

High Pressure Ignition Chemistry of Alternative Fuels

Bryan W. Weber

Prepared for Ph.D. Defense

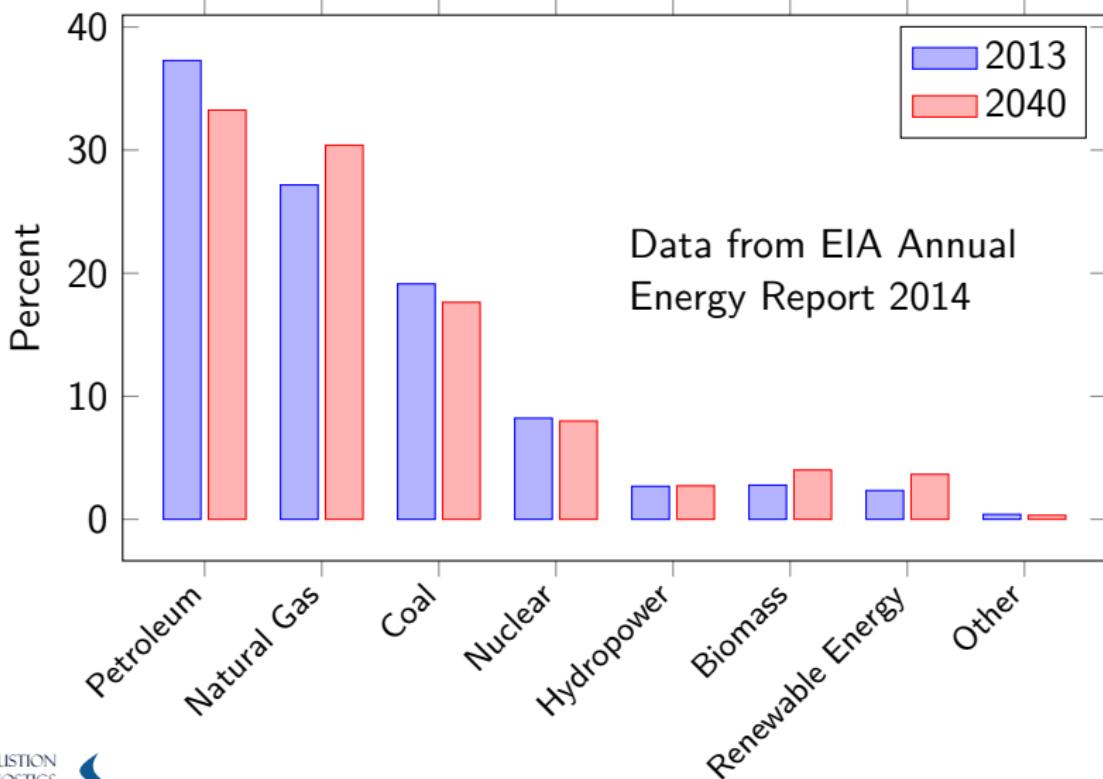
June 19, 2014

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

Combustion drives the energy economy

United States Energy Consumption by Fuel Source



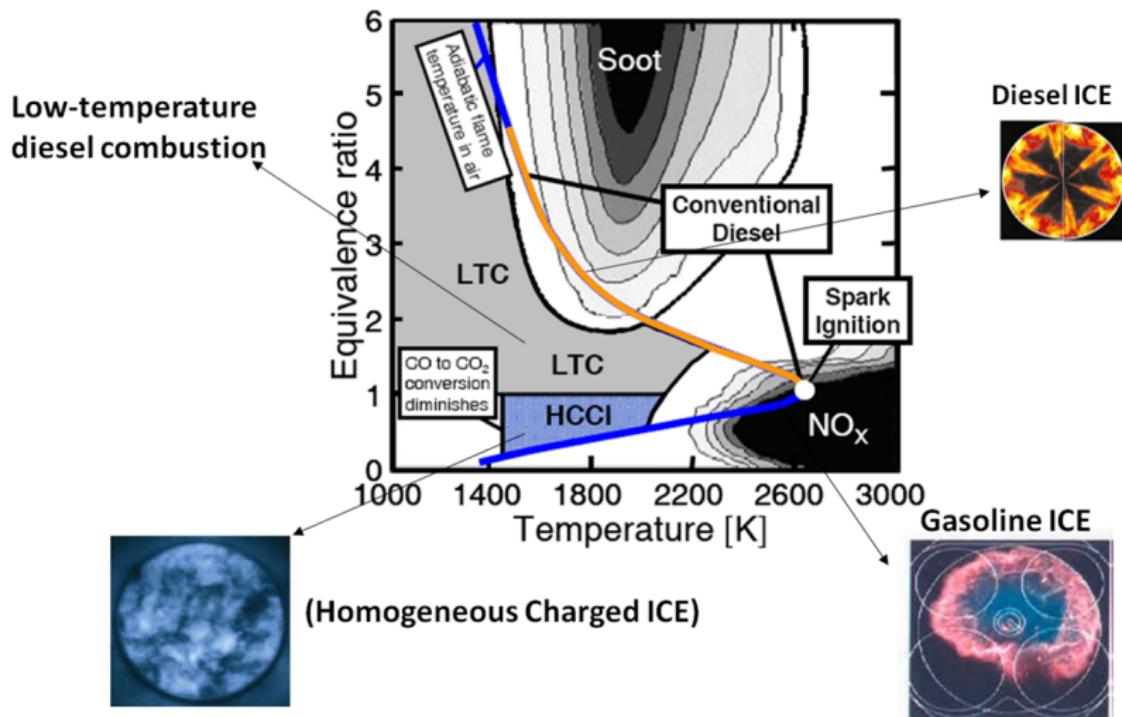
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Better engines have higher efficiency and lower emissions



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

Combustion drives the energy economy

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- ▶ Two solutions have been proposed:
 - ▶ Better engines
 - ▶ **Better fuels**

Better fuels have lower emissions and reduce dependence on fossil fuels

- ▶ Better fuels help move us away from traditional fuel sources

Methylcyclohexane is a major component in stepping-stone fuels

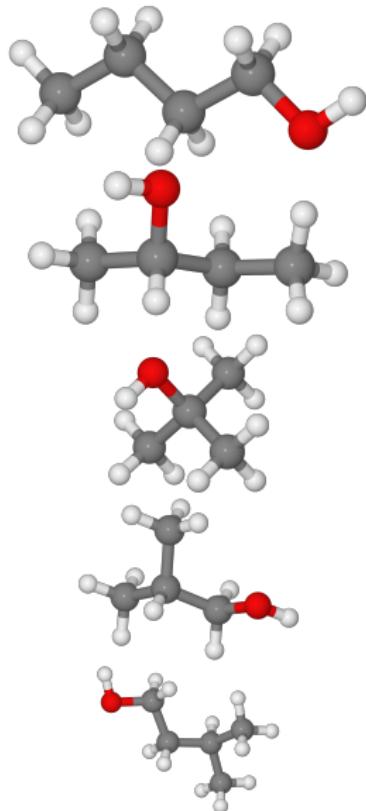
- ▶ Methylcyclohexane (MCH) is an important component of fuels produced from alternative petroleum sources, such as shale oil
- ▶ Models of real transportation fuels are difficult to construct and use due to the chemical complexity of the fuels
- ▶ Surrogate models use a limited number of components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

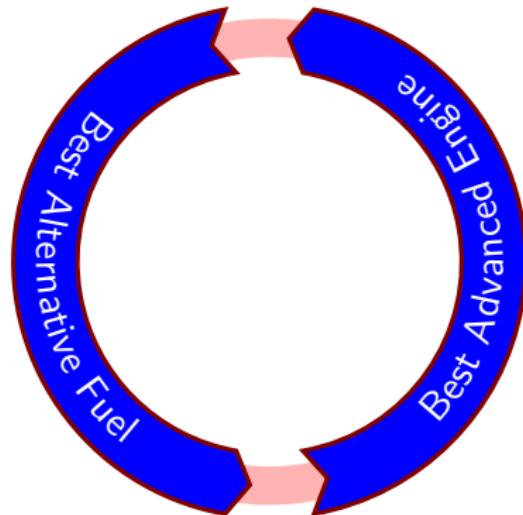
Bio-alcohol fuels can be sustainably produced to reduce well-to-wheel emissions

- ▶ 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



We need both solutions to make substantial progress

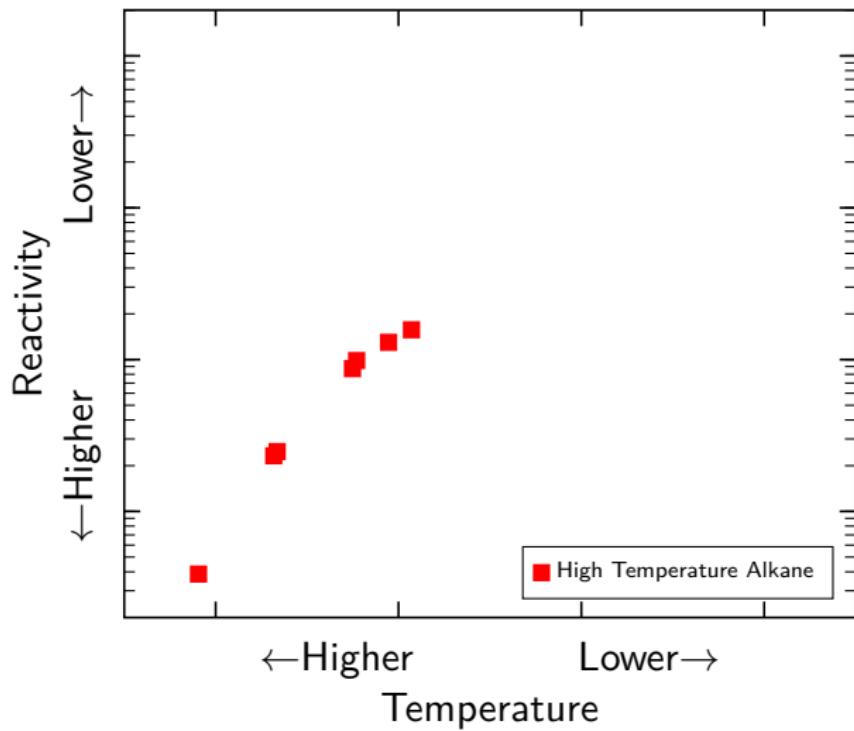
- ▶ Selecting the “best” alternative fuel requires knowledge of the “best” engine, which depends on which alternative fuel is selected...
- ▶ Testing every fuel in every engine is prohibitively expensive and time consuming

