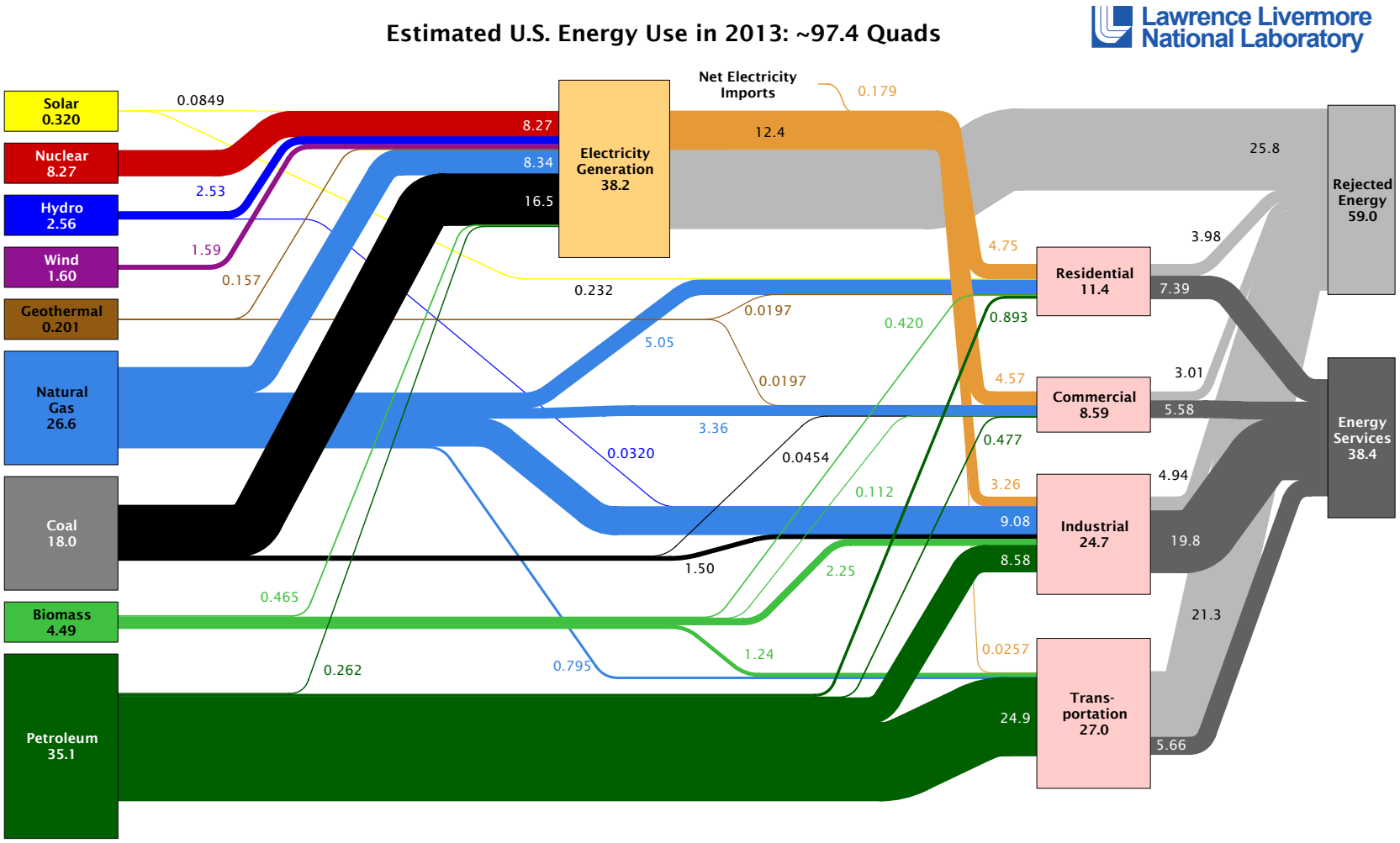
High Pressure Ignition Chemistry of Alternative Fuels

Bryan W. Weber

Prepared for Ph.D. Defense

June 19, 2014

We use a lot of fuels to power the world



Source: LLNL 2014. Data is based on DOE/EIA-0035(2014-03), 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 auspices 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

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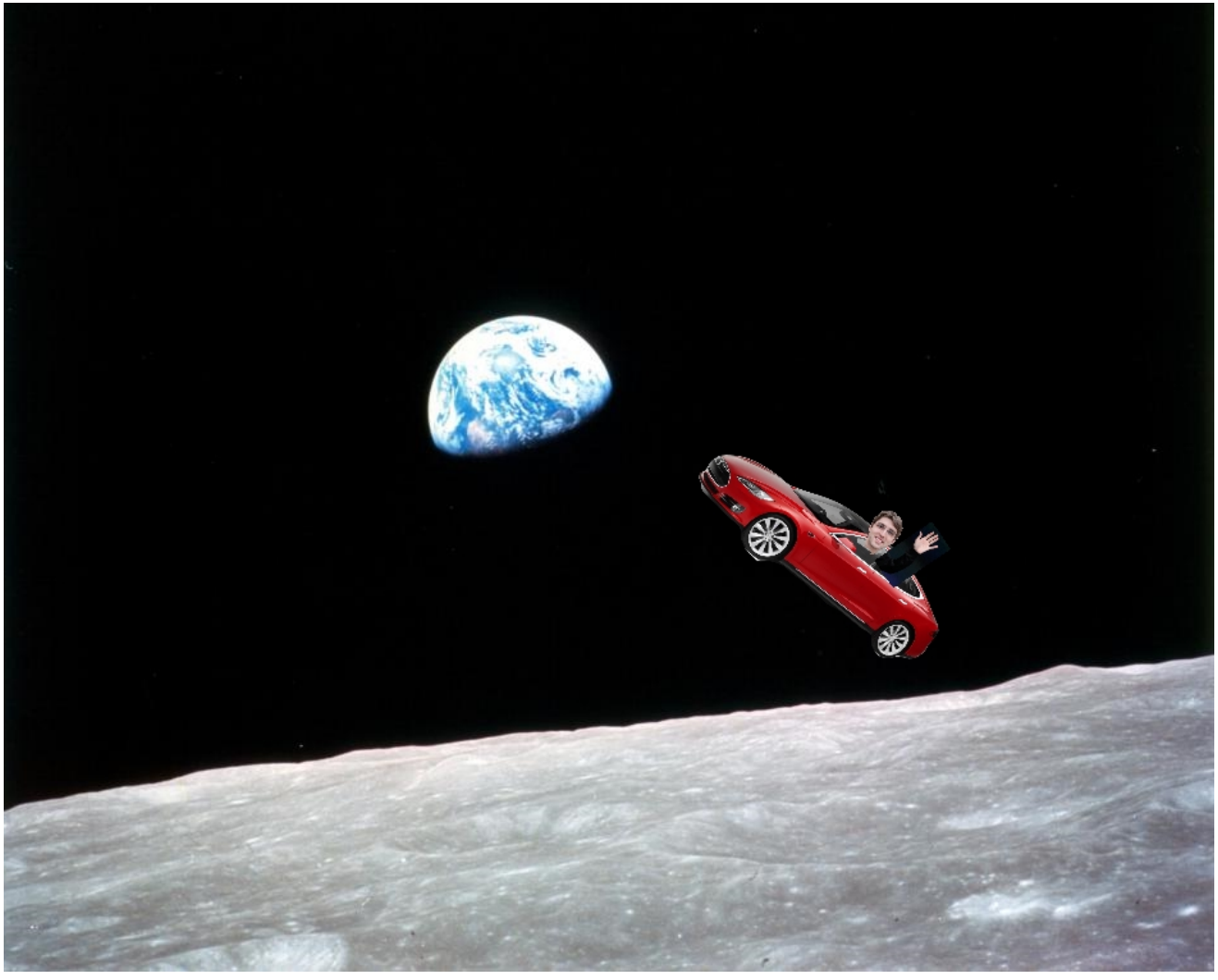

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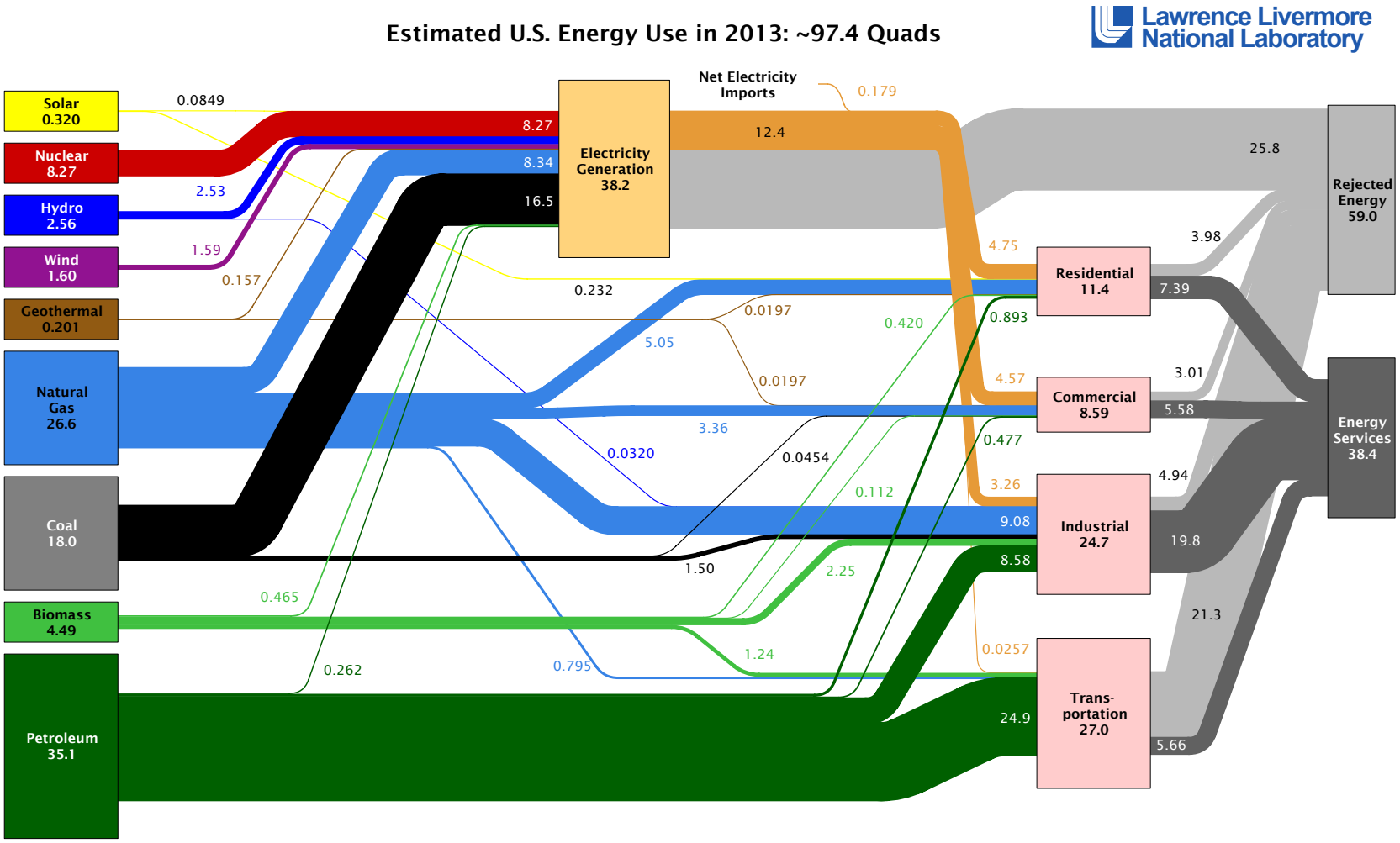

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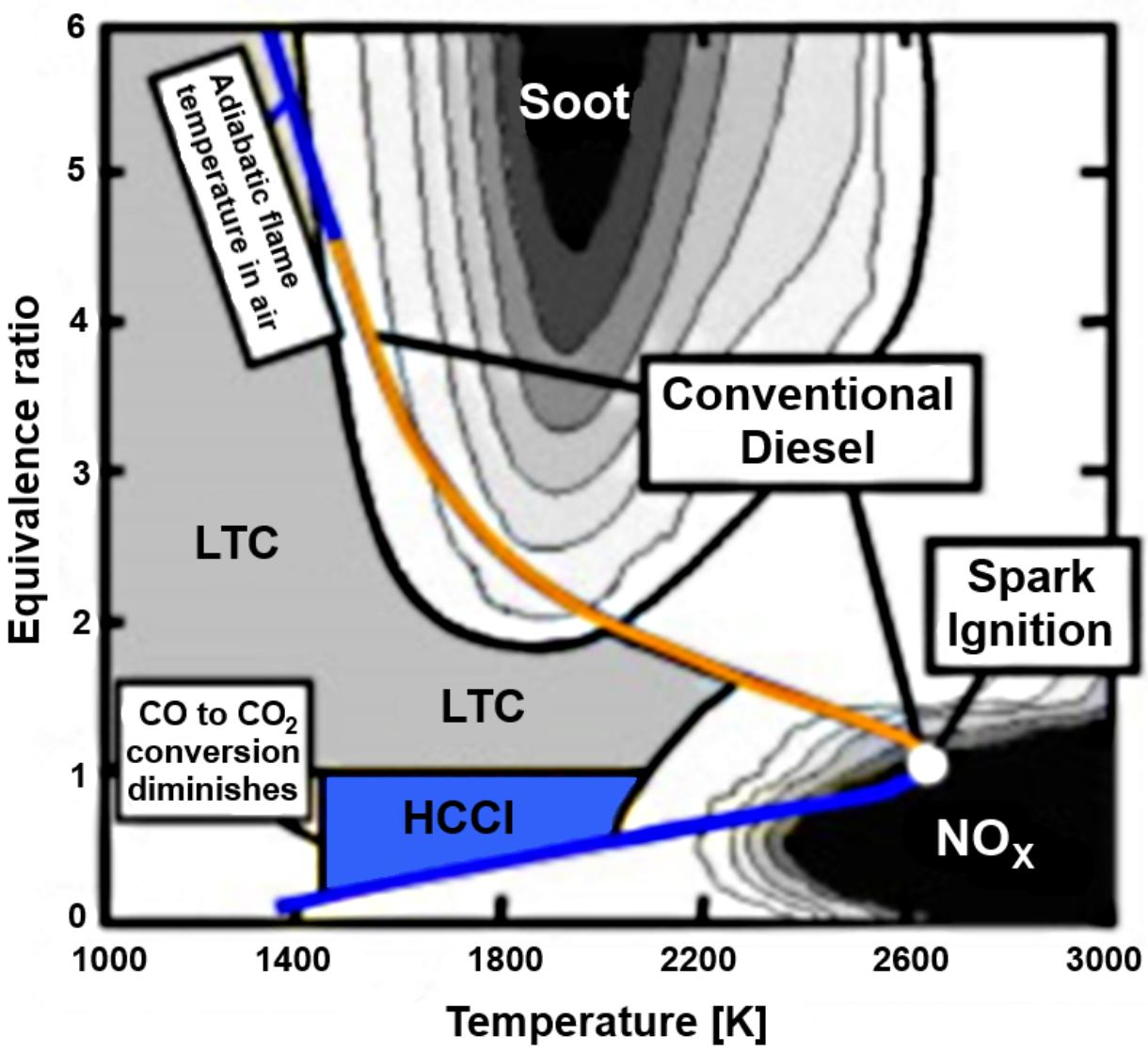
We use a lot of fuels to power the world

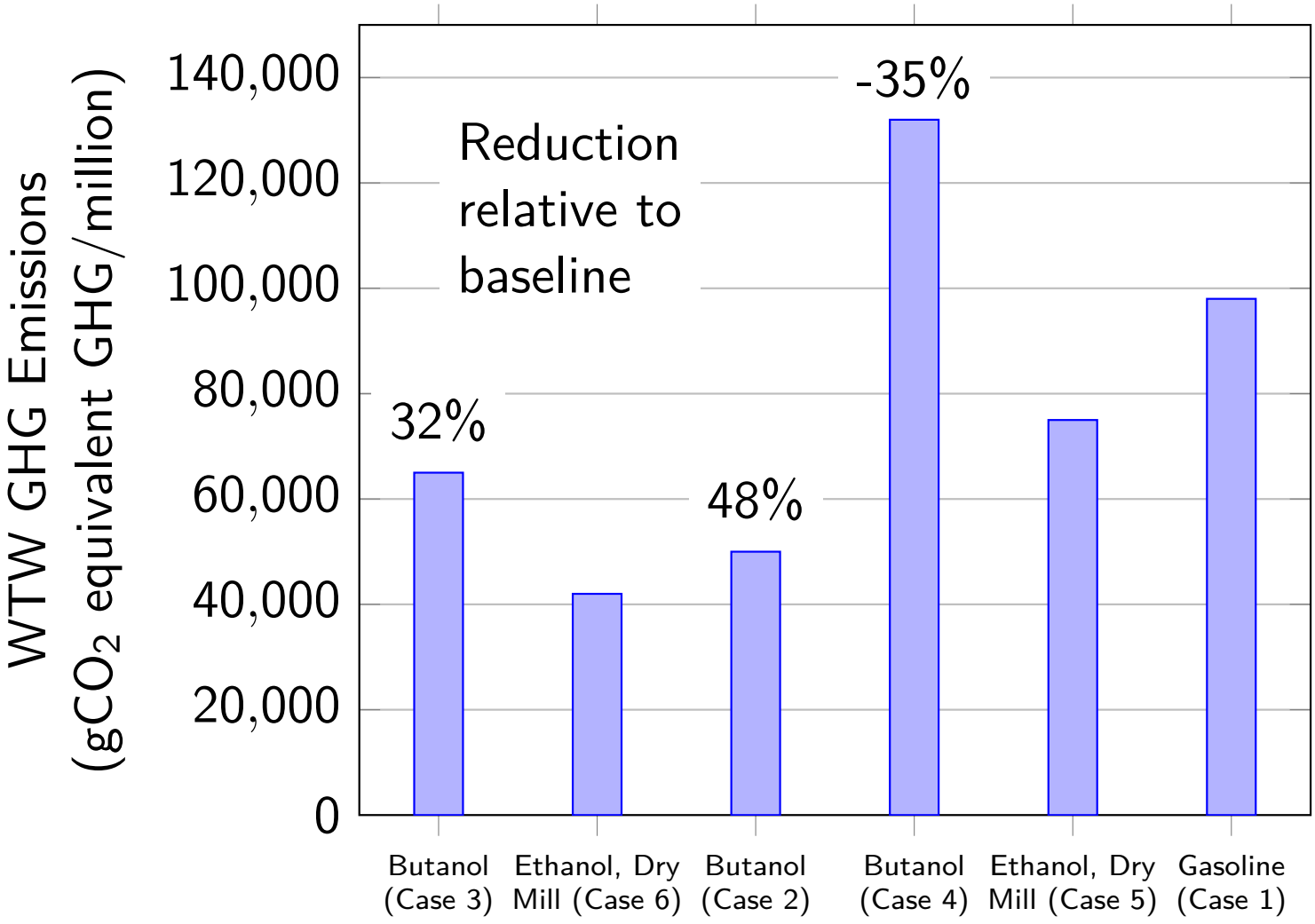
- Combustion is predicted to remain the dominant energy conversion process for many years into the future
- The combustion of fossil fuels has been implicated in a number of harmful effects on human health, the environment, and the economy
- Two solutions have been proposed:
  - Better engines
  - Better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

