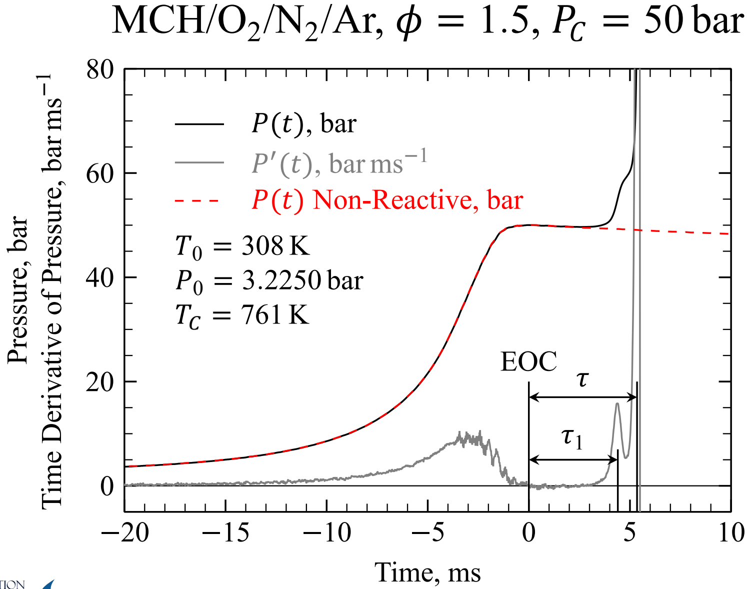
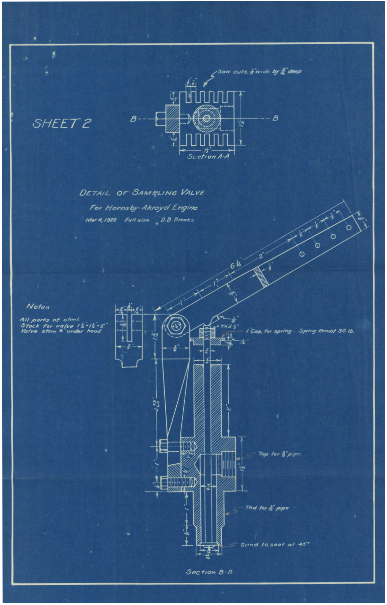


Rapid Sampling Apparatus

- Sampling apparatuses have been used since the 1920's to study combustion chemistry



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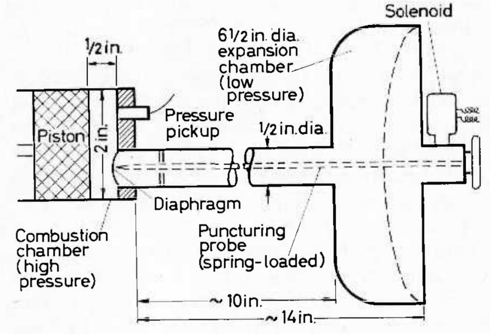

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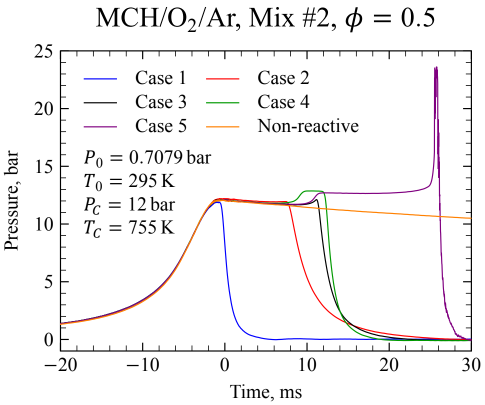

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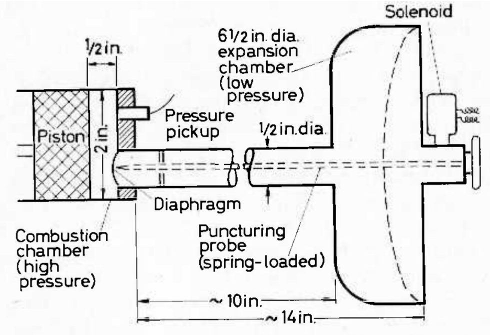

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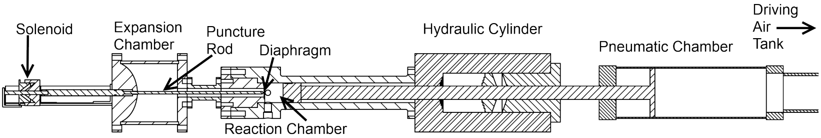