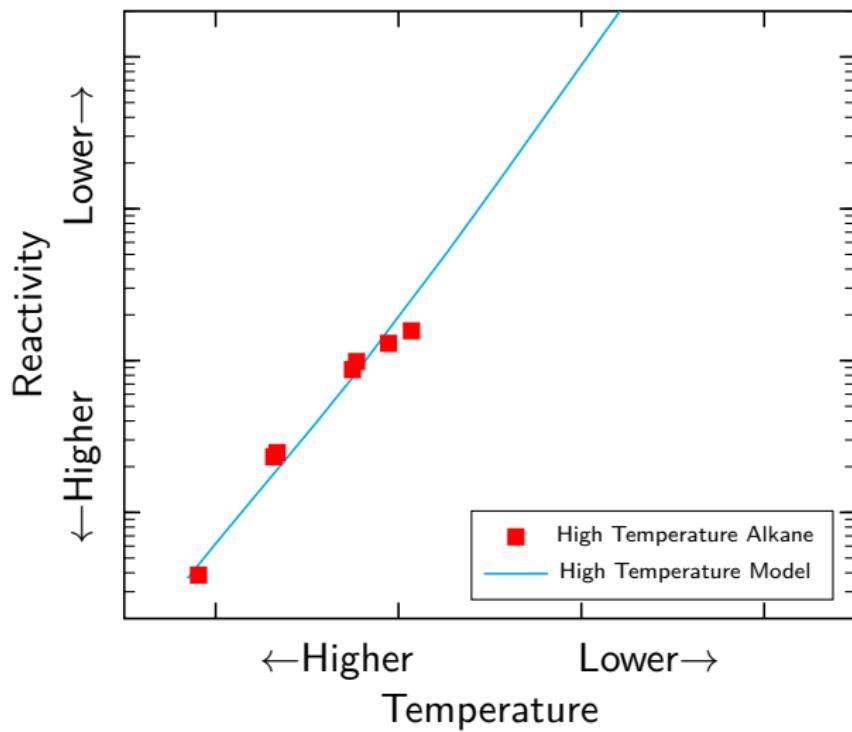


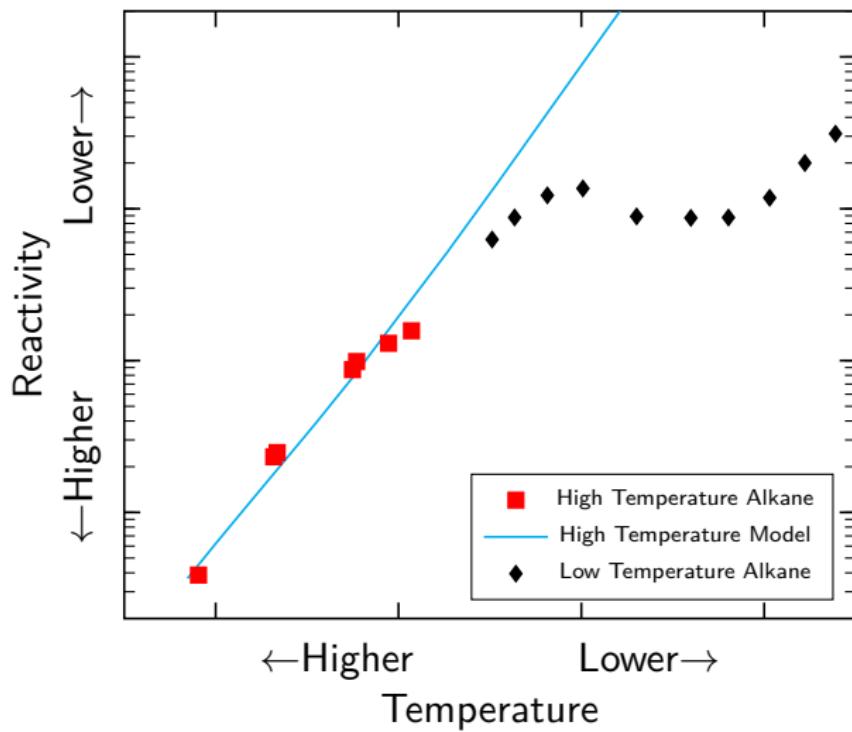
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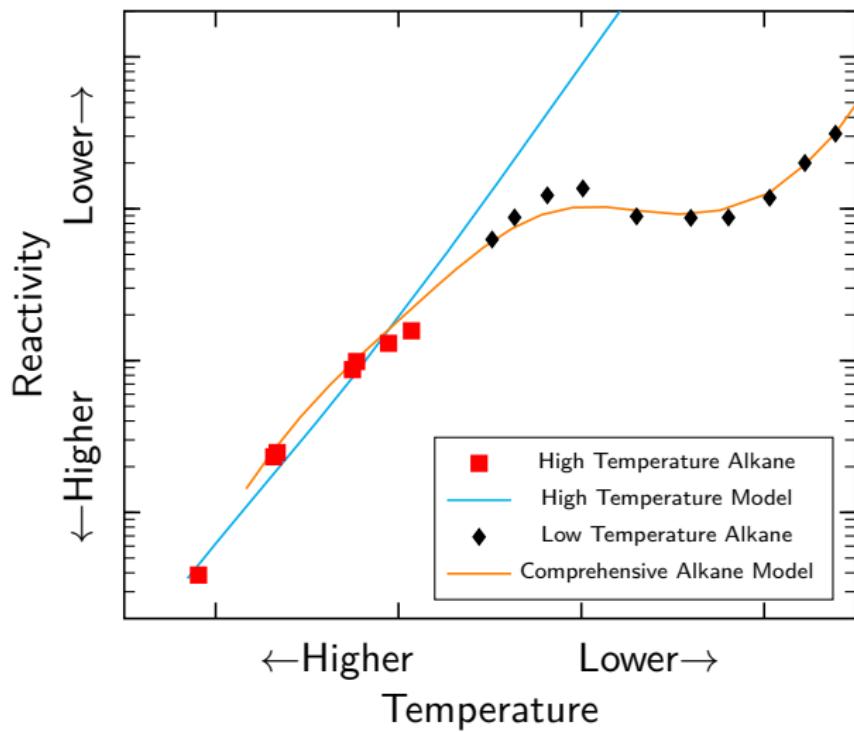
- ▶ Selecting the “best” alternative fuel requires knowledge of the “best” engine, which depends on which alternative fuel is selected...
- ▶ Testing every fuel in every engine is prohibitively expensive and time consuming
- ▶ Computer-aided design can be employed to create fuel-flexible engines **if the fuel models are predictive under LTC conditions**