Better engines have higher efficiency and lower emissions



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

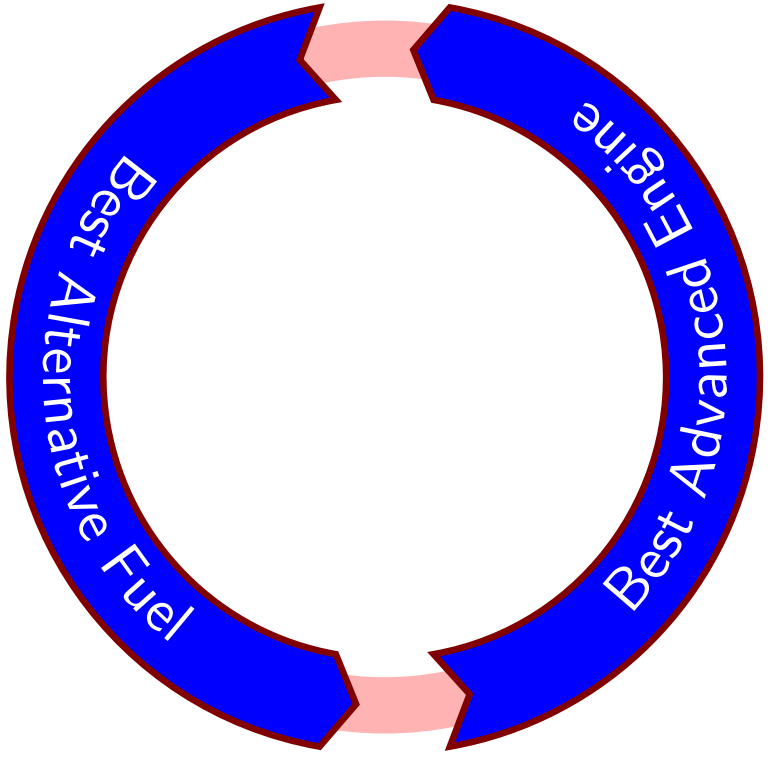
Better fuels reduce emissions and reduce dependence on fossil fuels



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

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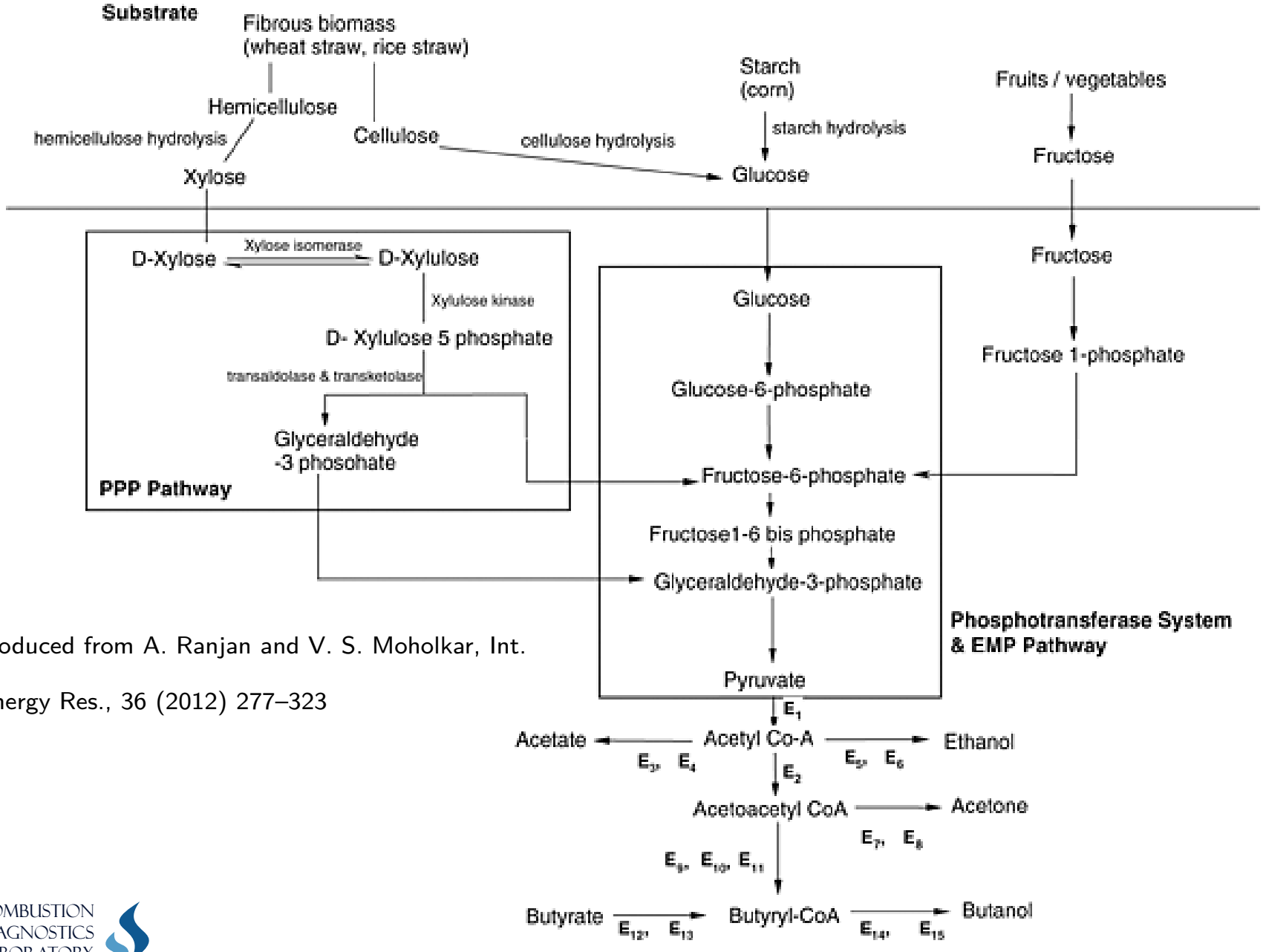
- Selecting the “best” alternative fuel requires knowledge of the “best” engine, which depends on which alternative fuel is selected. . .
- Testing every fuel in every engine is prohibitively expensive and time consuming
- Computer-aided design can be employed to create fuel-flexible engines if the fuel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

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 affect engine performance

- 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

- Cetane Number
- Octane Number
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Fundamental Studies

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  - Quantum chemical modeling
  - Reaction mechanisms
  - Computational fluid dynamics

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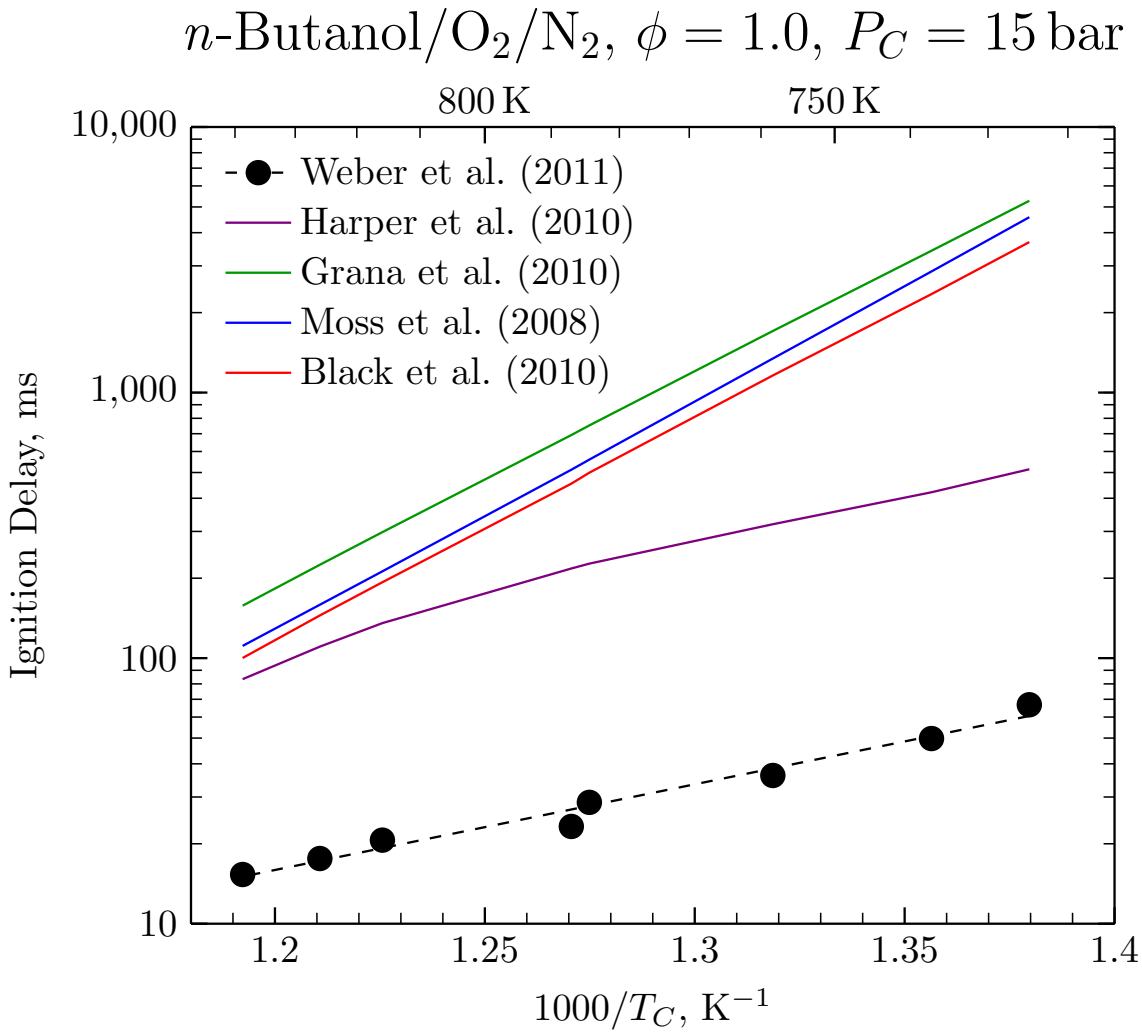
These efforts are complementary!

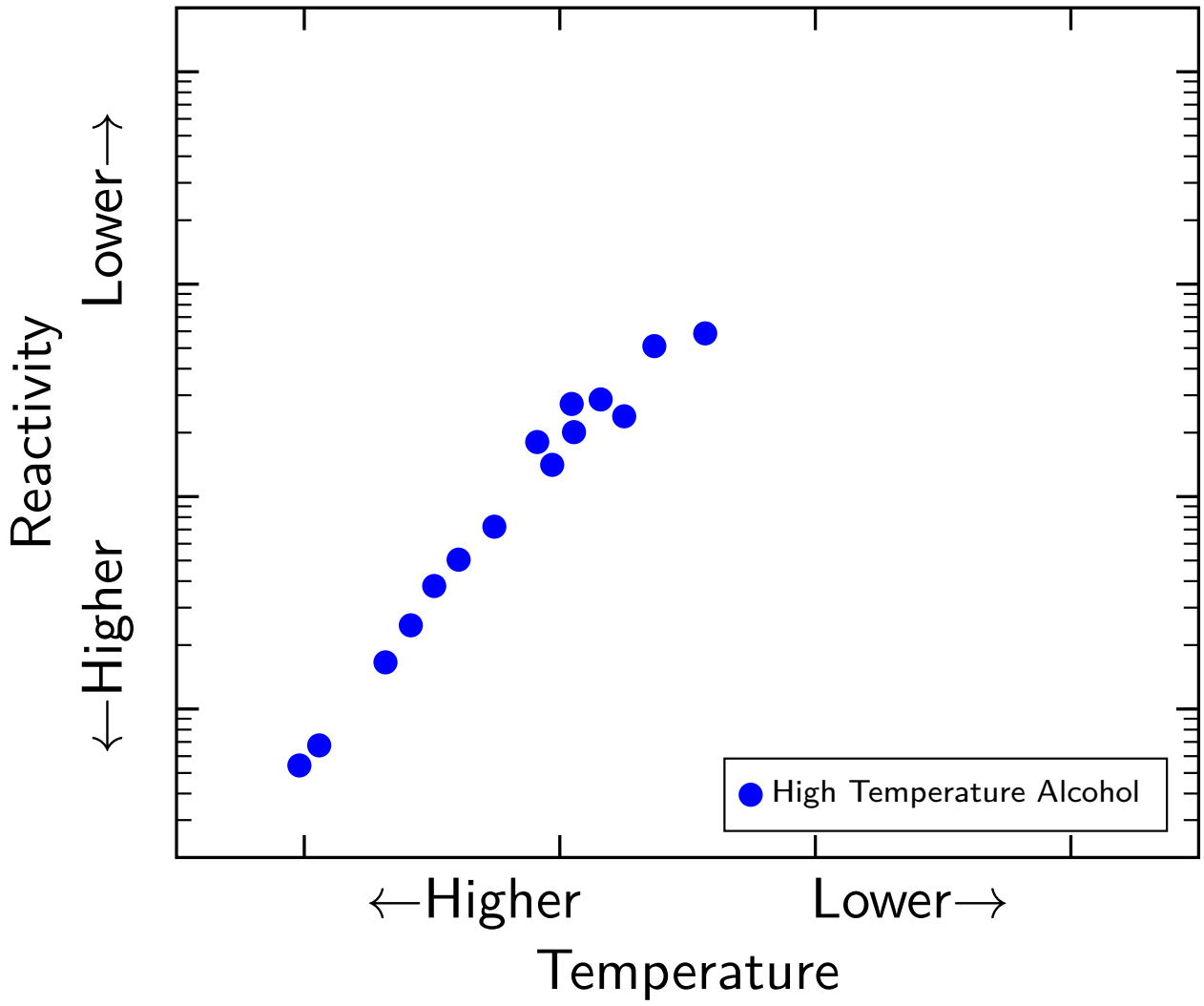
What phenomena am I trying to understand?

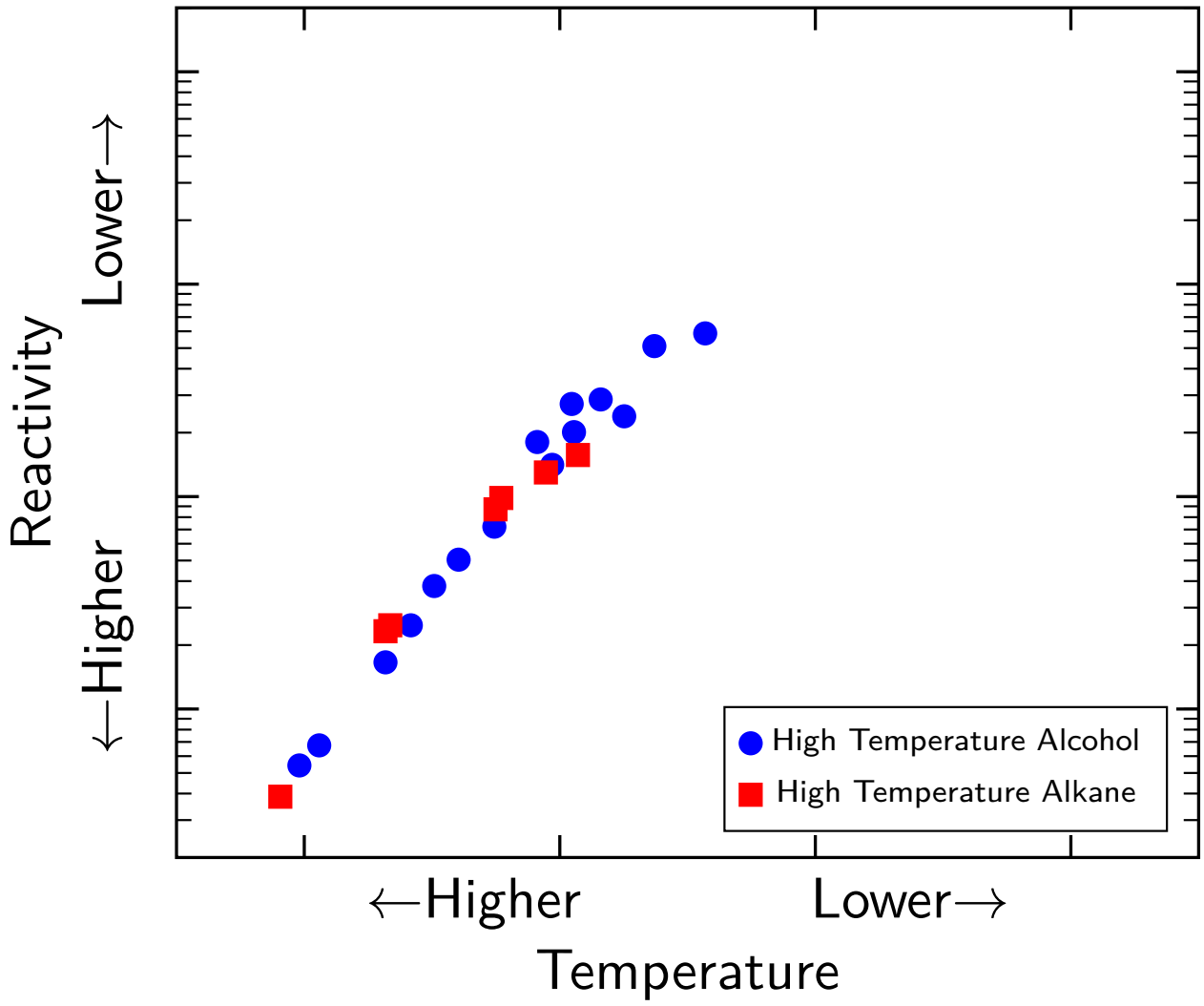
How do alternative fuels react at engine-relevant conditions?

