

High Pressure Ignition Chemistry of Alternative Fuels

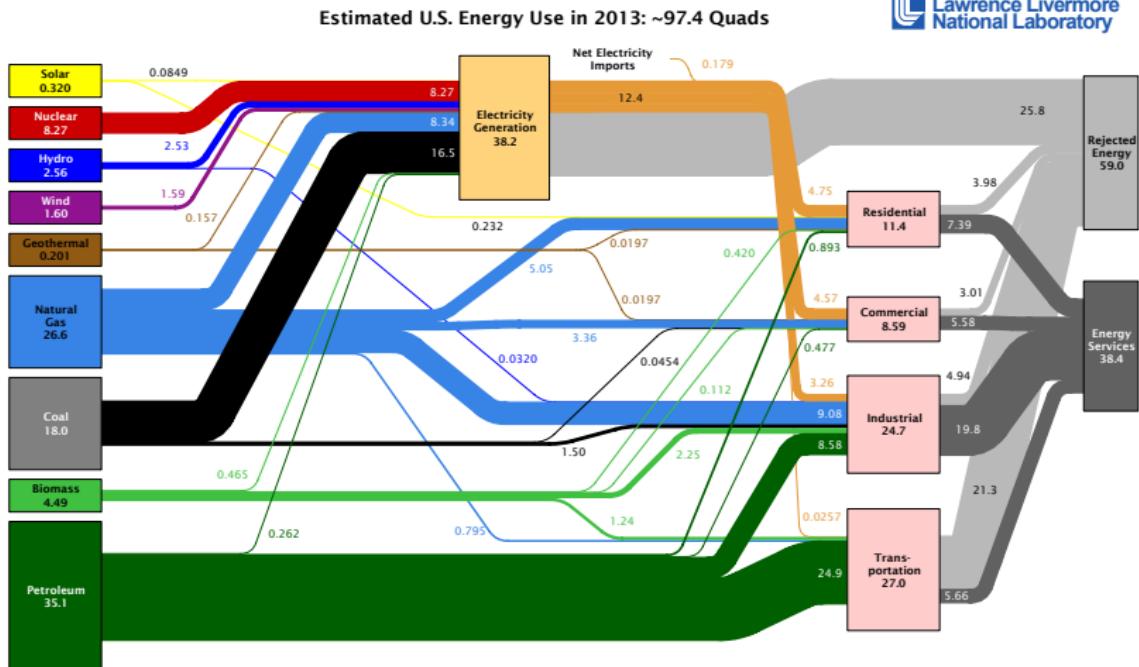
Bryan W. Weber

Prepared for Ph.D. Defense

June 19, 2014

We use a lot of fuels to power the world

Lawrence Livermore National Laboratory

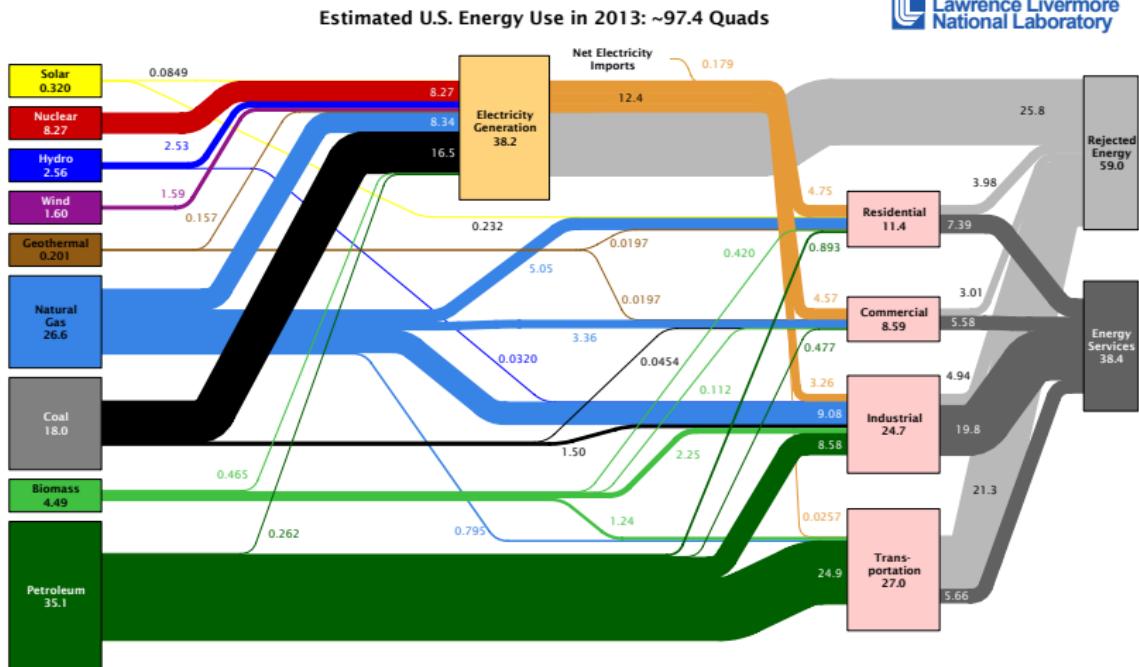


We use a lot of fuels to power the world

Could drive to the moon and back over 180 million times in a Tesla Model S with the amount of energy we use annually

We use a lot of fuels to power the world

Lawrence Livermore National Laboratory



Source: LLNL 2014. Data is based on DOE/EIA-0435(2014-0B), March, 2014. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy under whose project the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports consumption of renewable resources (i.e., hydro, wind, geothermal and solar) for electricity in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." *The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 65% for the residential and commercial sectors 80% for the industrial sector, and 21% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

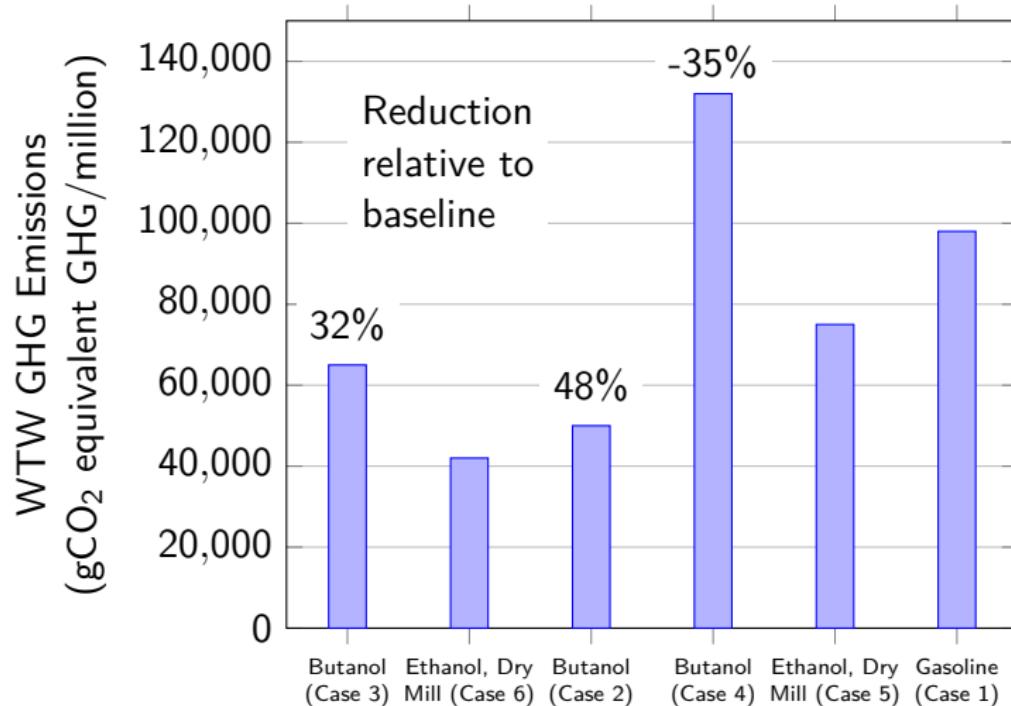
We use a lot of fuels to power the world

- ▶ 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

Better engines have higher efficiency and lower emissions

John Dec image

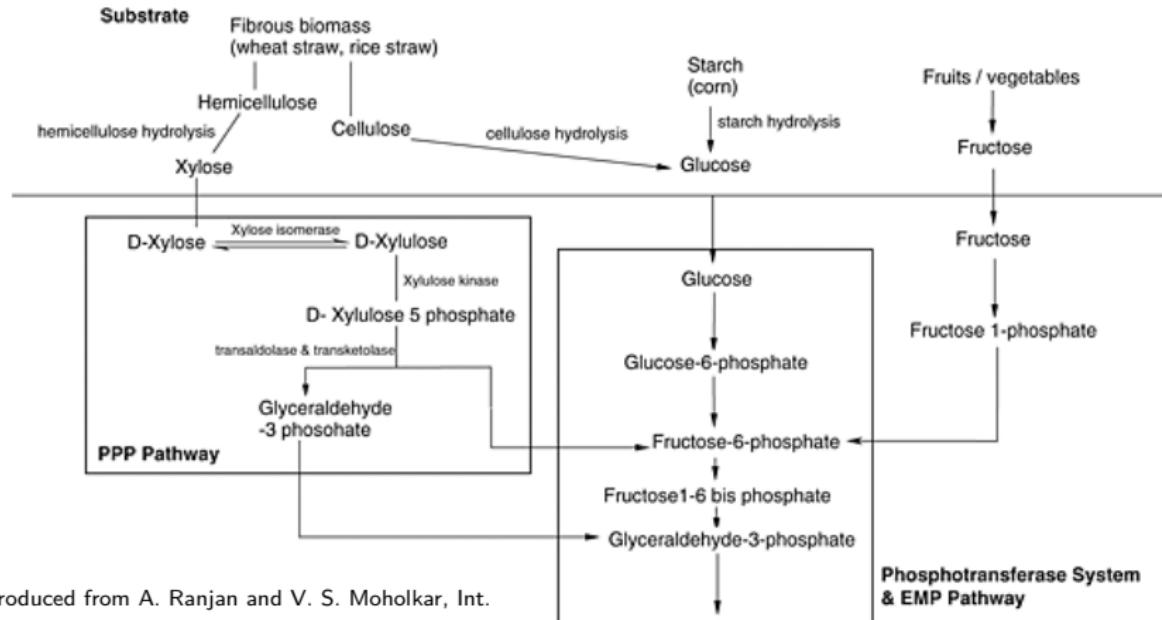
Better fuels reduce emissions and eliminate dependence on fossil fuels



Reproduced from M. Wu, M. Wang, J. Liu, H. Huo, Biotechnol. Prog. 24 (2008) 1204–1214.