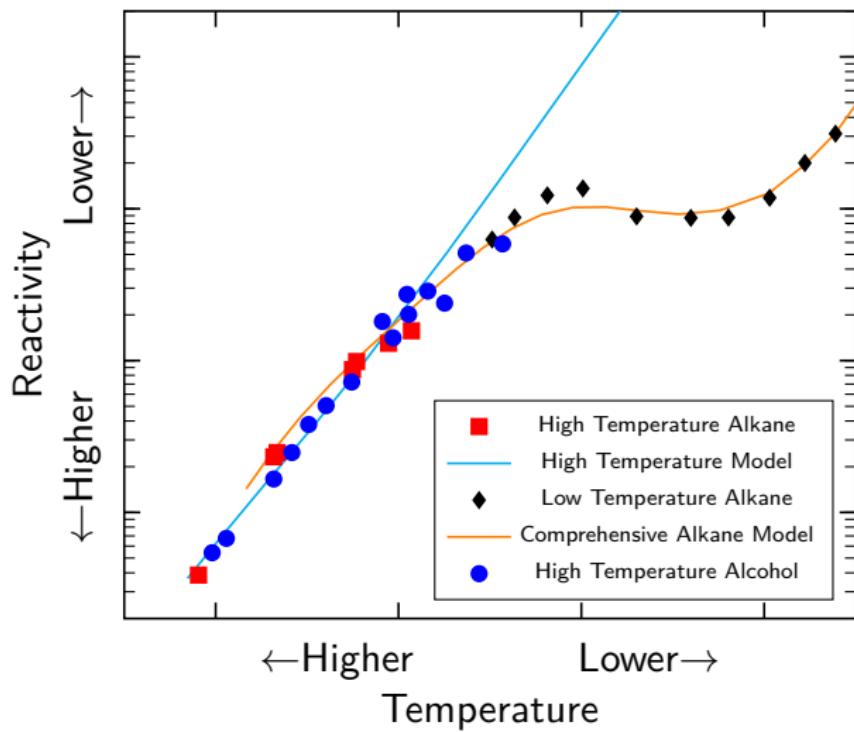


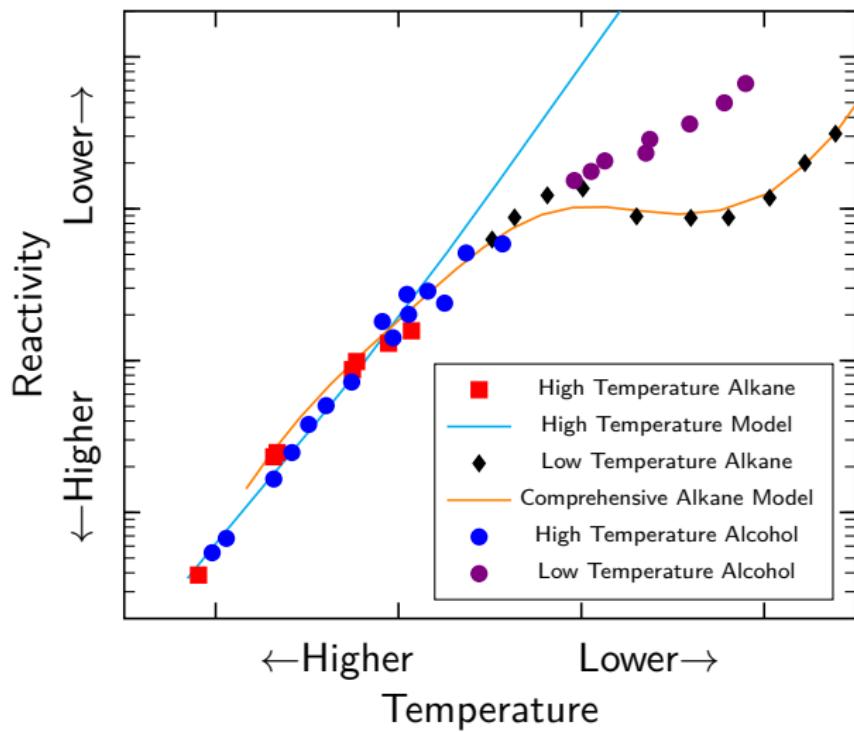


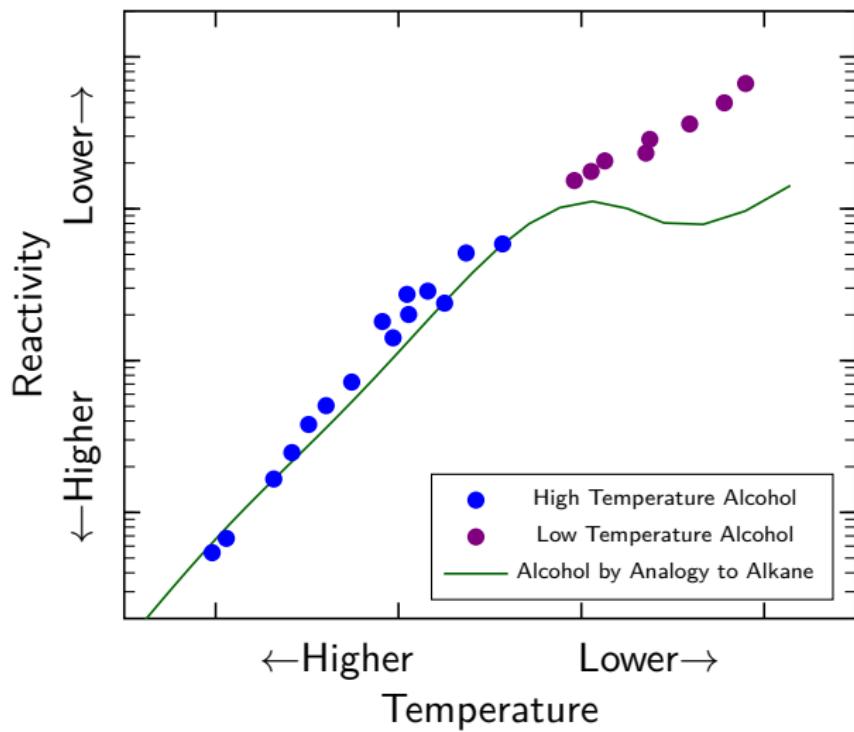


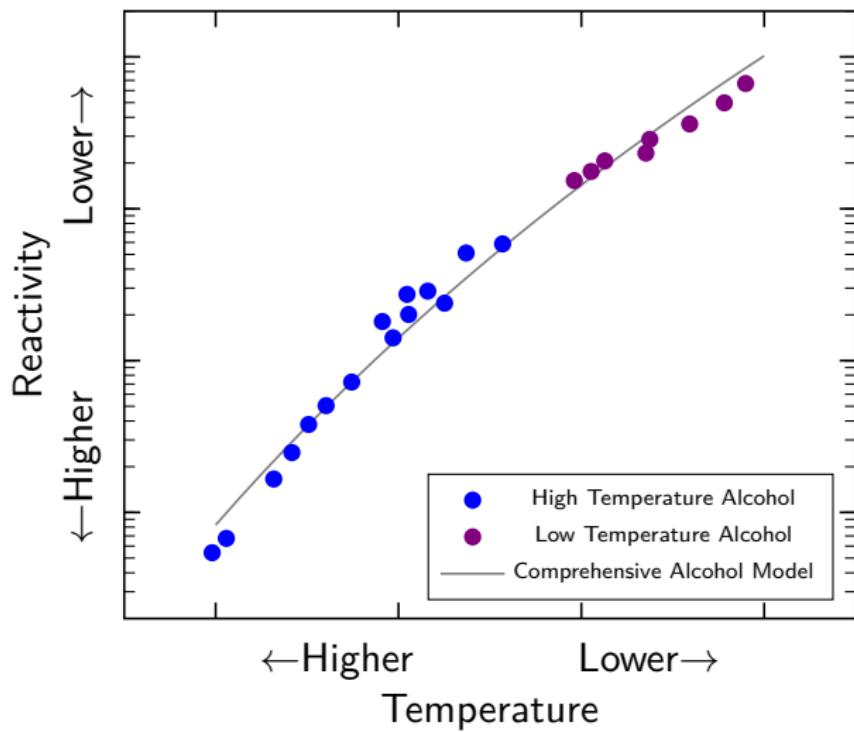












How can we understand the effect of better fuels on better engines?

- ▶ 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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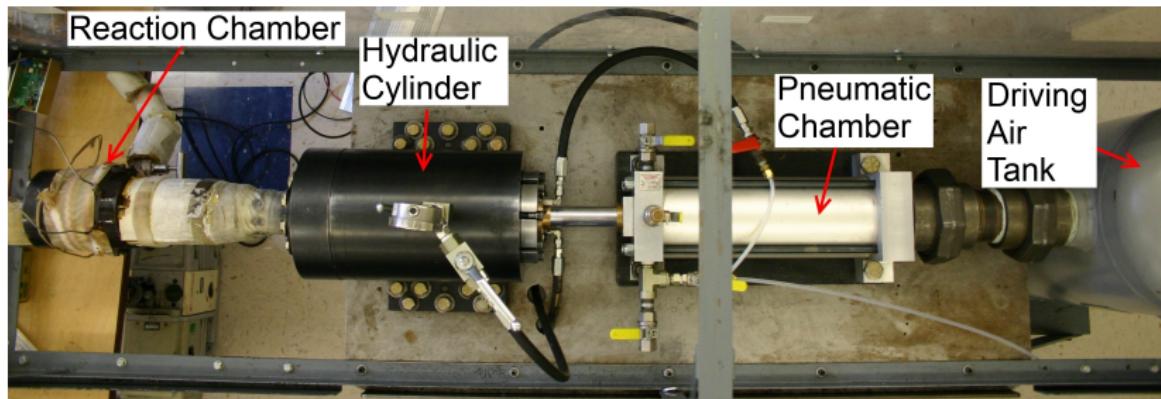
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 - ▶ Reactivity ← Ignition Delay
 - ▶ **Pollutant Production ← Detailed reaction pathways**
 - ▶ ...

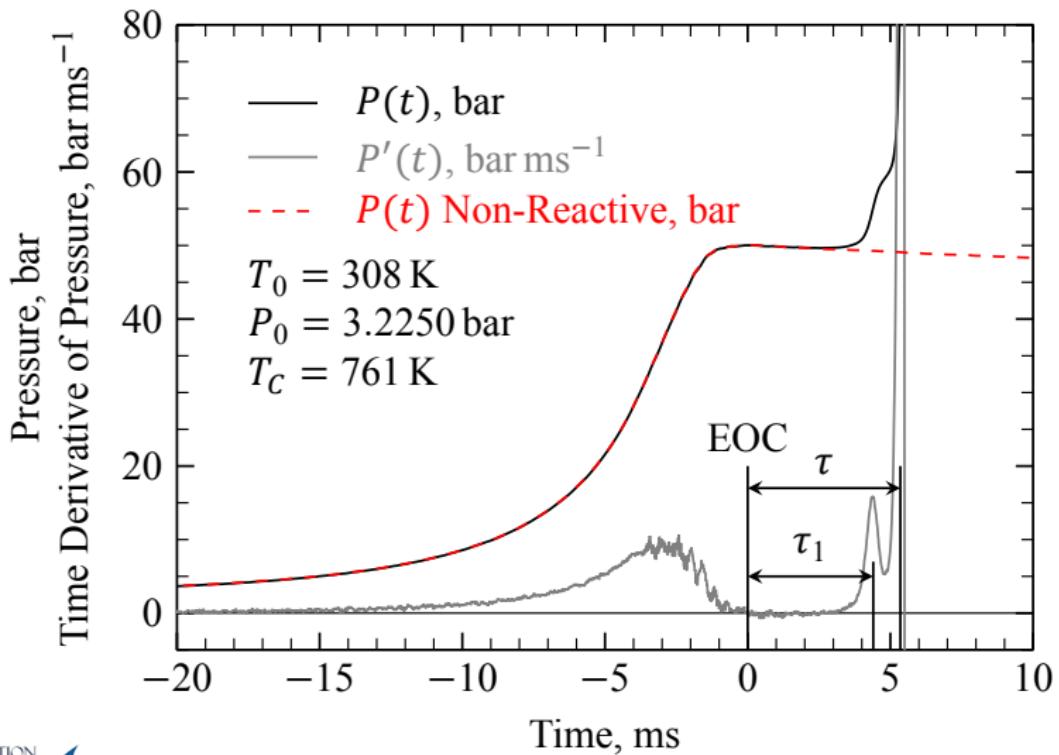
Experimental Methods

Rapid Compression Machine



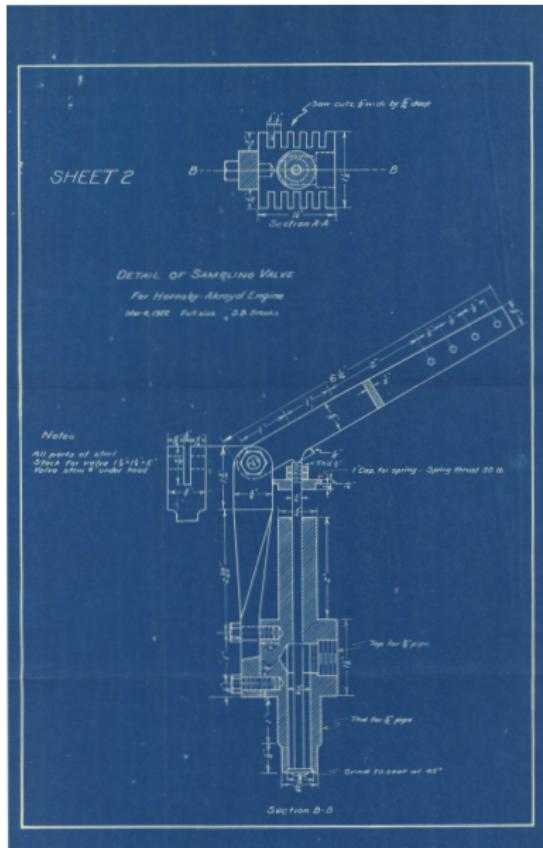
Rapid Compression Machine

MCH/O₂/N₂/Ar, $\phi = 1.5$, $P_C = 50$ bar



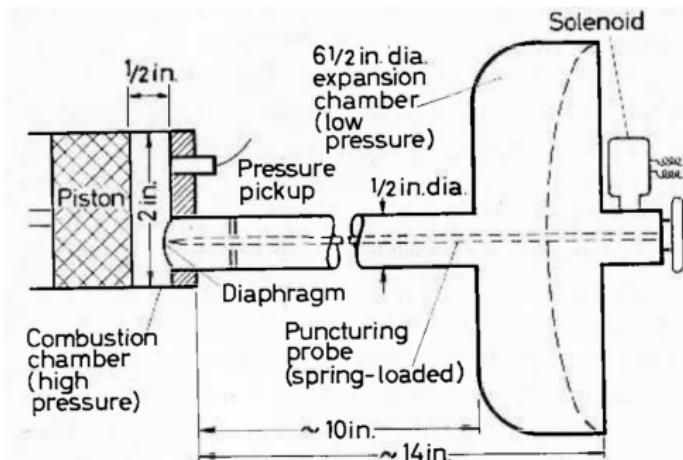
Rapid Sampling Apparatus

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



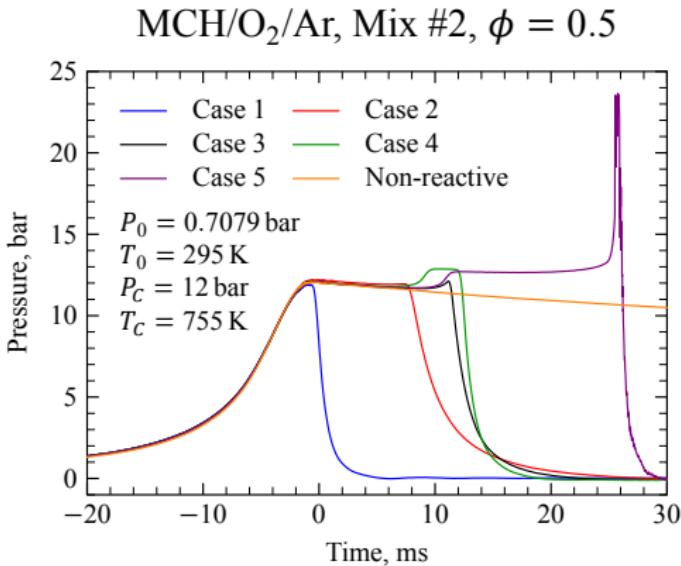
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- ▶ In the 1960's, the first sampling apparatus was adapted for an RCM



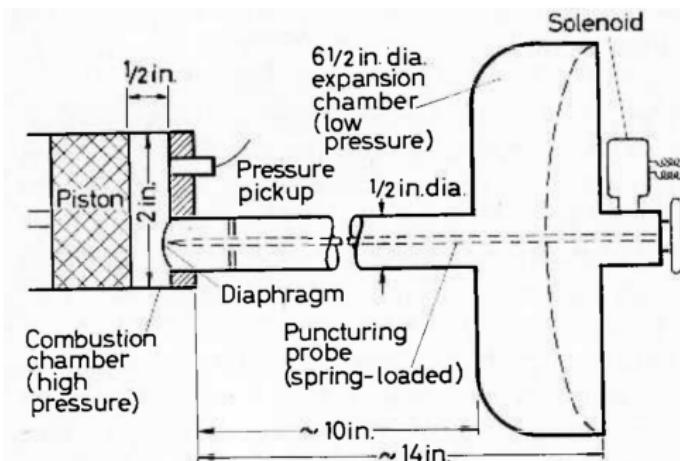
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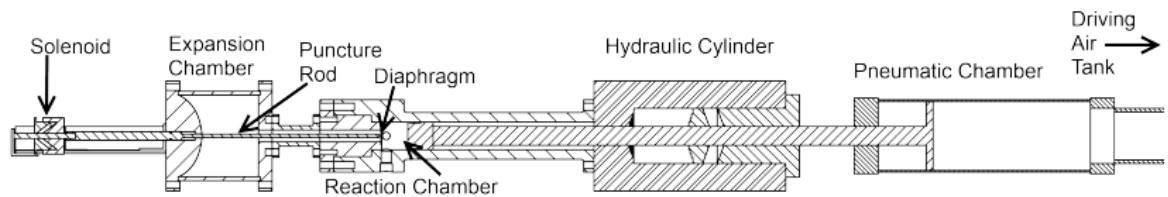