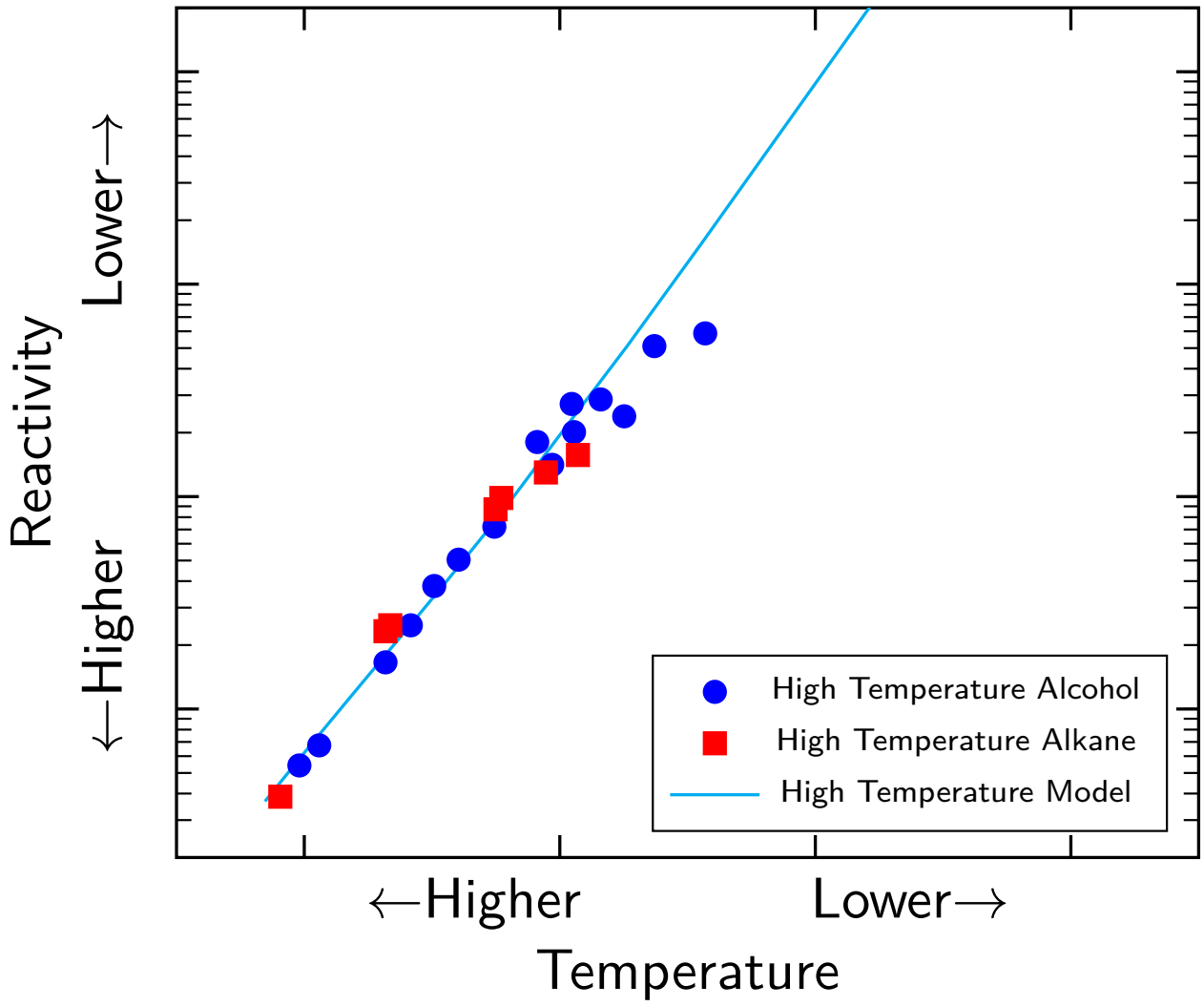
What phenomena am I trying to understand?

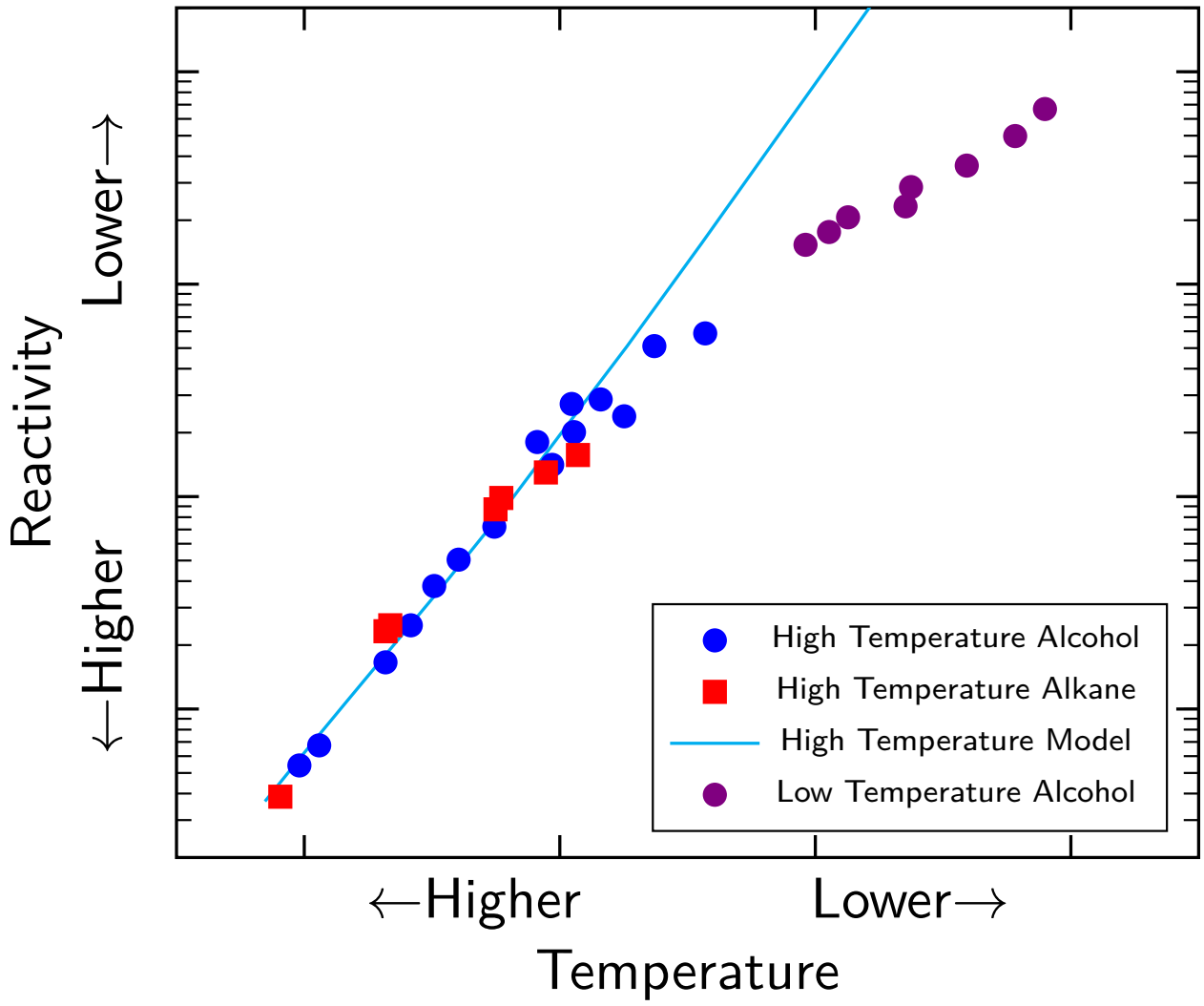


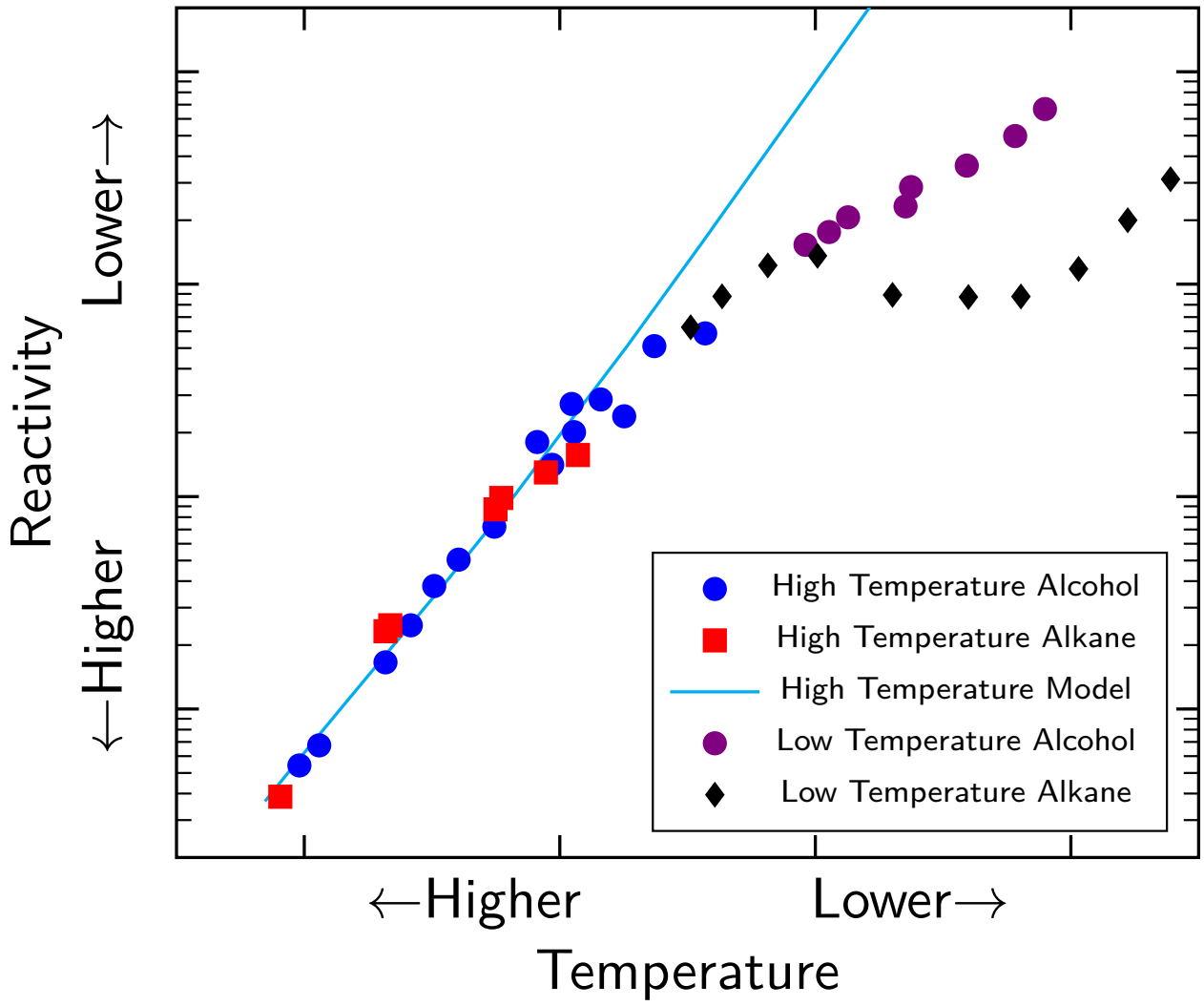
Alternative fuels may undergo reactions that have not been described before

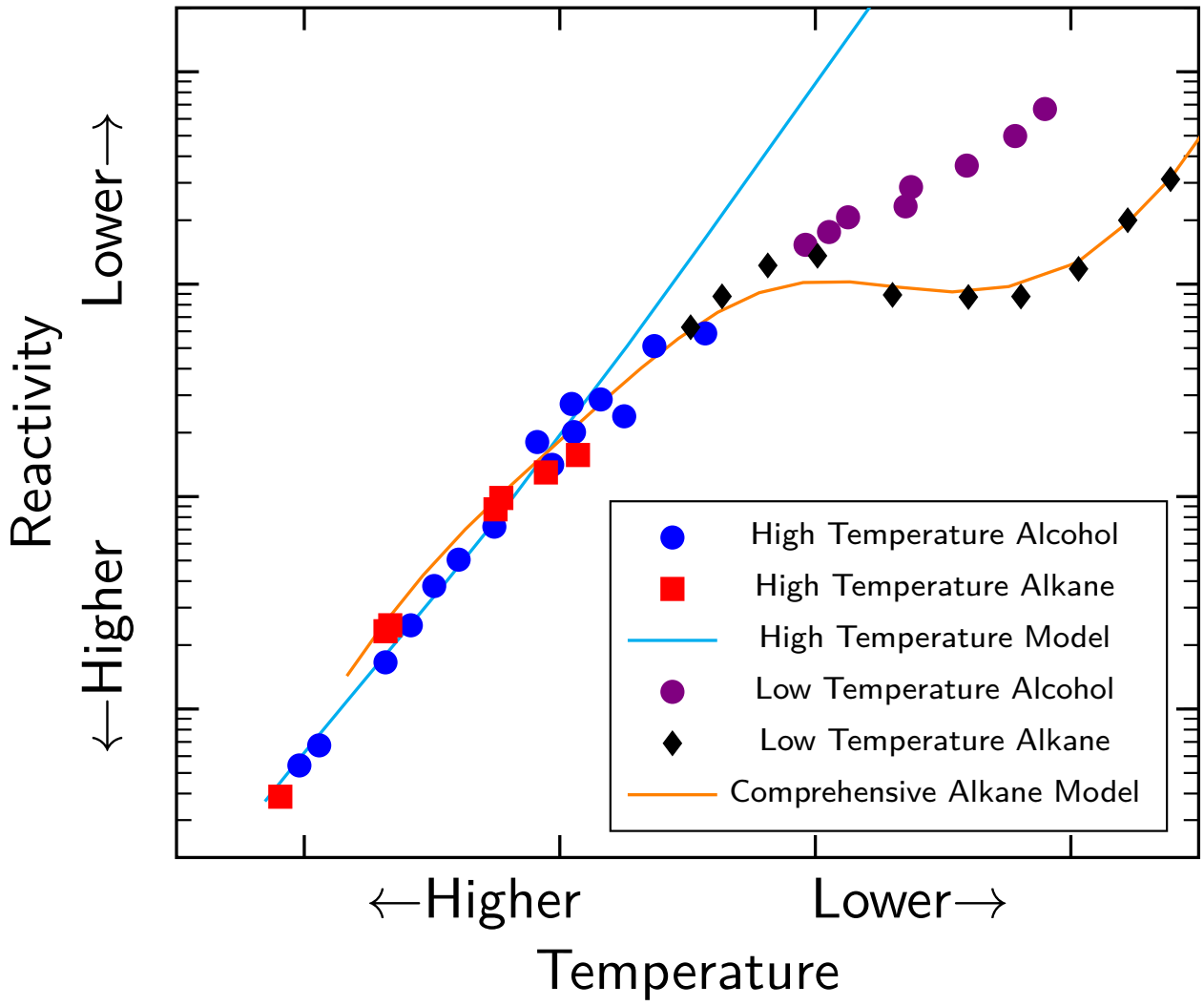

Reactivity
←Higher
Lower→
High Temperature Alcohol
←Higher
Lower→
Temperature

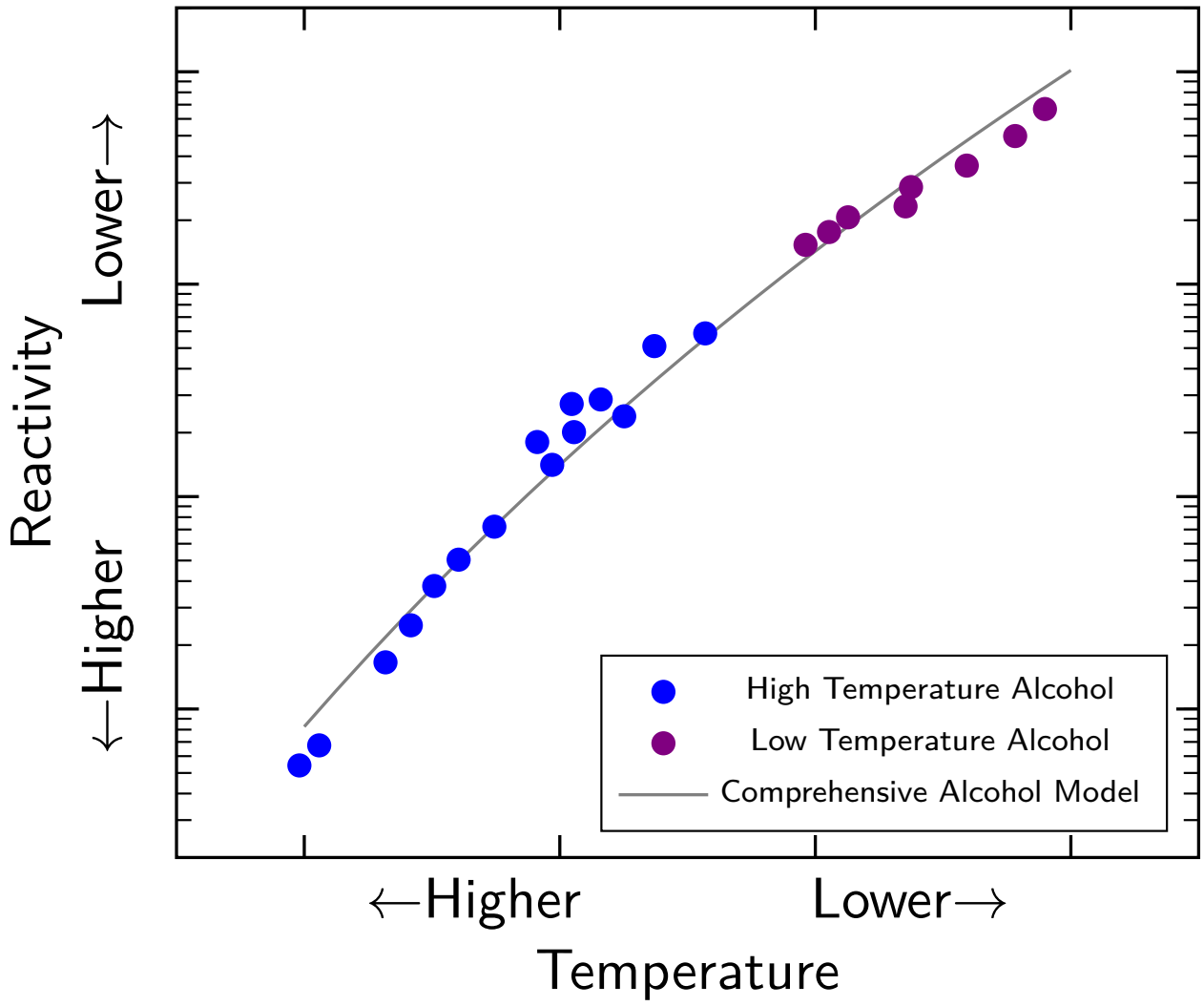

Reactivity
←Higher
Lower→
←Higher
Lower→
Temperature
High Temperature Alcohol
High Temperature Alkane