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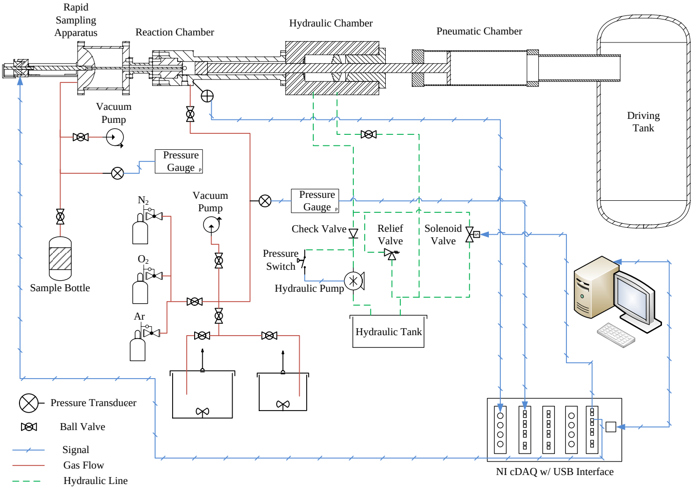

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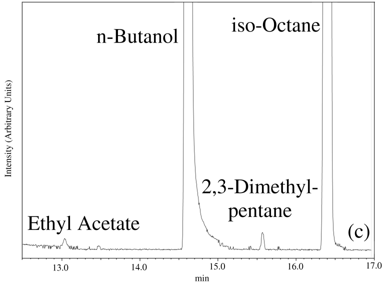
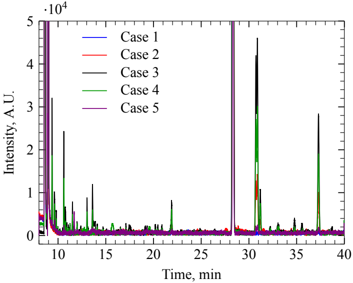
Gas Chromatograph/Mass Spectrometer

- Standard piece of chemistry lab equipment, commercially supplied (Shimadzu GCMS-QP2010S)

Gas Chromatograph/Mass Spectrometer

- Separates, identifies, and quantifies chemical species





Numerical Methods

- Computational analysis complements experimental work
- Direct comparisons can be made between the computed and experimental ignition delays as well as the pressure traces
- Detailed analysis of chemical kinetic models can deepen the understanding of the experimental data

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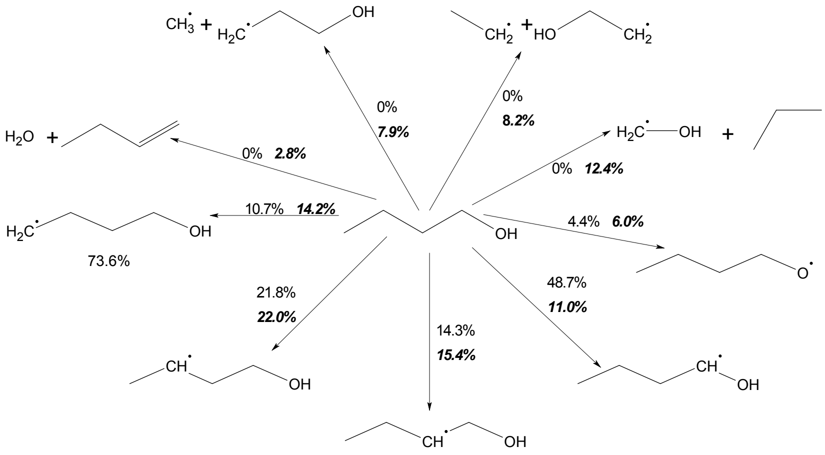
Path Flux Analysis



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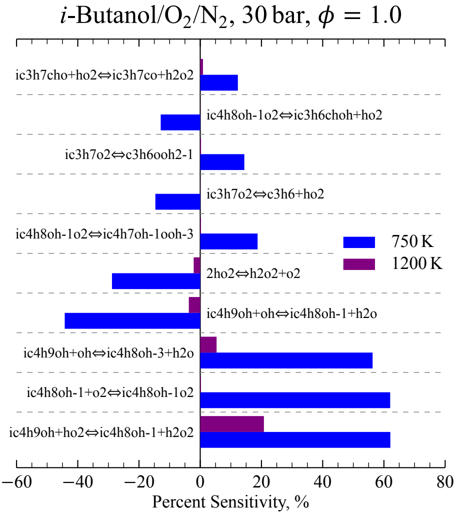
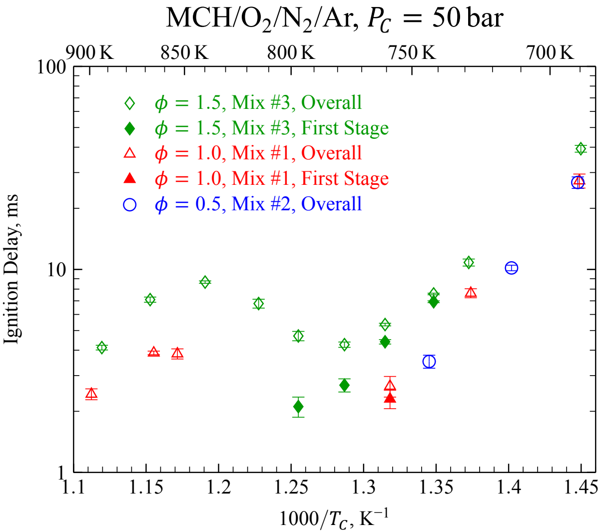
  - Sensitivity Analysis helps find important reactions and how they affect reactivity