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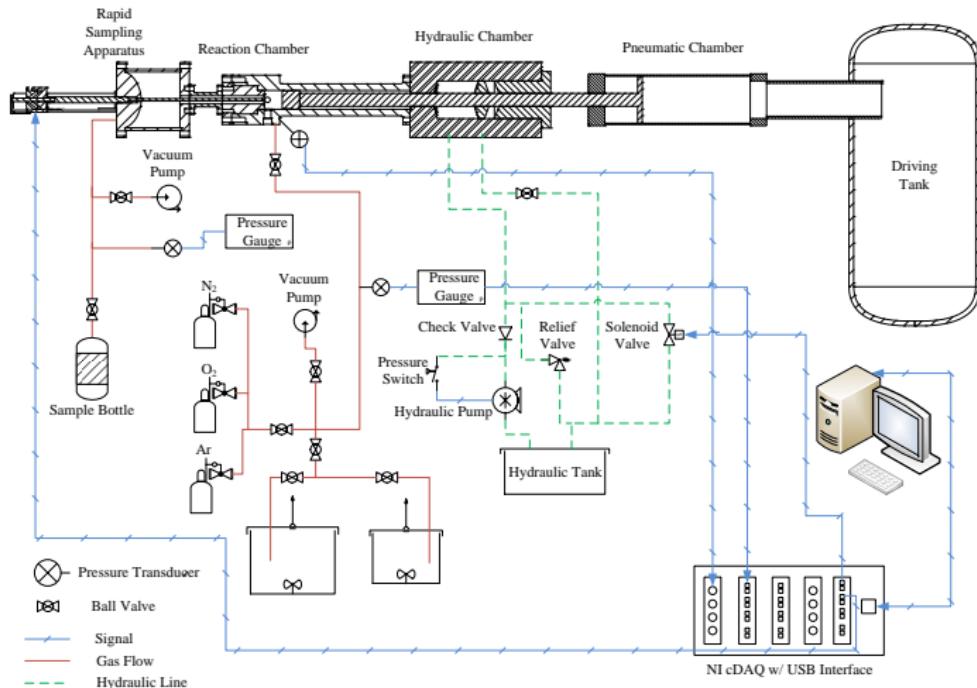
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Rapid Compression Machine



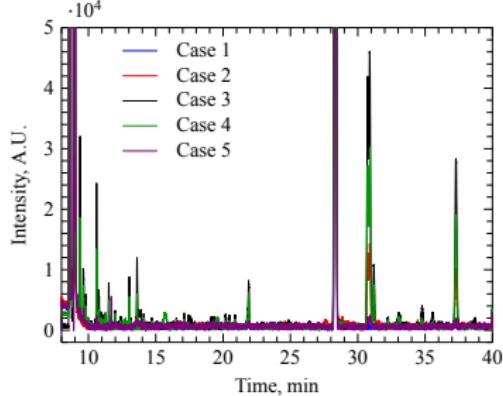
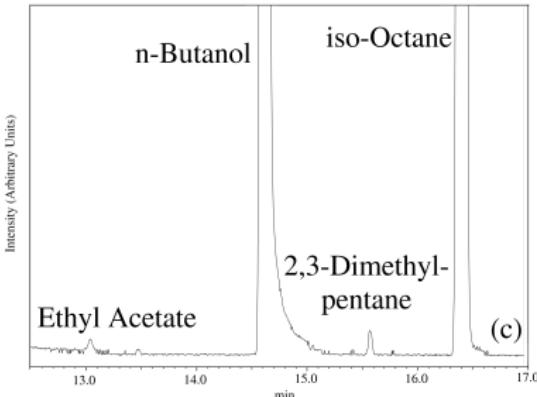
Gas Chromatograph/Mass Spectrometer

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



Gas Chromatograph/Mass Spectrometer

- ▶ Separates, identifies, and quantifies chemical species



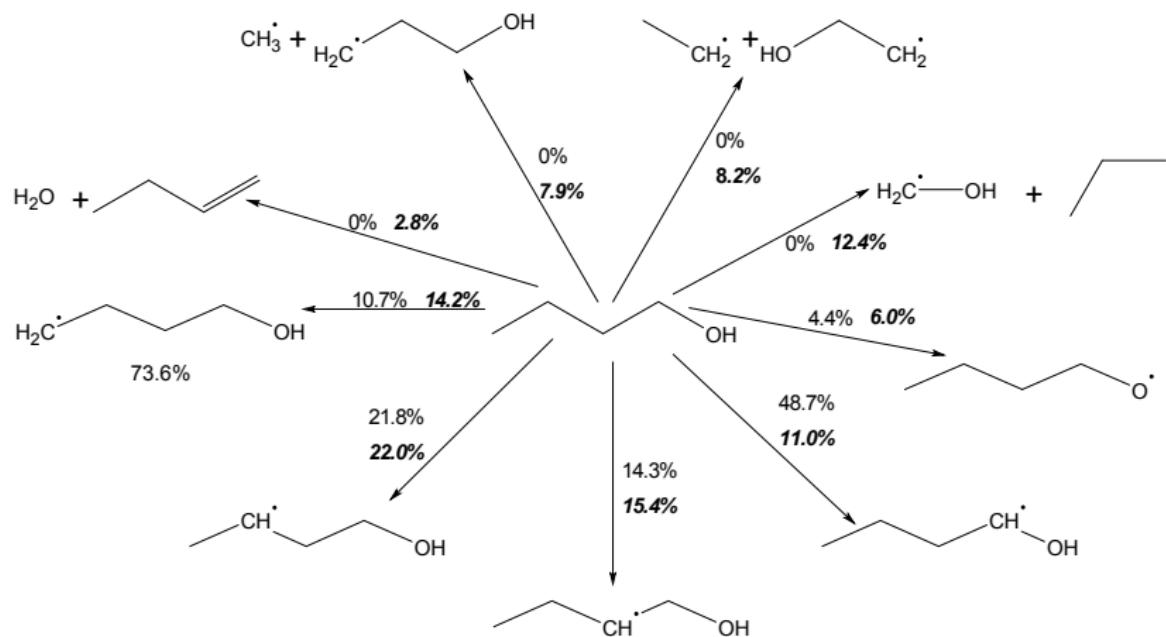
Numerical Methods

- ▶ Computational analysis complements experimental work
- ▶ Direct comparisons can be made between the computed and experimental ignition delays as well as the pressure traces
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Path Flux Analysis

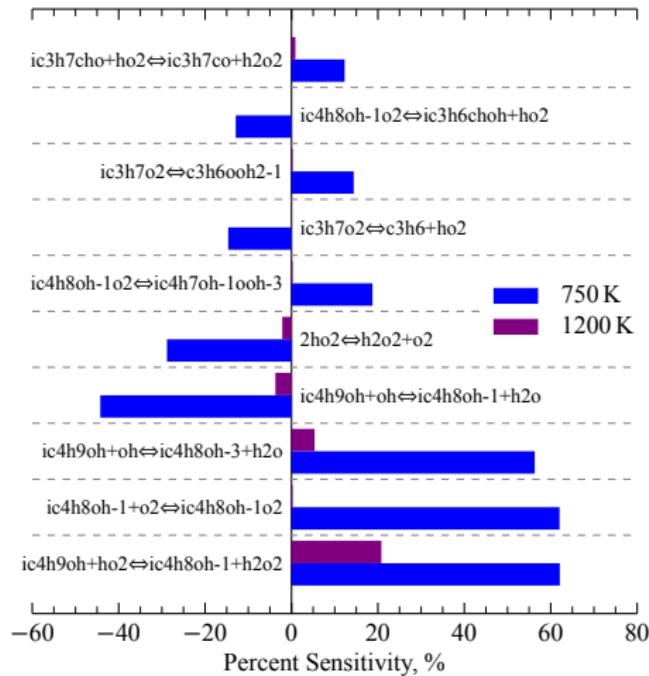


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 - ▶ Path Flux Analysis helps determine important reaction pathways
 - ▶ Sensitivity Analysis helps find important reactions and how they affect reactivity

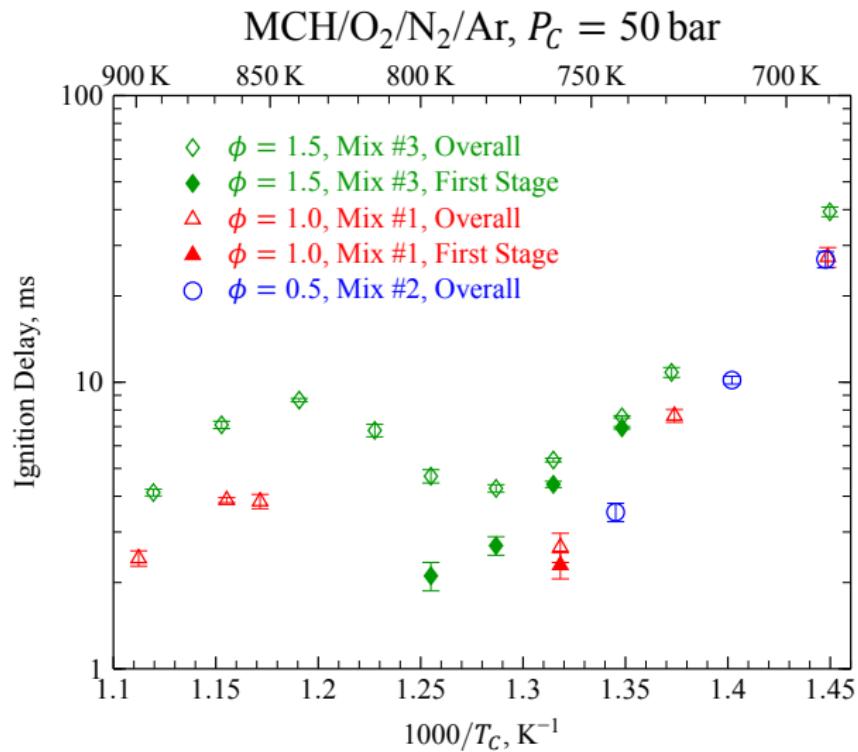
Sensitivity Analysis

i-Butanol/O₂/N₂, 30 bar, $\phi = 1.0$



Methylcyclohexane

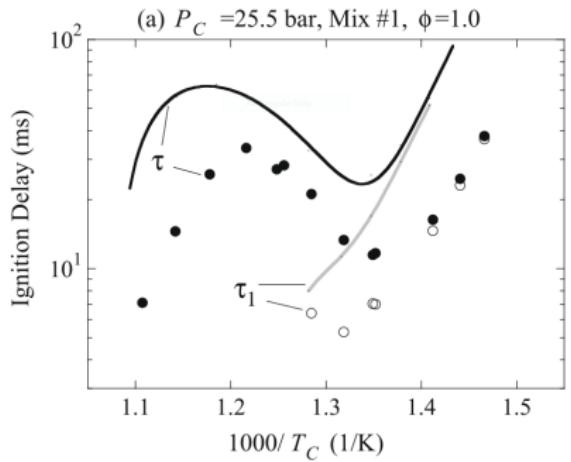
Ignition delays were measured at new conditions



