Comparative Investigation of the High Pressure Autoignition of the Butanol Isomers

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Presenting: Bryan Weber

A Short PR Digression

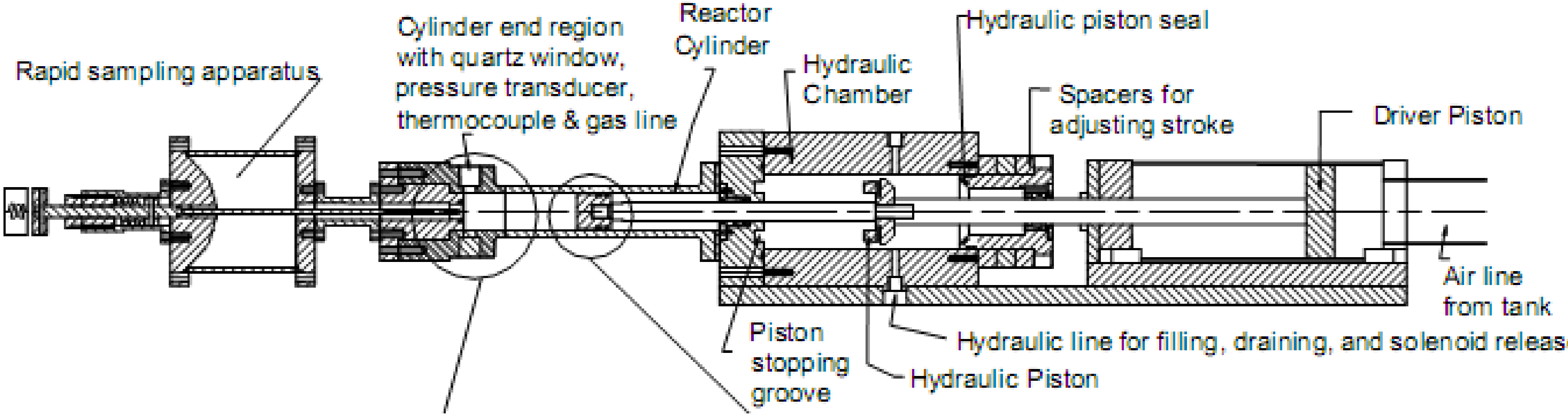
Introduction

- Butanols – 4 carbon alcohol with 4 isomers
- Motivation – Why Butanol?
  - *n*-Butanol is a second generation biofuel with the potential to replace ethanol and gasoline
  - The isomers of butanol have potential as high-octane gasoline additives
  - The butanol system is the smallest alcohol system with primary, secondary and tertiary alcohol groups

Objectives

- Investigate the butanol isomers to help determine their suitability for replacing traditional fuels in transportation applications
- Low-temperature ignition delays provide a key measure of performance related to compression or spark ignition engines
- Provide ignition delay data for all four butanol isomers at engine relevant conditions
- Evaluate the ability of chemical kinetic models to predict the ignition delays

Rapid Compression Machine (1)



- Single, retractable piston
- Piston is pneumatically driven and hydraulically stopped, with compression time around 30 ms
- Piston is machined with crevices to contain roll-up vortex created by piston motion