What kind of research can we do to push these solutions along?

We can do biological research to produce the fuels



Reproduced from A. Ranjan and V. S. Moholkar, Int.

J. Energy Res., 36 (2012) 277–323

We can do engineering research on how the fuels will behave

- ▶ We need to know the physical properties
 - ▶ Density
 - ▶ Viscosity
 - ▶ ...
- ▶ We need to know the combustion properties
 - ▶ Heat of combustion
 - ▶ Propensity to generate pollutants
 - ▶ Reactivity
 - ▶ ...

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What tools does combustion research use?

Phenomenological Studies

- ▶ Engine Studies
- ▶ Octane Number
- ▶ ...

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Fundamental Studies

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- ▶ Product Speciation
- ▶ ...

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- ▶ Modeling

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 - ▶ Computational fluid dynamics

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These efforts
are complementary!

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Fundamental Studies

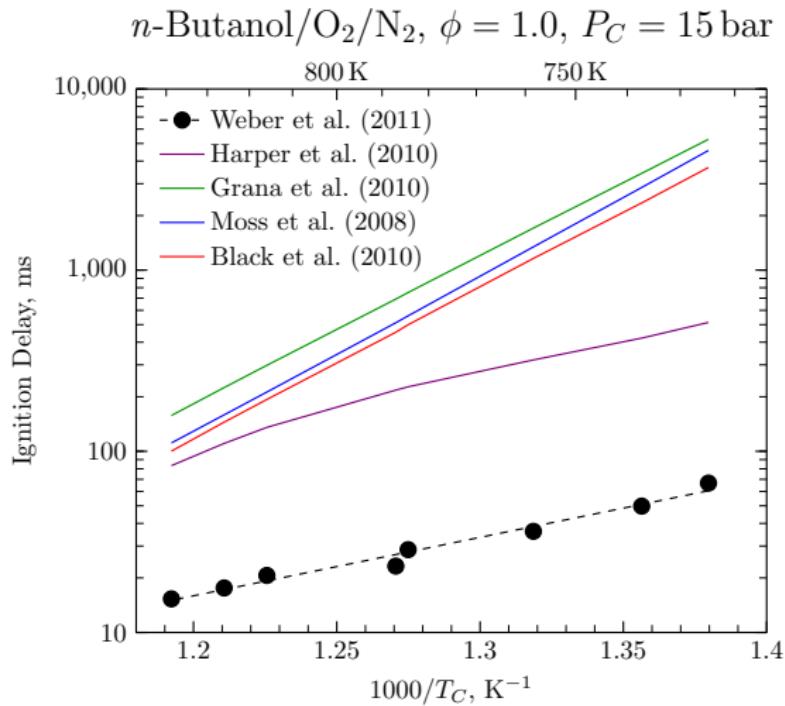
- ▶ Ignition Delay
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 - ▶ **Reaction mechanisms**
 - ▶ Computational fluid dynamics

What phenomena am I trying to understand?

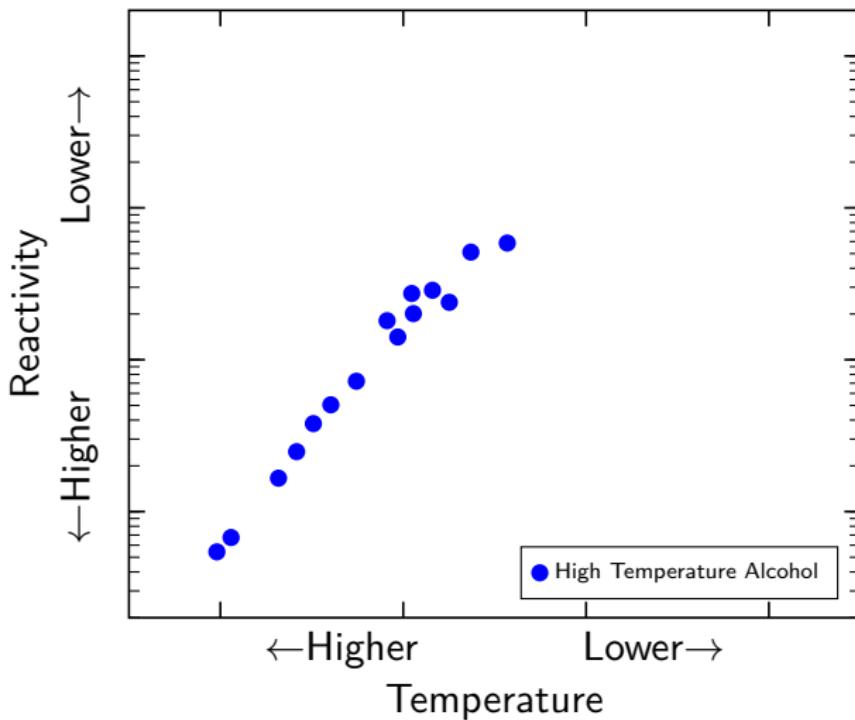
How do alternative fuels react at engine-relevant conditions?

What phenomena am I trying to understand?

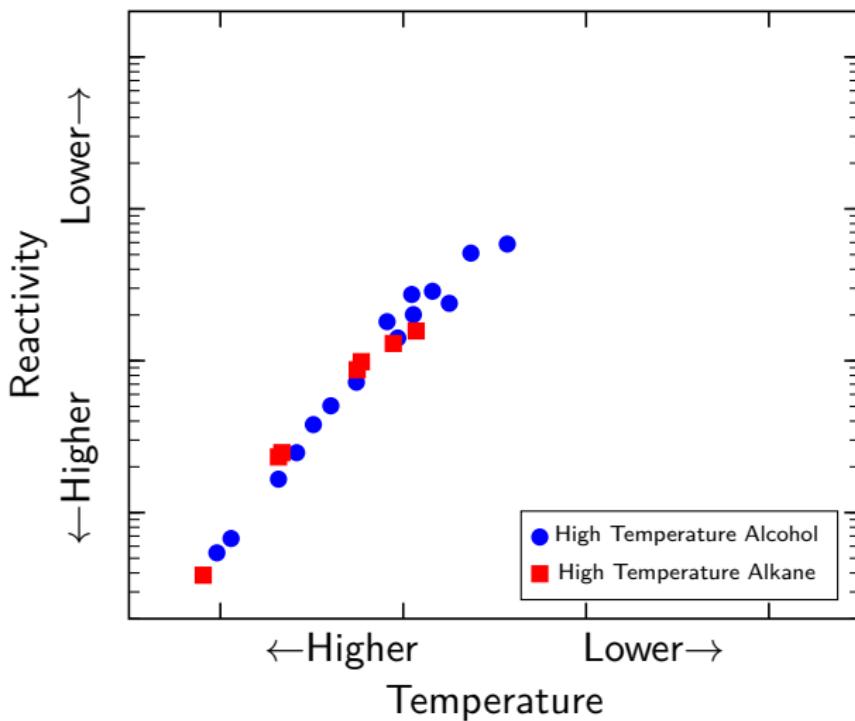


Until 2011, no one was aware that low-temperature chemistry would be important for alcohol fuels!

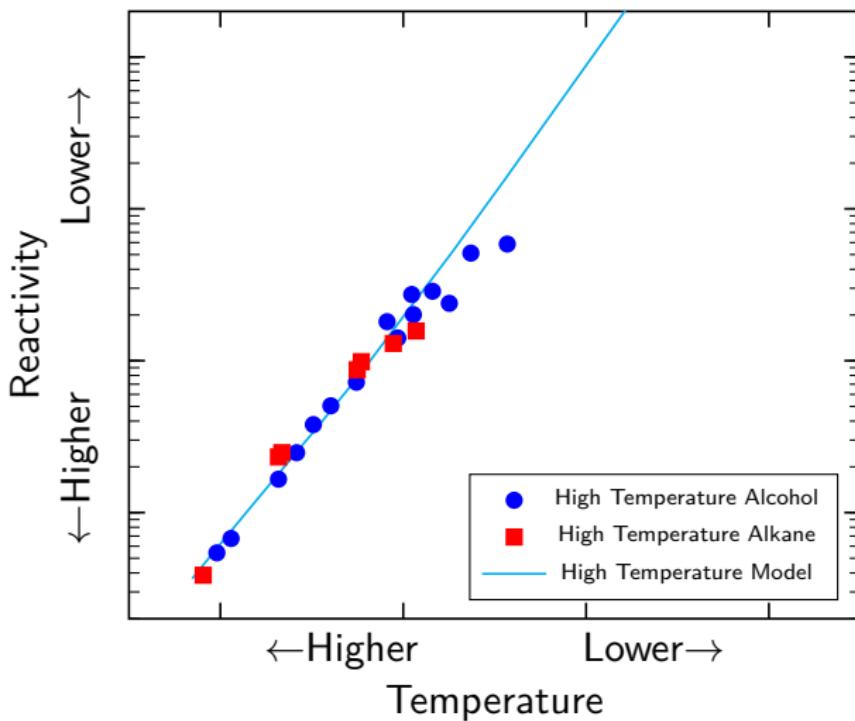
What is low-temperature chemistry?



