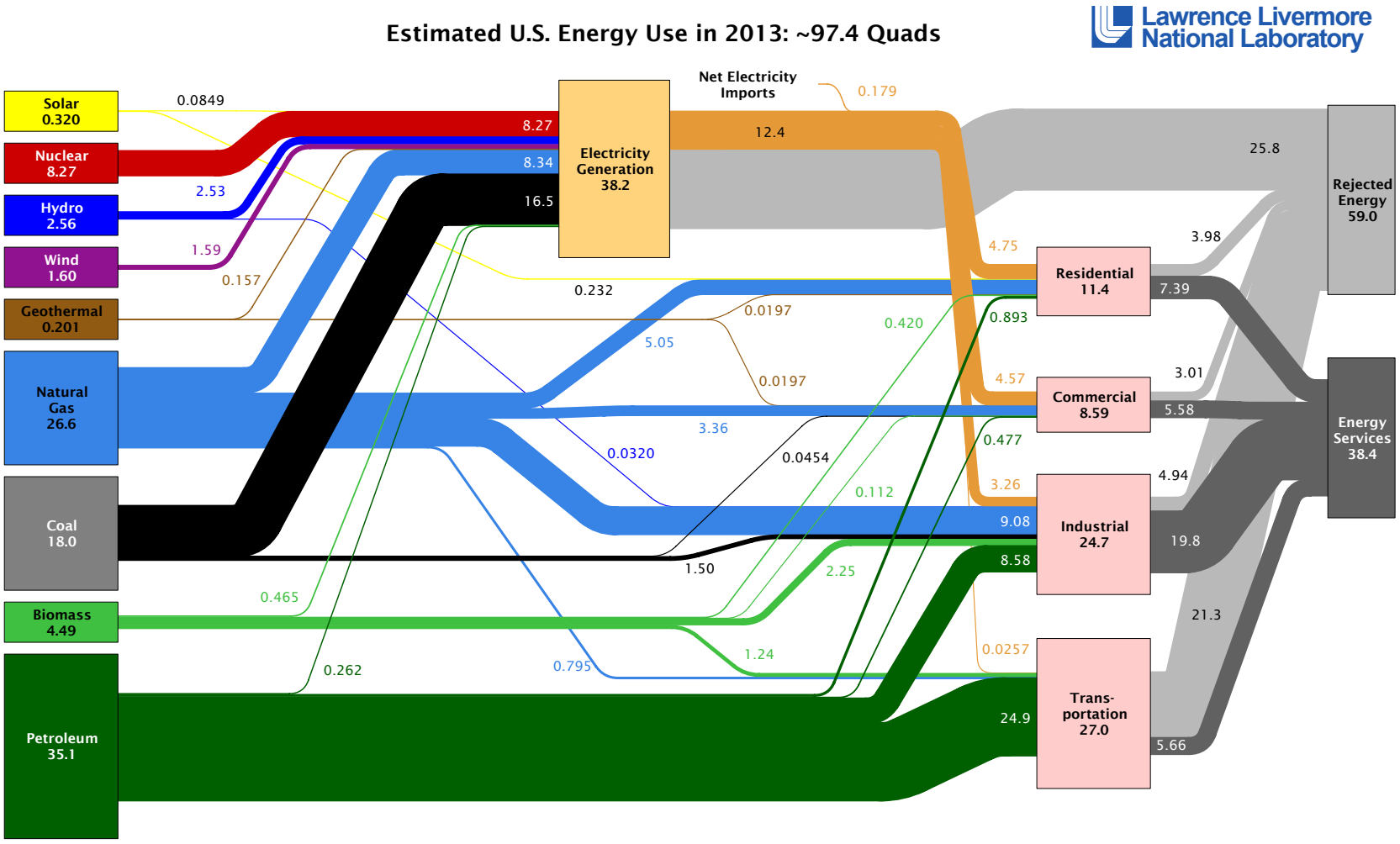
High Pressure Ignition Chemistry of Alternative Fuels

Bryan W. Weber

Prepared for Ph.D. Defense

June 19, 2014

We use a lot of fuels to power the world

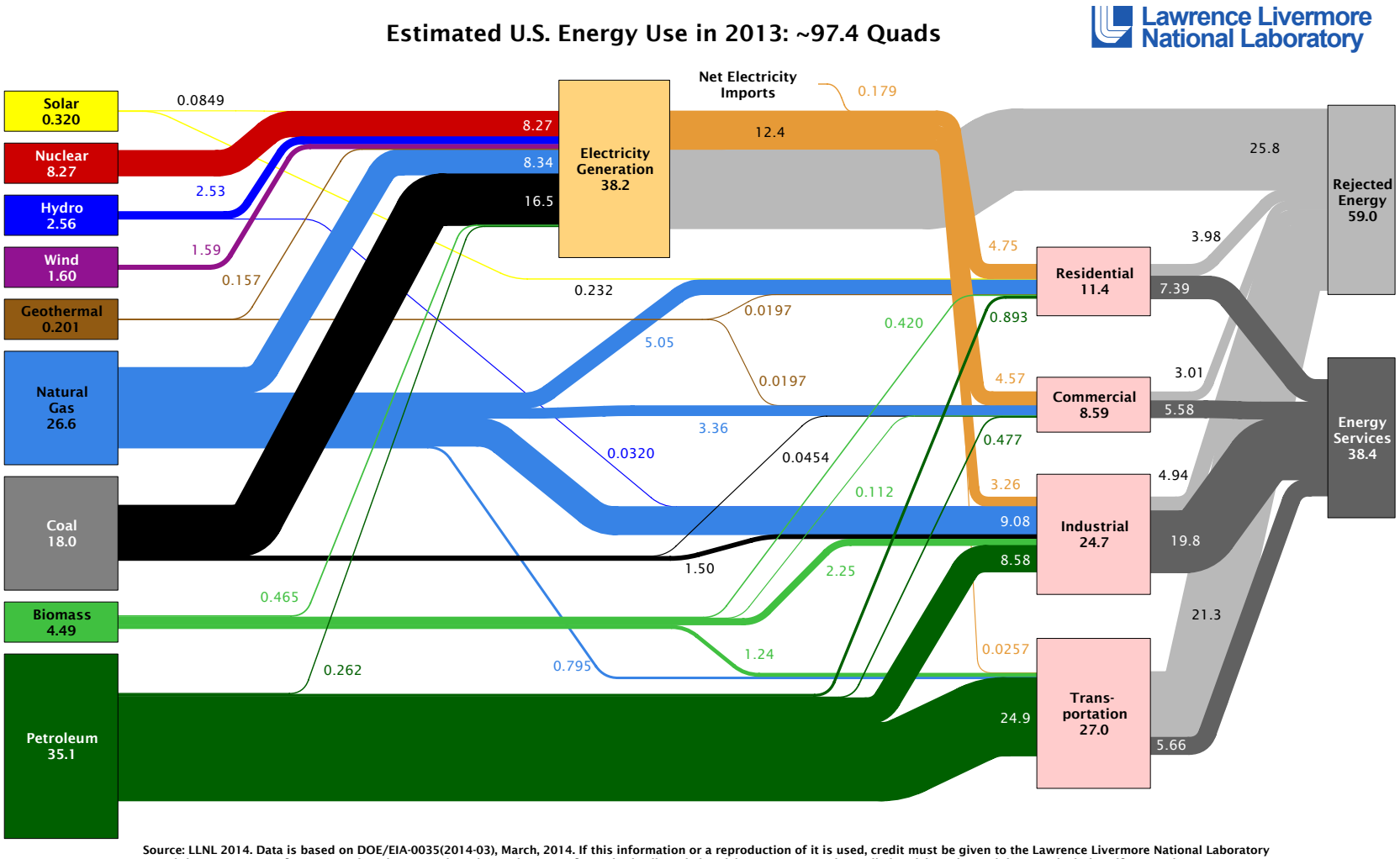


Source: LLNL 2014. Data is based on DOE/EIA-0035(2014-03), March, 2014. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents 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