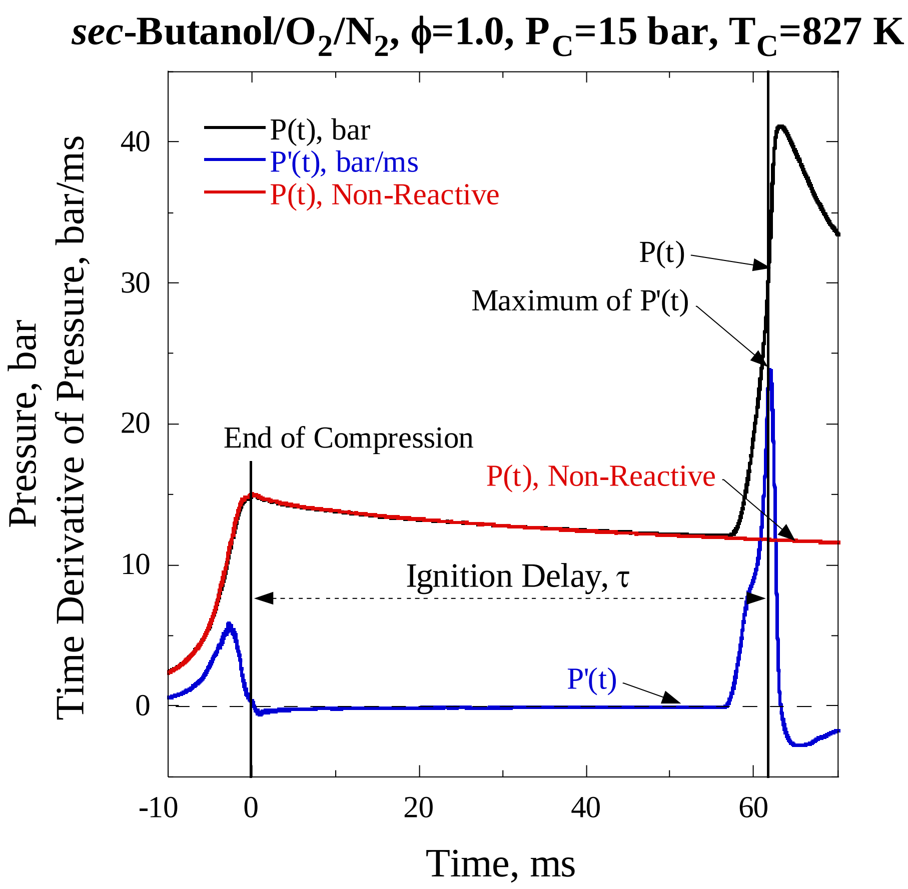
Rapid Compression Machine (2)

- Pressure and Temperature from Top Dead Center (TDC) are reported as "compressed conditions", P_C and T_C
- Ability to vary P_C and T_C independently
  – P_C up to 45 bar
  – T_C between 660-1100 K (CR:7-15)
- Fuel and oxidizer are preheated (60°C – 140°C) and mixed by magnetic stirrer in a 15 L mixing tank to ensure homogeneity

Experimental Conditions

- Overall Compressed Temperature Range: 680 K to 860 K
- Overall Compressed Pressure Range: 15 and 30 bar
- Overall Equivalence Ratio Range:
$$\phi = 0.5, 1.0, 2.0$$
- Not all fuels have been studied at all conditions (yet)

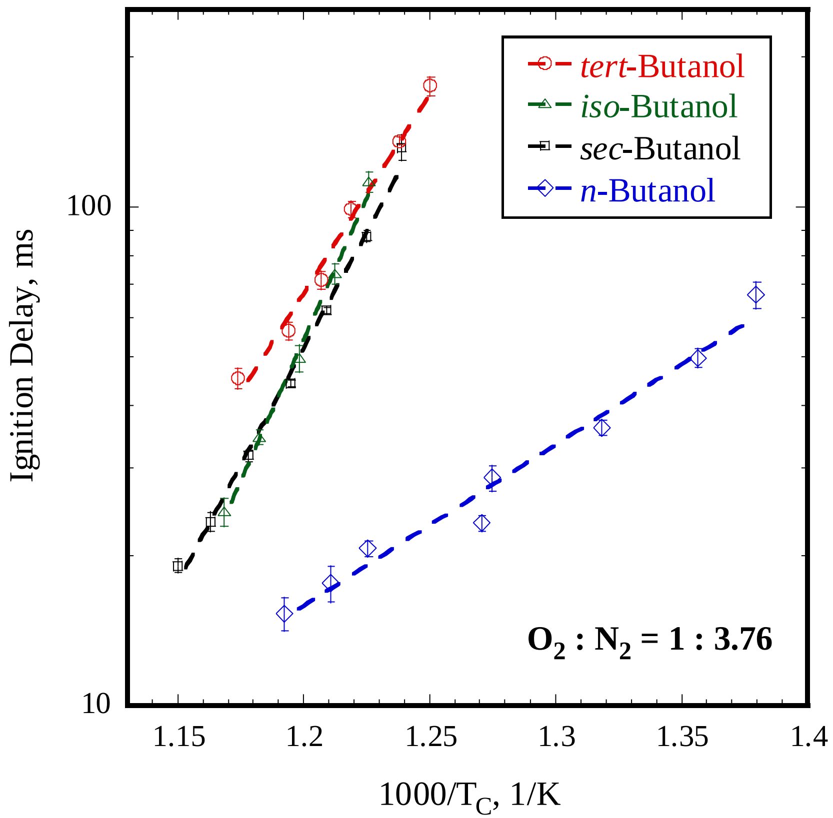
Definition of Ignition Delay



- Ignition criteria is the maximum rate of pressure rise
- Ignition delay is the time difference from the end of compression to ignition point
- Each condition is repeated at least 5 times to ensure repeatability
- Non-reactive case replaces O_2 with inert to quantify effect of heat loss to the reactor walls