Sensitivity Analysis



Methylcyclohexane

Ignition delays were measured at new conditions



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Many improvements to the kinetic model for MCH were made

- The C_1–C_4, aromatics, and cyclohexane chemistry have been updated
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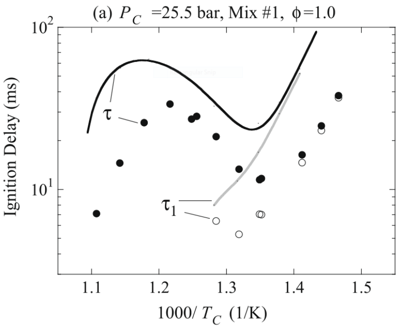
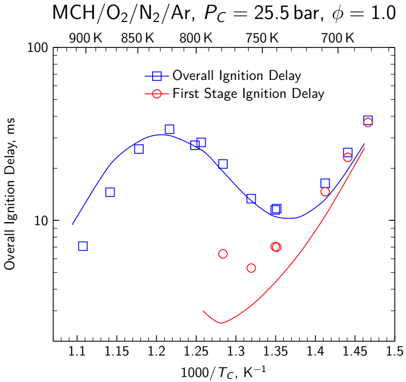


Mittal and Sung Combust. Flame 2009



Weber et al. Combust. Flame 2014

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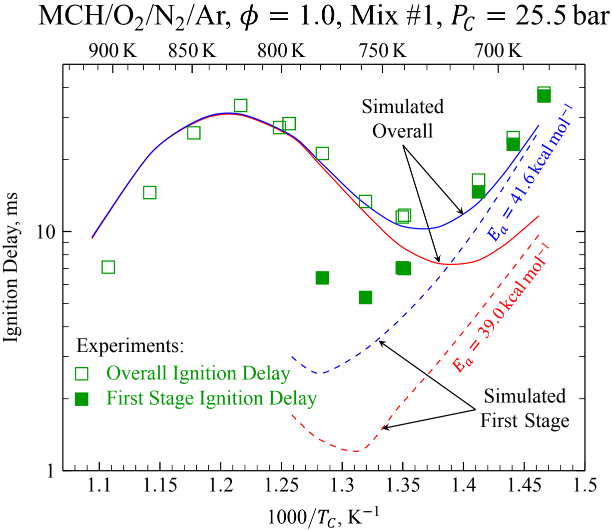

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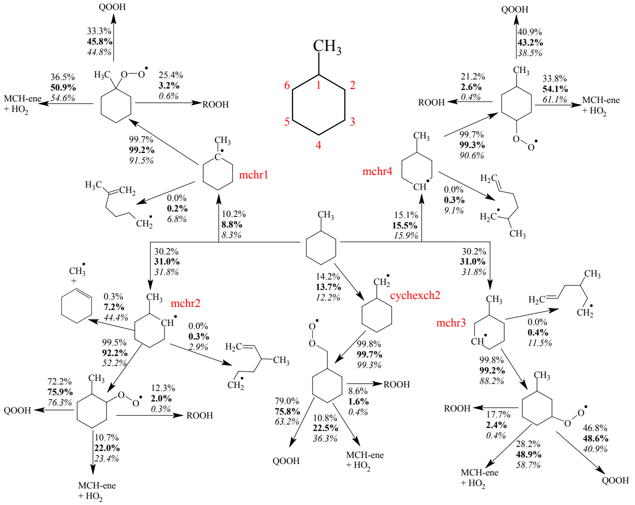
- New pathways involving species with unsaturated rings were added to enable prediction of species such as methylcyclohexenes