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

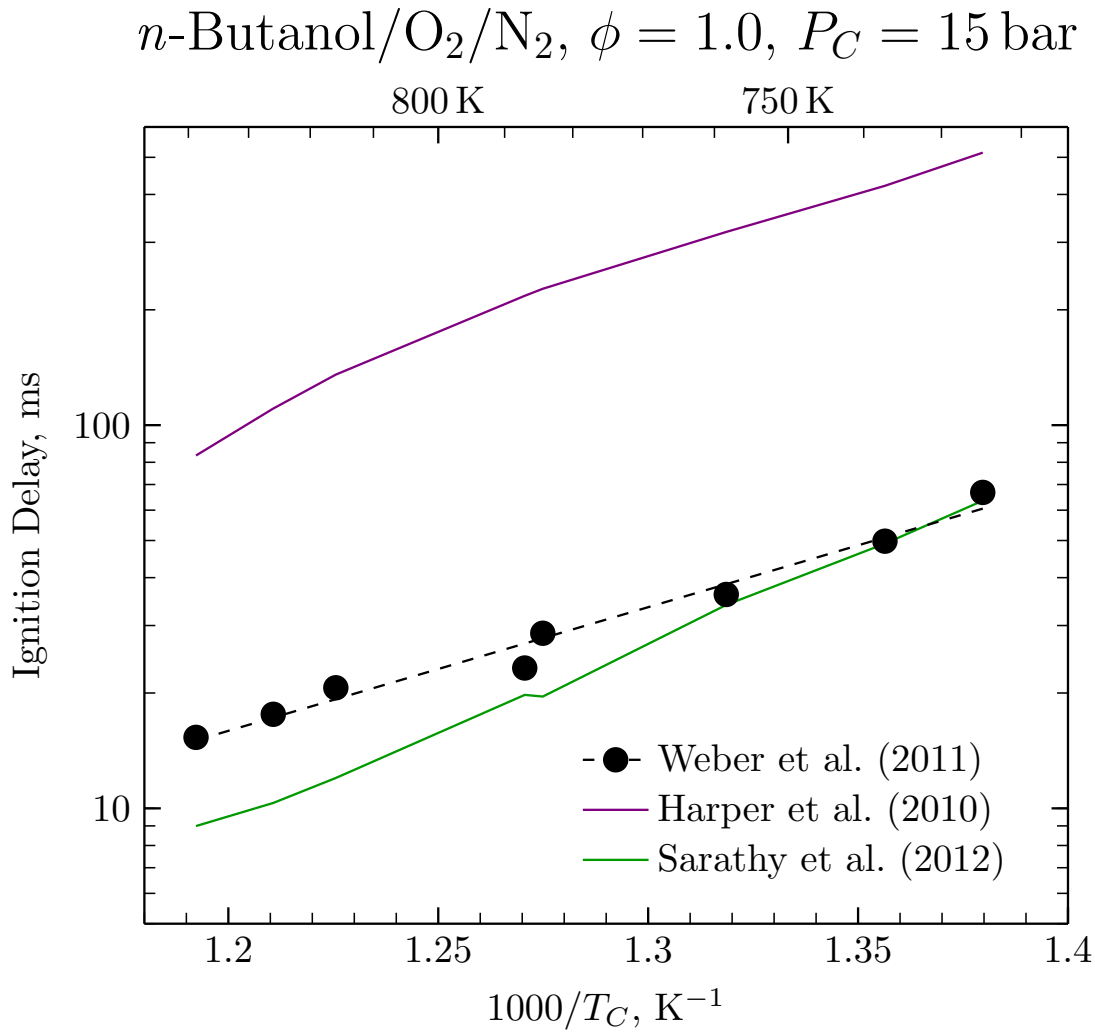

Reactivity
←Higher
Lower→
←Higher
Lower→
Temperature
High Temperature Alcohol
High Temperature Alkane
High Temperature Model
Low Temperature Alcohol


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


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


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

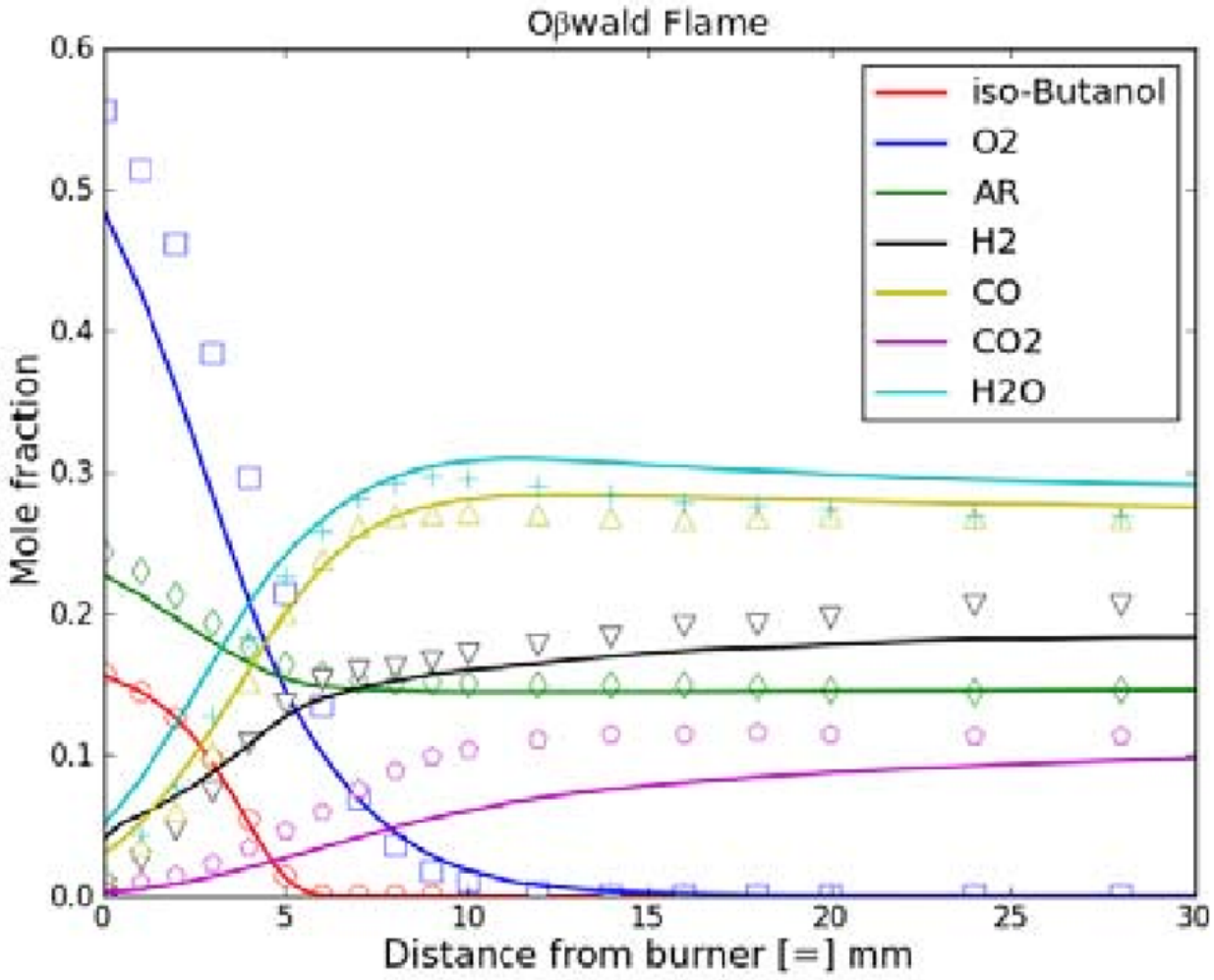
Updated models better predict the combustion phenomena



Sarathy et al. — With low temperature reactions

Harper et al. — Without low temperature reactions

Updated models better predict the combustion phenomena



Reproduced from Hansen et al. Combust. Flame 160 (2013) 2343–2351

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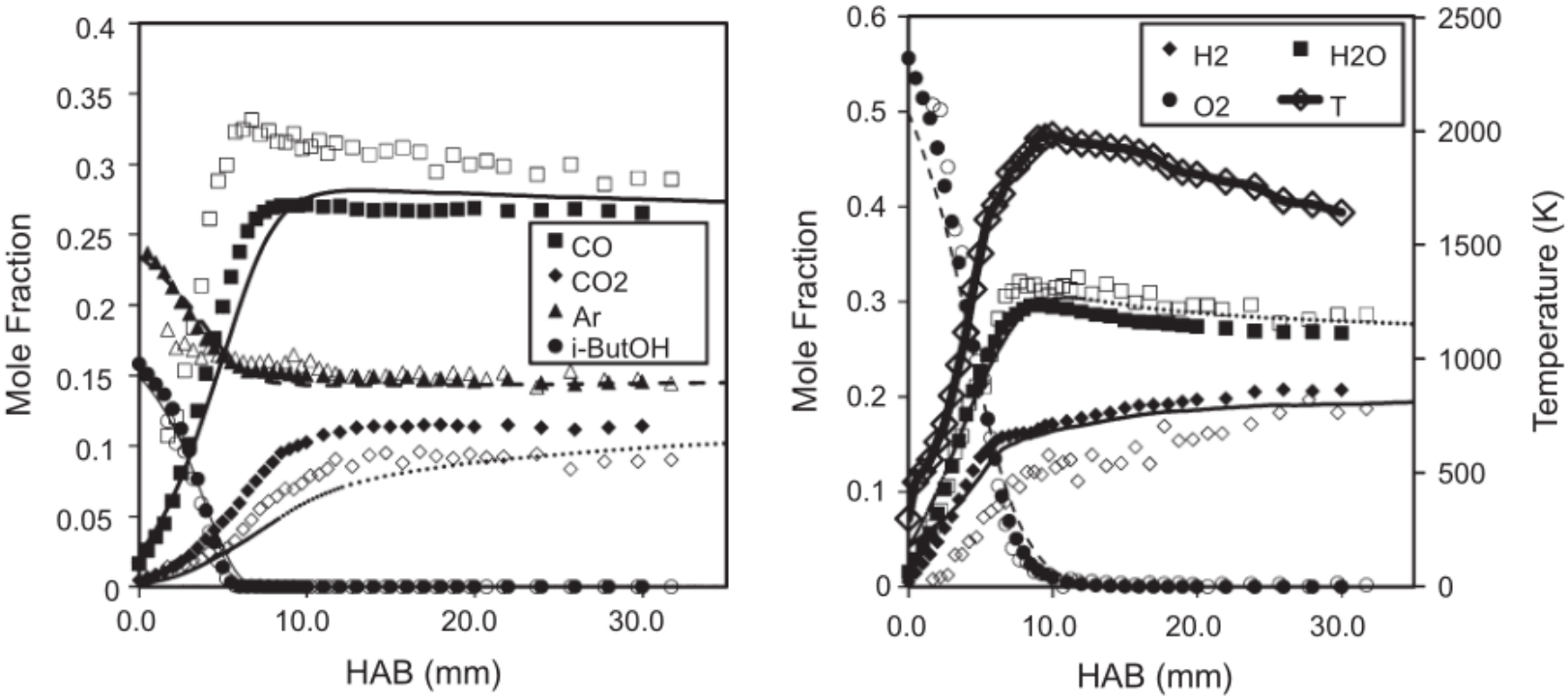

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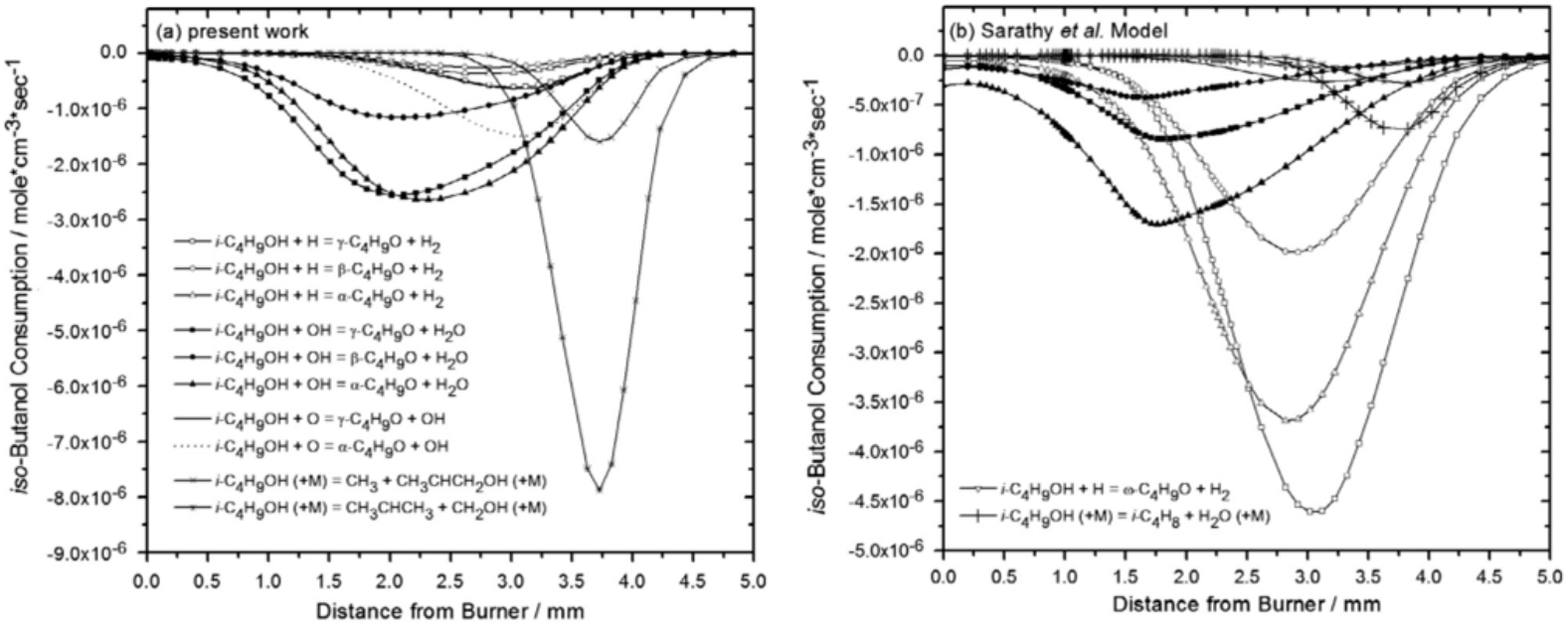

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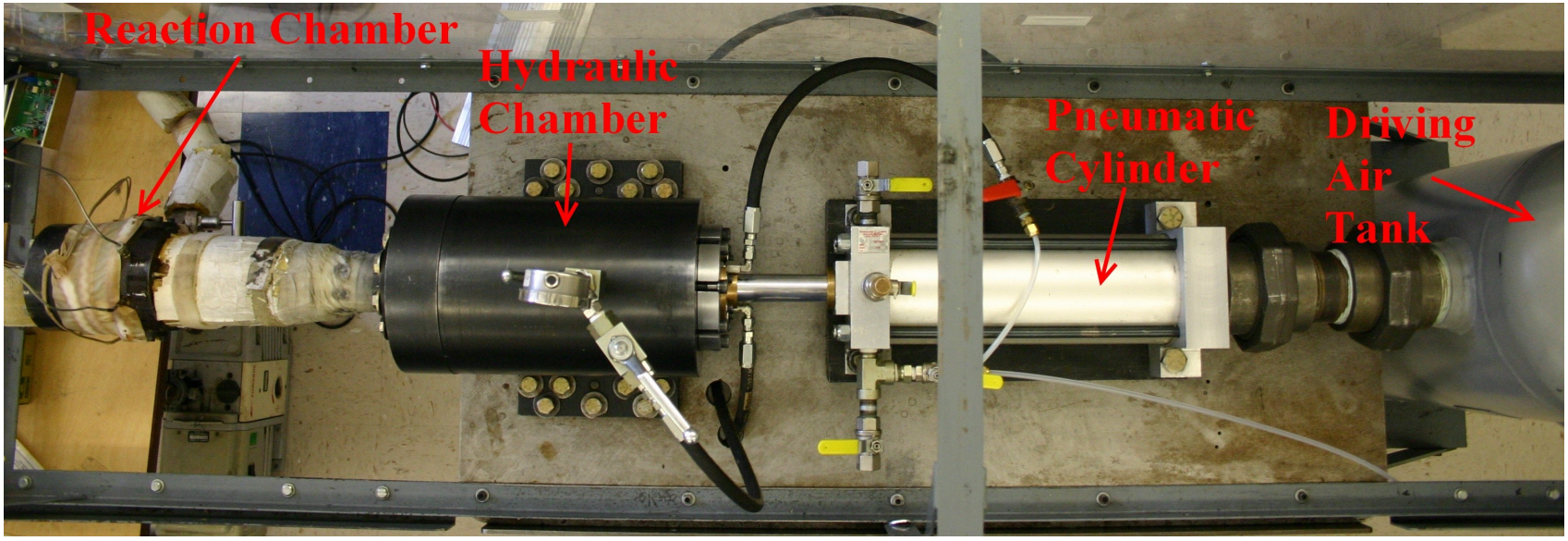
Experimental Apparatuses

Rapid Compression Machine



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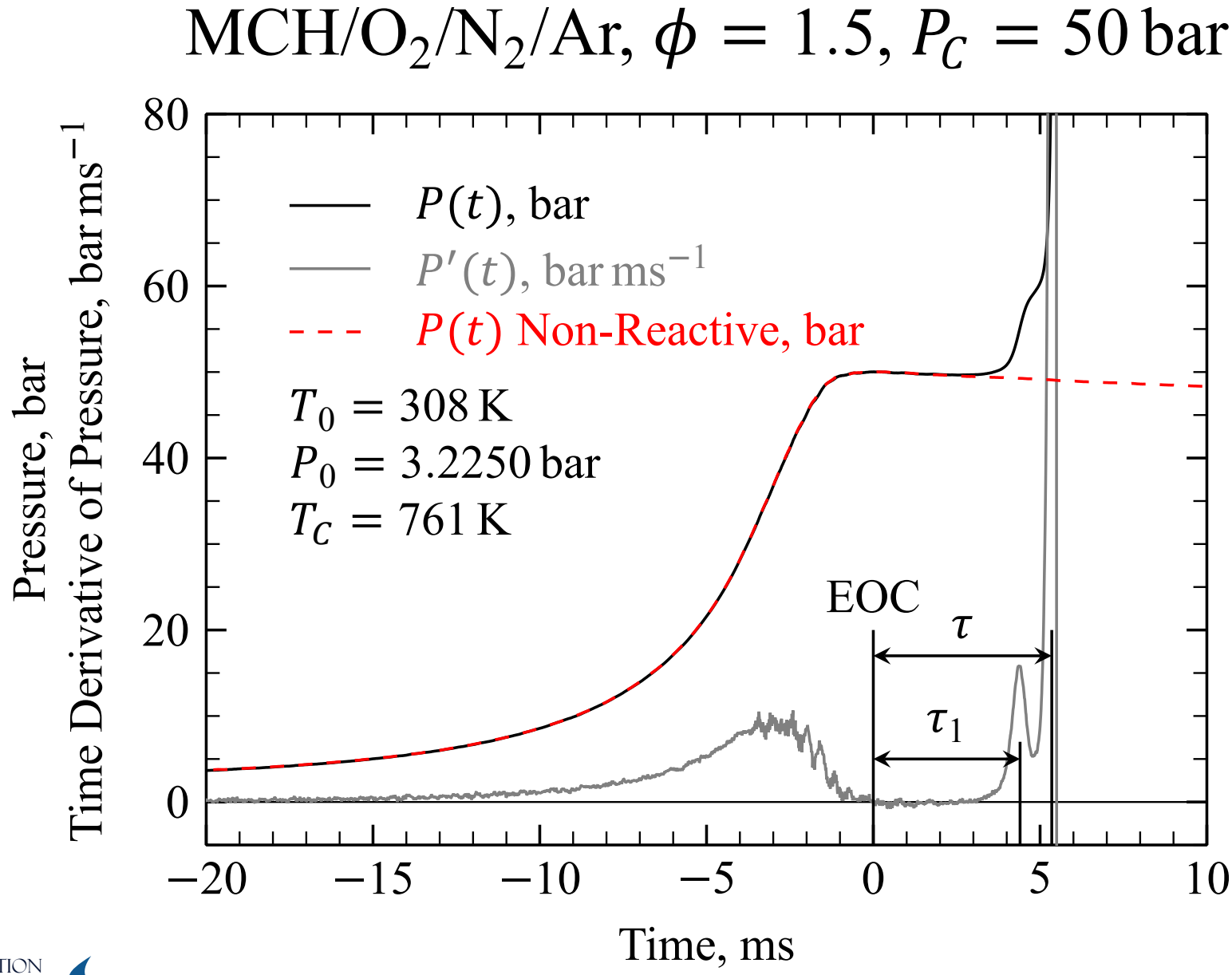
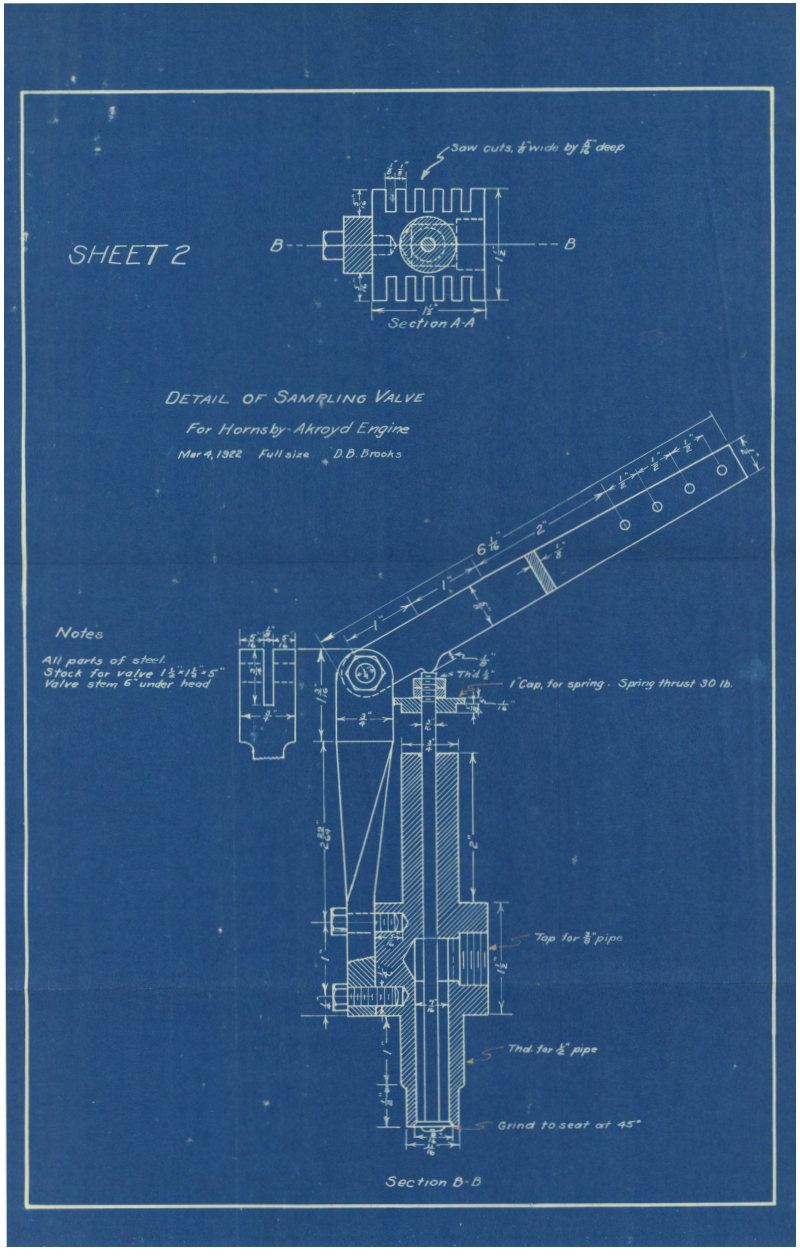