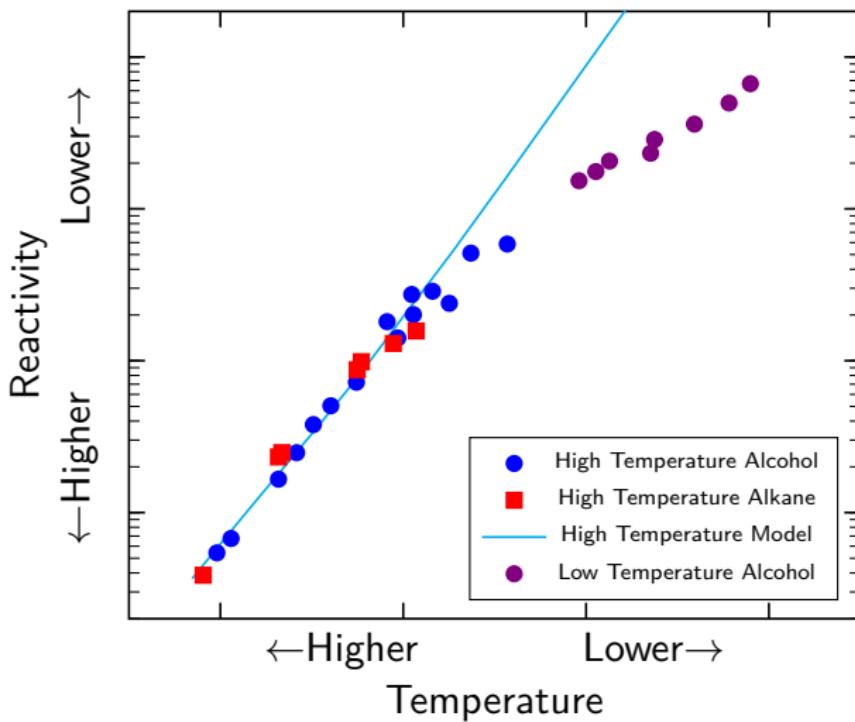
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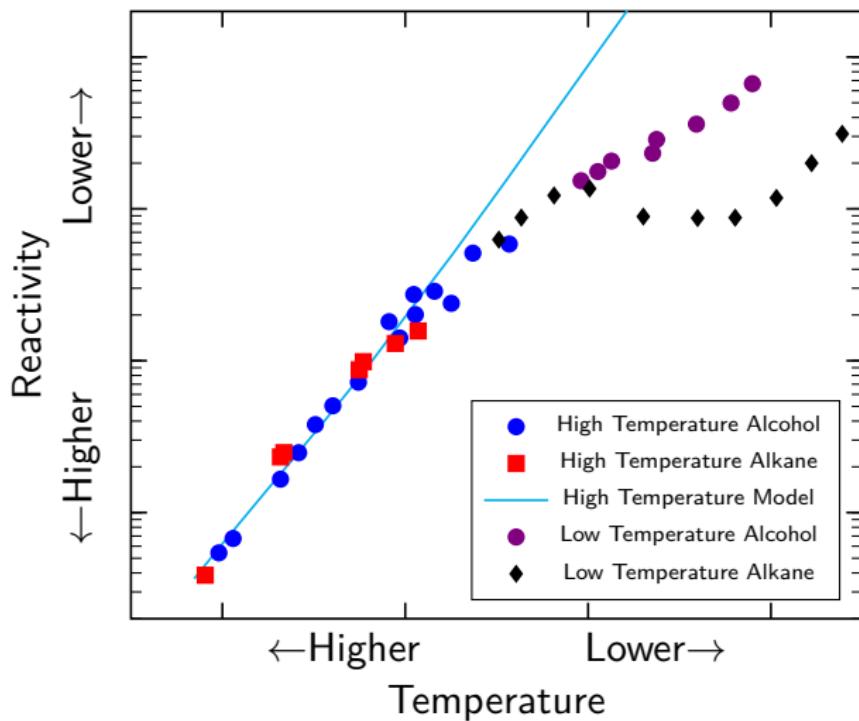
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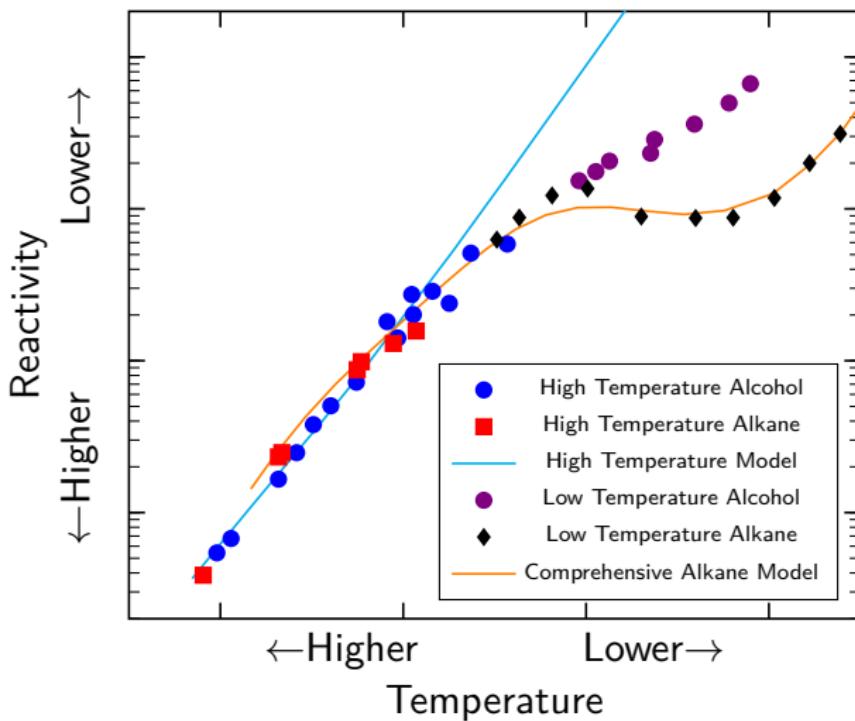
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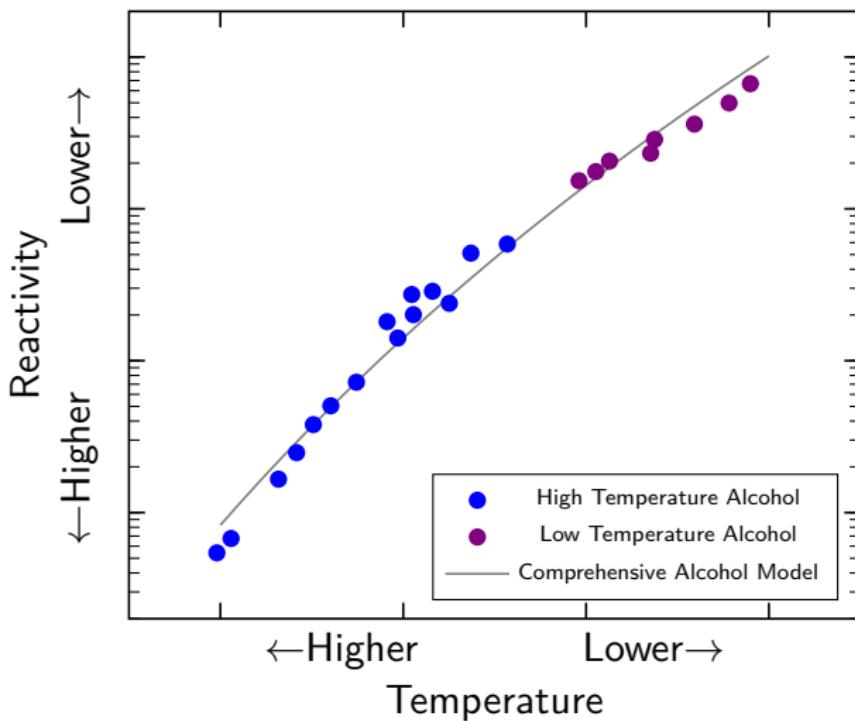
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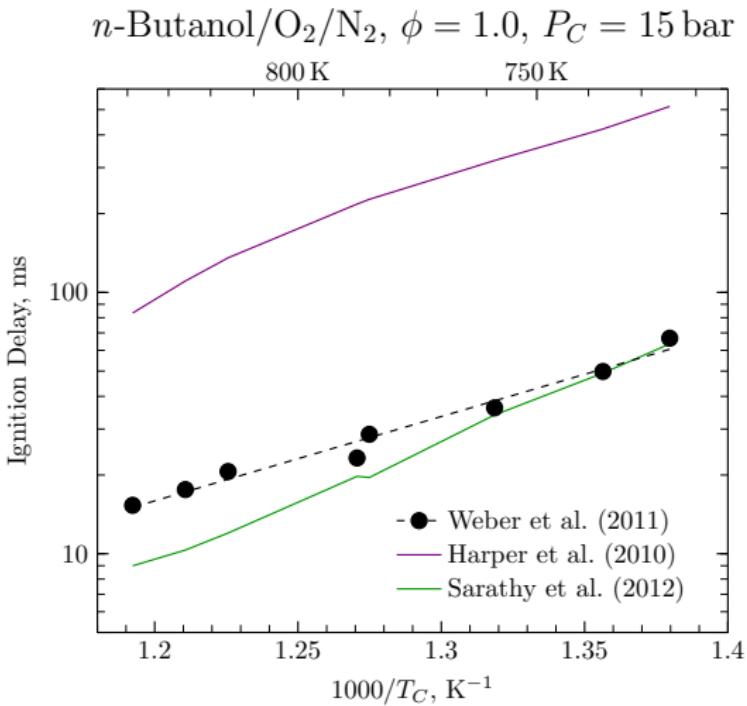
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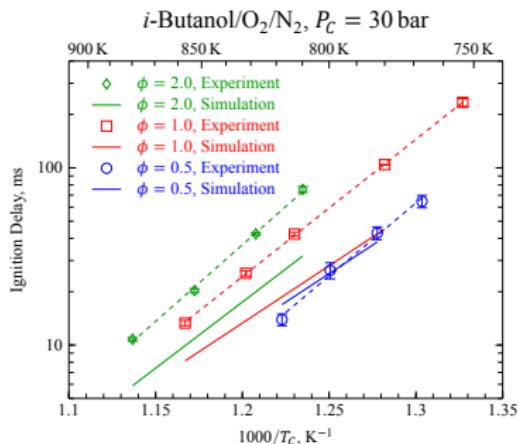
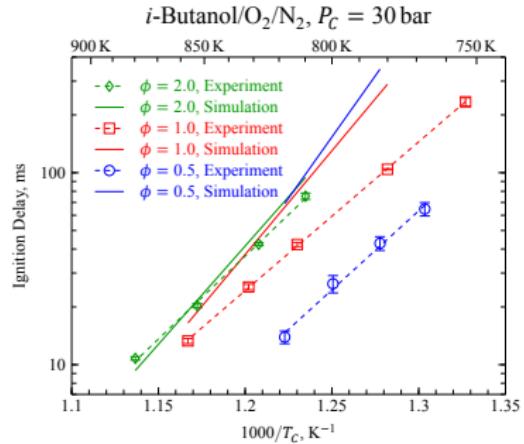


What phenomena am I trying to understand?