Path flux analysis shows the important reaction pathways



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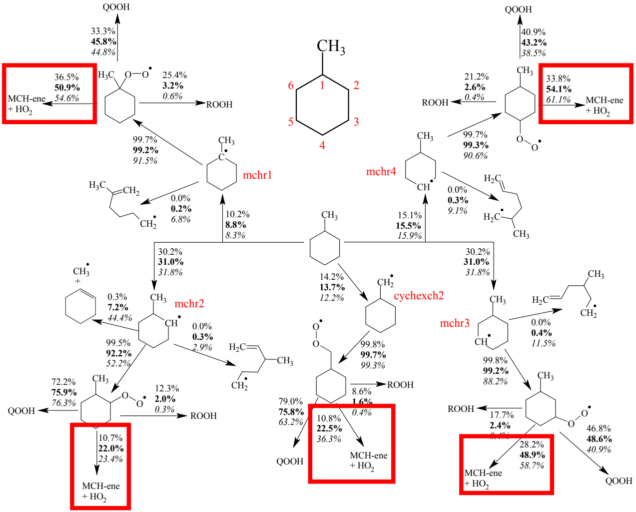
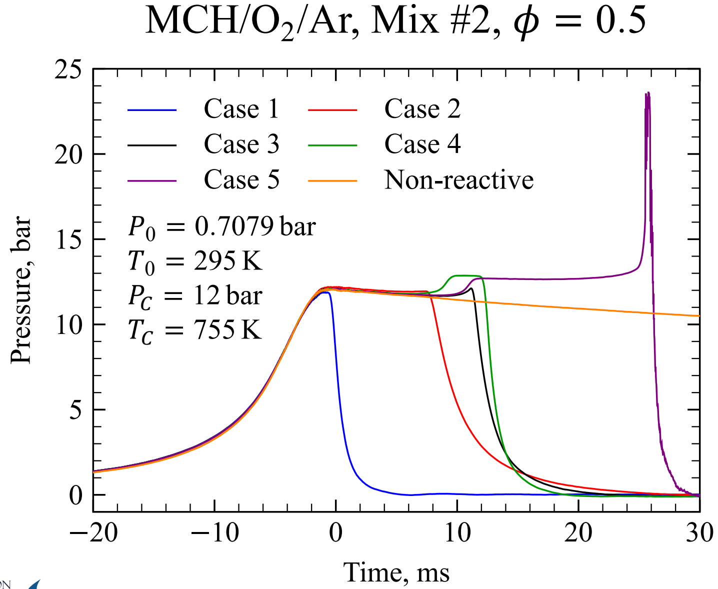


New sampling data can test the newly added pathways



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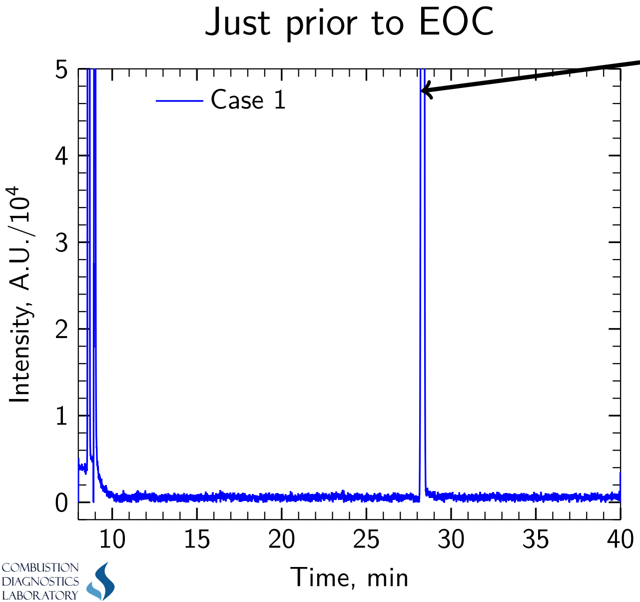

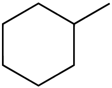

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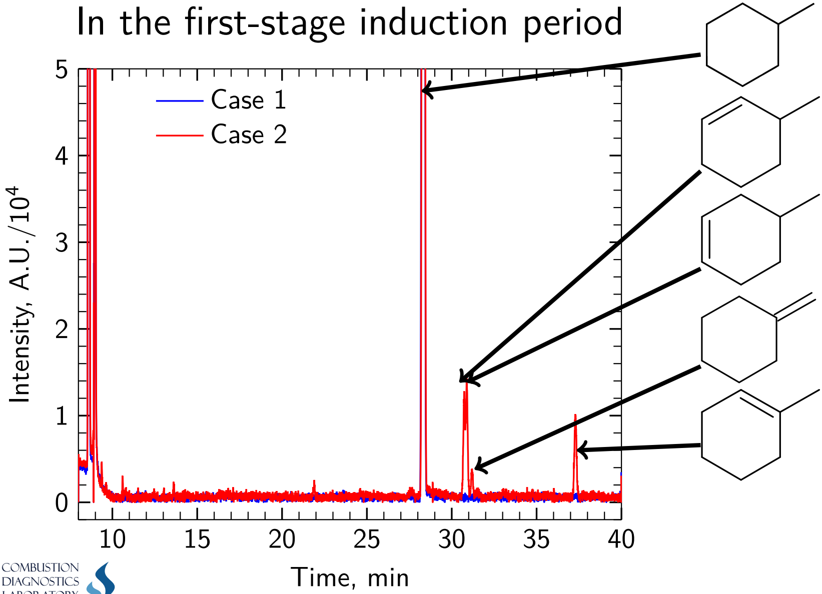