We use a lot of fuels to power the world

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

We use a lot of fuels to power the world



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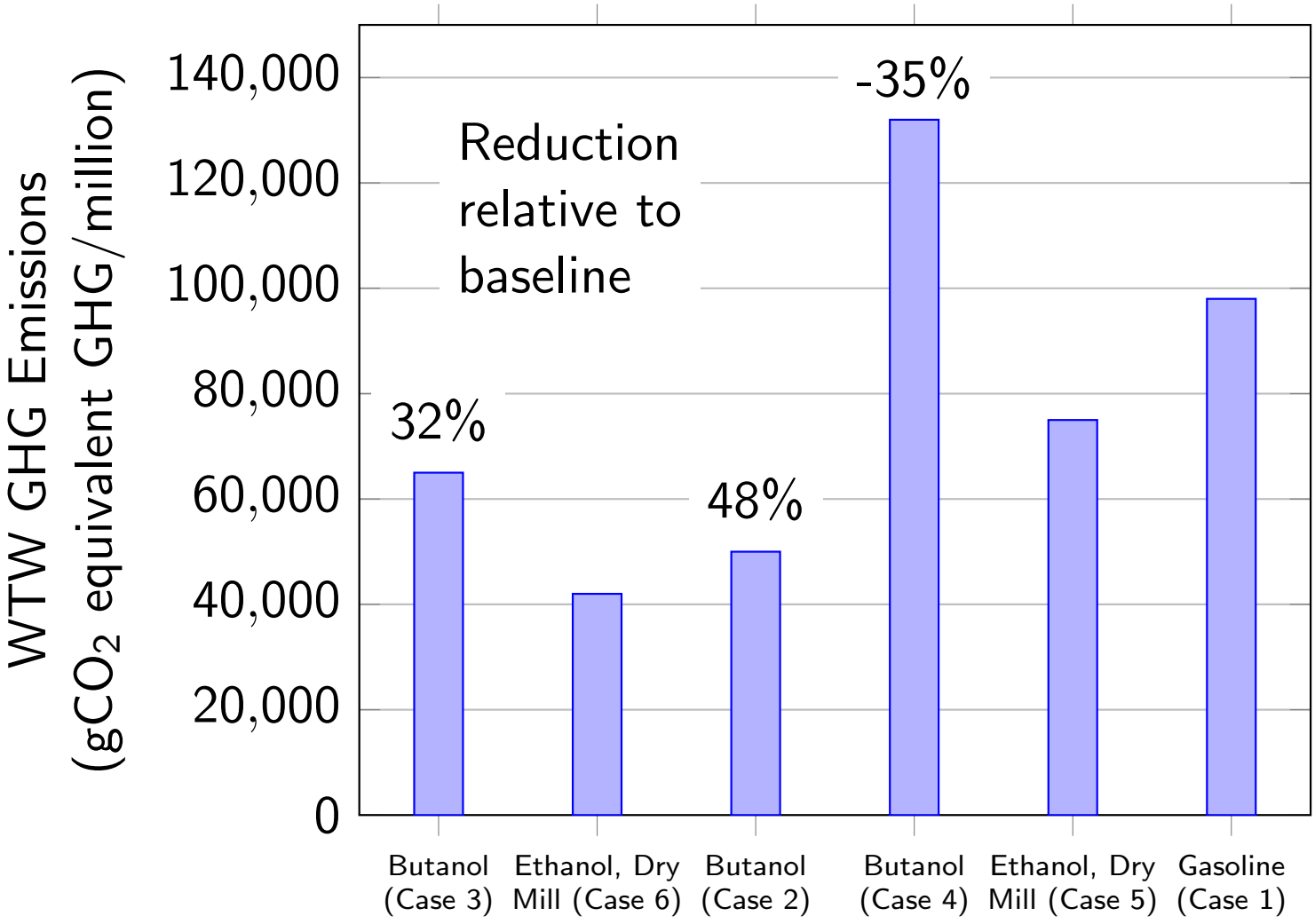
We use a lot of fuels to power the world

- 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

John Dec image

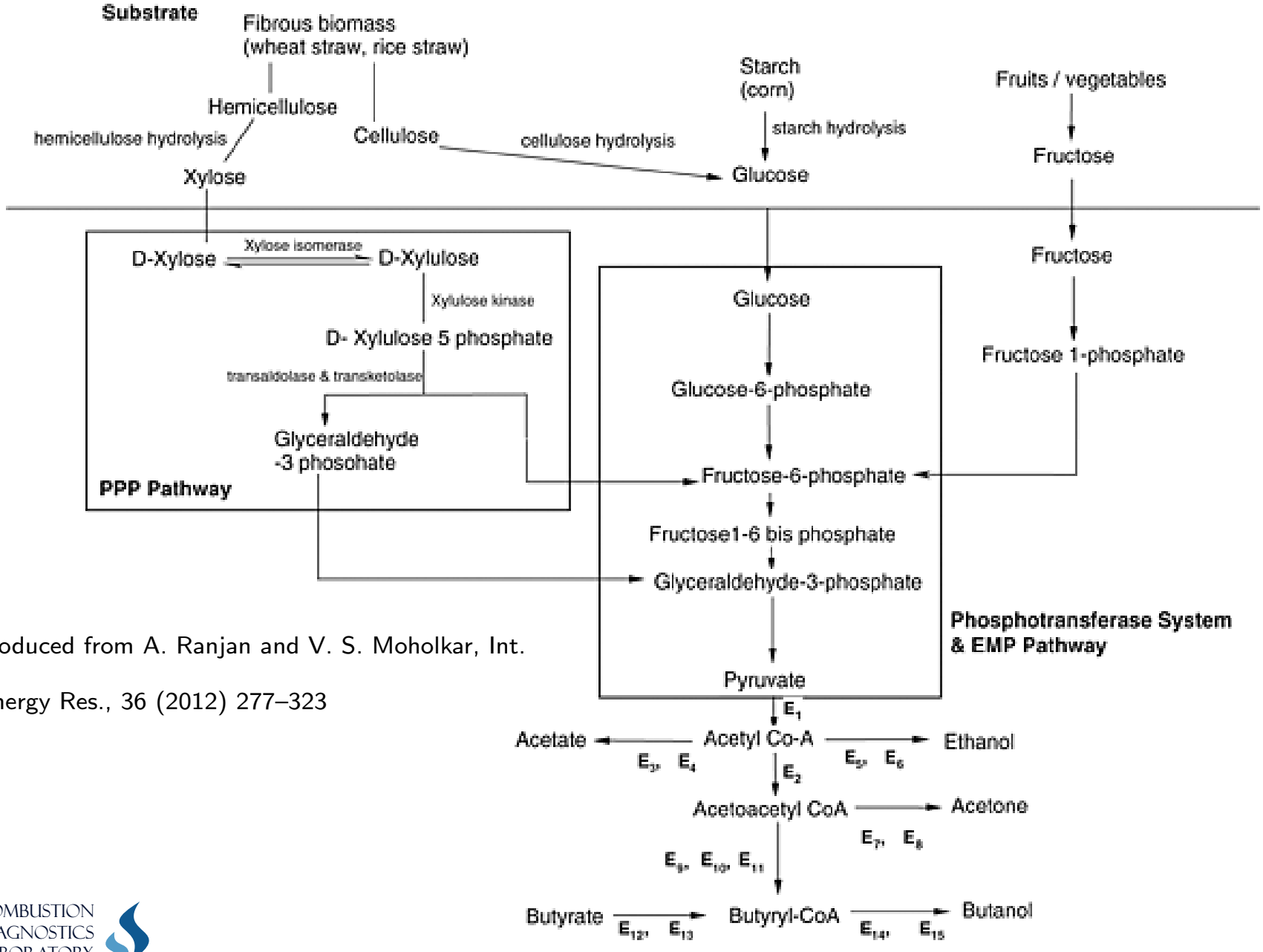
Better fuels reduce emissions and eliminate dependence on fossil fuels



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 can combustion research use?