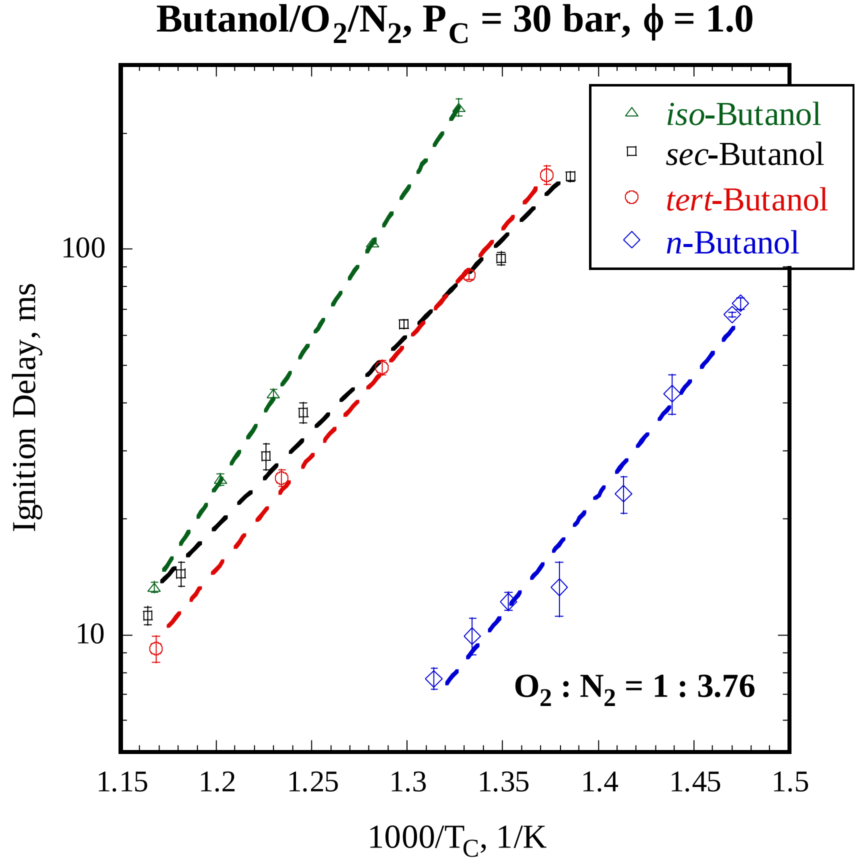
Experimental Results (1)

Butanol/O_2/N_2, P_C = 15 bar, ϕ = 1.0



- Reactivity at 15 bar: $n-$butanol > $sec-$butanol ≈ $iso-$butanol > $tert-$butanol

Experimental Results (2)



- Reactivity at 30 bar: $n-$butanol > $tert-$butanol > $sec-$butanol > $iso-$butanol
- Why does $tert-$butanol become relatively more reactive at higher pressures?