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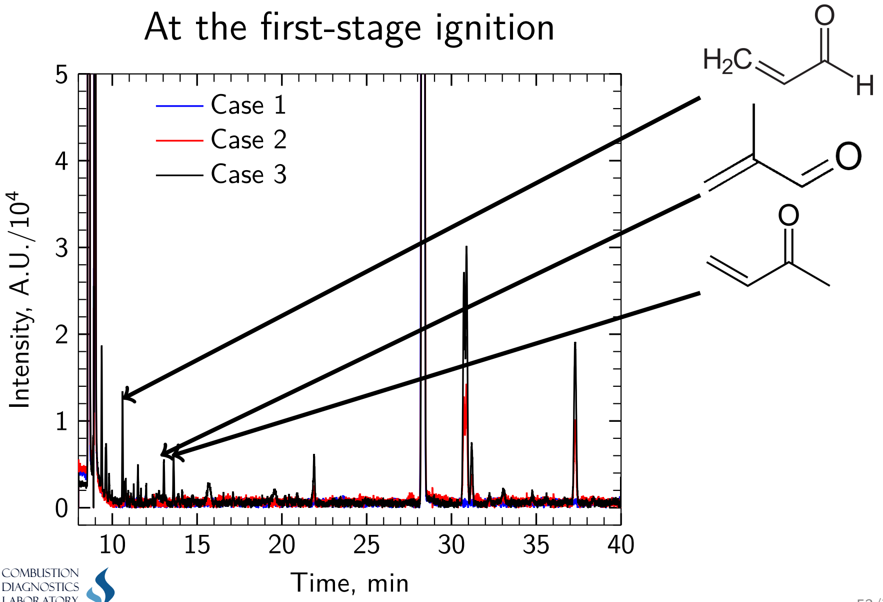

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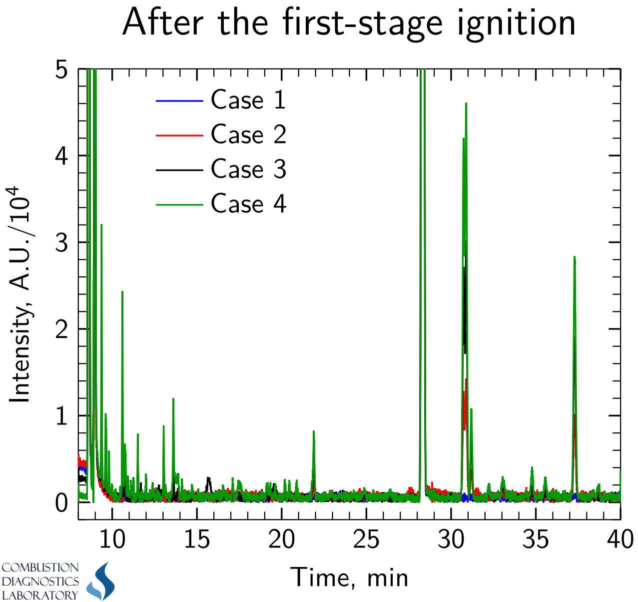

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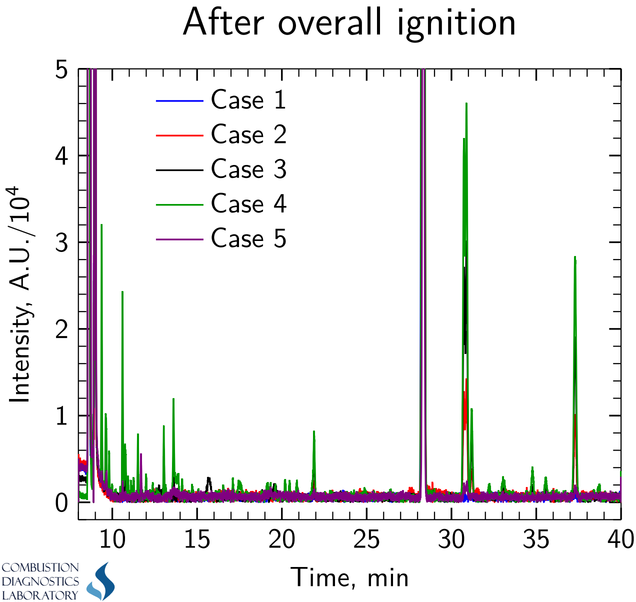