Phenomenological Studies

- Engine Studies
- Octane Number
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Fundamental Studies

- Ignition Delay
- Product Speciation
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- Experiments

- Modeling

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  - Engine experiments
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  - Quantum chemical modeling
  - Reaction mechanisms
  - Computational fluid dynamics

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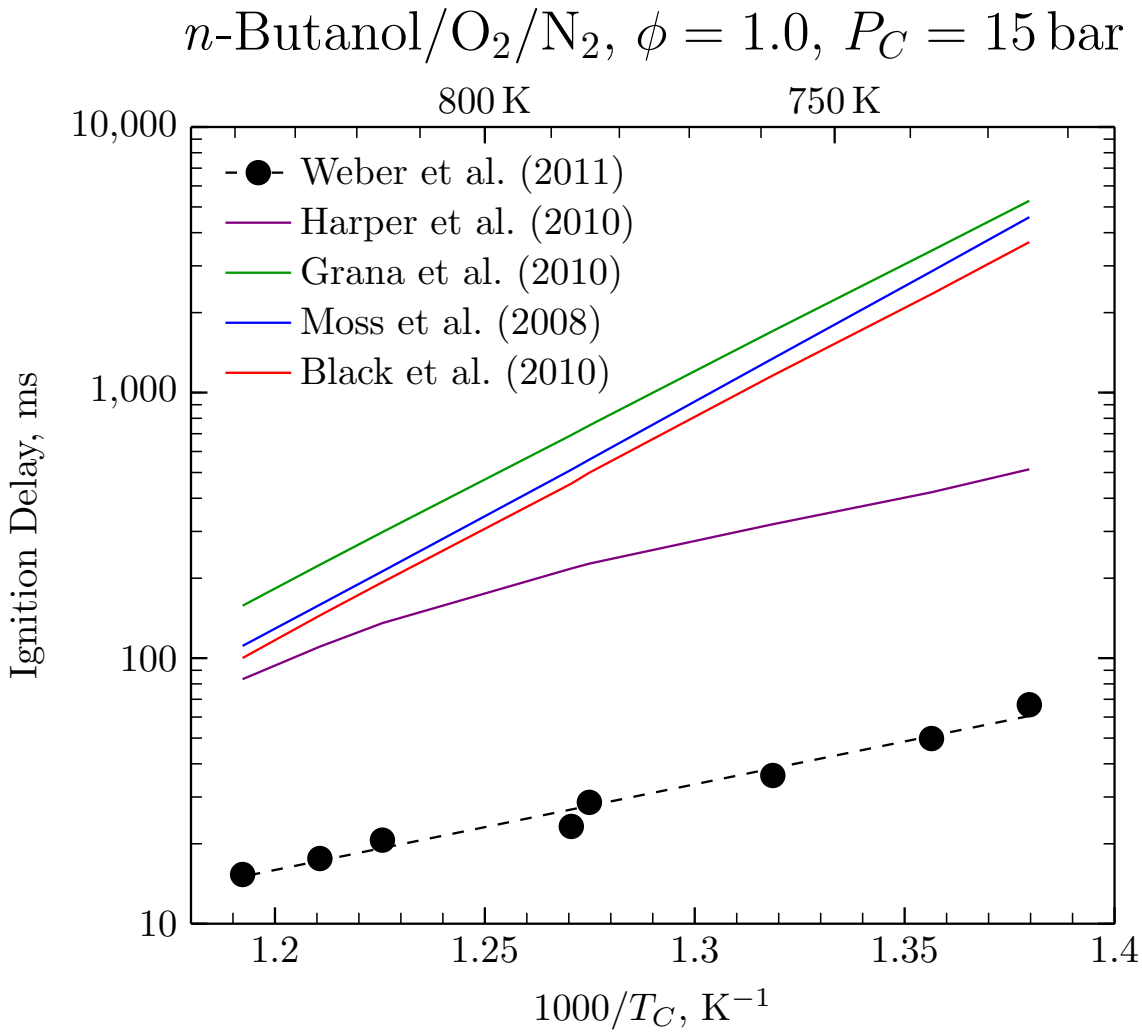
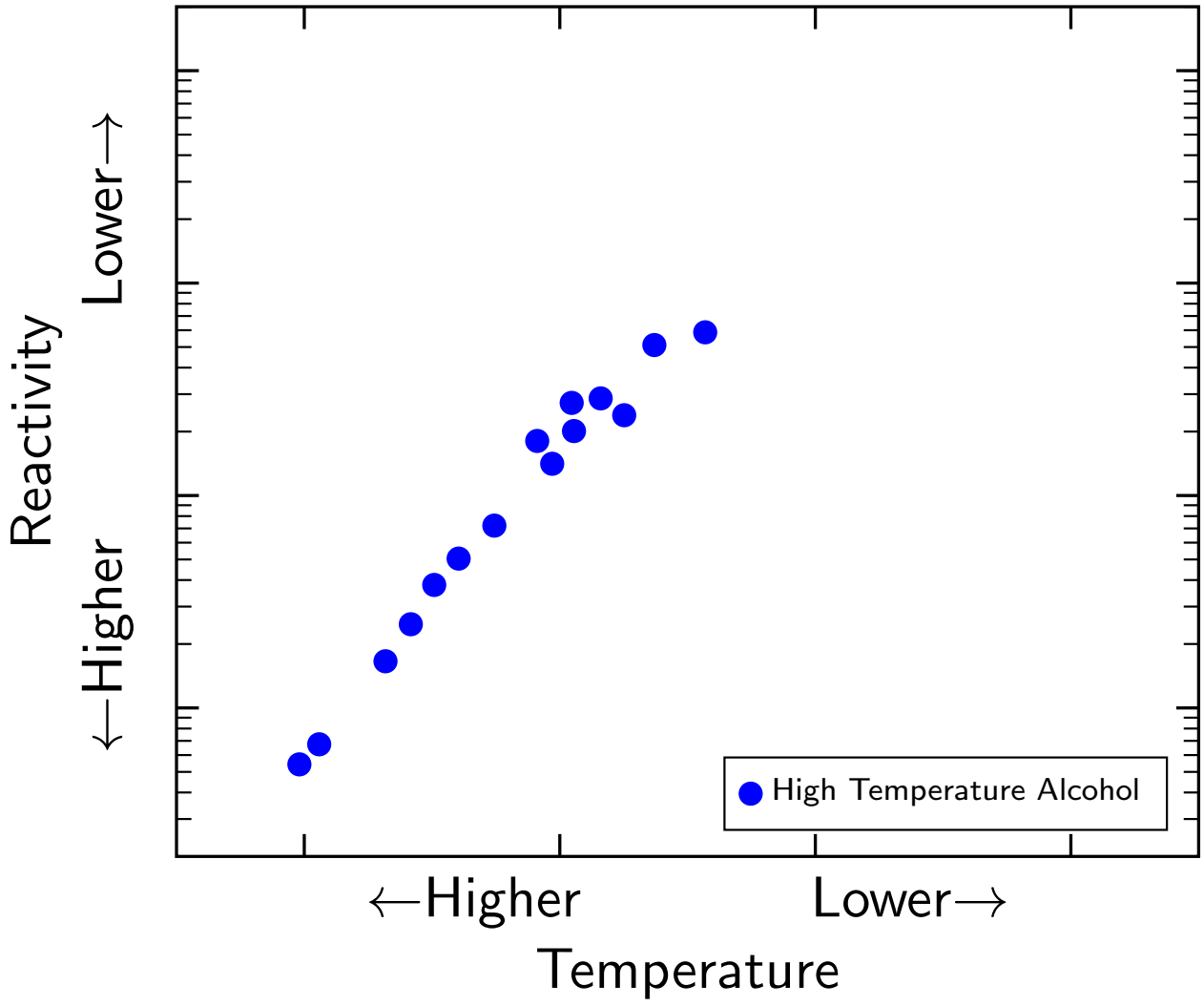
These efforts are complementary!