With low-temperature reaction classes added, models can better predict the ignition delay.

What phenomena am I trying to understand?



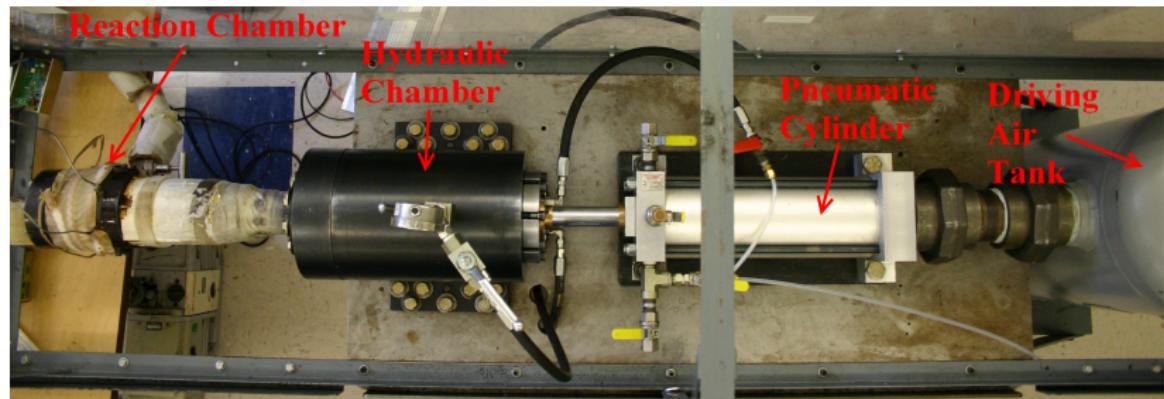
Weber et al. 8th US National Combustion Meeting 2013

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

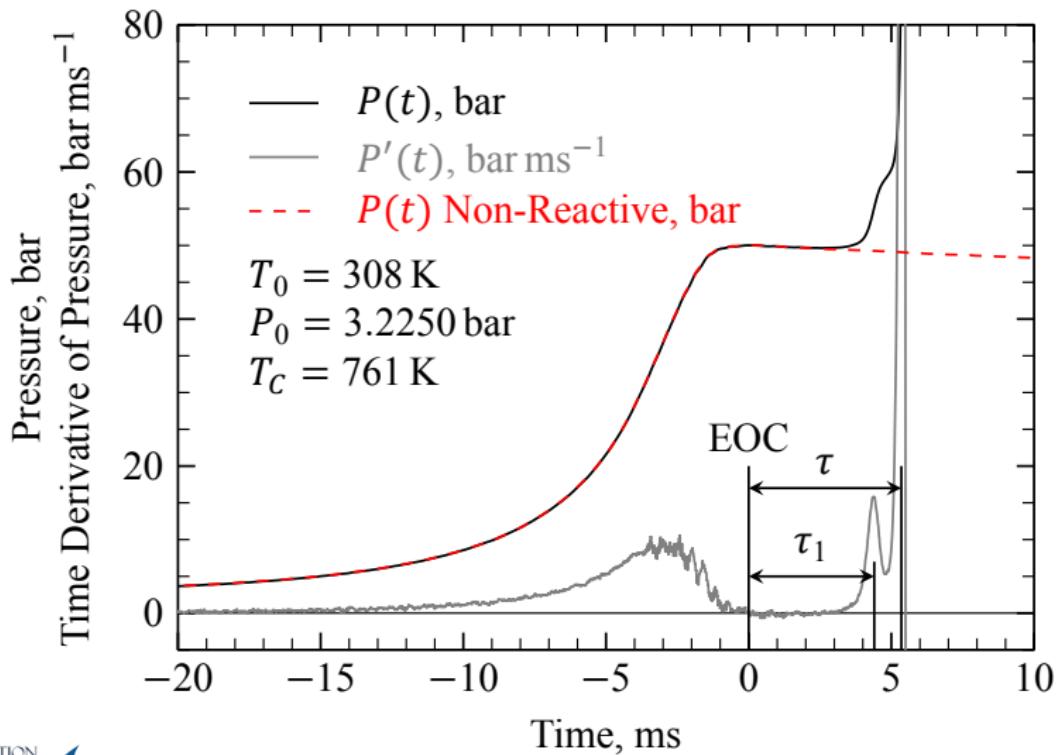
Experimental Apparatuses

Rapid Compression Machine



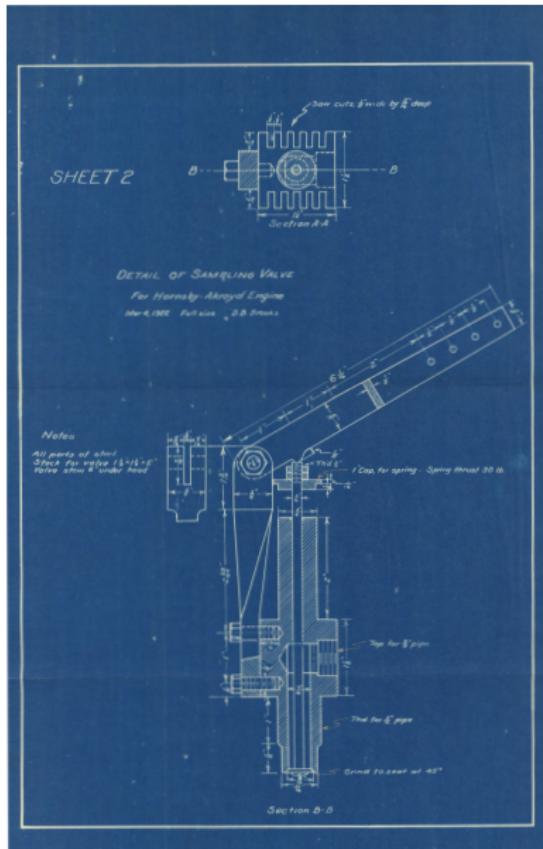
Rapid Compression Machine

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



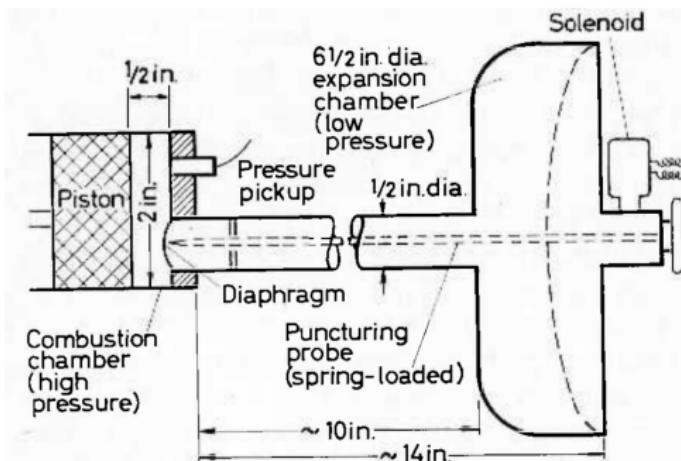
Rapid Sampling Apparatus

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



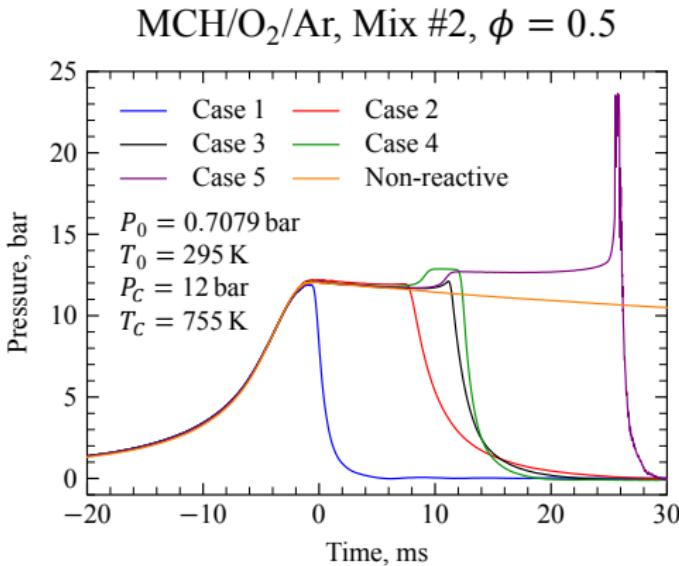
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- ▶ In the 1960's, the first sampling apparatus was adapted for an RCM