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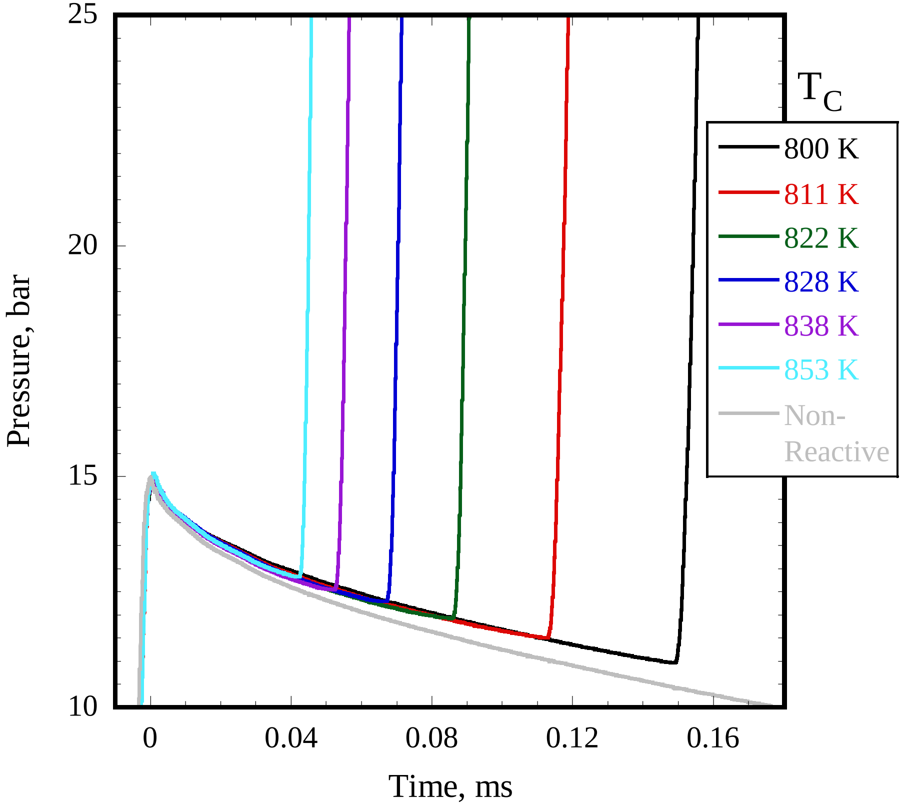
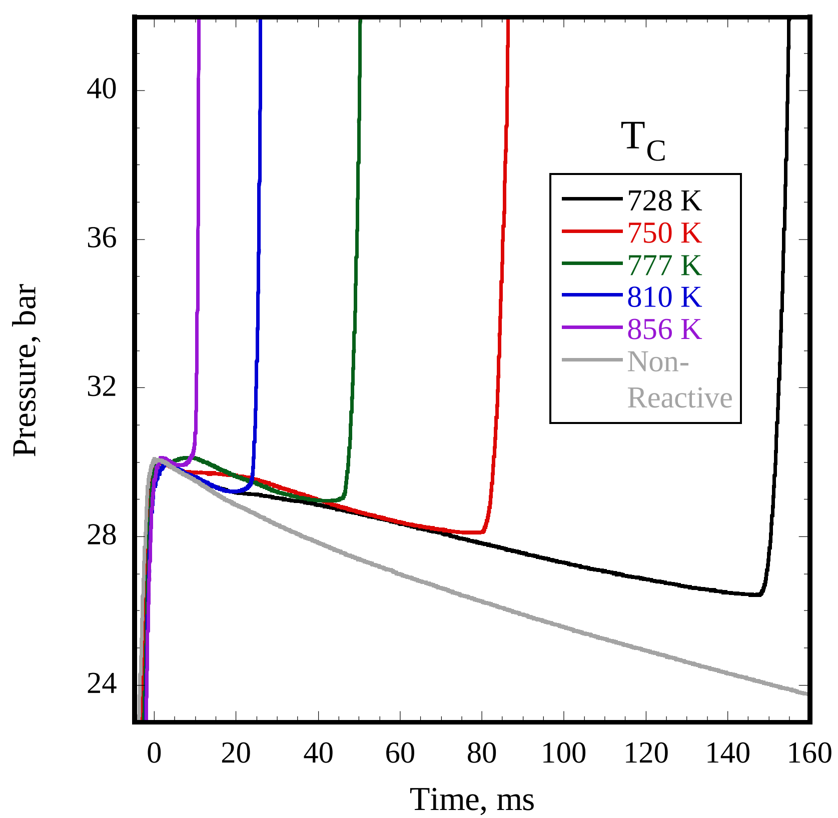
Experimental Results (3)