What problem am I trying to solve?



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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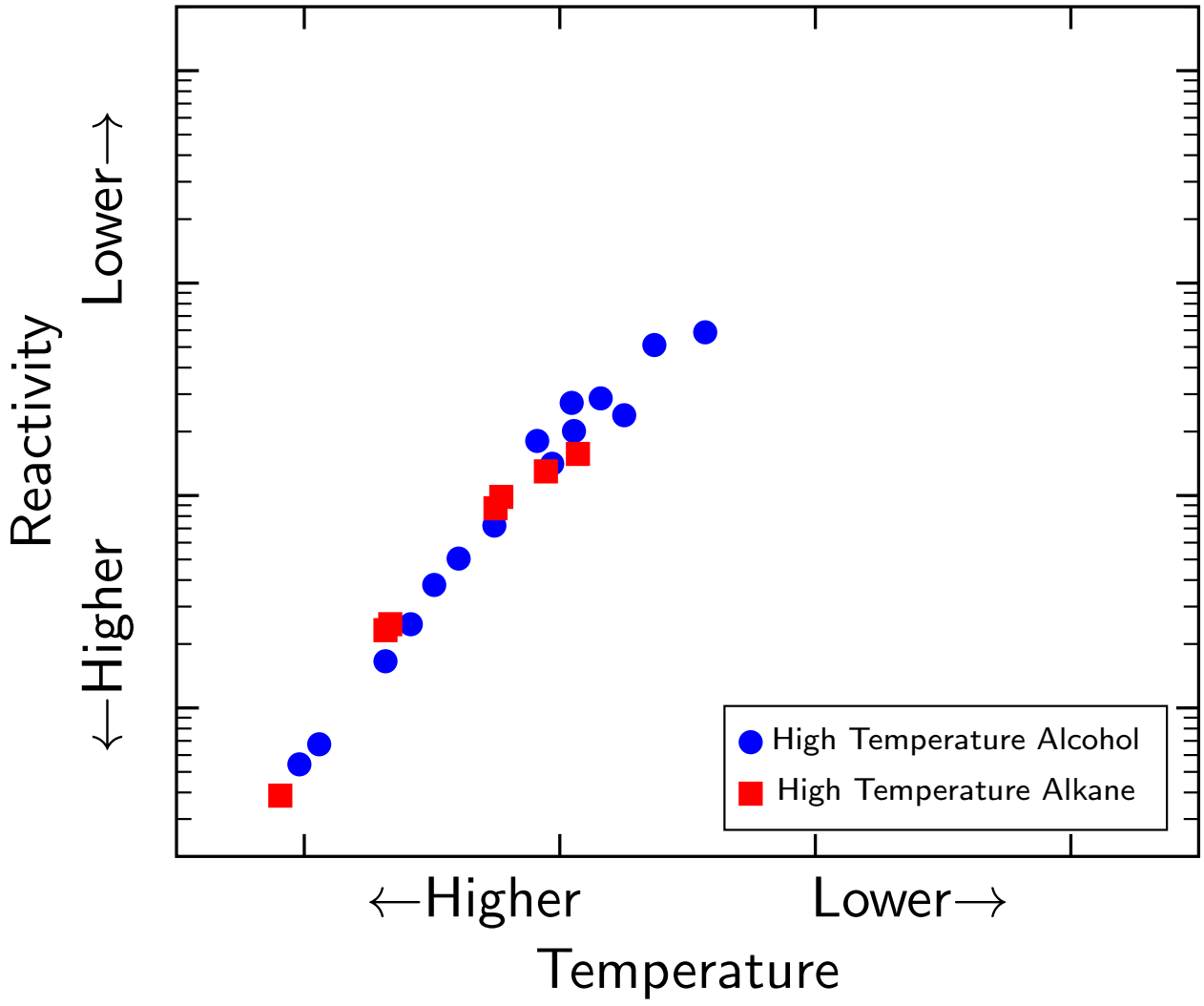

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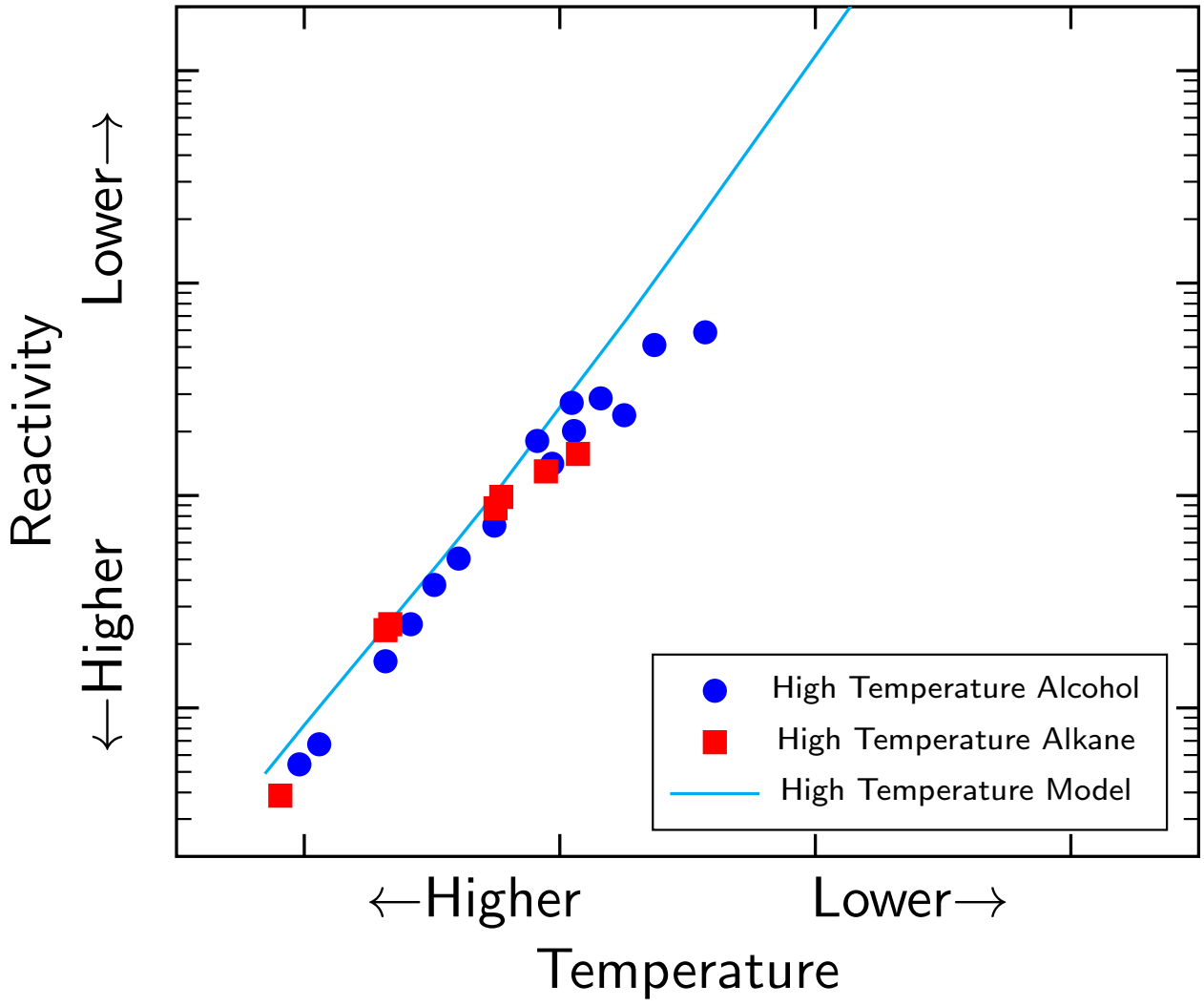