Rapid Sampling Apparatus

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



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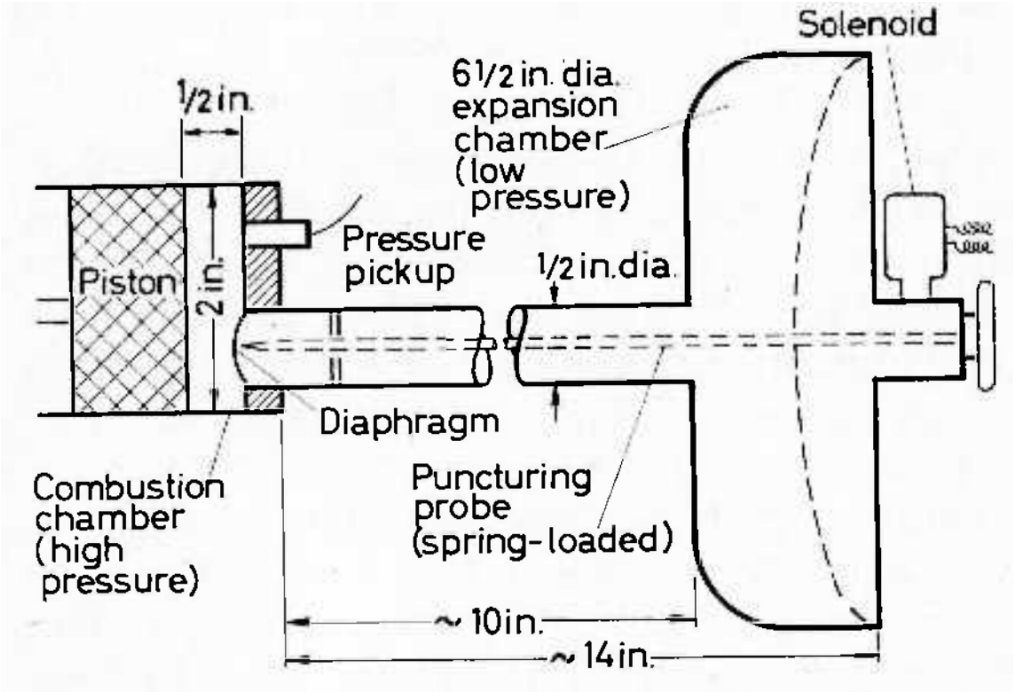

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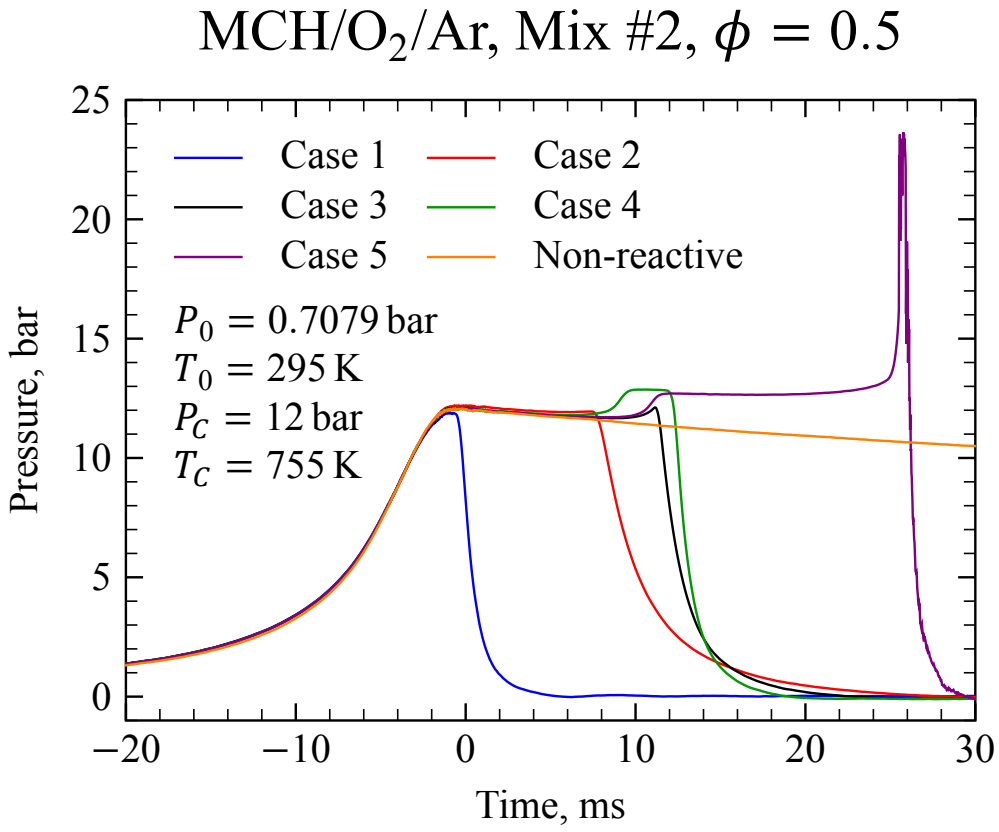
- Sampling devices rapidly quench ongoing reactions so that species are determined at a discrete point in time



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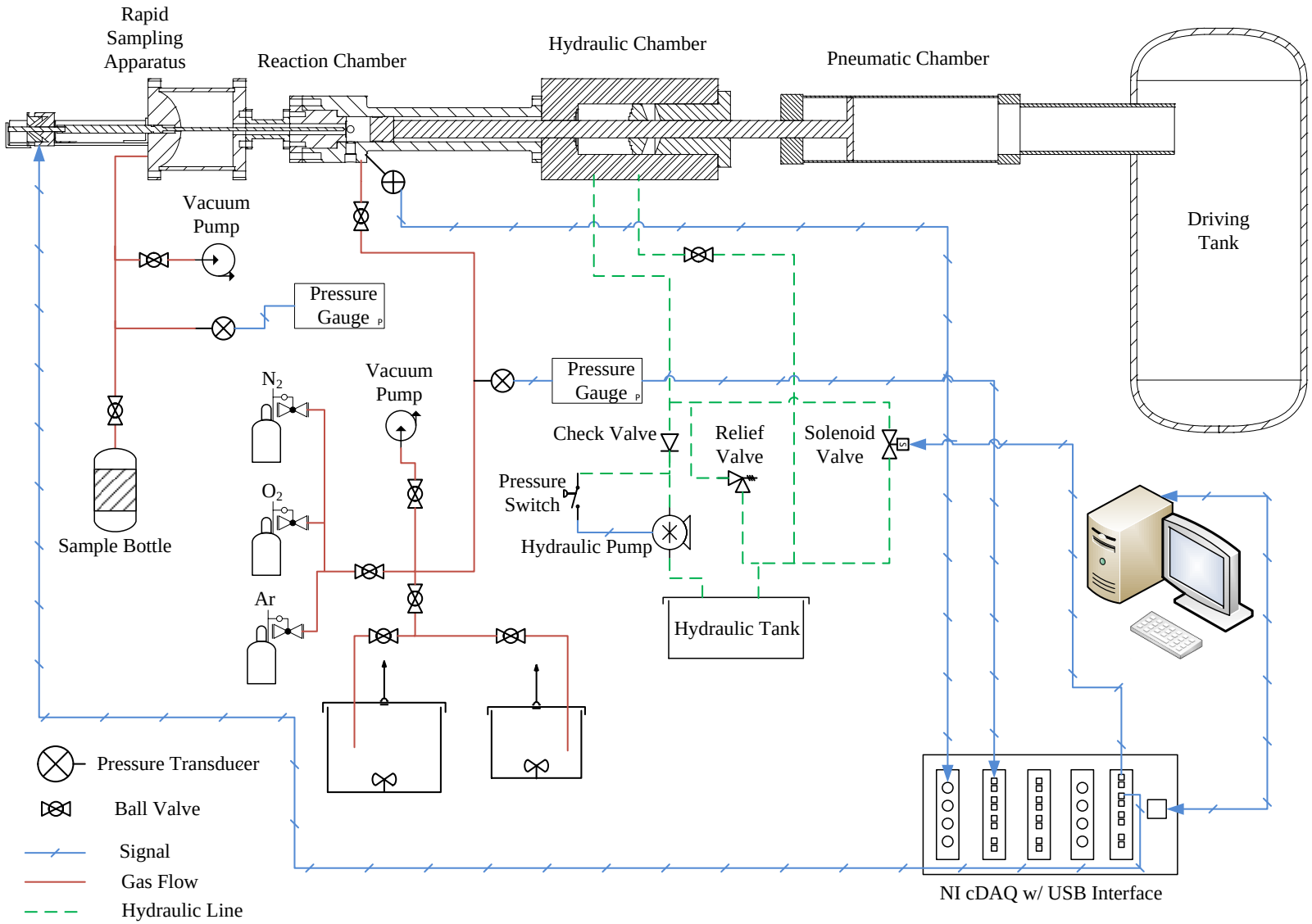
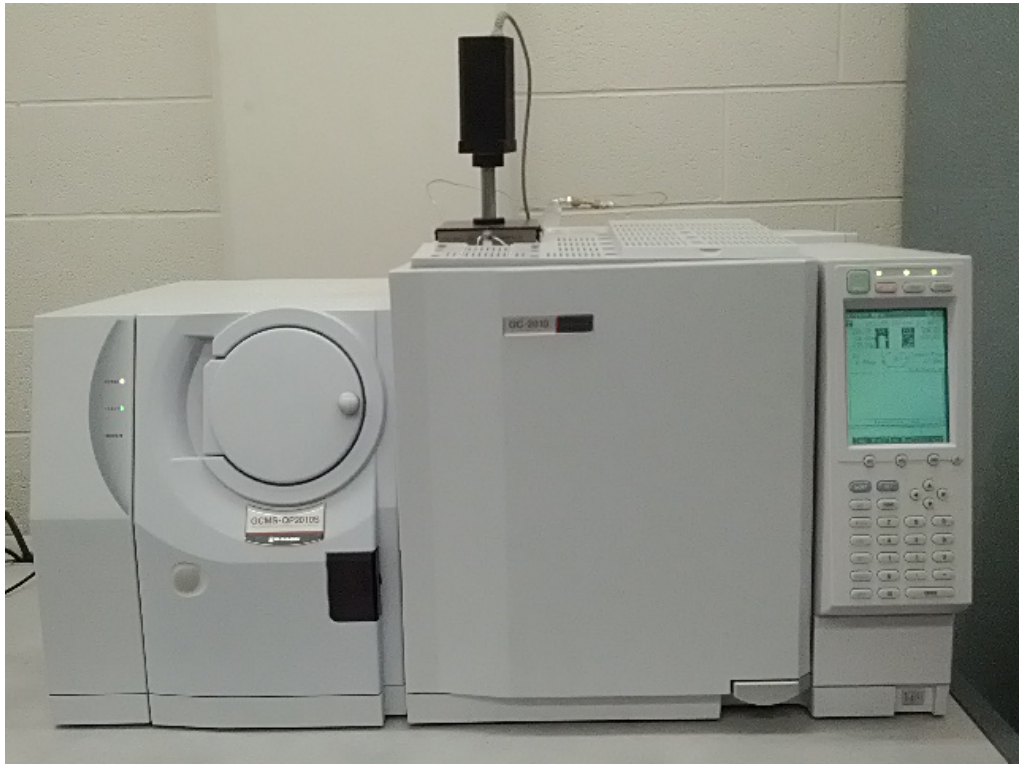


UCONN COMBUSTION DIAGNOSTICS LABORATORY

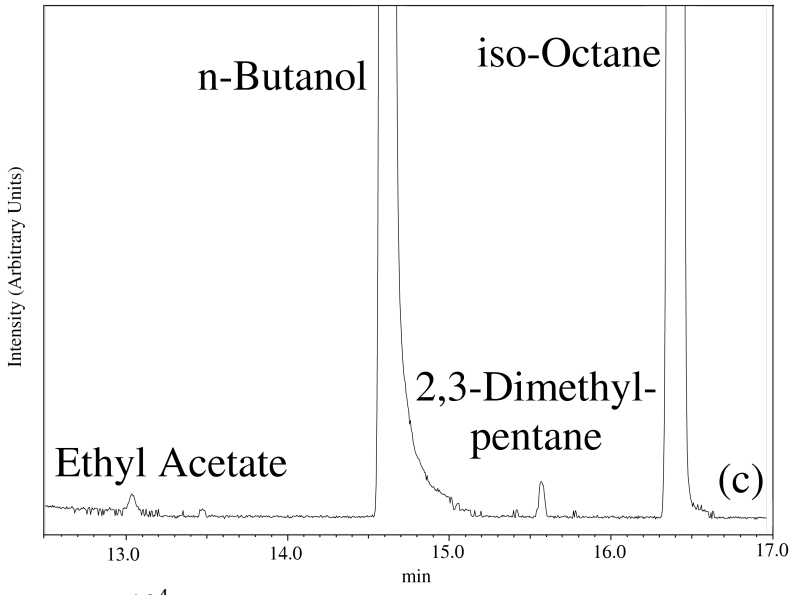
Gas Chromatograph/Mass Spectrometer

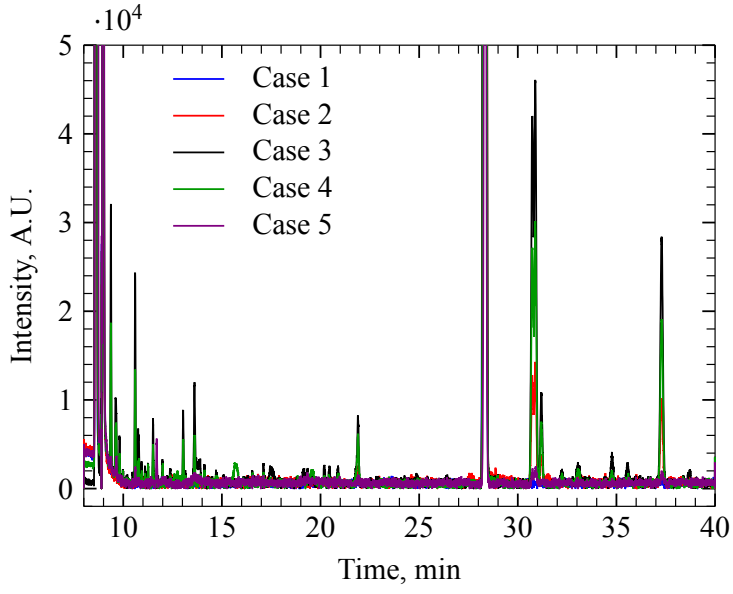
- Standard piece of chemistry lab equipment, commercially supplied (Shimadzu GCMS-QP2010S)