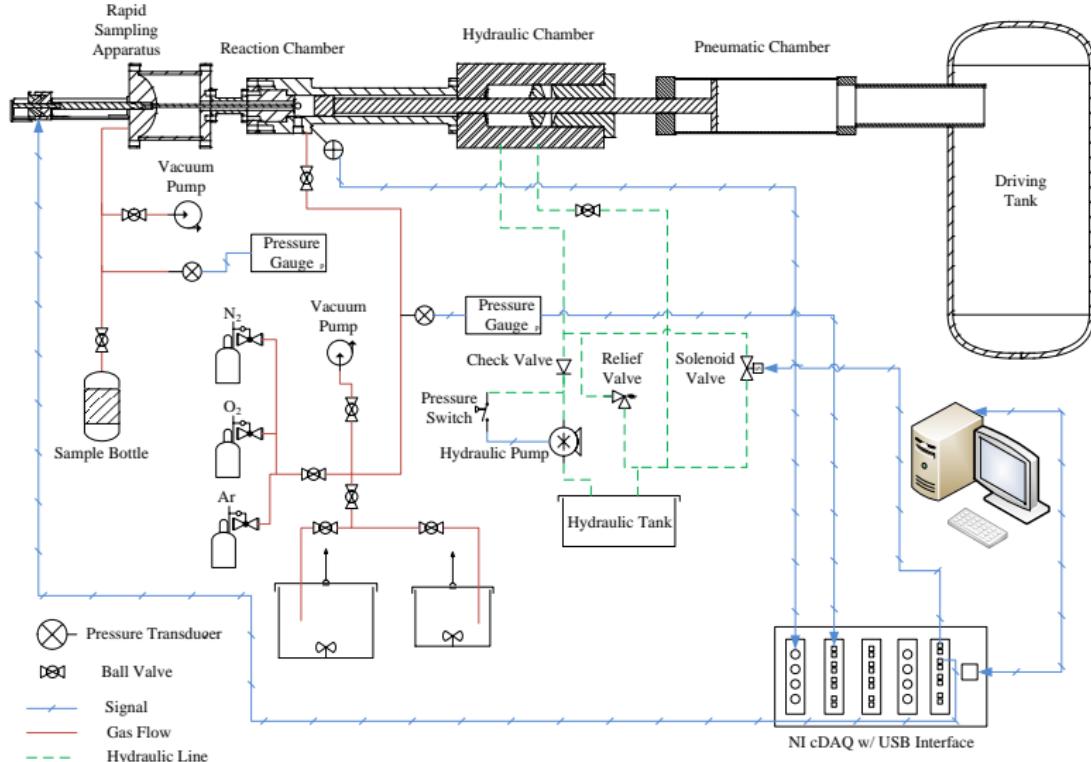


Rapid Sampling Apparatus

- ▶ Sampling apparatuses have been used since the 1920's to study combustion chemistry
- ▶ In the 1960's, the first sampling apparatus was adapted for an RCM
- ▶ Sampling devices rapidly quench ongoing reactions so that species are determined at a discrete point in time



Rapid Sampling Apparatus



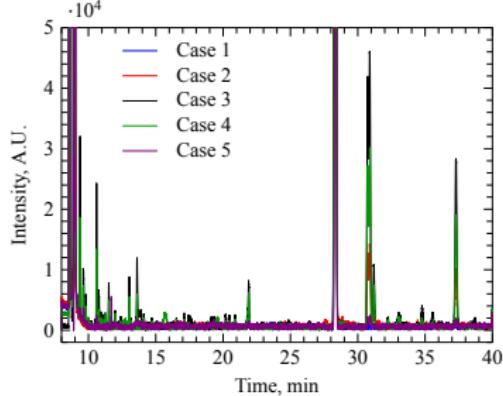
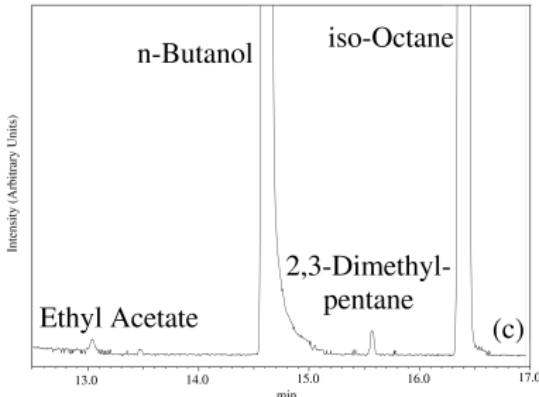
Gas Chromatograph/Mass Spectrometer

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



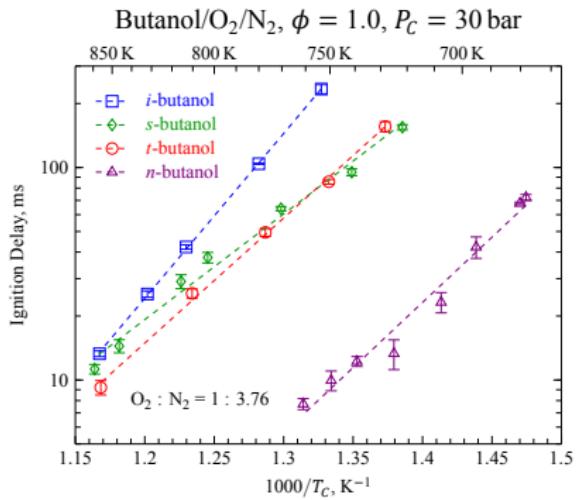
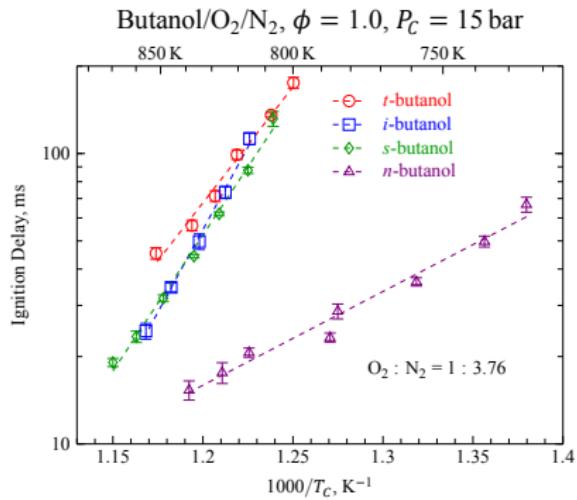
Gas Chromatograph/Mass Spectrometer