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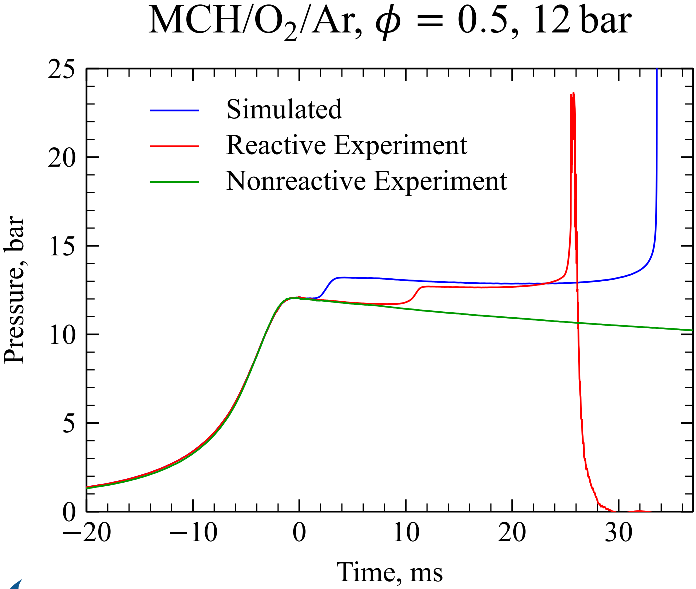

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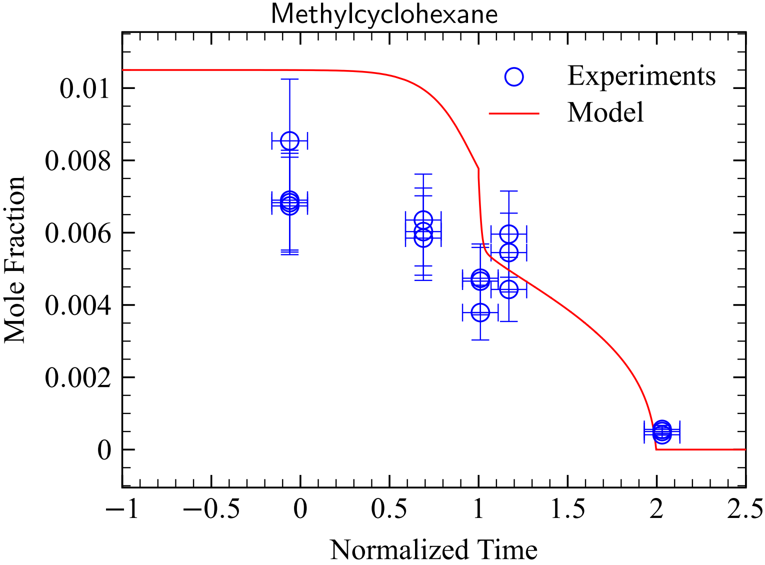

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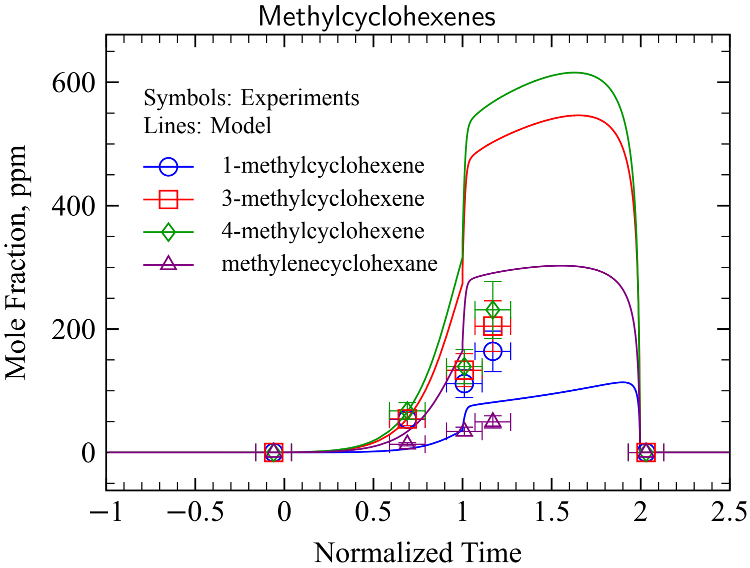