Gas Chromatograph/Mass Spectrometer

- Separates, identifies, and quantifies chemical species

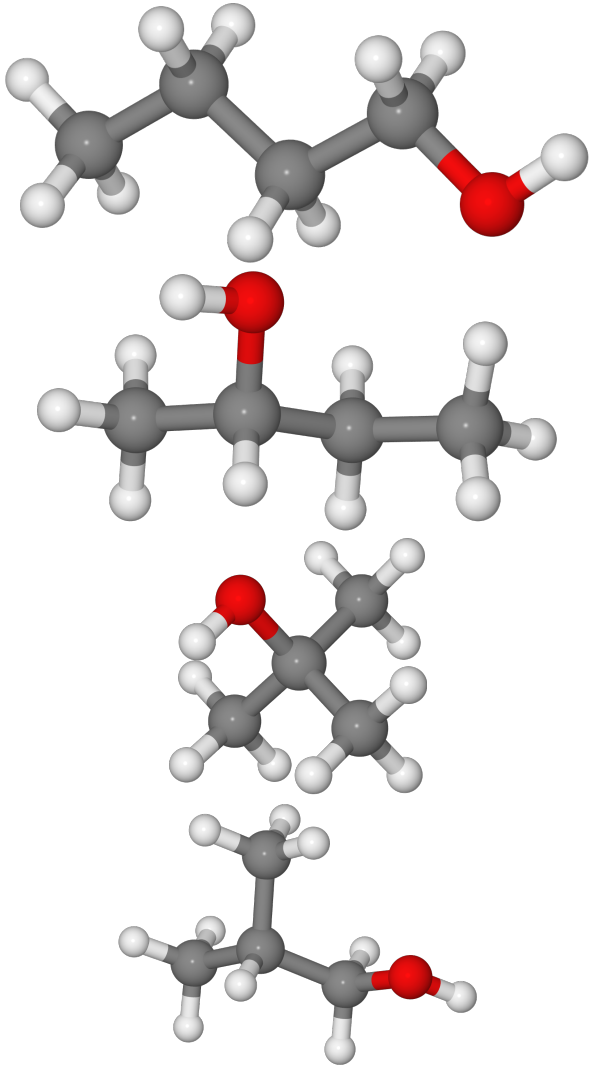




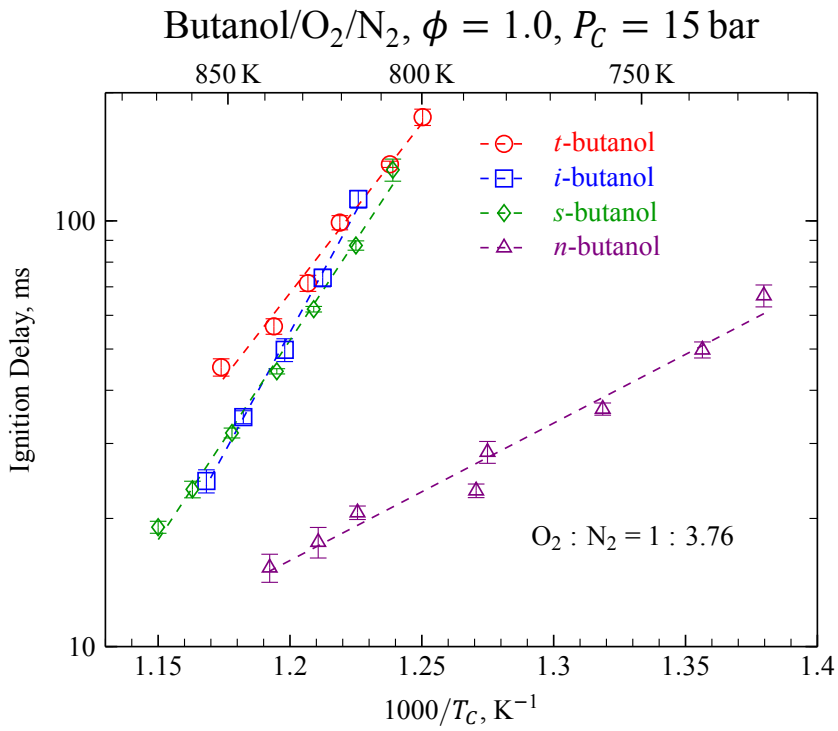
Butanol Isomers

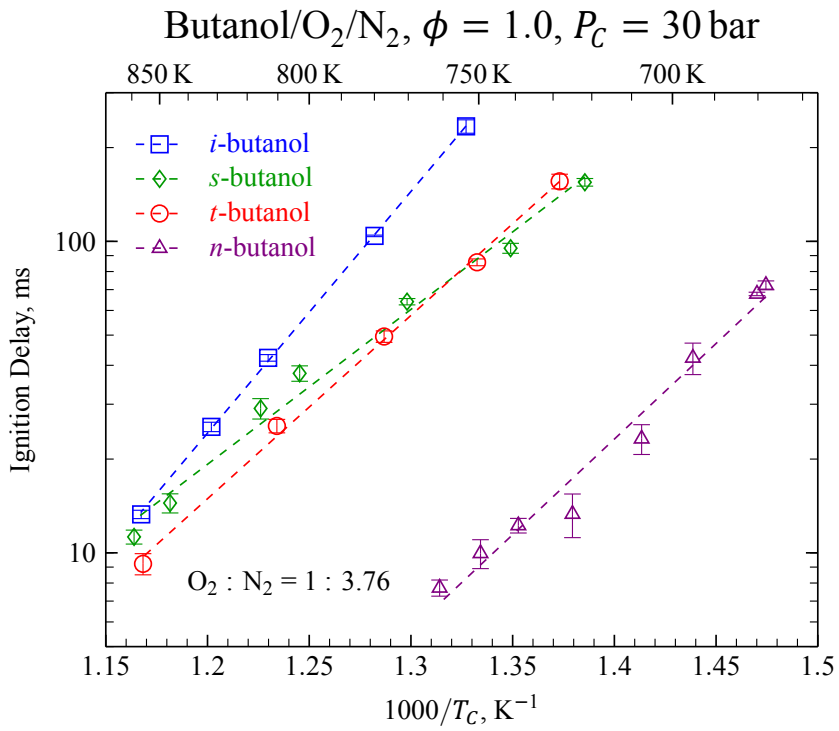
Why butanol?

- There are four isomers of butanol
- Butanol can be produced from bio-based and waste sources
- Butanol is the smallest alcohol with each type of C-O bond



The reactivity of the butanol isomers depends on the pressure





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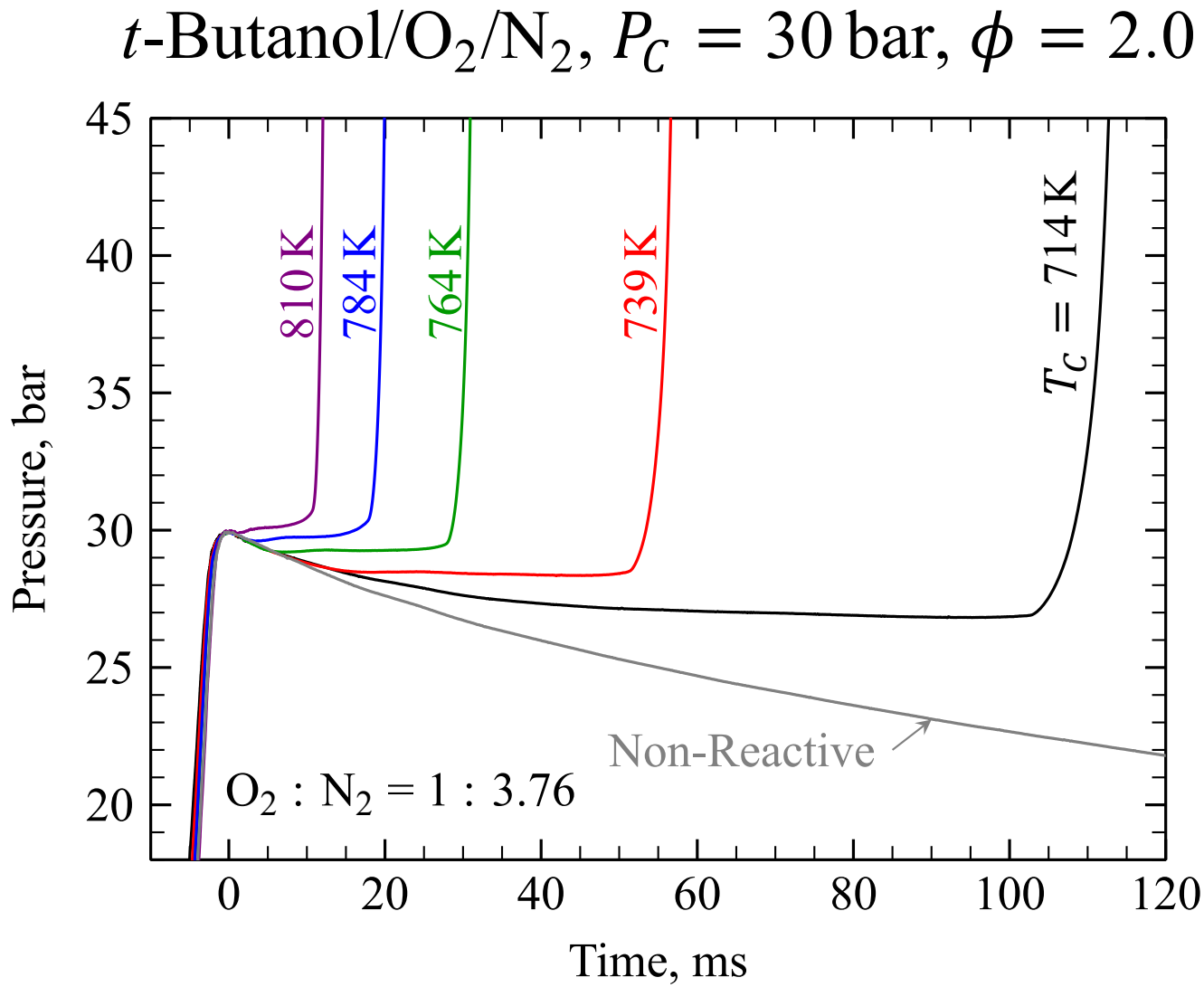
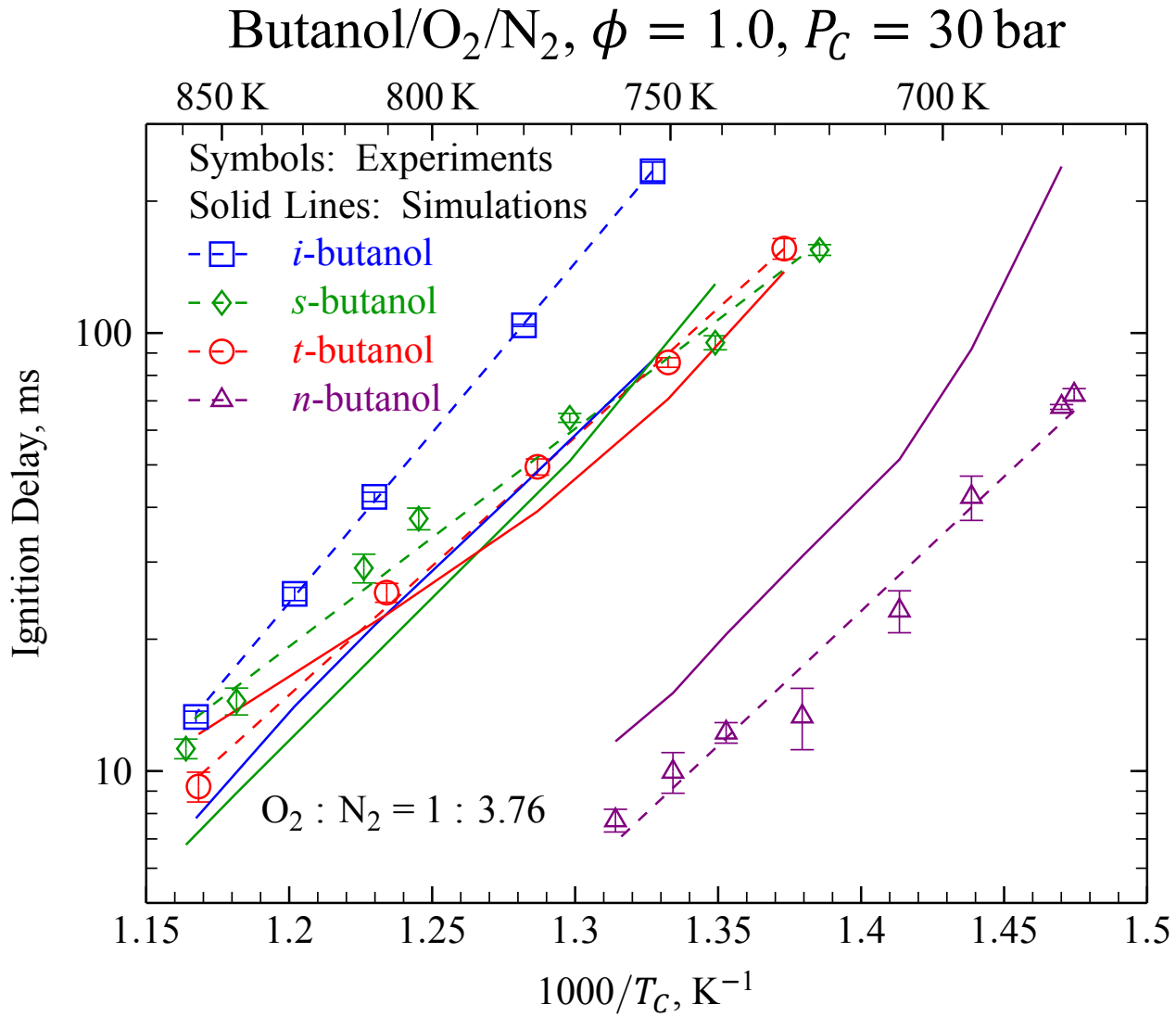


The reactivity trend can be predicted by a detailed understanding of the chemistry



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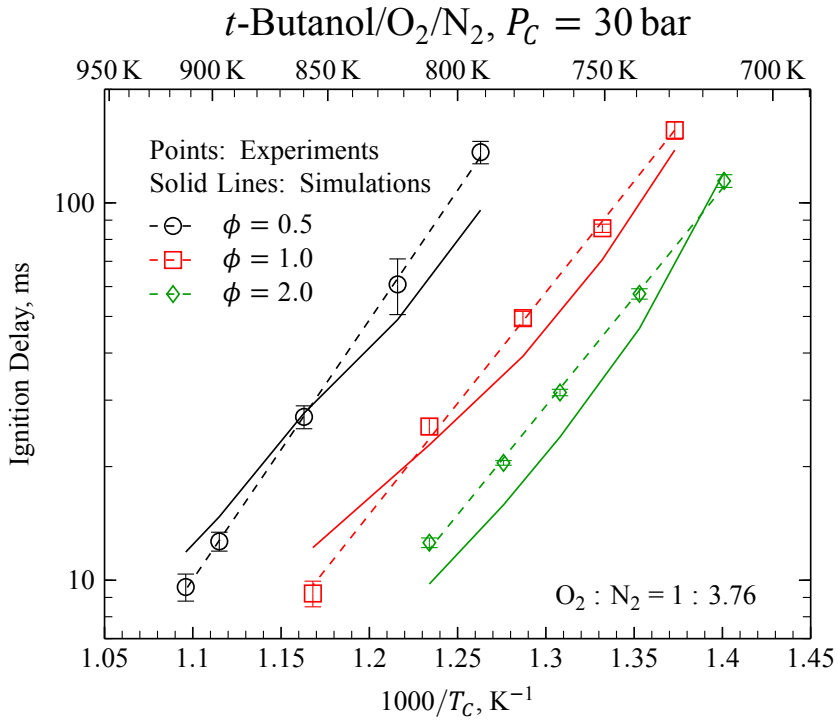
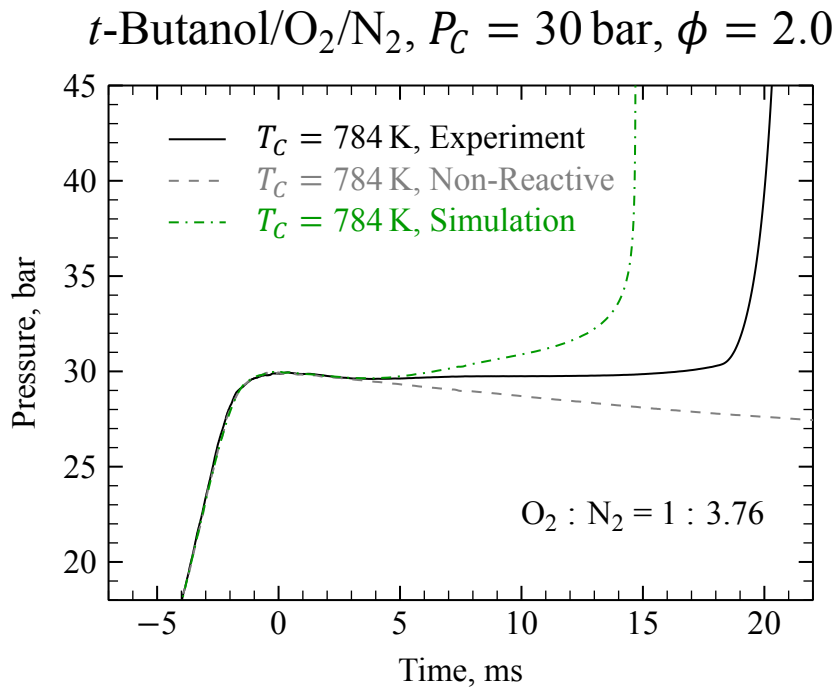


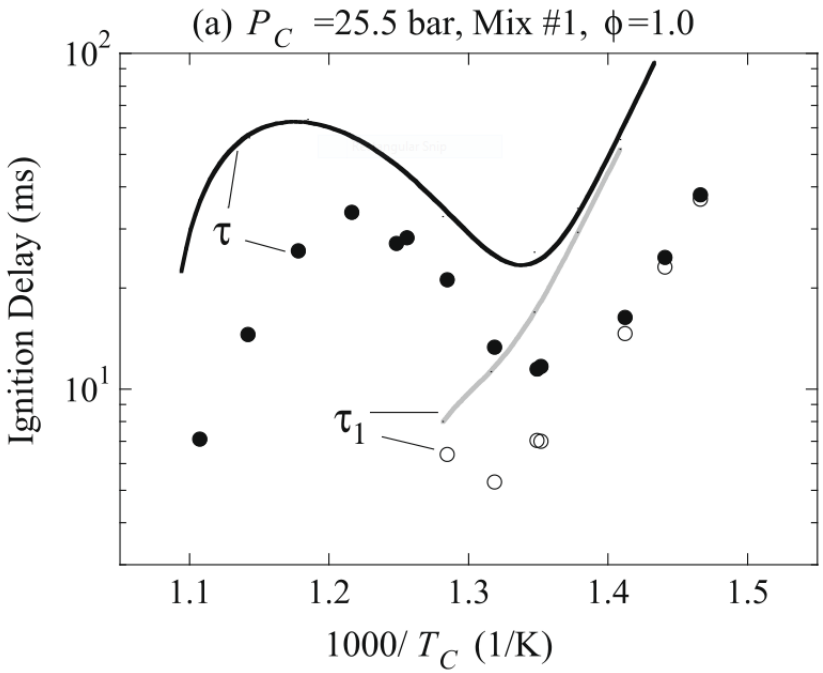


Methylcyclohexane

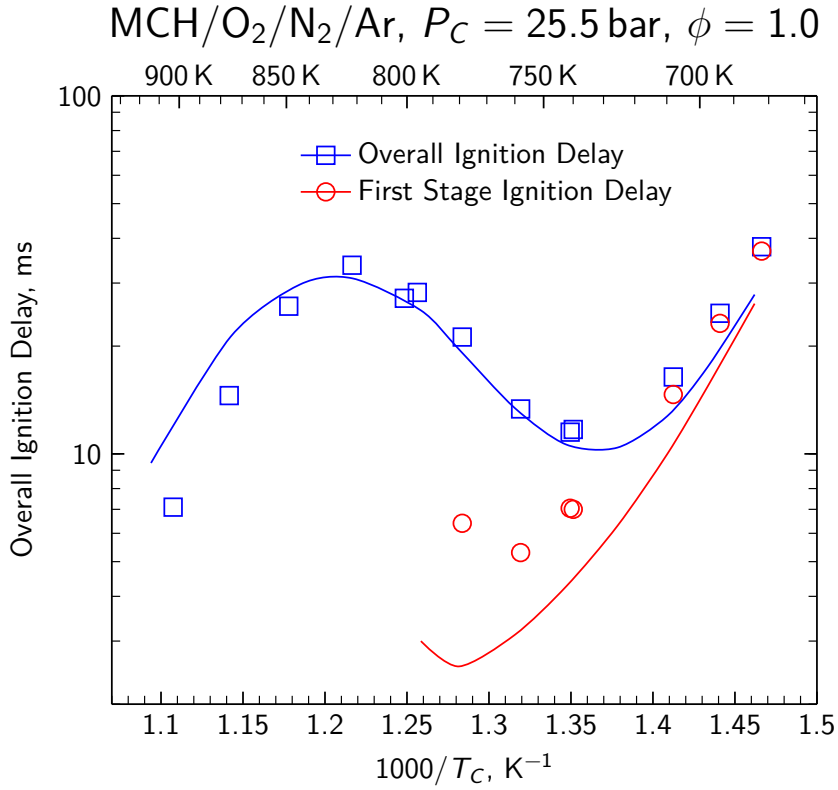
Why methylcyclohexane?