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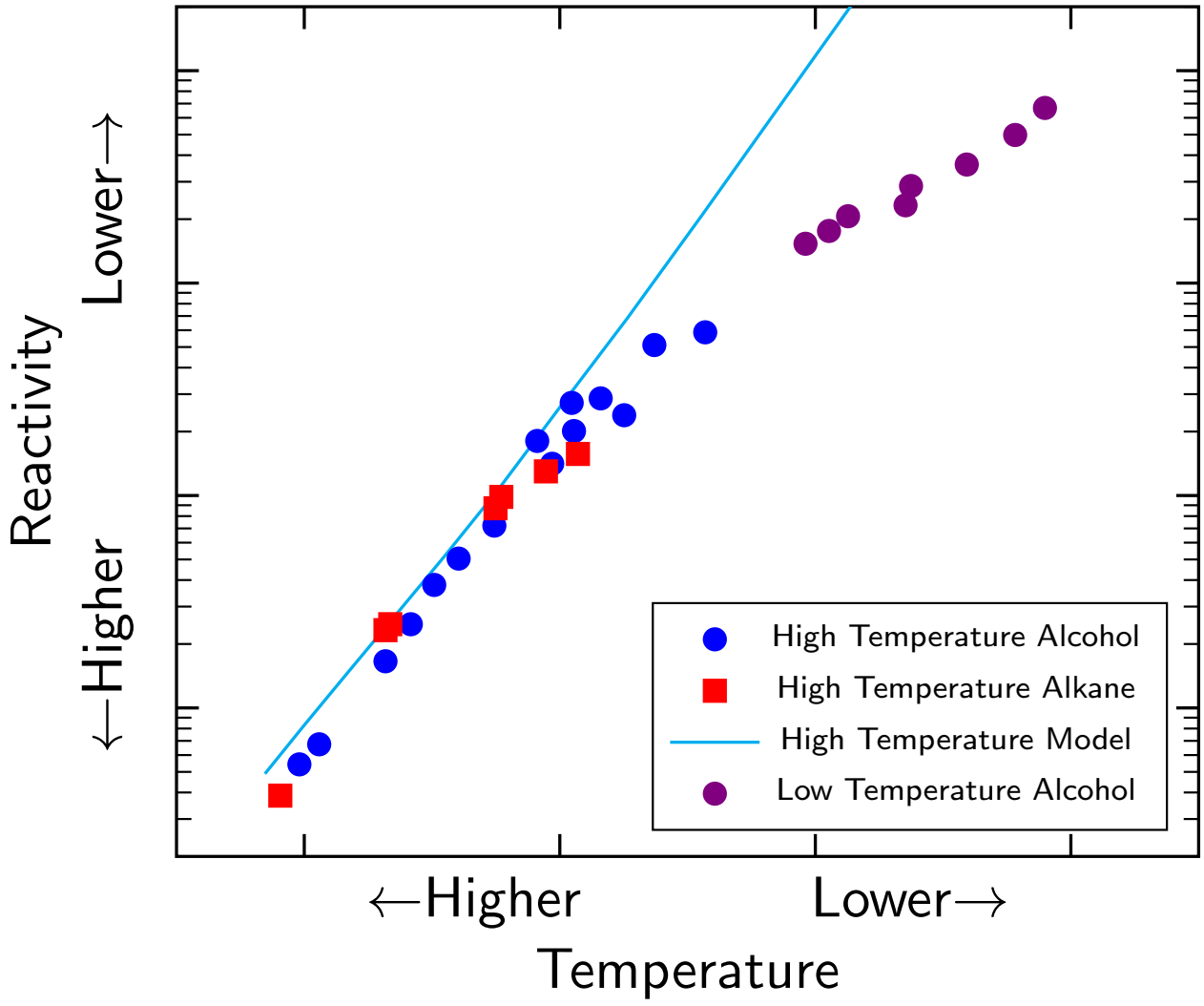

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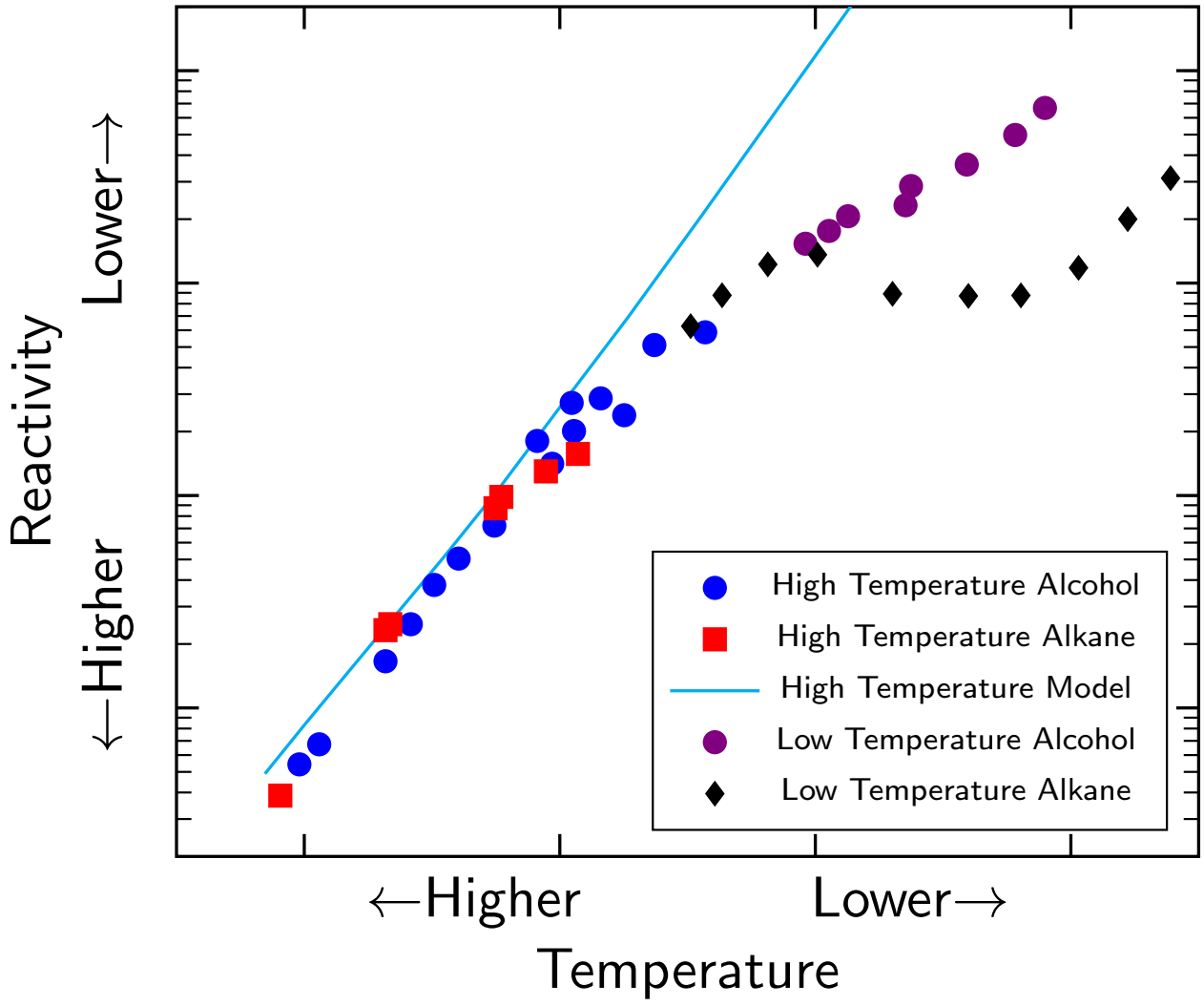