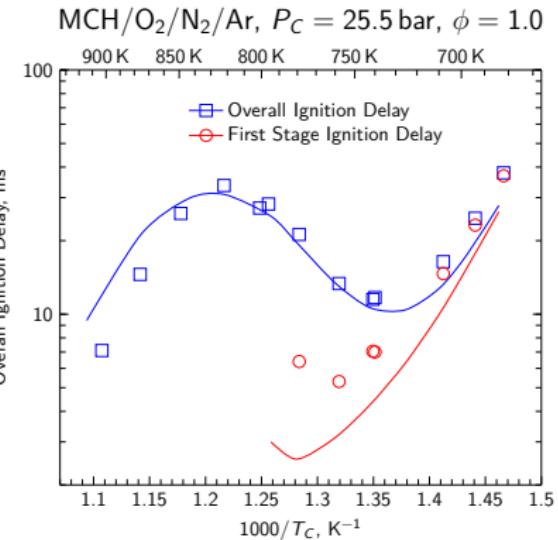
Many improvements to the kinetic model for MCH were made

- ▶ The C₁–C₄, aromatics, and cyclohexane chemistry have been updated
- ▶ Important fuel decomposition reaction rates have been updated based on experimental measurements and quantum chemical calculations
- ▶ These changes have improved prediction of the overall ignition delay substantially

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Mittal and Sung Combust. Flame
2009

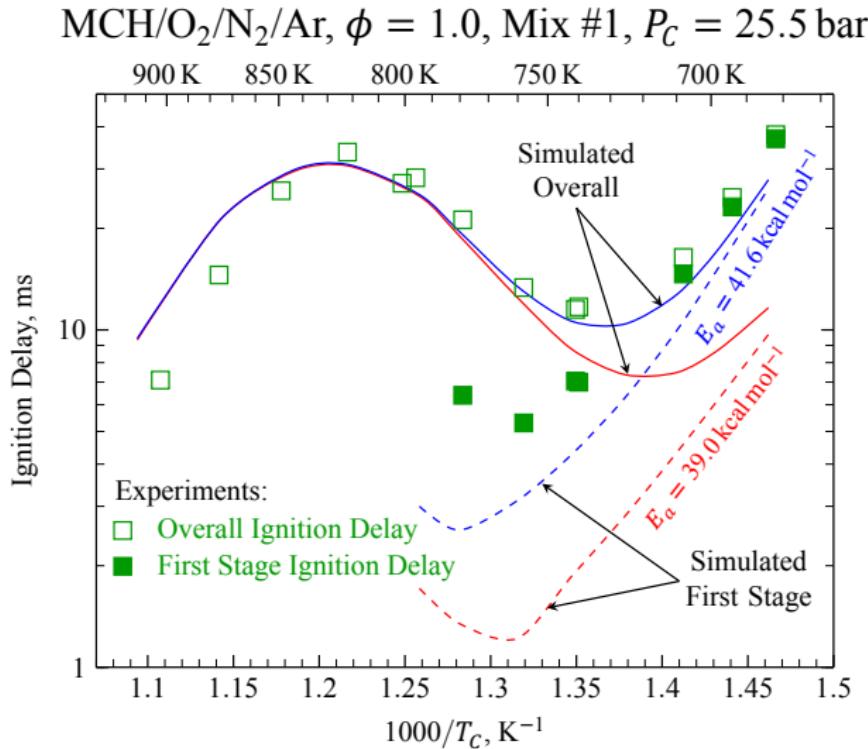


Weber et al. Combust. Flame
2014

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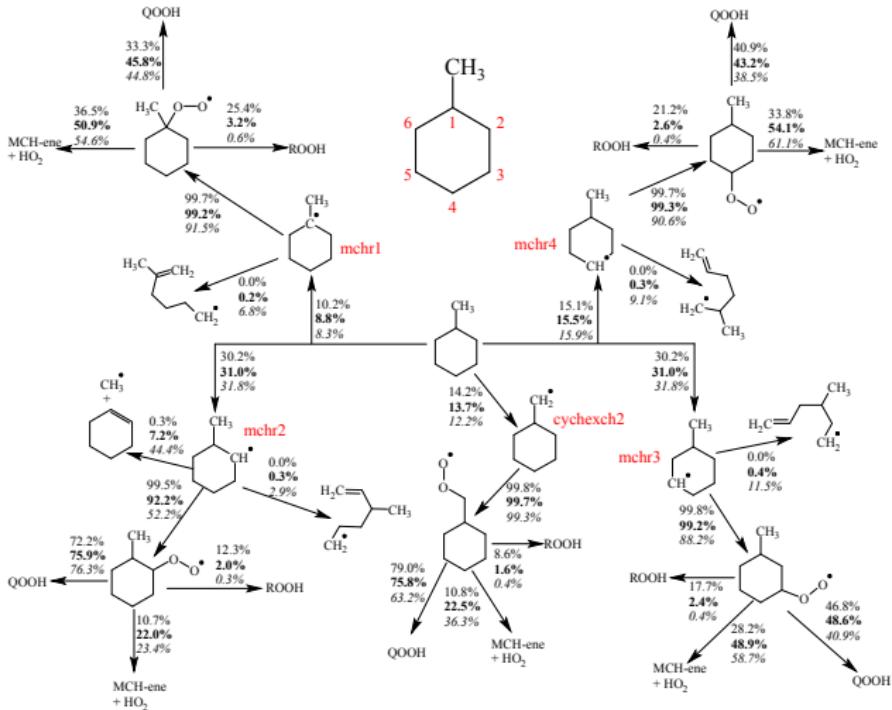
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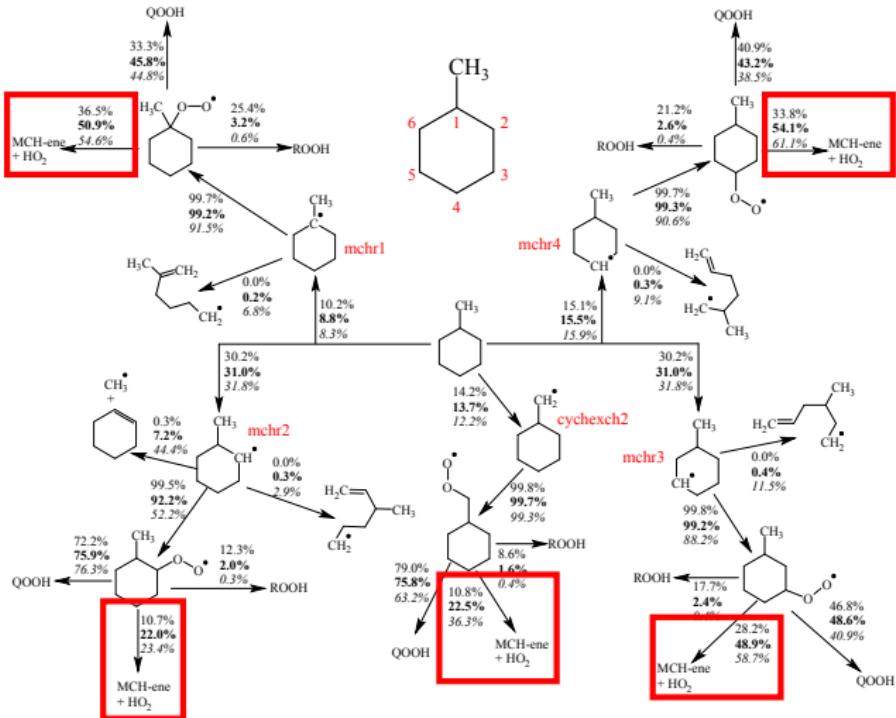
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- ▶ New pathways involving species with unsaturated rings were added to enable prediction of species such as methylcyclohexenes

Path flux analysis shows the important reaction pathways

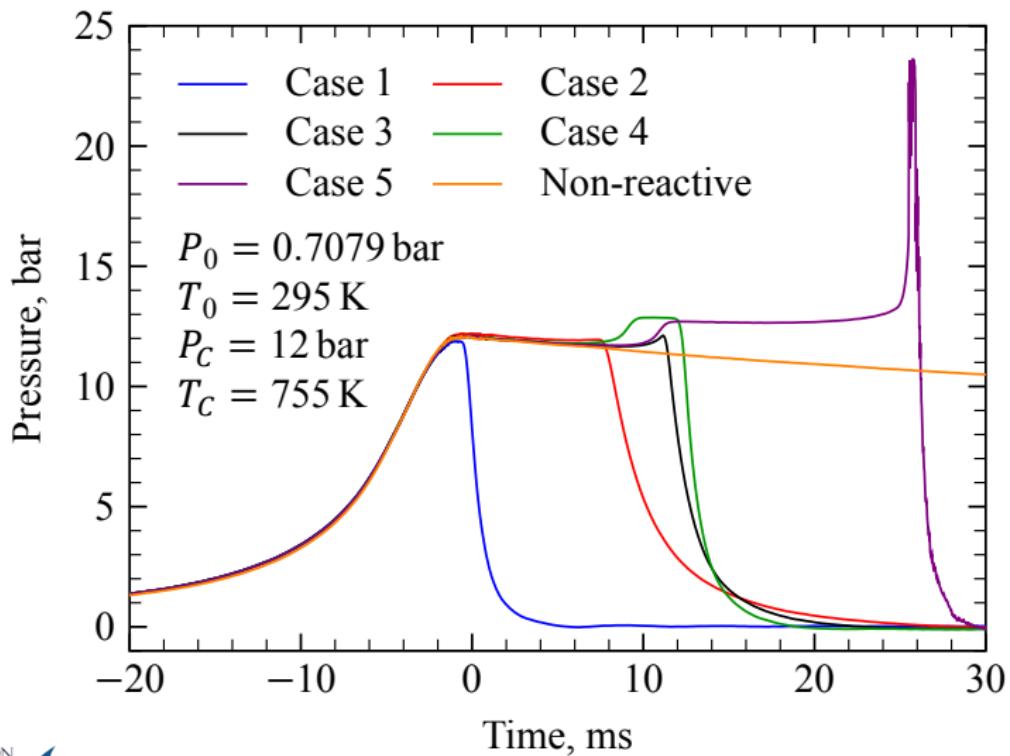


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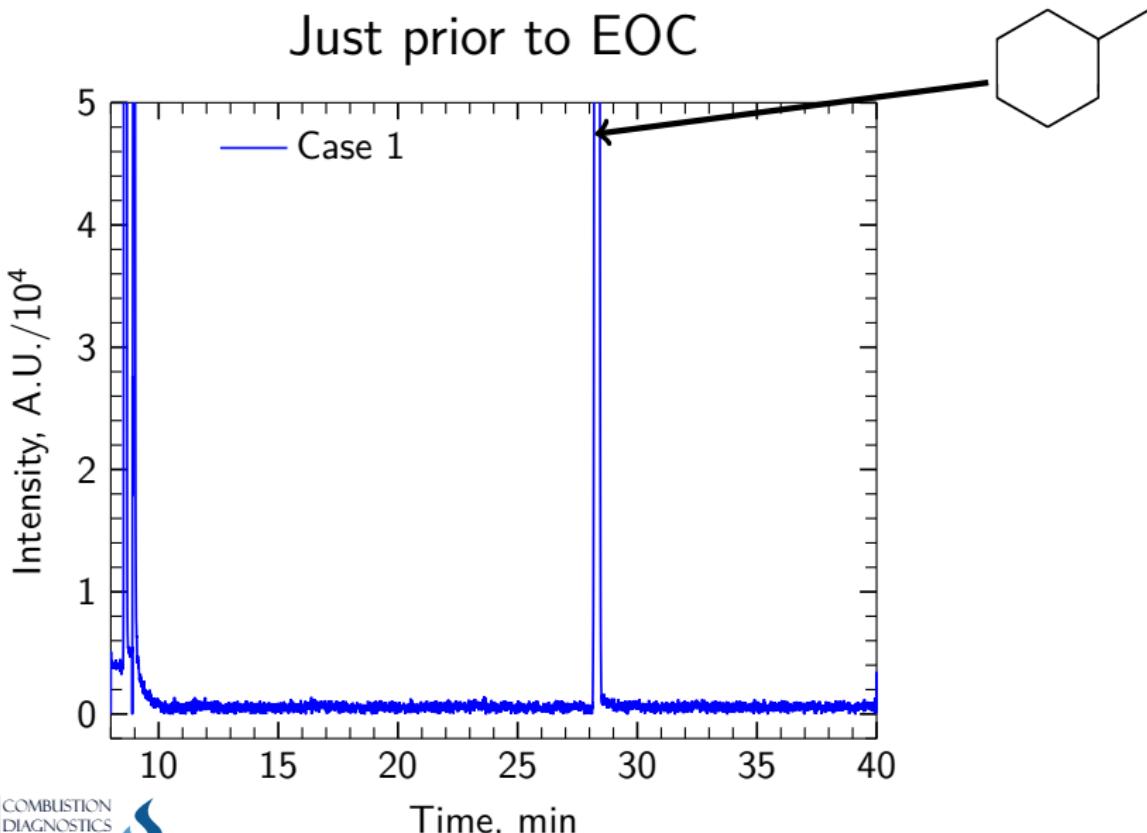