tert-Butanol/O_2/N_2, ϕ=1.0, P_C = 15 bar

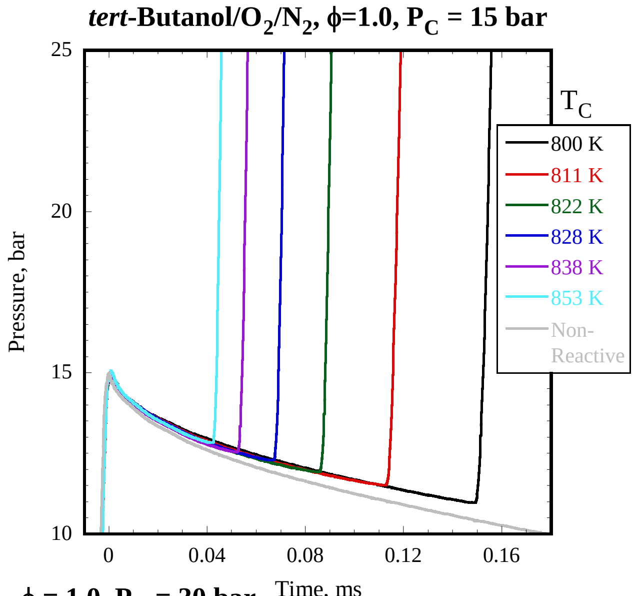


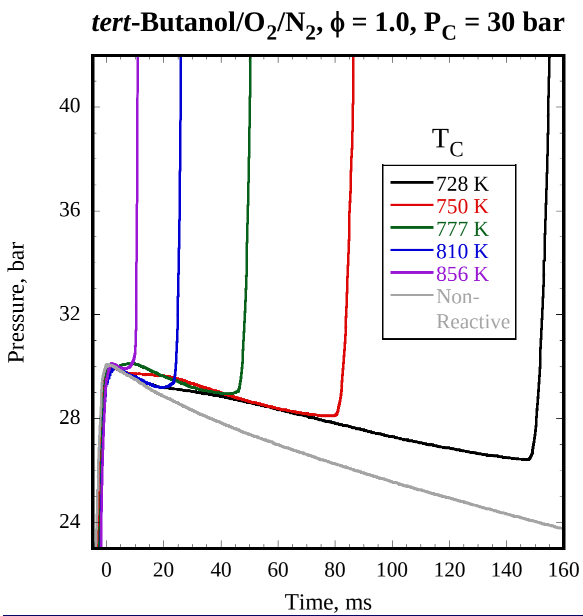
tert-Butanol/O_2/N_2, ϕ = 1.0, P_C = 30 bar



- Pressure traces from the RCM show clearly that there is pre-ignition heat release

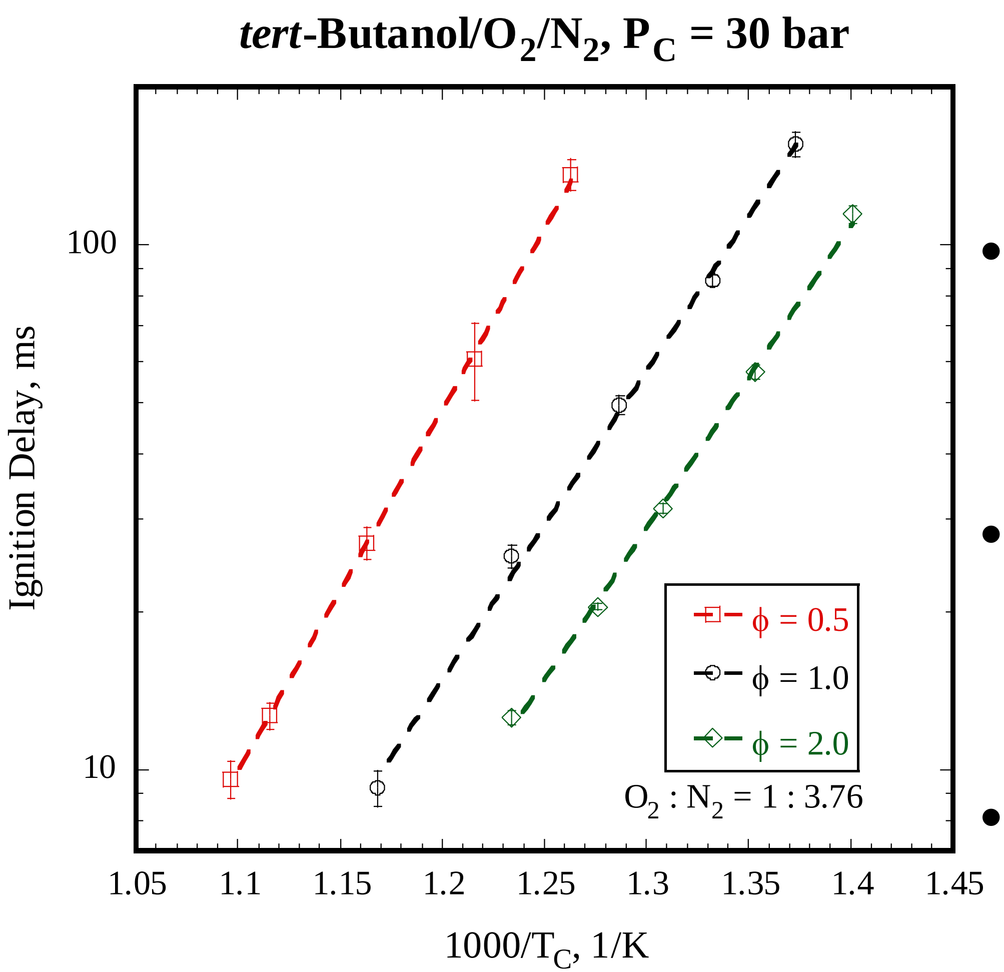
Experimental Results (4)