- 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
- Models need to be developed and validated for the neat components as well as for their blends
- MCH is a component in many surrogate transportation fuel formulations

Methylcyclohexane ignition



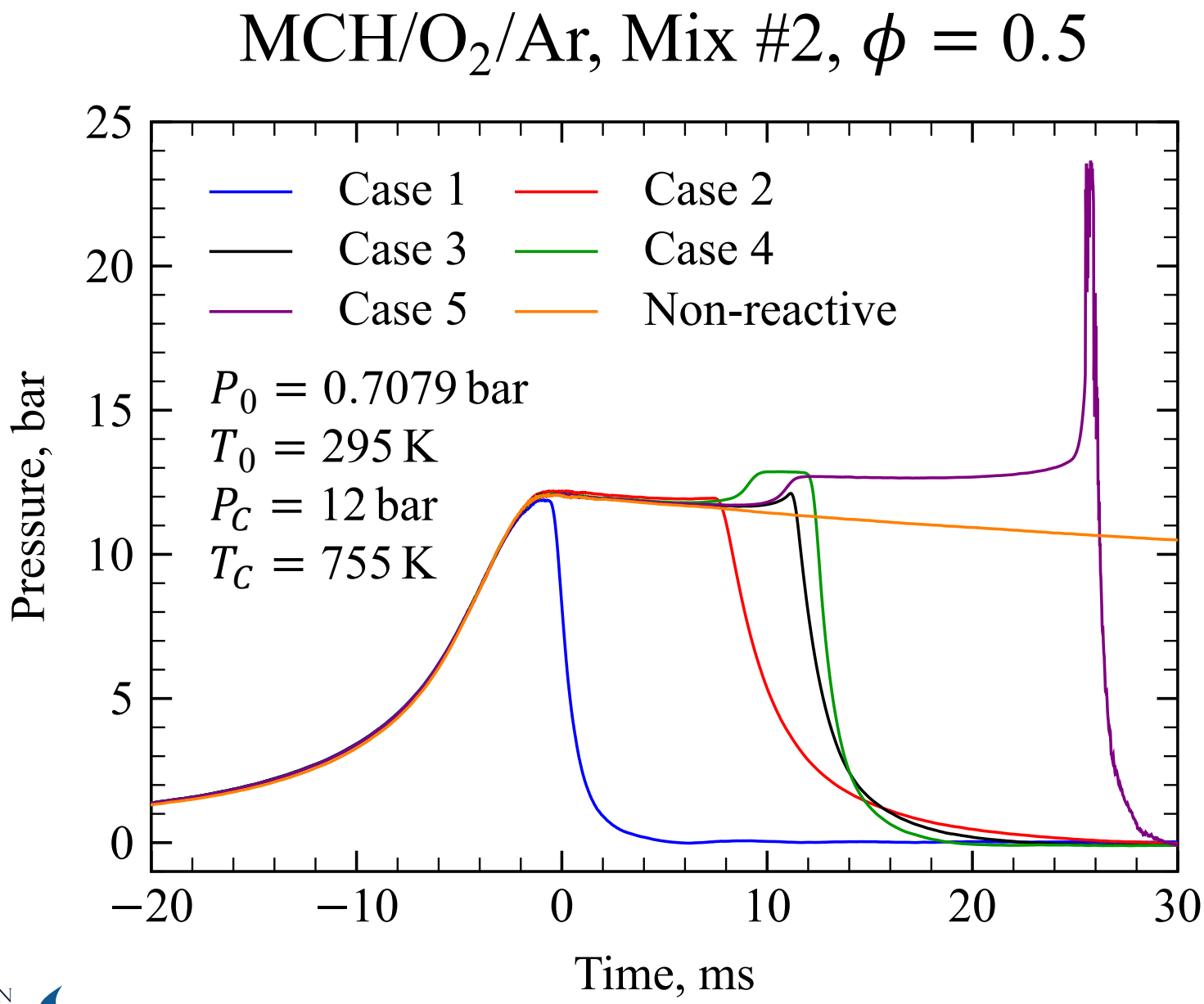
Mittal et al. Combust. Flame 2009



Weber et al. Combust. Flame 2014

Reaction mechanisms for MCH are improving but something is still missing

Sampling results



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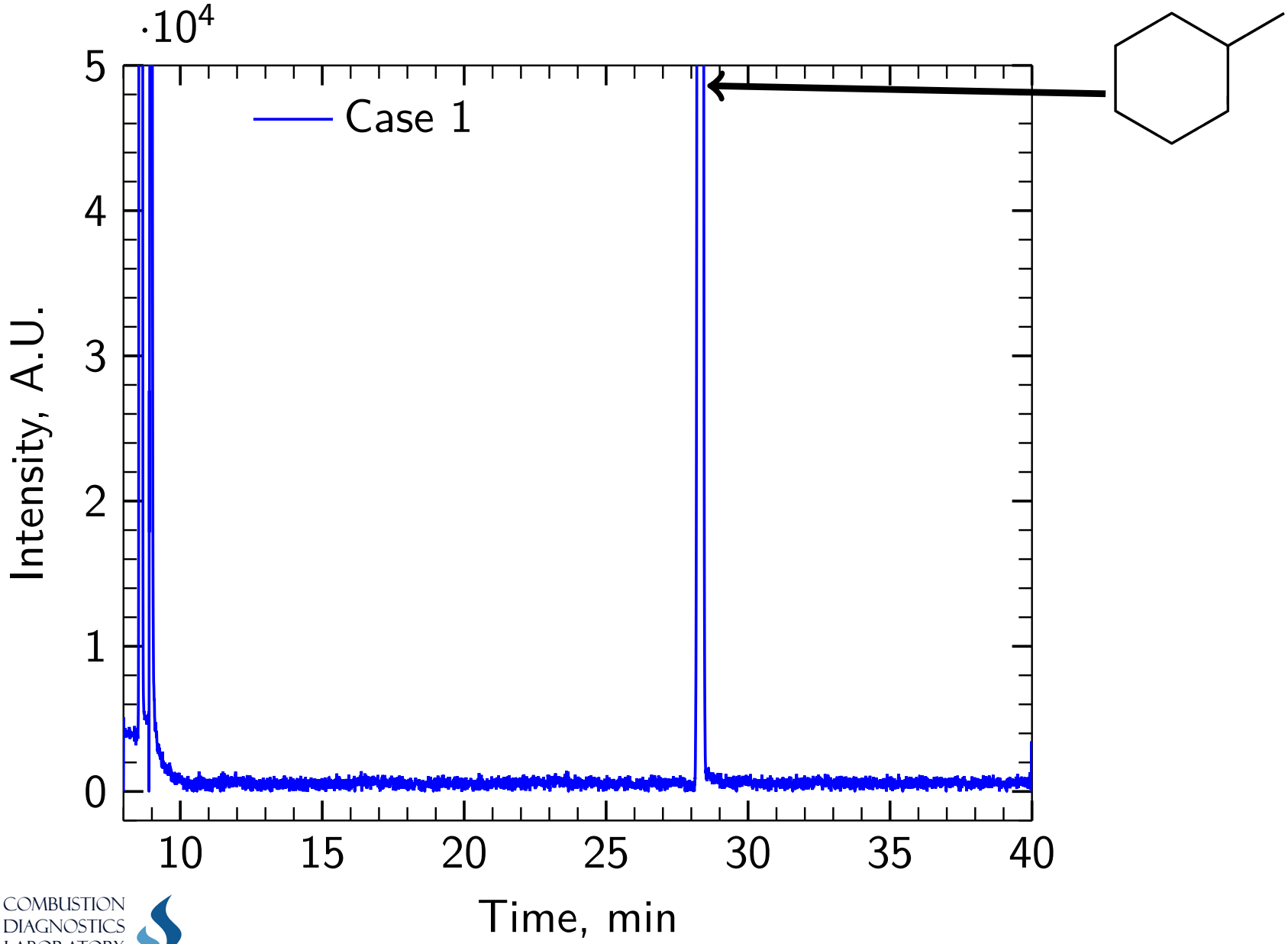

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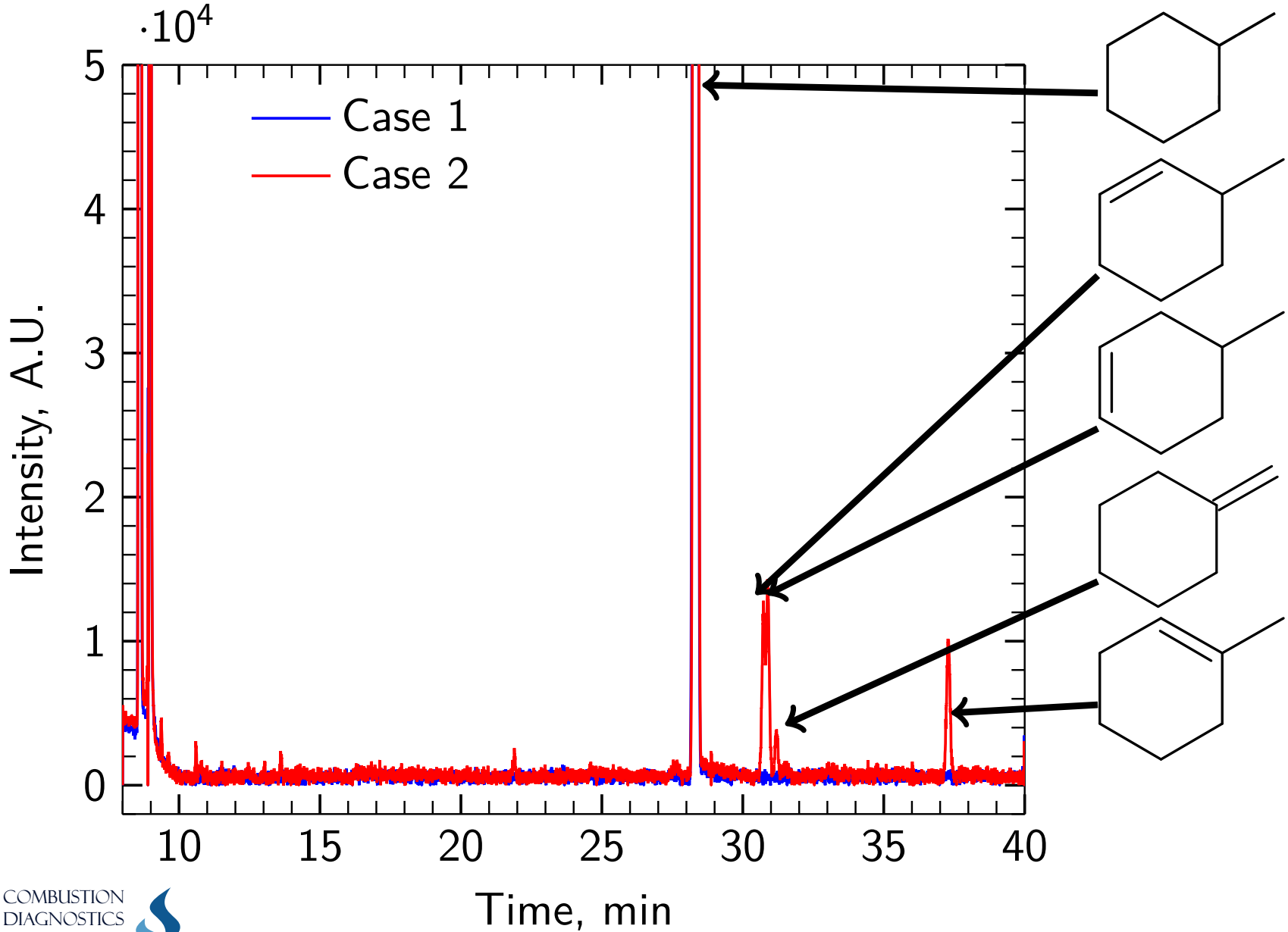

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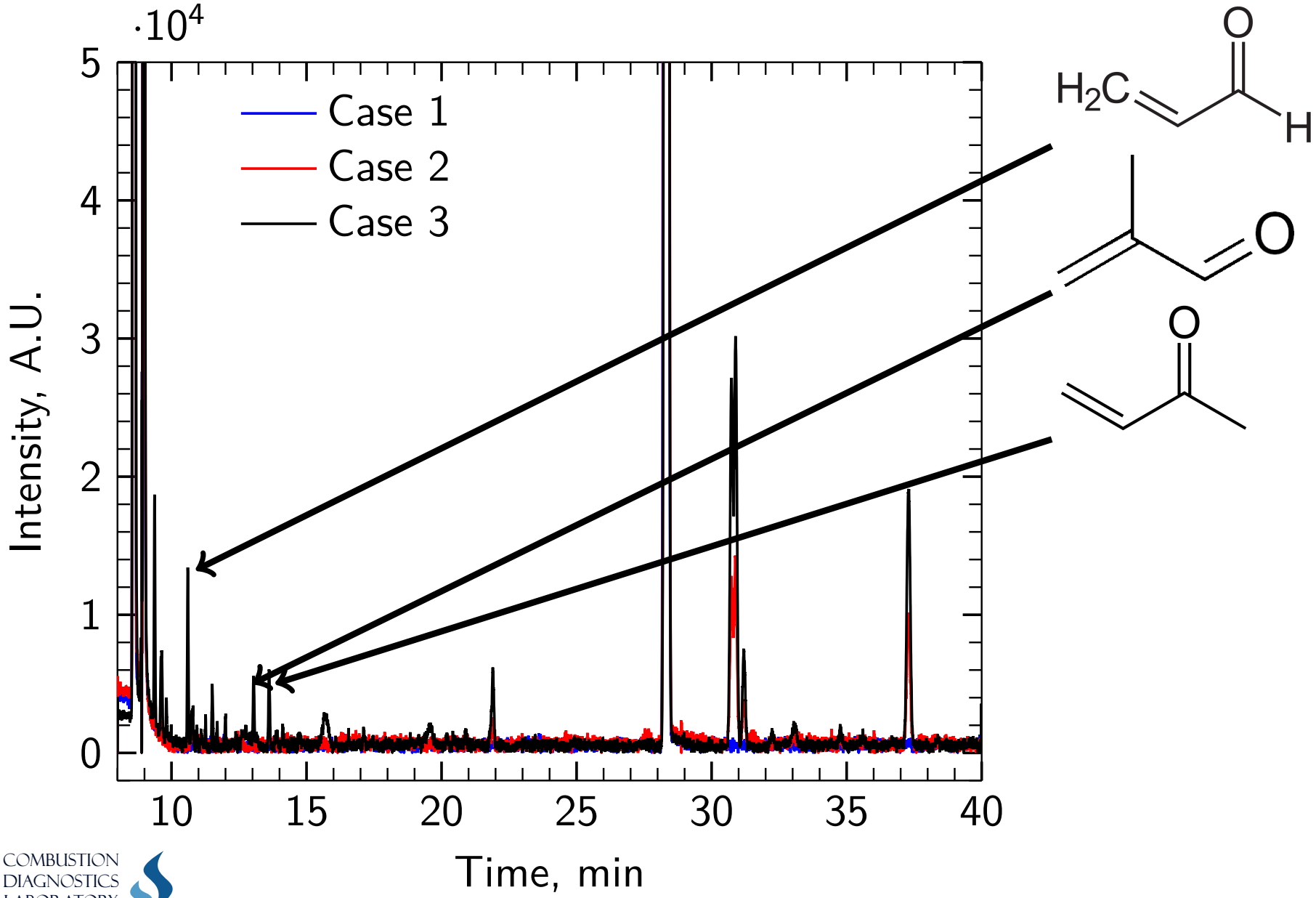

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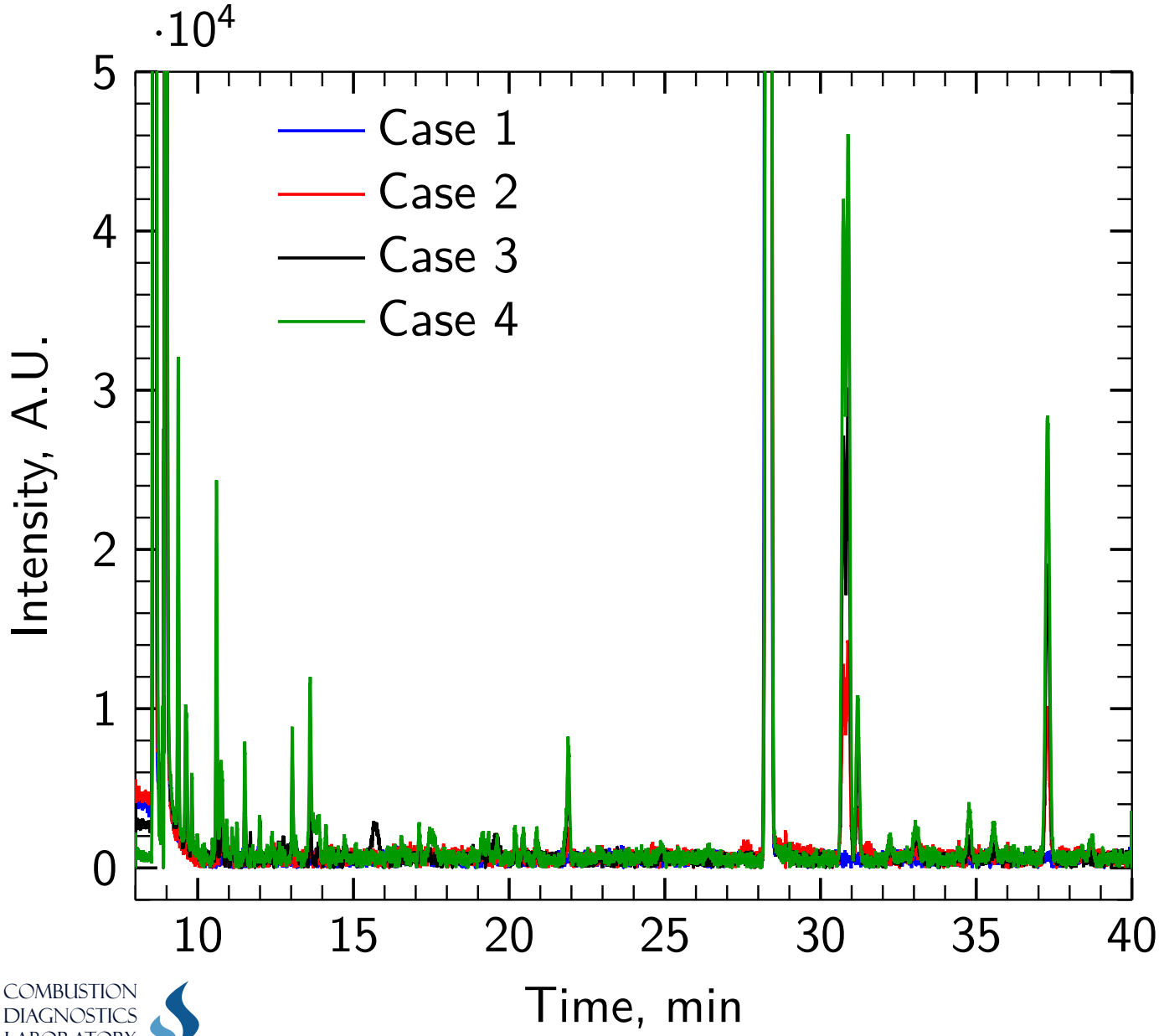