New sampling data can test the newly added pathways

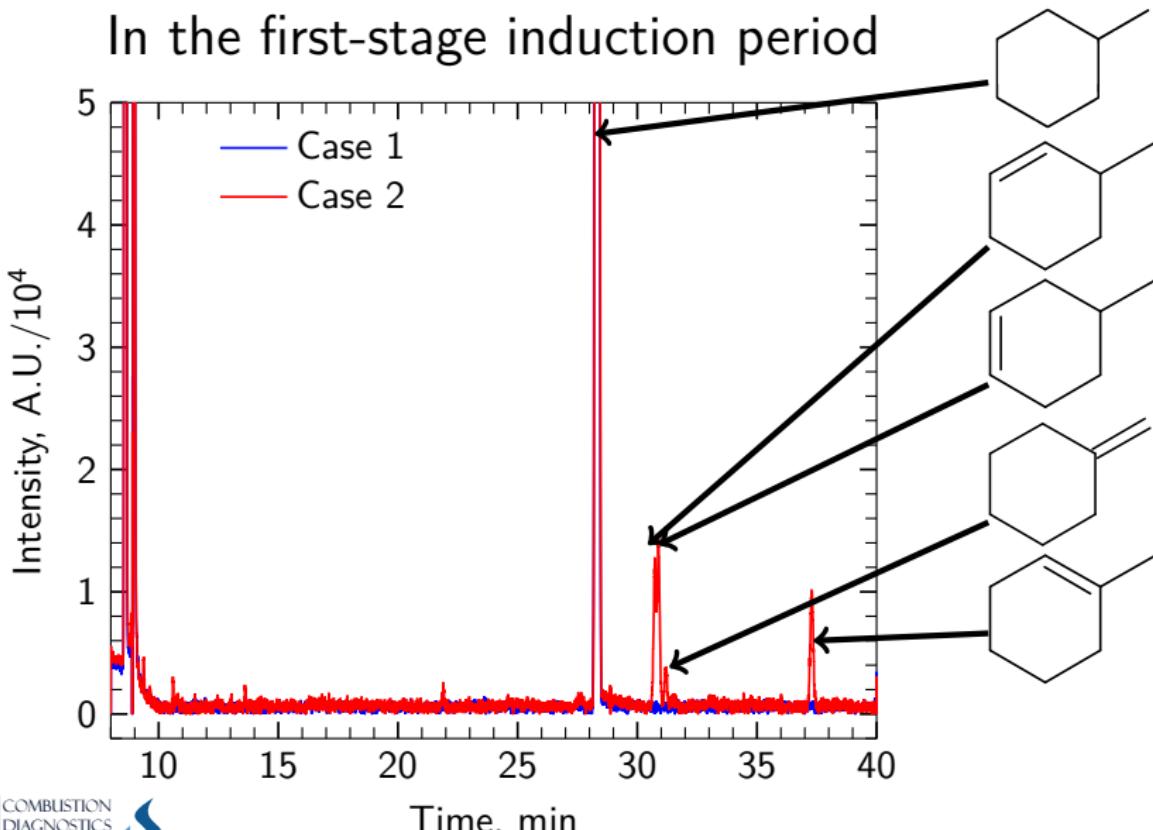
MCH/O₂/Ar, Mix #2, $\phi = 0.5$



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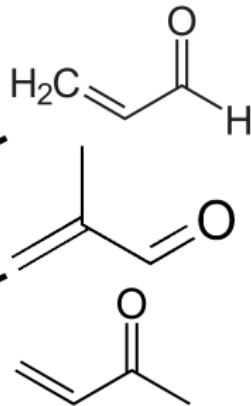
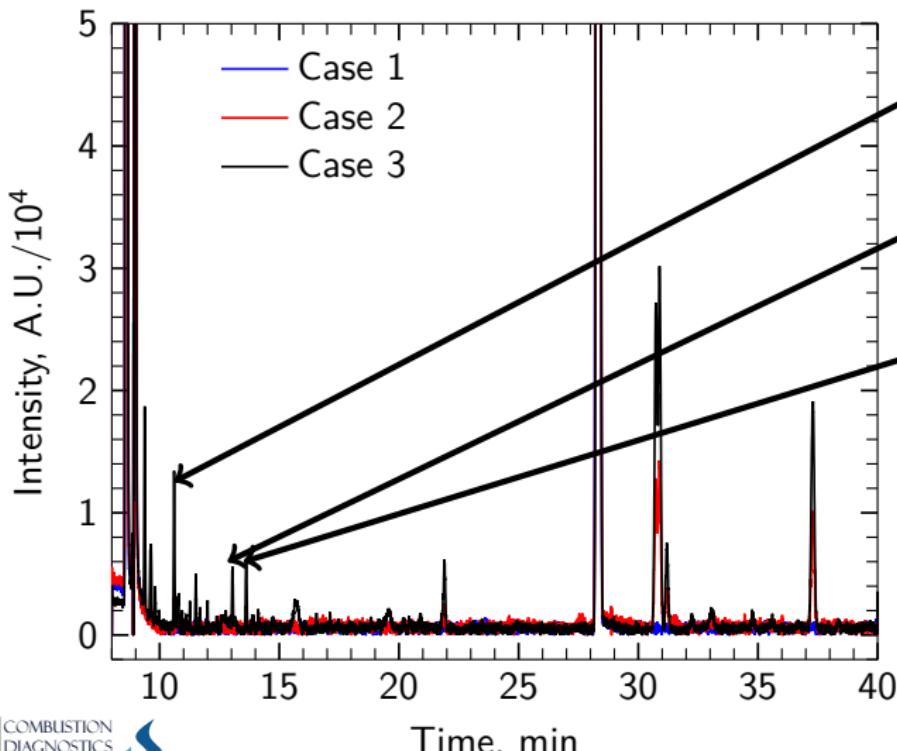


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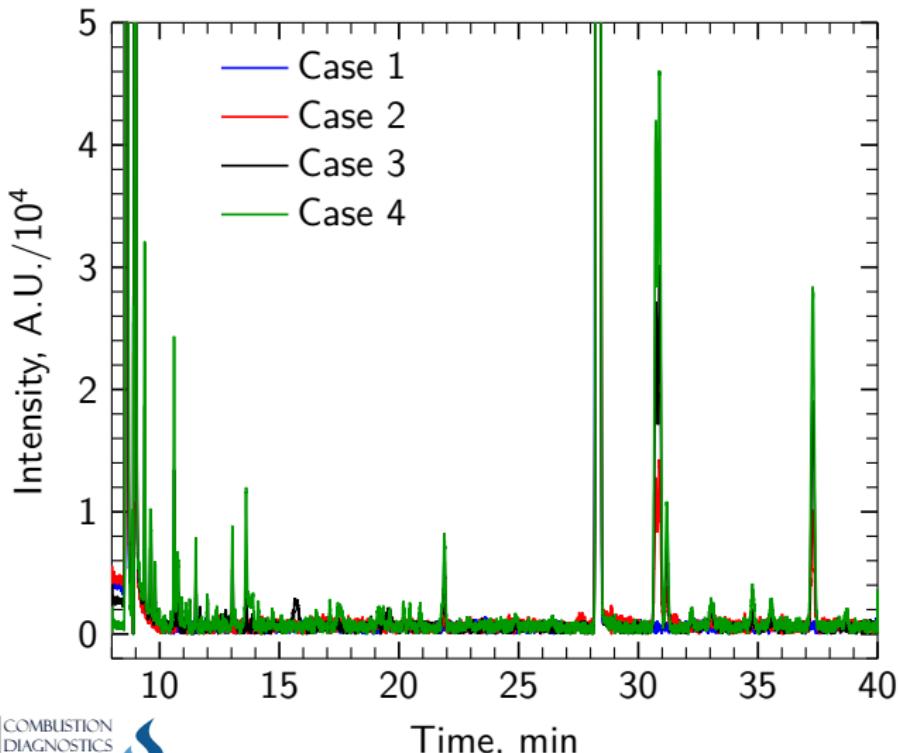
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At the first-stage ignition



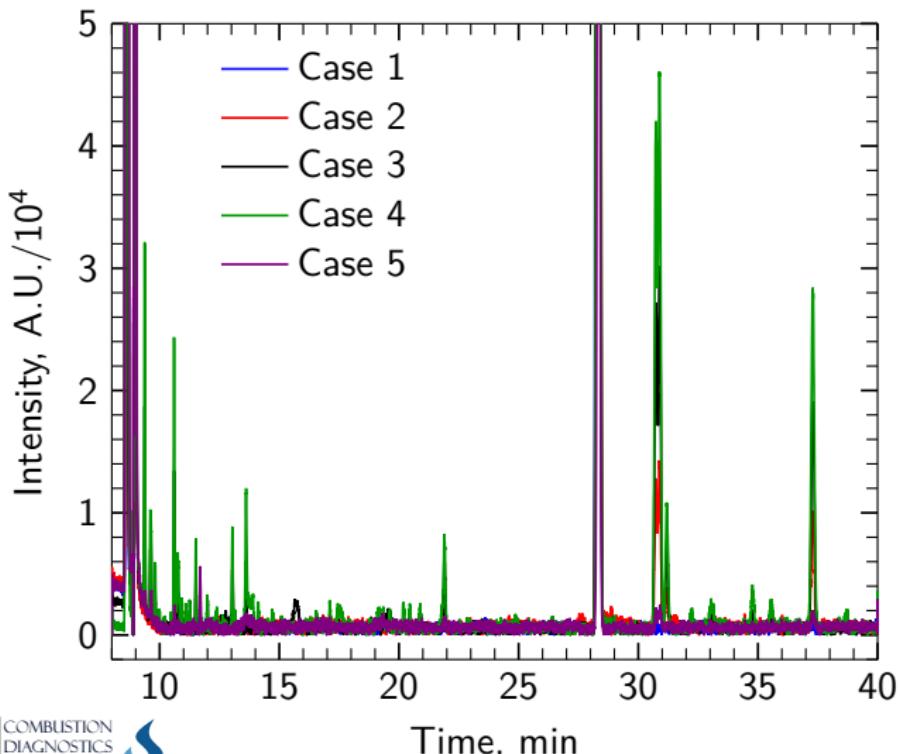
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After the first-stage ignition