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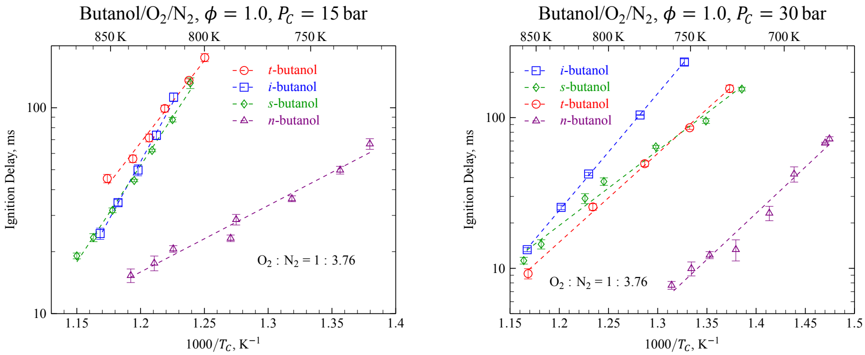
Butanol Isomers

The reactivity of the butanol isomers depends on the pressure



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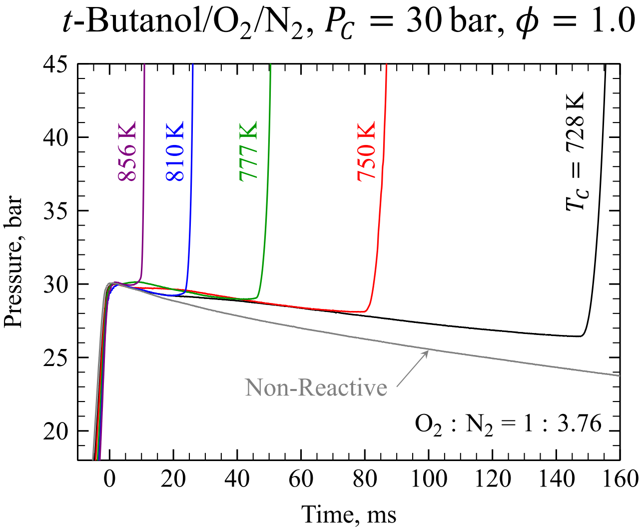

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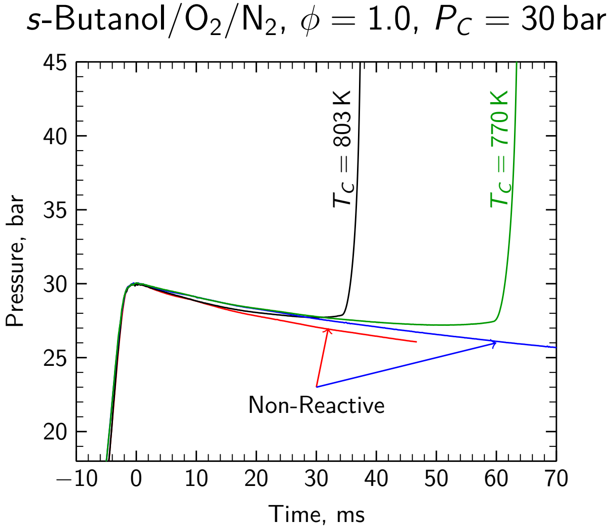

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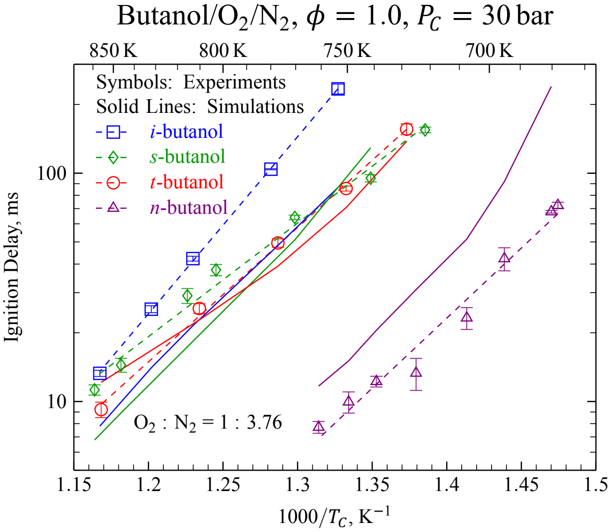
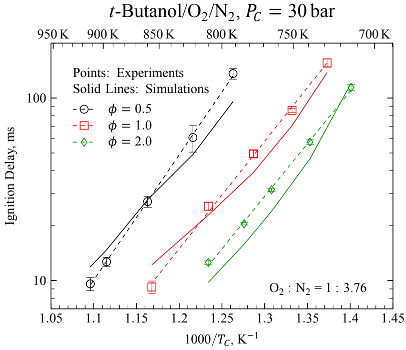
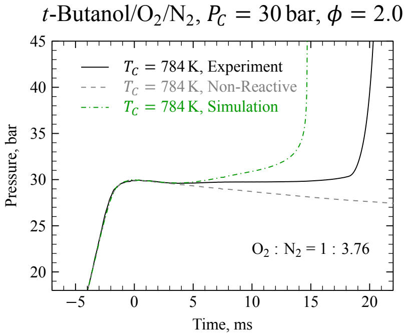
Understanding the detailed chemistry enables modeling of biofuel ignition