- ▶ Separates, identifies, and quantifies chemical species



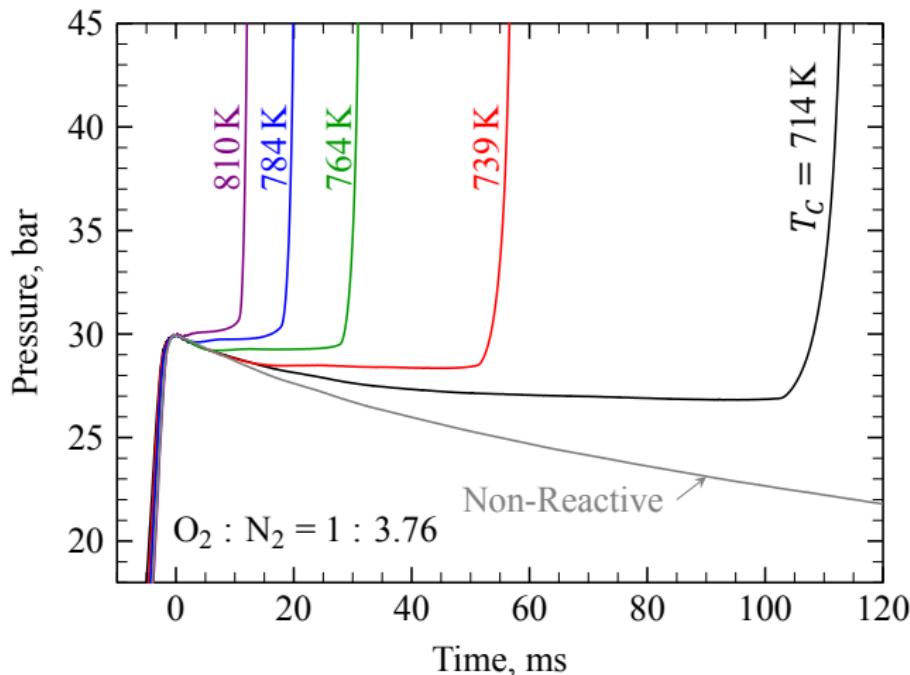
Results, Butanol Isomers

The reactivity of the butanol isomers depends on the pressure

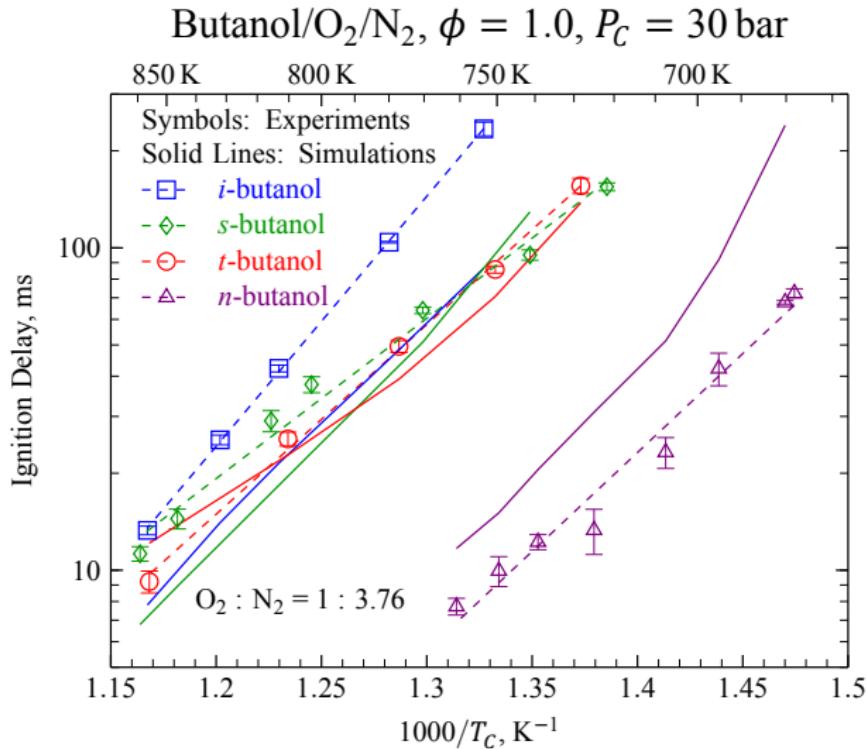


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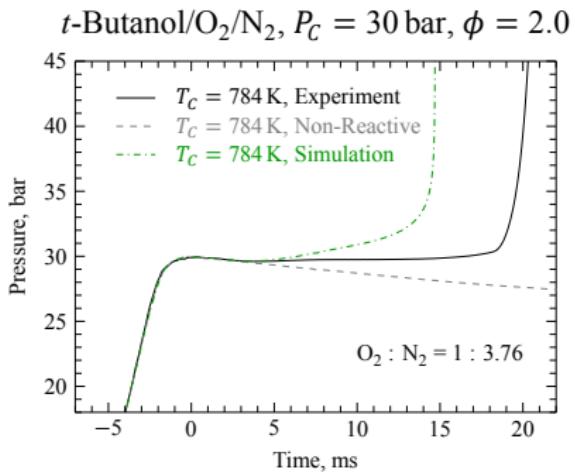
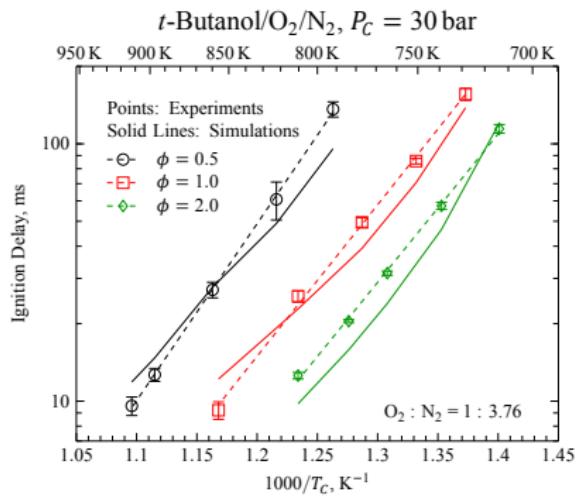
t-Butanol/O₂/N₂, $P_C = 30$ bar, $\phi = 2.0$



The reactivity trend can be predicted by a detailed understanding of the chemistry

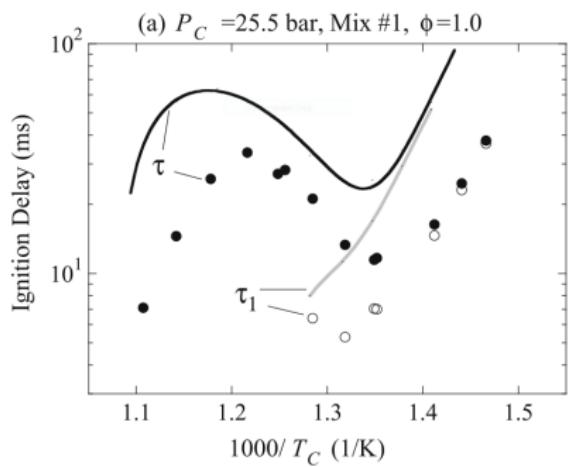


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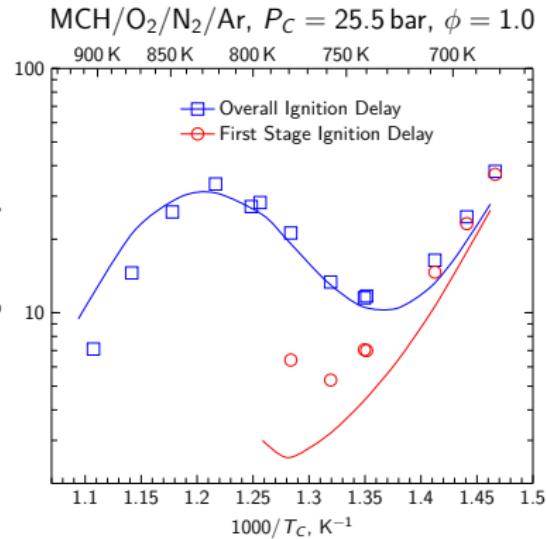