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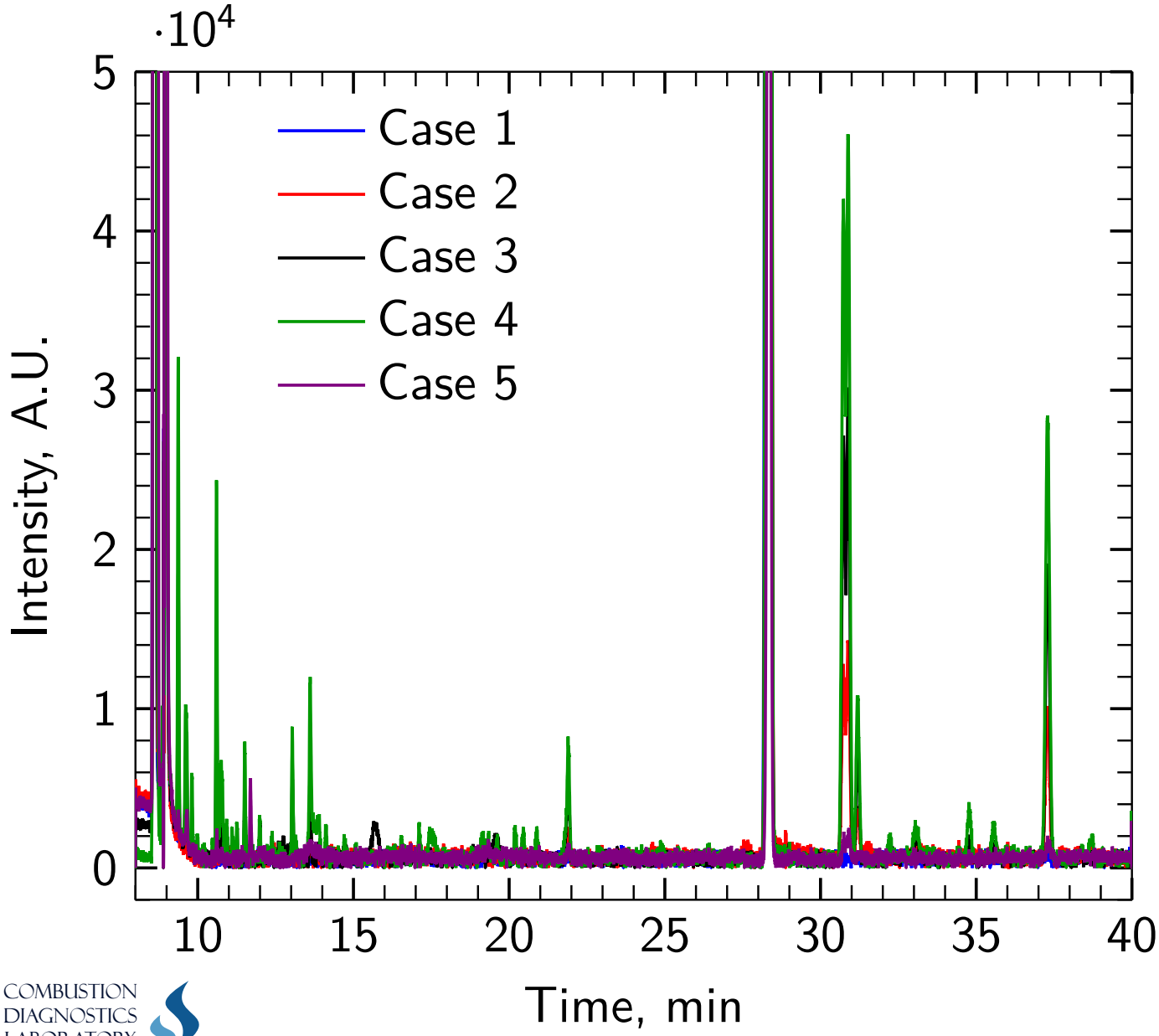

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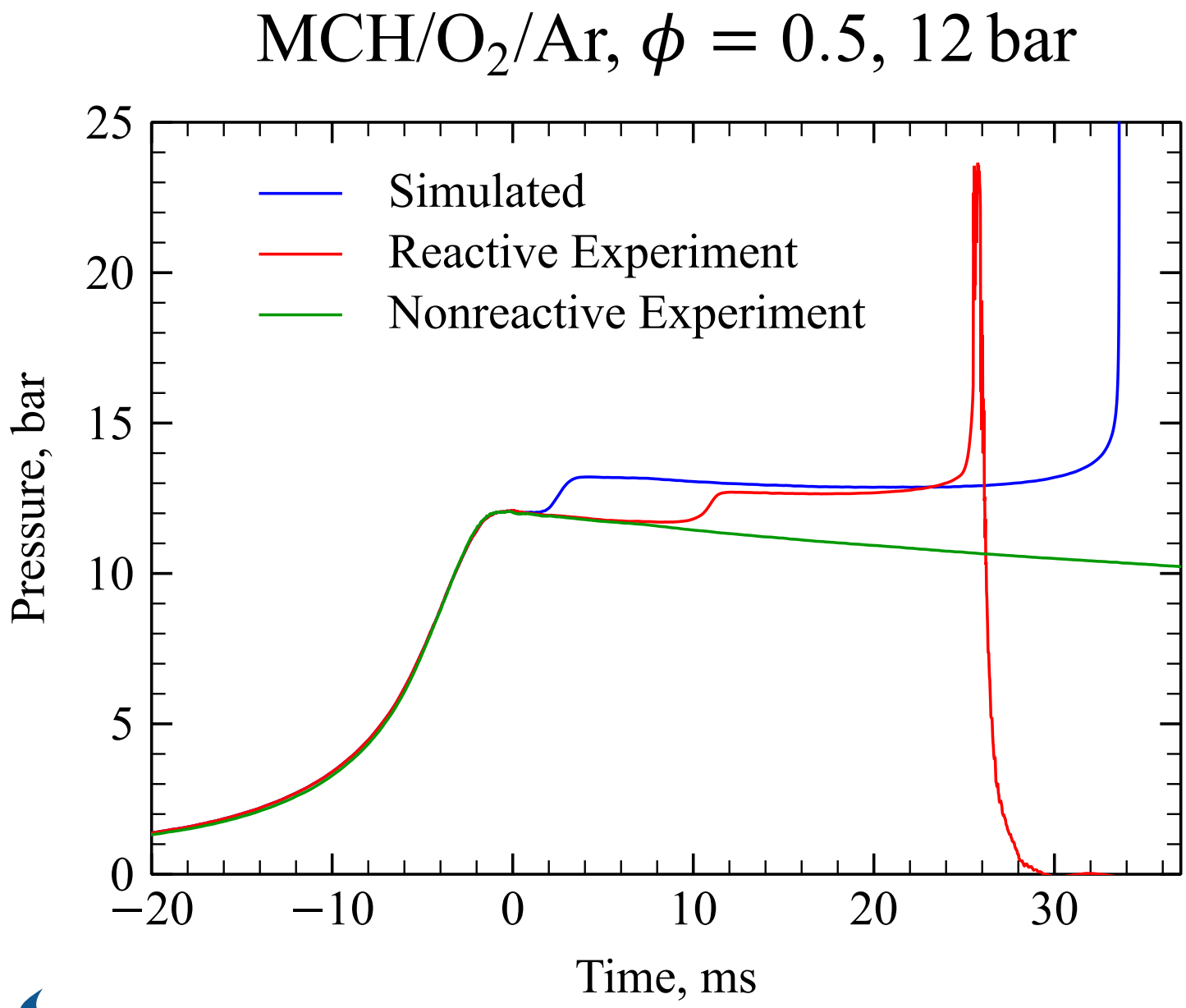
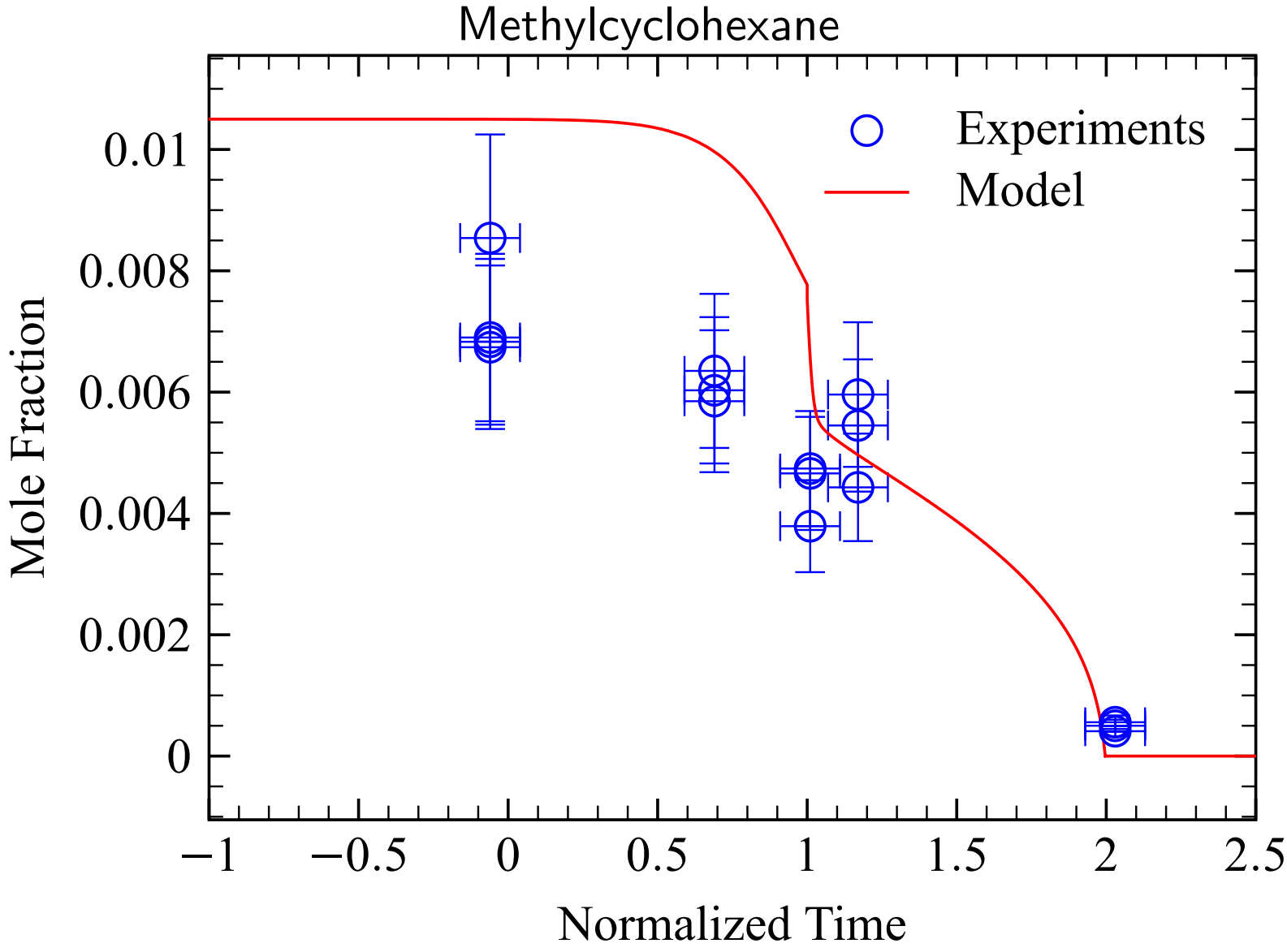
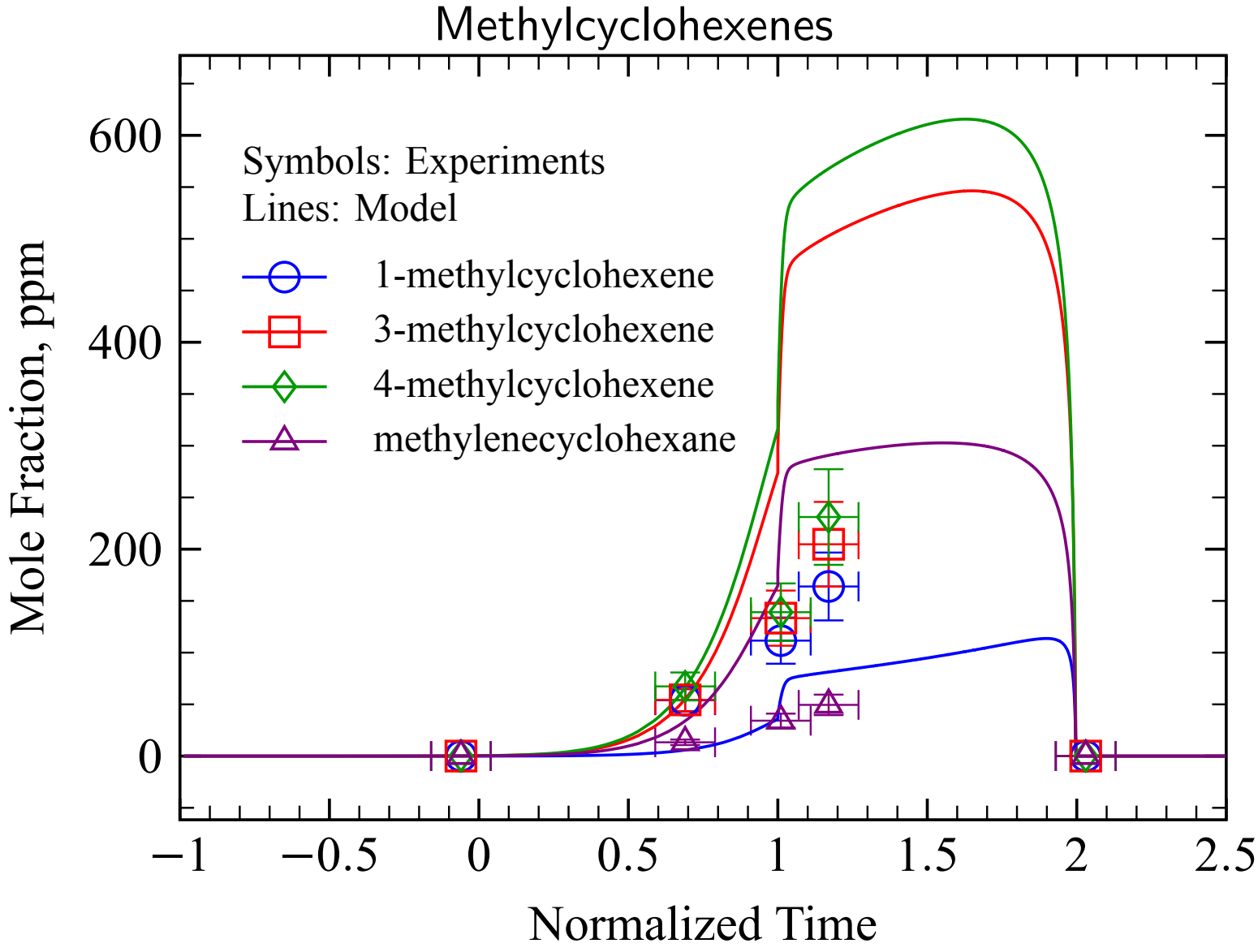


Sampling results



Sampling results



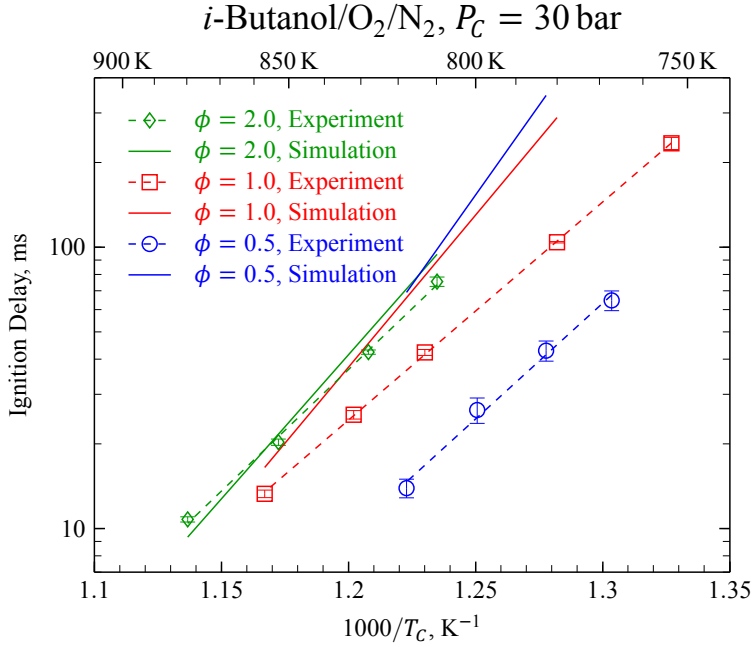
Summary

- 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

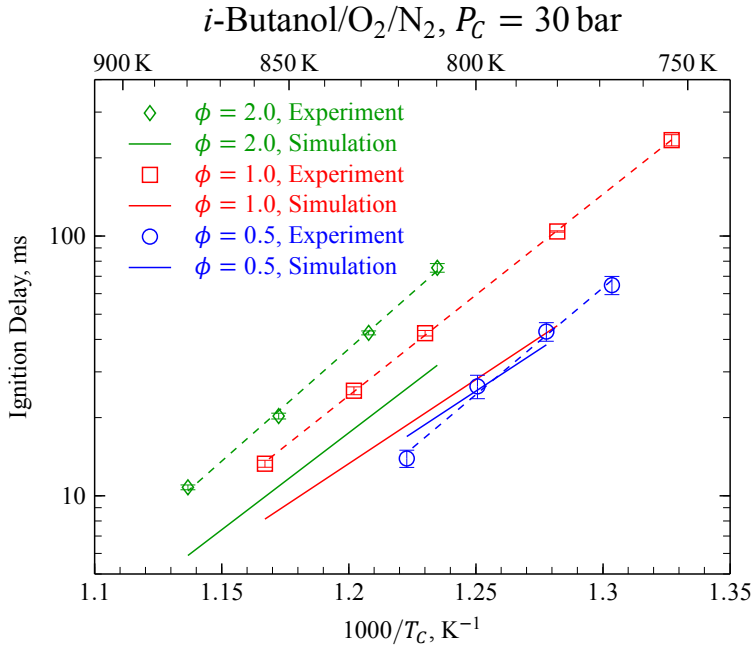
Future work

- Calibration for more species of importance
- Resolve discrepancies at early sampling times
- Consider more conditions and more fuels

Future work



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

Thank you!
Questions?