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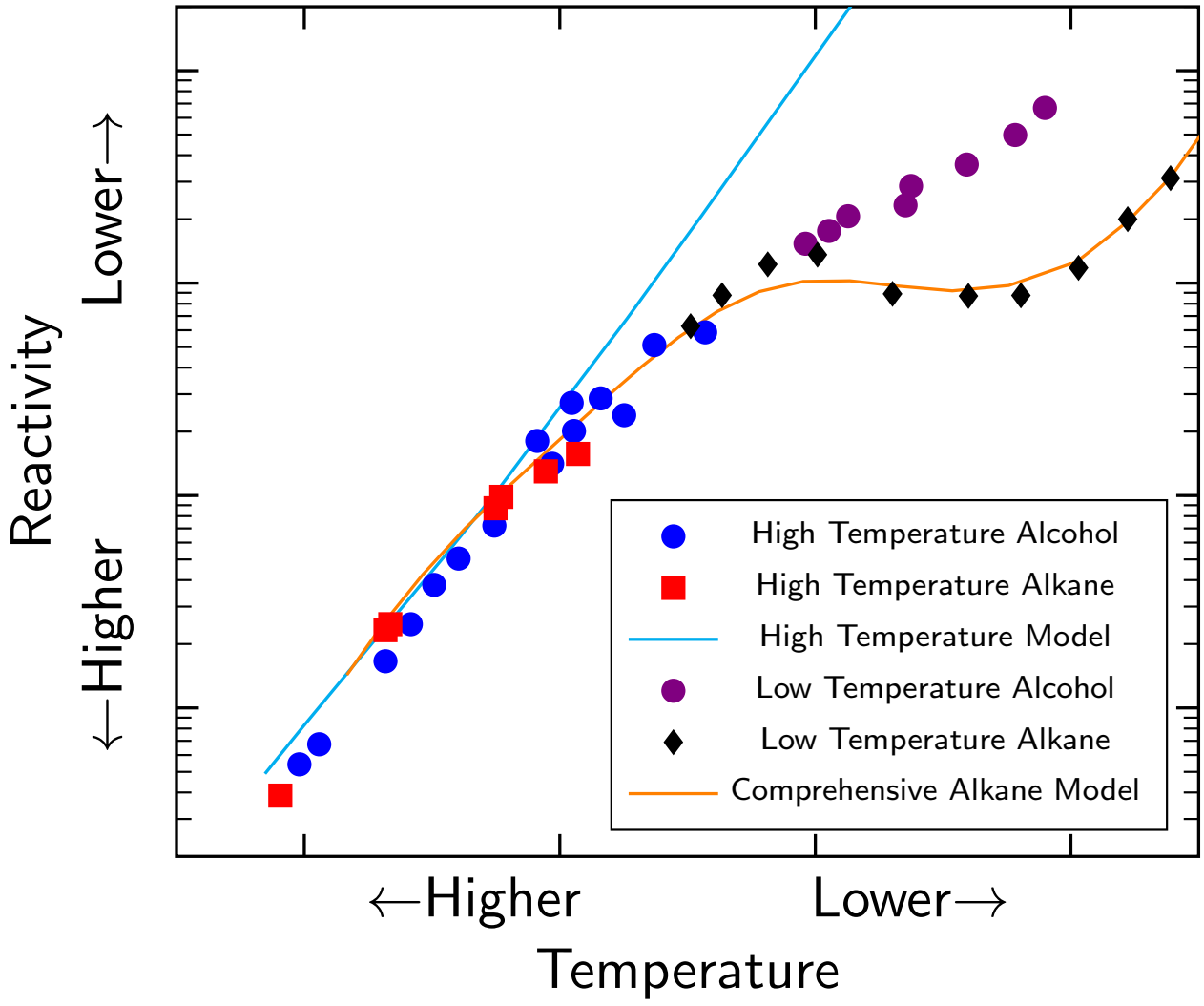

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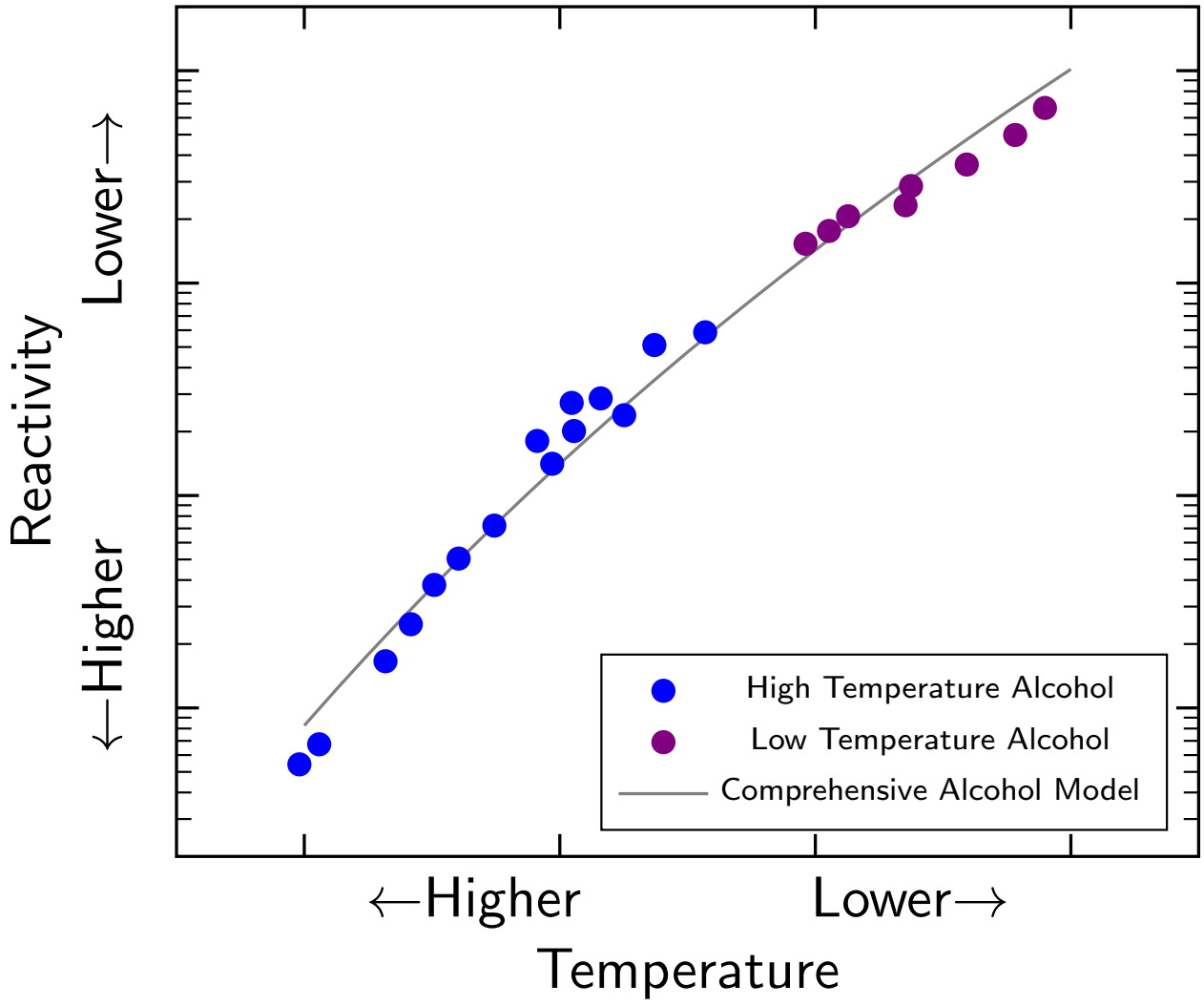