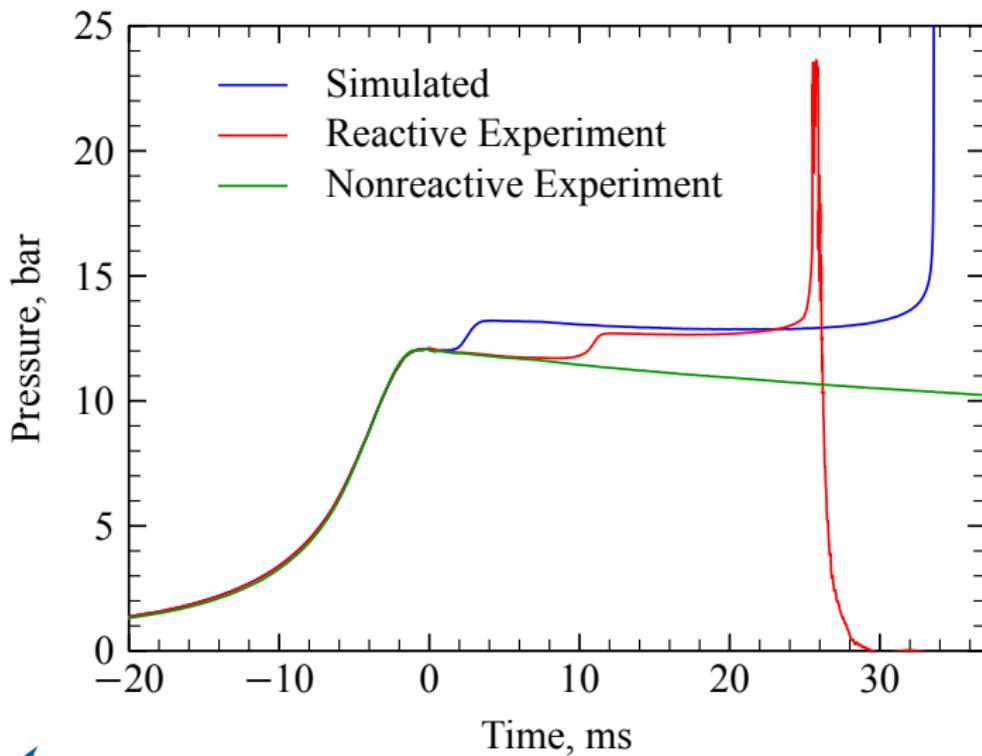
New sampling data can test the newly added pathways

After overall ignition

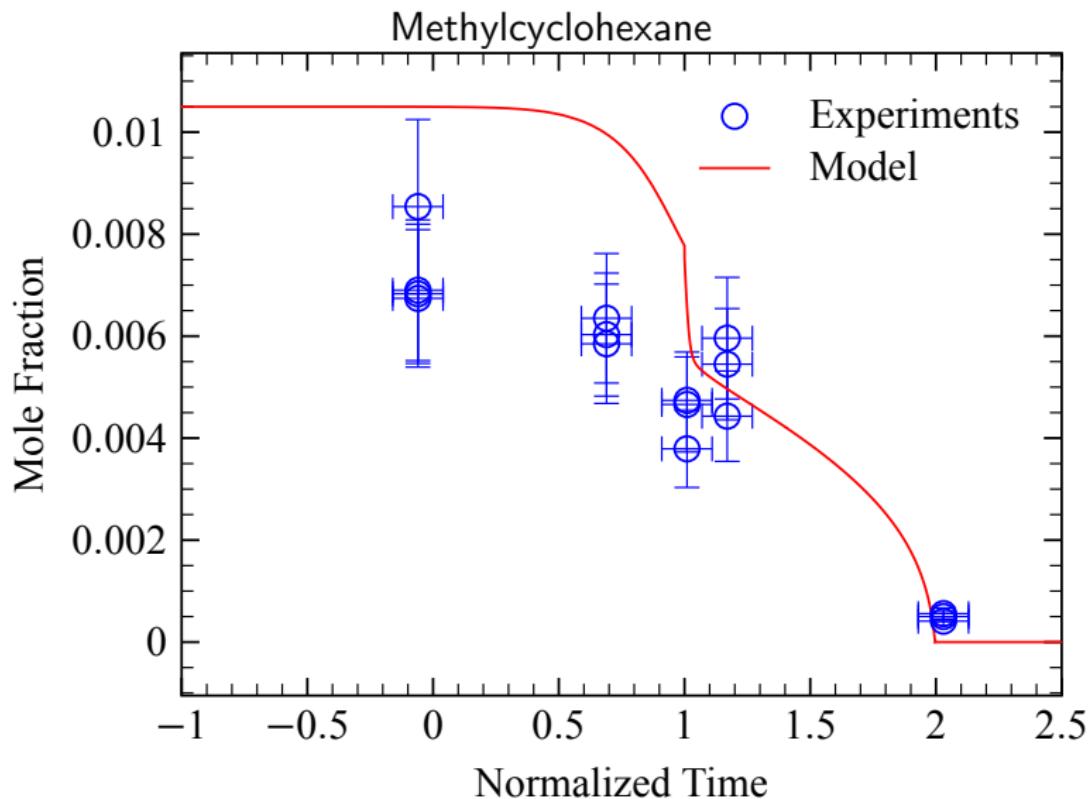


New sampling data can test the newly added pathways

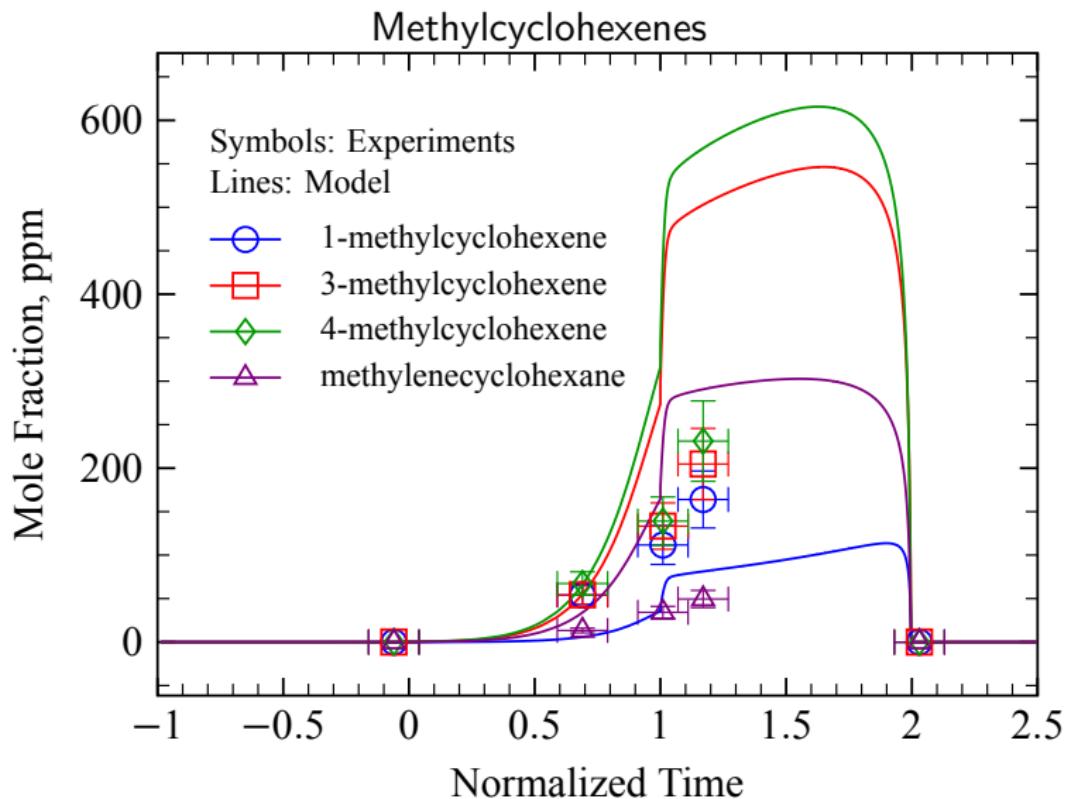
MCH/O₂/Ar, $\phi = 0.5$, 12 bar



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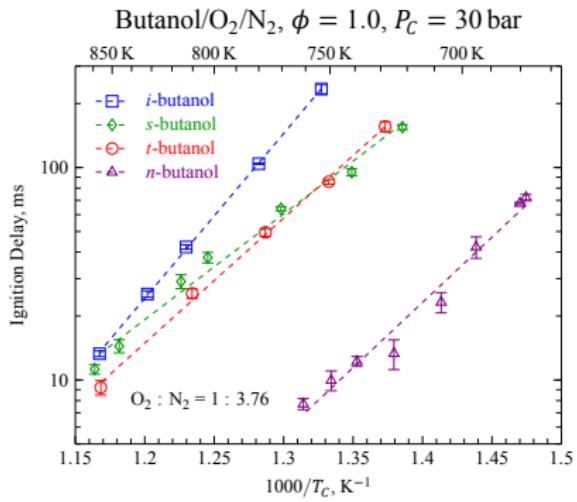
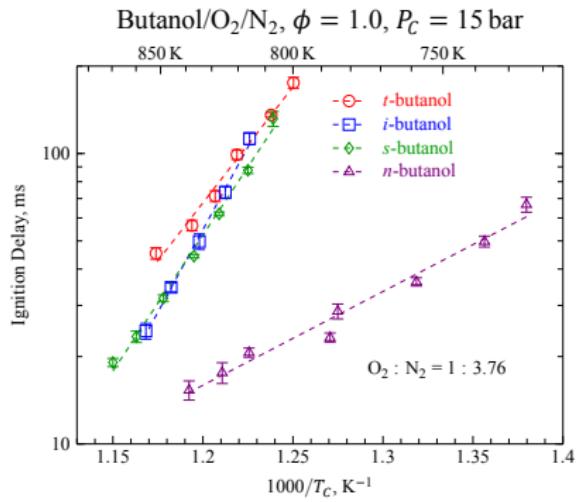


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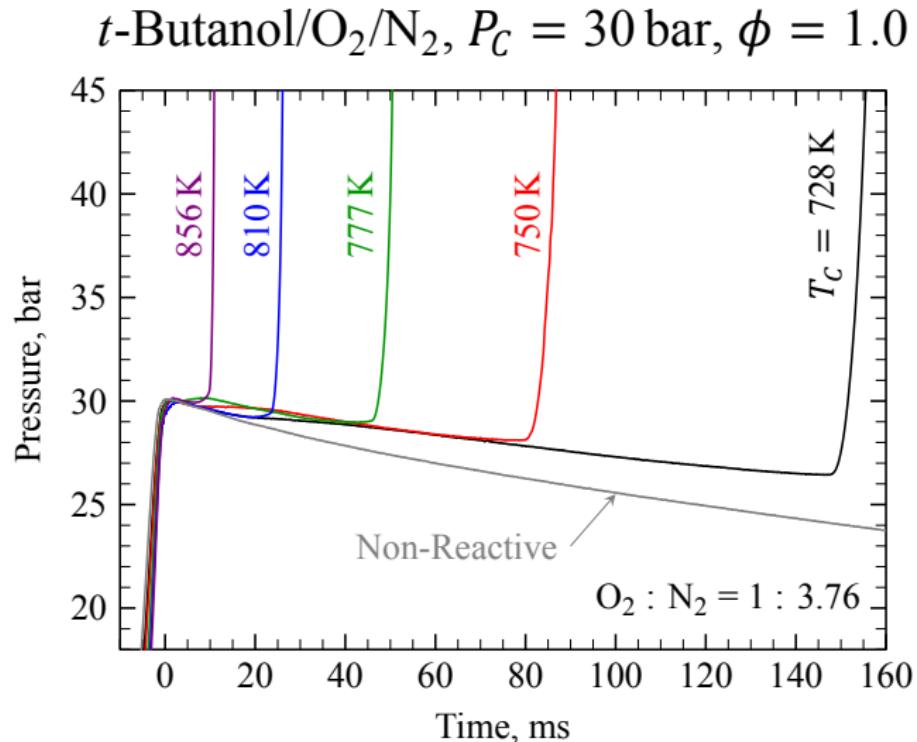