Results, Methylcyclohexane

Methylcyclohexane ignition



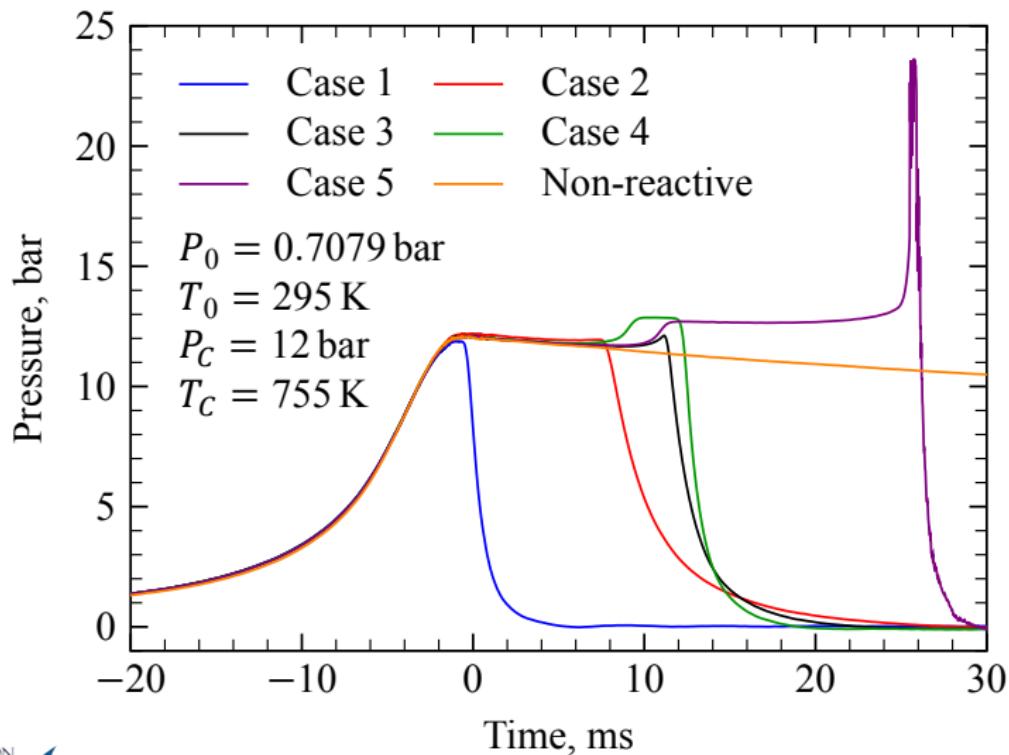
Mittal et al. Combust. Flame
2009



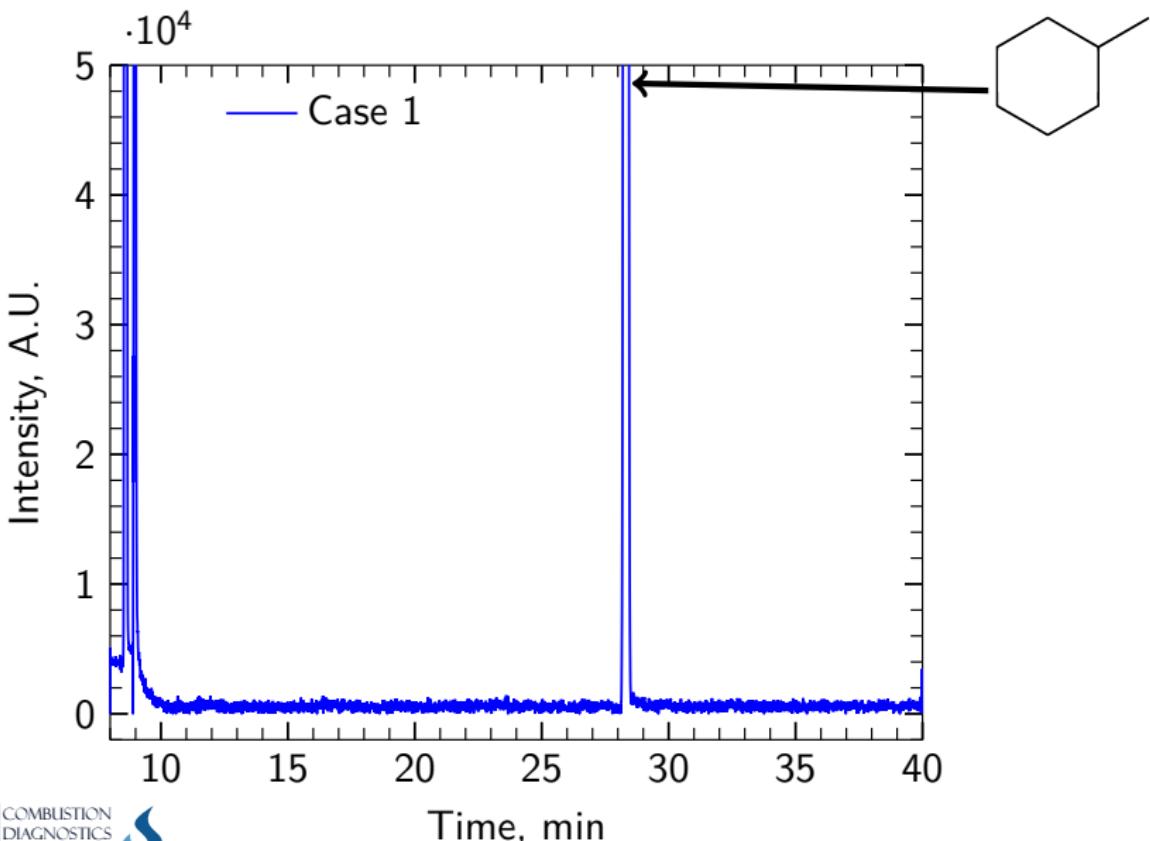
Weber et al. Combust. Flame
2014

Sampling results

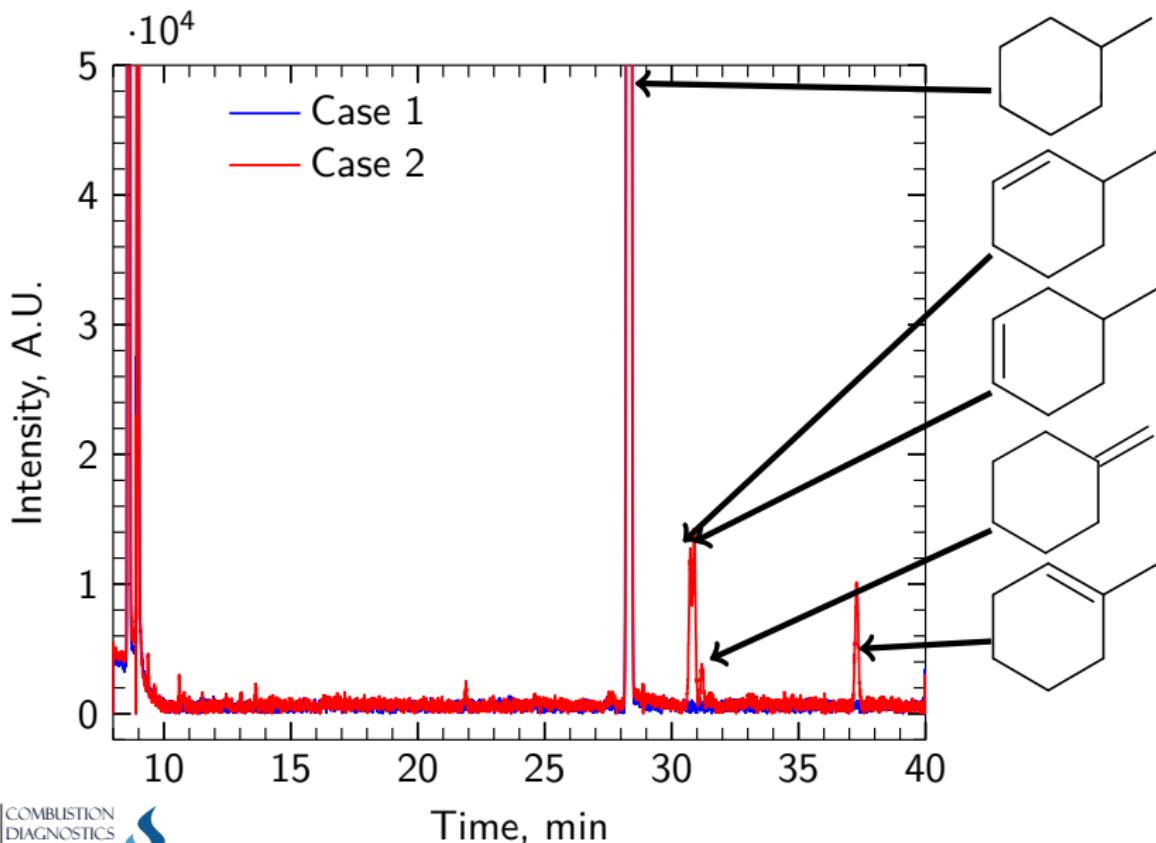
MCH/O₂/Ar, Mix #2, $\phi = 0.5$



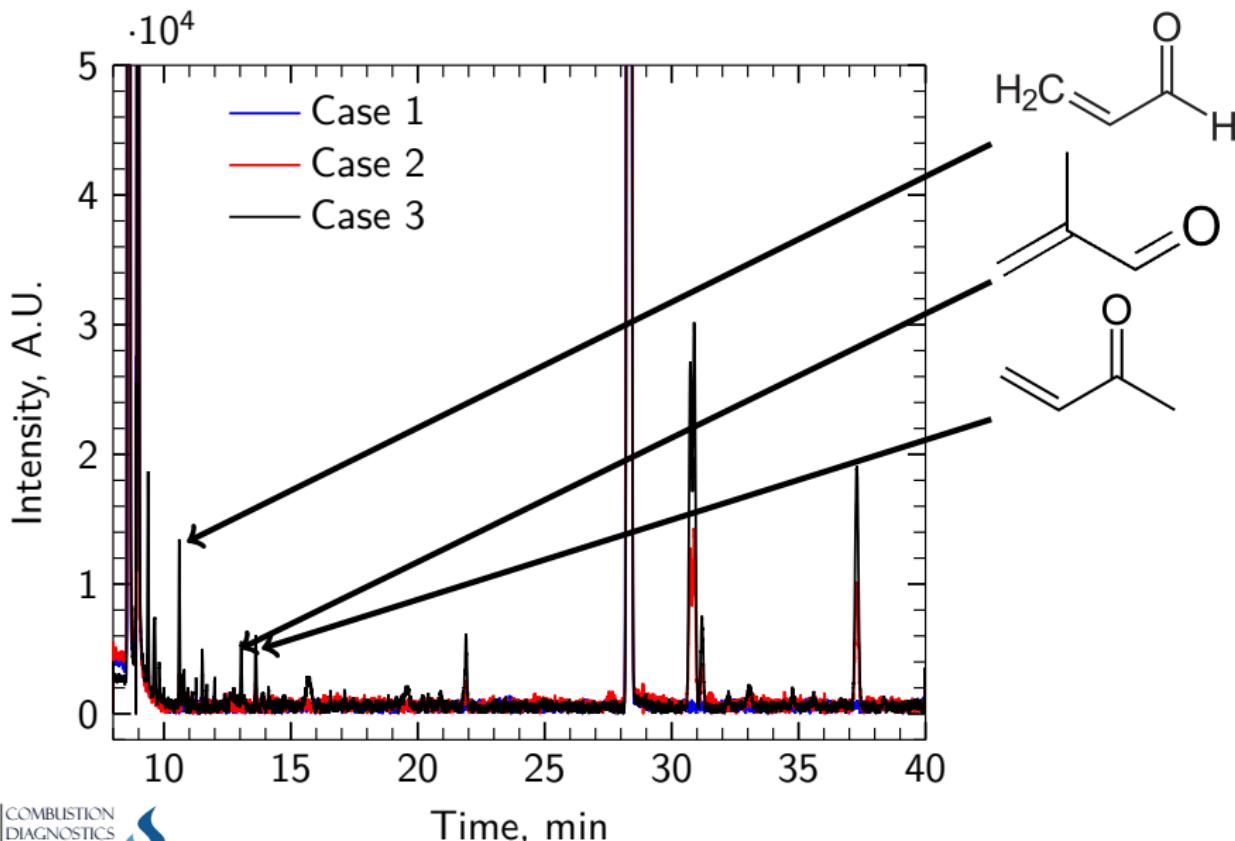
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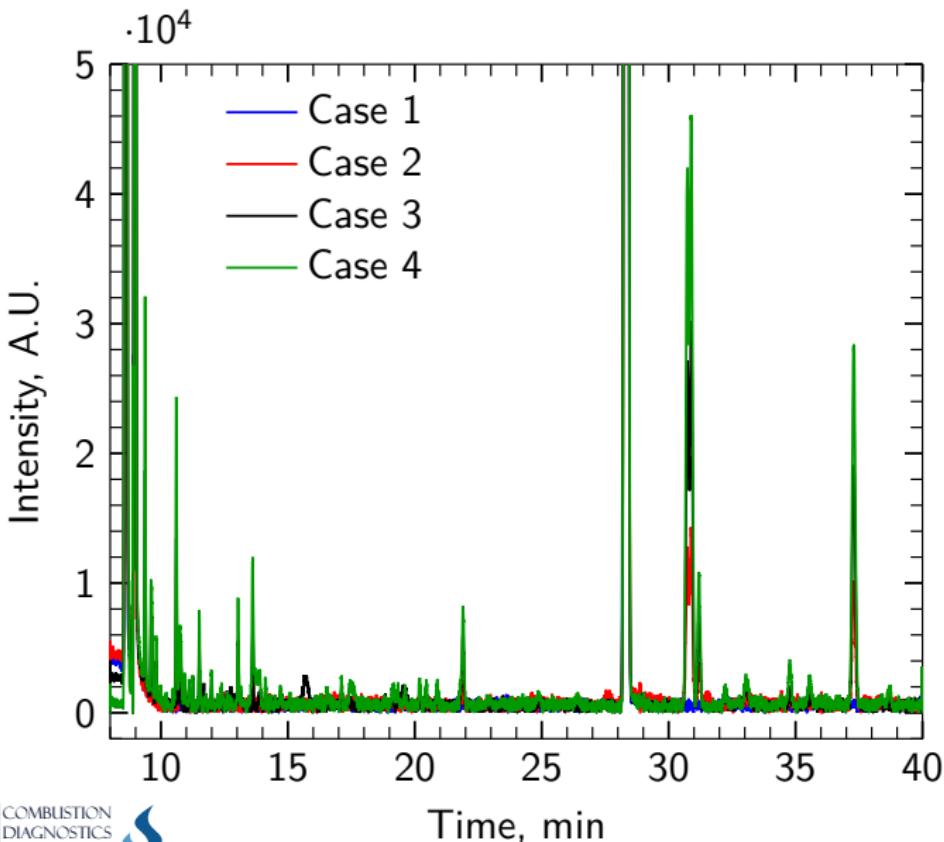
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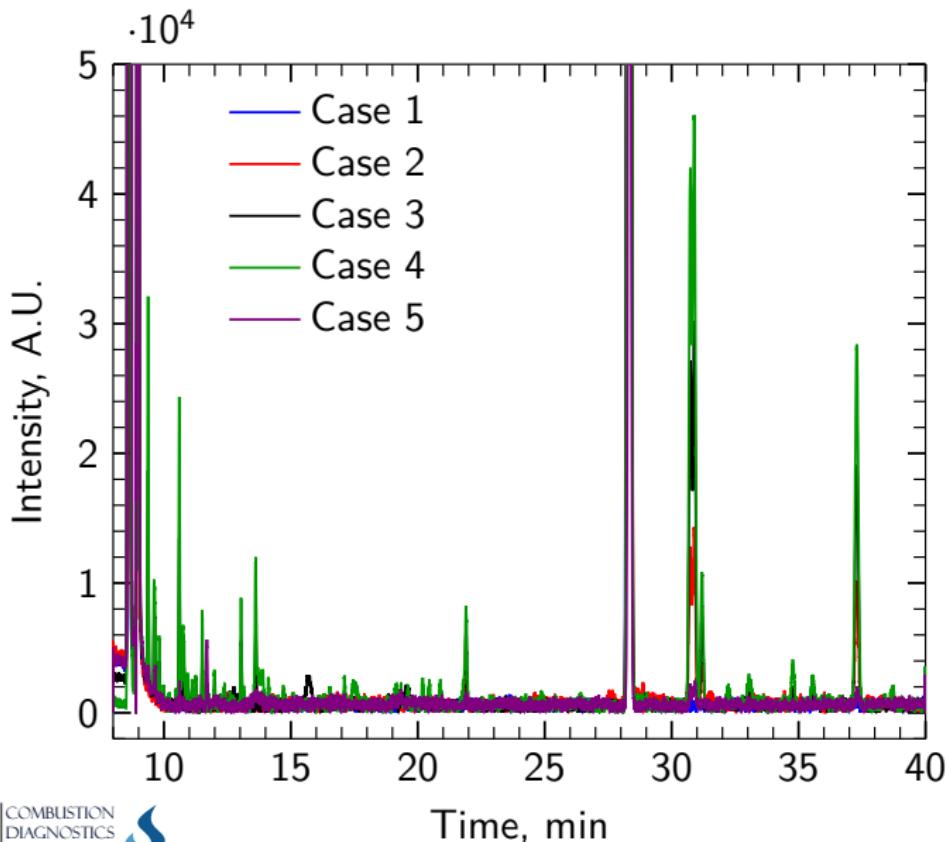
Sampling results