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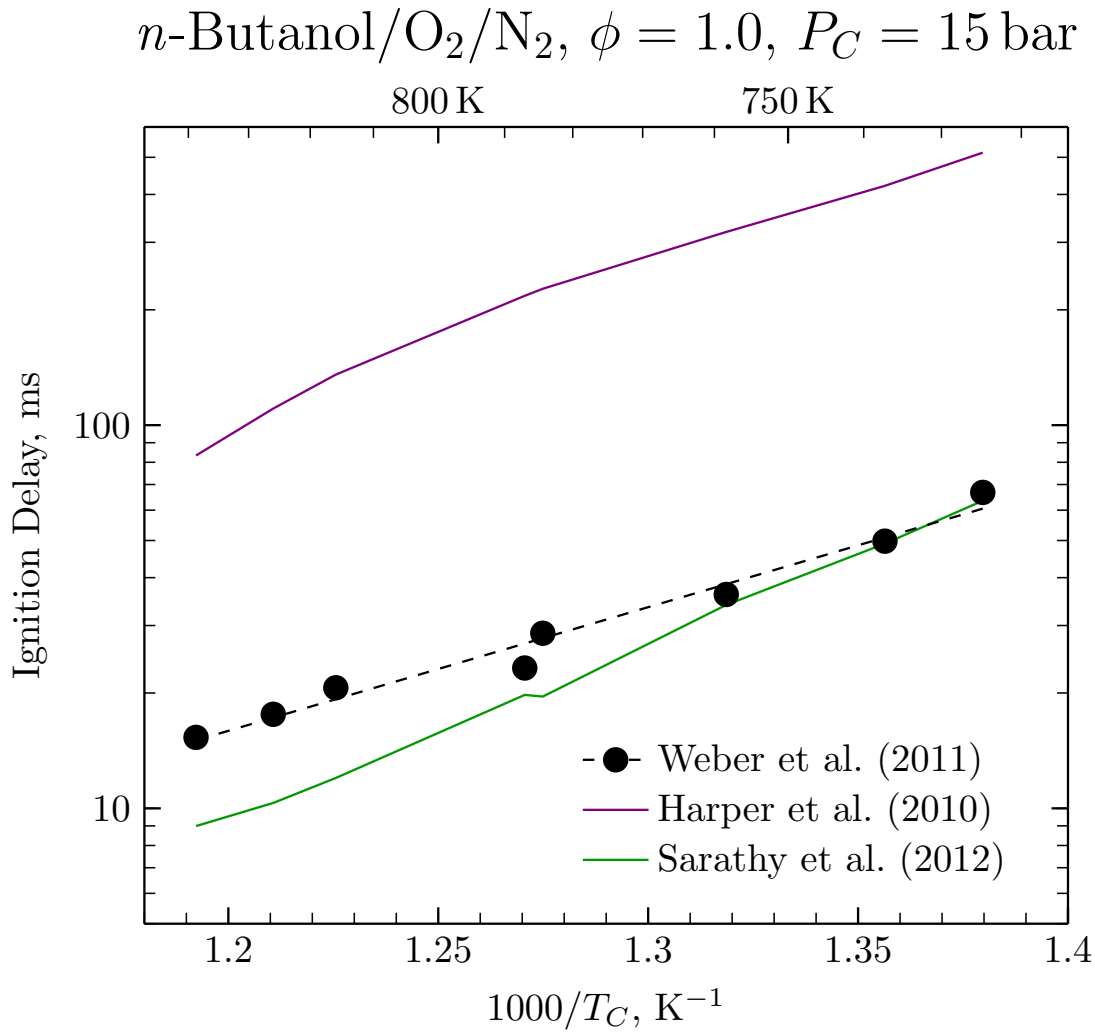


With low-temperature reaction classes added, models can better predict the ignition delay.

Combustion models are hierarchical

- In this, "combustion models" = "kinetic models" = "reaction mechanisms"
- Combustion chemistry is important! Studied since at least the advent of IC engines to understand knock; later for emissions and pollutants.
- Need to ensure that the models for small molecules are thoroughly validated when including them in models for large molecules
- A number of research efforts (past and present) have focused on this goal

H_2, CO

Combustion models are hierarchical

- Model validation for larger molecule combustion must proceed in parallel to the small molecule chemistry because the models are needed now!
- Validation data for alcoholic alternative fuels has focused on the isomers of butanol (C4 alcohols) and i-pentanol (C5 alcohol)

Combustion models are hierarchical

- Models can predict the combustion of alcohols well for a variety conditions
- Models fail to predict certain engine relevant conditions, such as ignition delay dependence on $[O_2]$

Combustion models are hierarchical

- 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

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

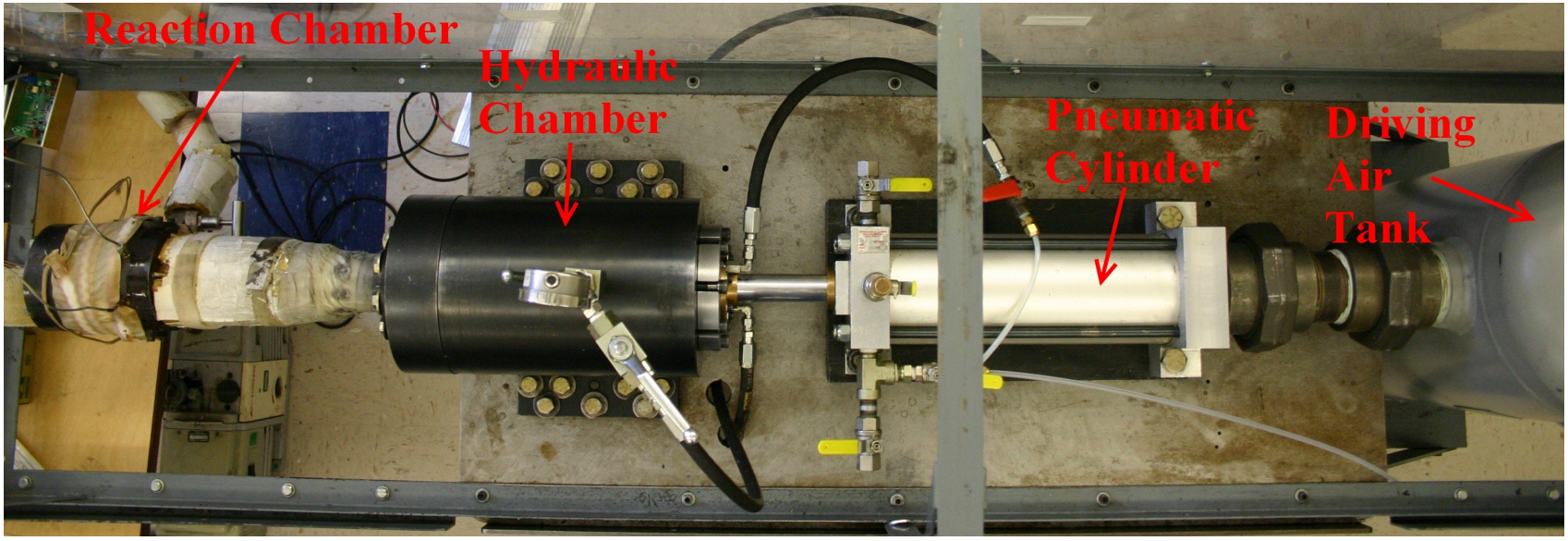
Why Bio-Alcohols?