Butanol Isomers

The reactivity of the butanol isomers depends on the pressure

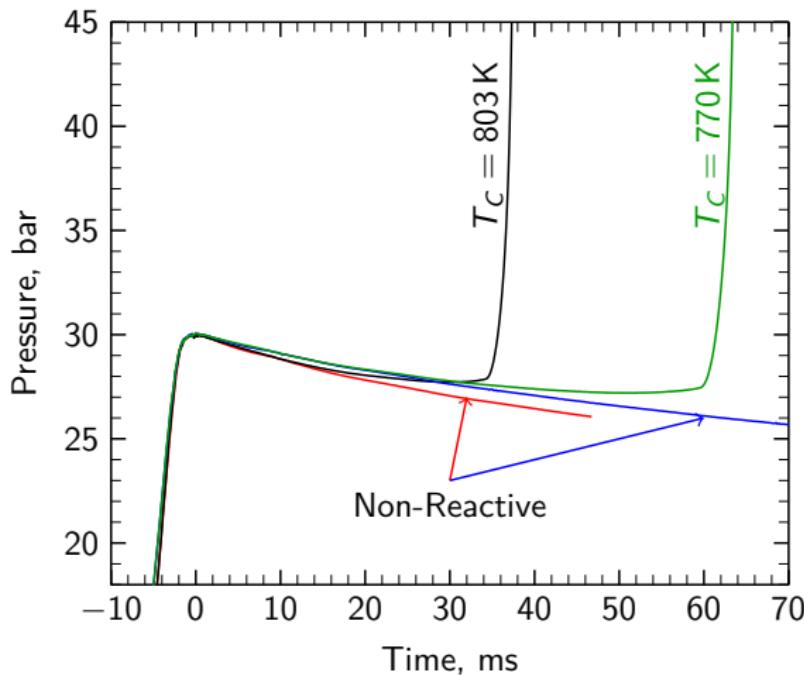


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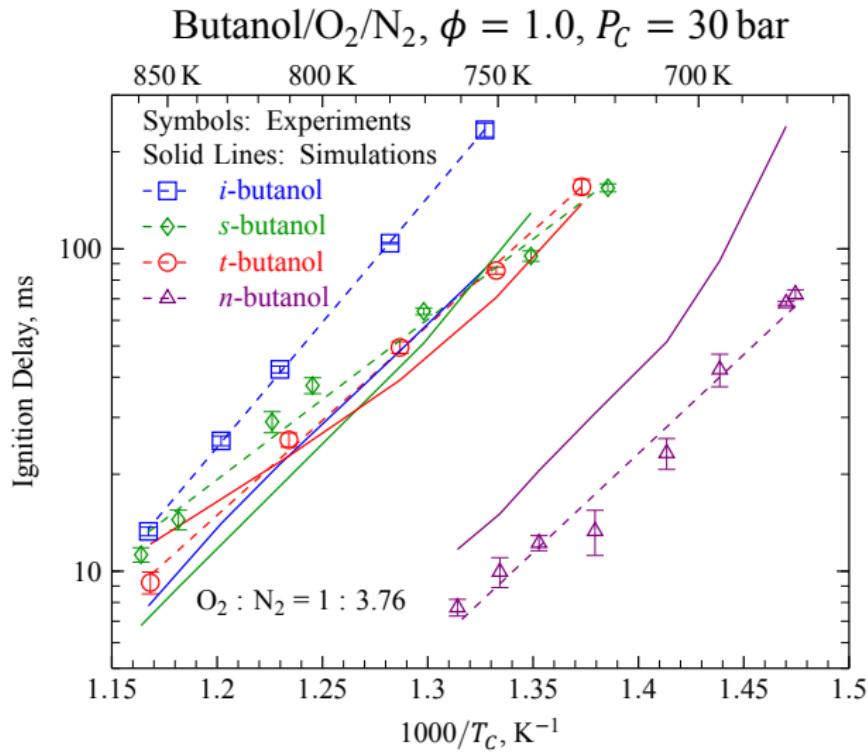


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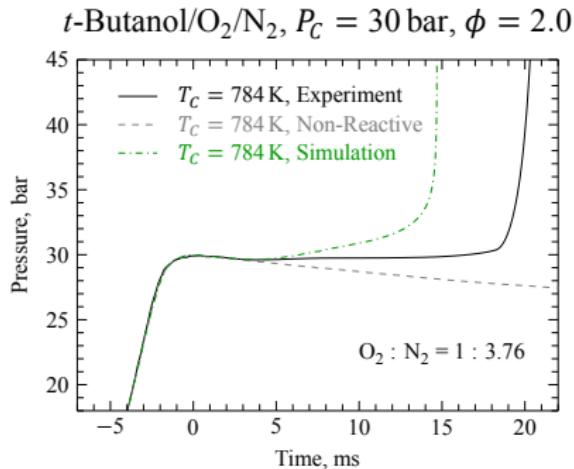
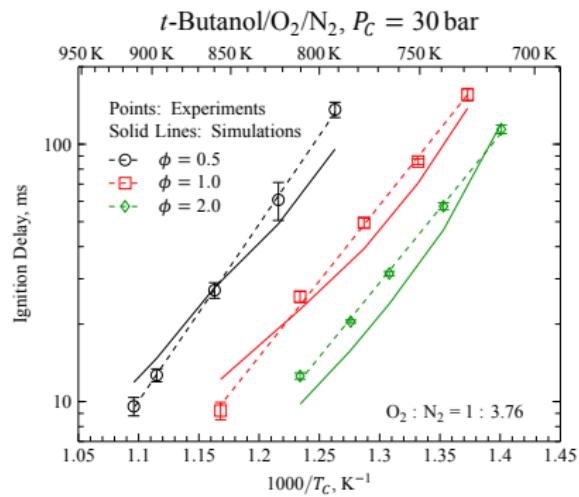
s-Butanol/O₂/N₂, $\phi = 1.0$, $P_C = 30$ bar



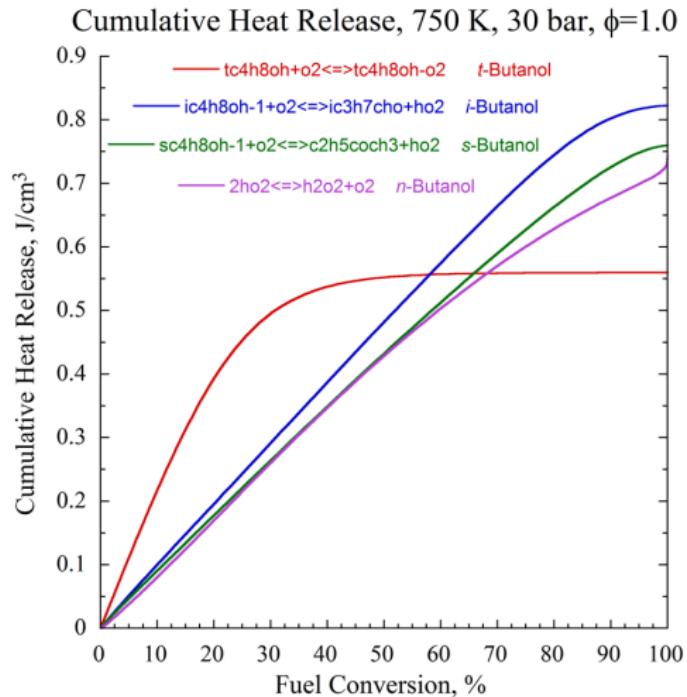
Understanding the detailed chemistry enables modeling of biofuel ignition



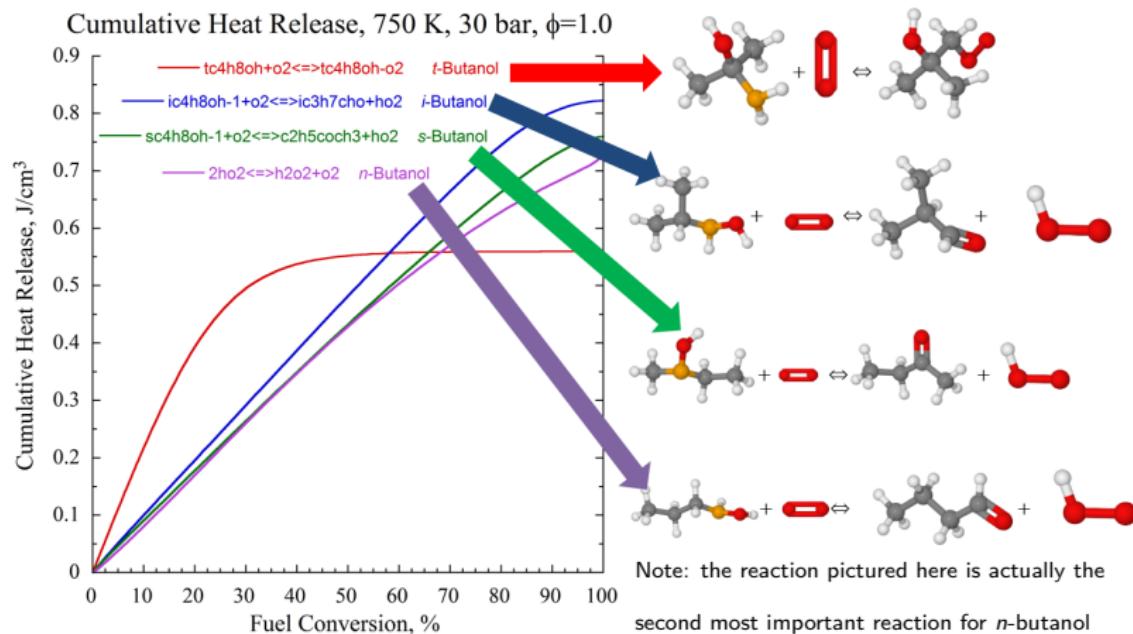
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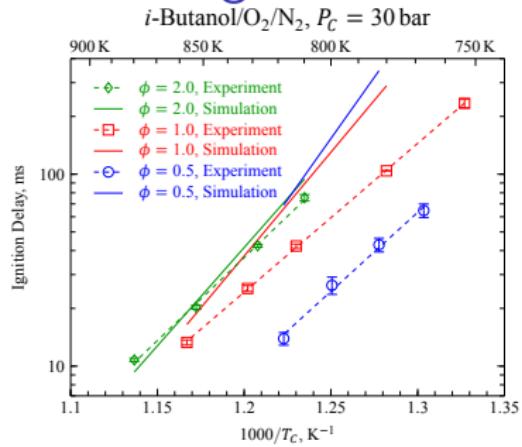
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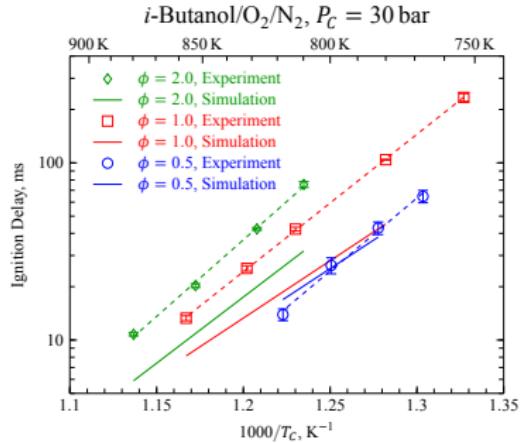
Understanding the detailed chemistry enables modeling of biofuel ignition



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

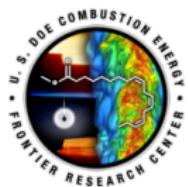
Future work

- ▶ 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?



COMBUSTION
DIAGNOSTICS
LABORATORY



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