Model from Sarathy et al. Combust. Flame 2012

Understanding the detailed chemistry enables modeling of biofuel ignition





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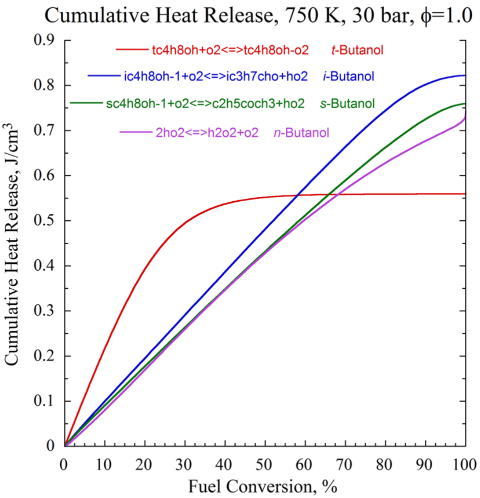

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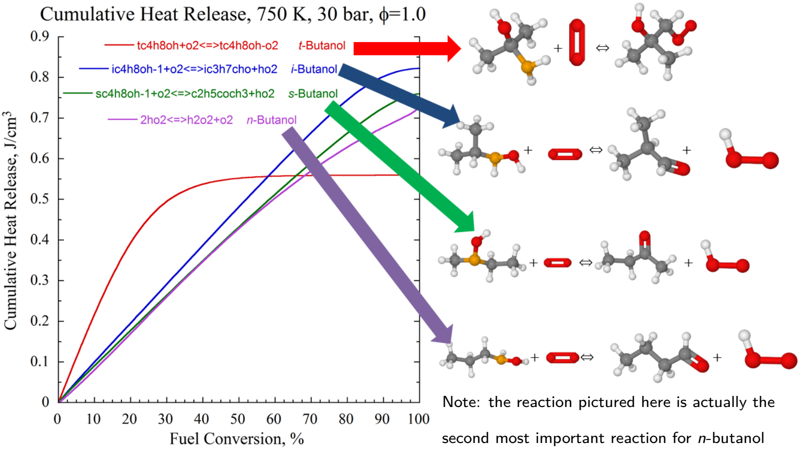

Note: the reaction pictured here is actually the second most important reaction for *n*-butanol

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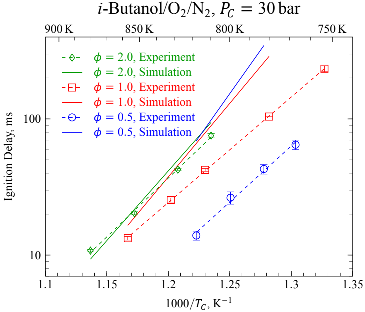
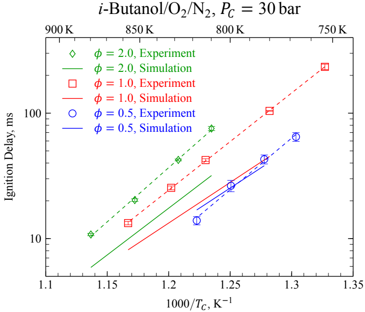
The models cannot predict the combustion behavior at some LTC engine-relevant conditions



Model from Weber et al. 8th US National Combustion Meeting 2013



Model from Sarathy et al. Combust. Flame 2012

There is still some critical information missing from our understanding of high-pressure, low-temperature ignition of alternative fuels

Future work

- Calibration for more species of importance
- Provide quantitative speciation data for model comparison
- Consider more conditions and more fuels

Summary

- We need a better understanding of the fundamental combustion properties of alternative fuels, especially under engine-relevant conditions
- Using this understanding, we need to develop models that can predict the combustion behavior of new fuels in new engines
- Through experimental studies and detailed chemical kinetic analysis, my work has extended the state-of-the-art in our understanding of high-pressure ignition chemistry of alternative fuels

Thank you!
Questions?

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