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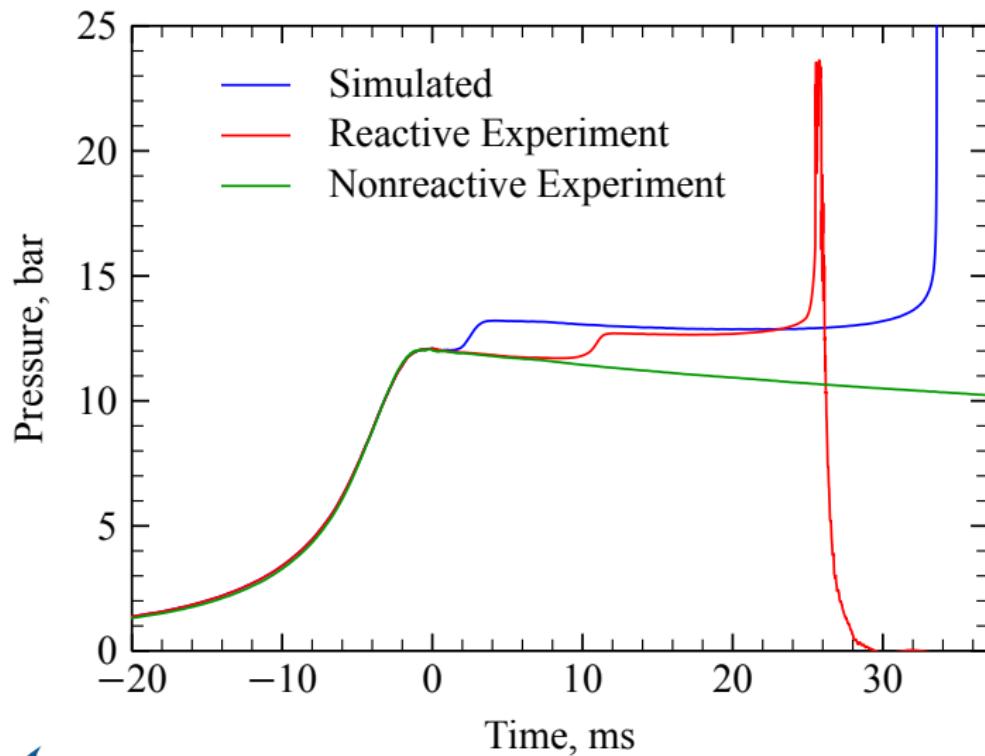


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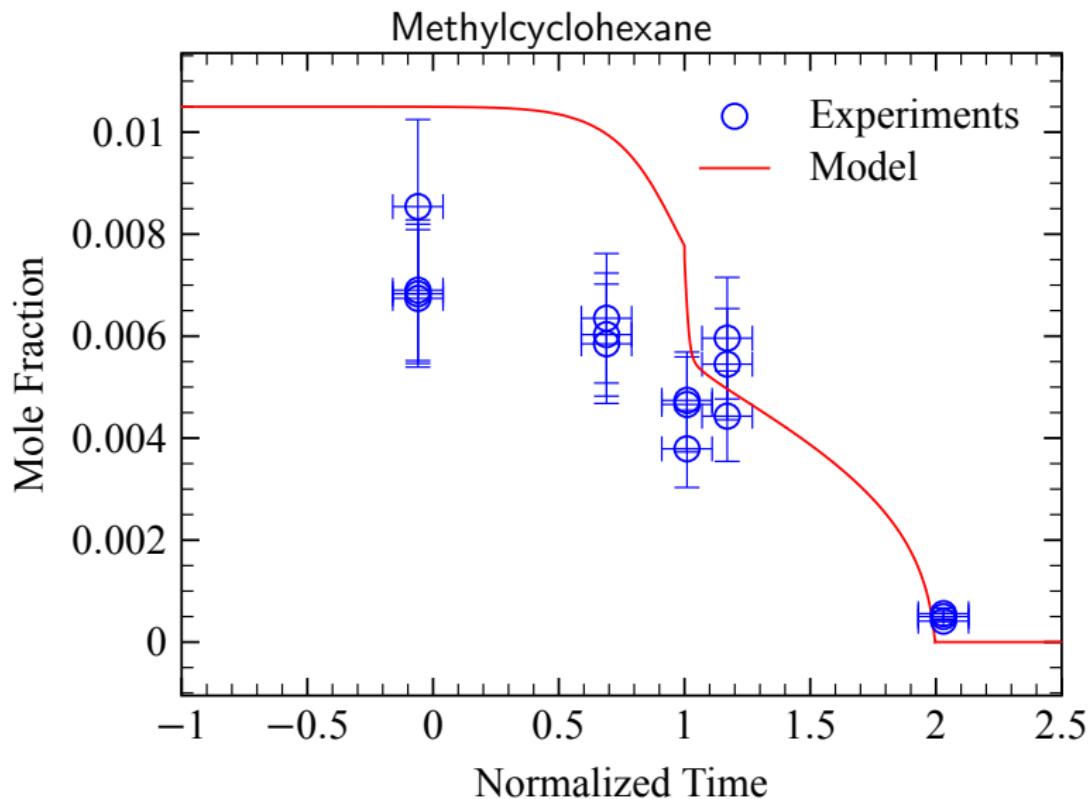


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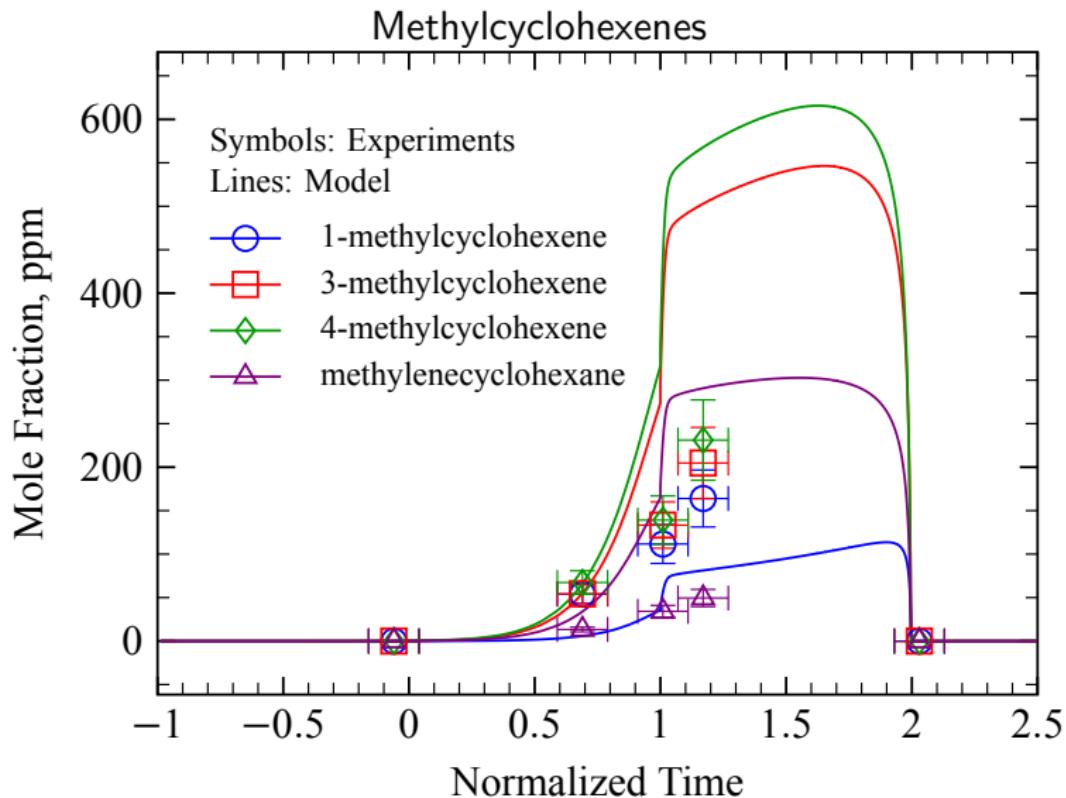
MCH/O₂/Ar, $\phi = 0.5$, 12 bar



Sampling results



Sampling results



Summary

- ▶ We need a better understanding of the combustion properties of fuels we use now, fuels for the medium-term, and fuels for the long-term 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
- ▶ My dissertation did x y z to advance these causes