Why MCH?

What are surrogates? (Has been touched on briefly previously)

Experimental Apparatuses

Rapid Compression Machine



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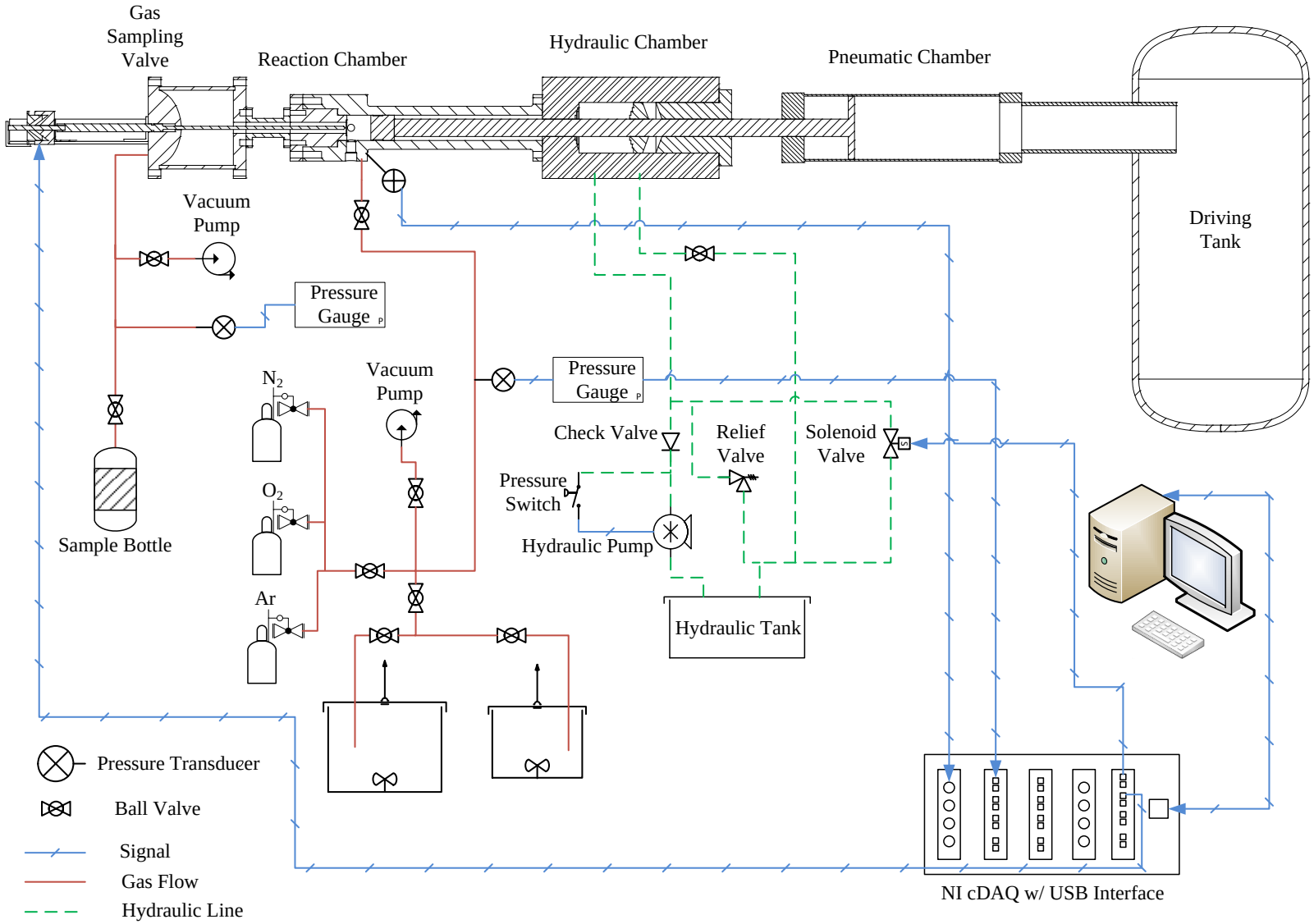
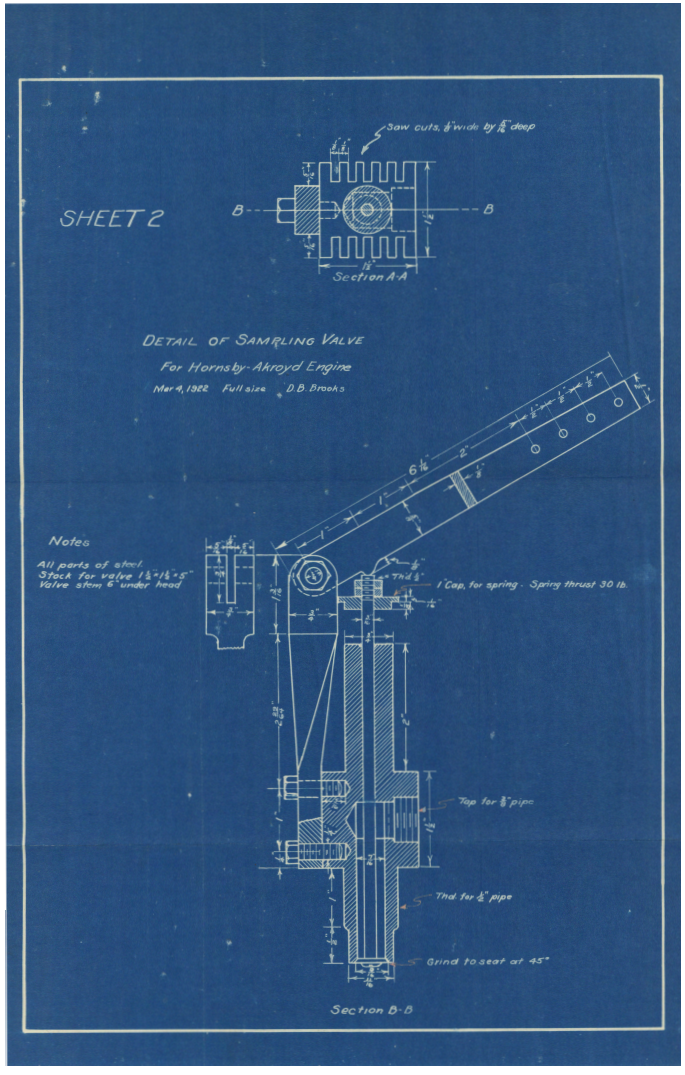


Rapid Sampling Apparatus

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



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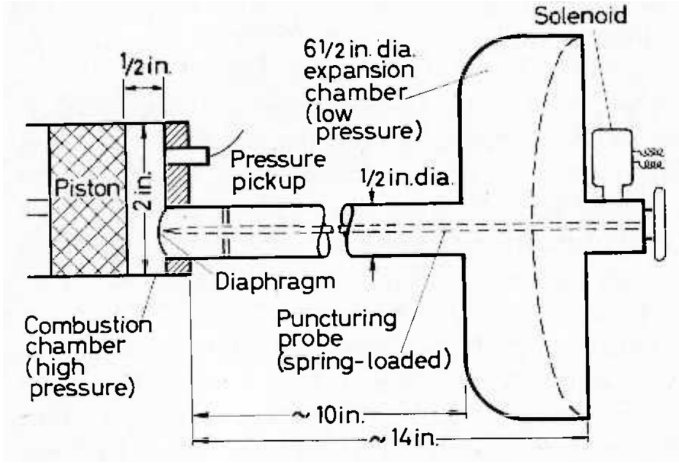

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- I have modified the design of Mittal to incorporate a solenoid instead of the electromagnet

Gas Chromatograph/Mass Spectrometer

- Standard piece of chemistry lab equipment, commercially supplied (Shimadzu)
- Separates, identifies, and quantifies chemical species