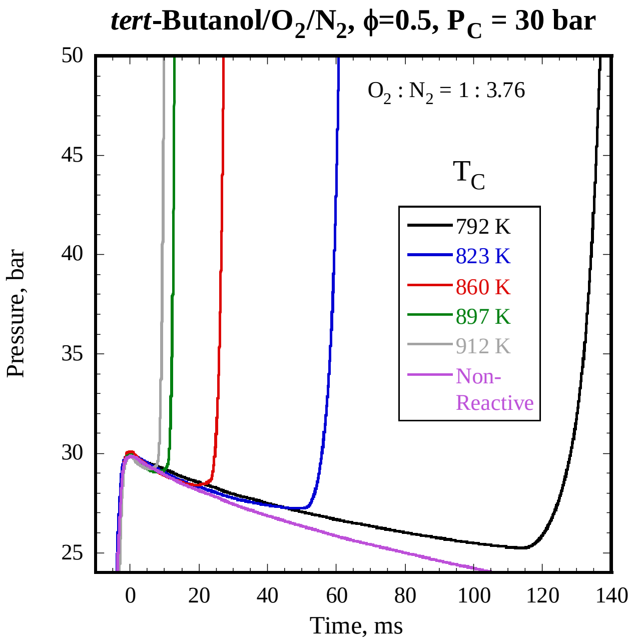
- No other isomers show this extreme behavior (n−butanol deviates slightly from its non-reactive traces)
- To help answer what is causing this heat release, we need data at different conditions
- How dependent on fuel concentration is the heat release?

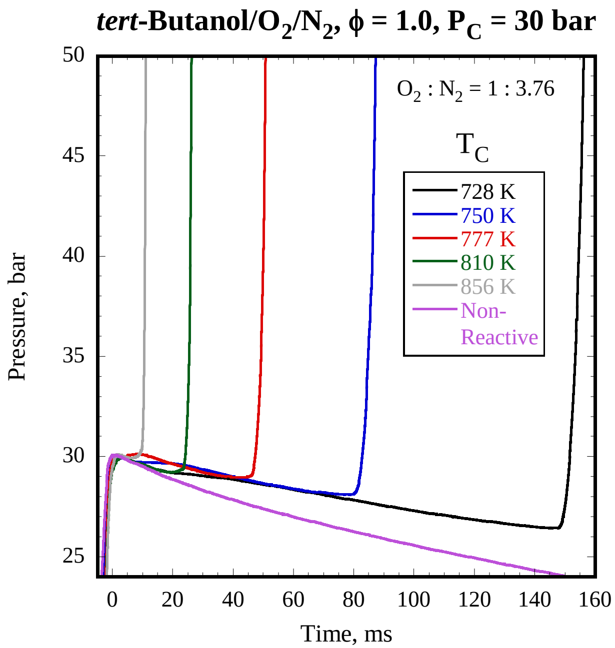
Experimental Results (5)

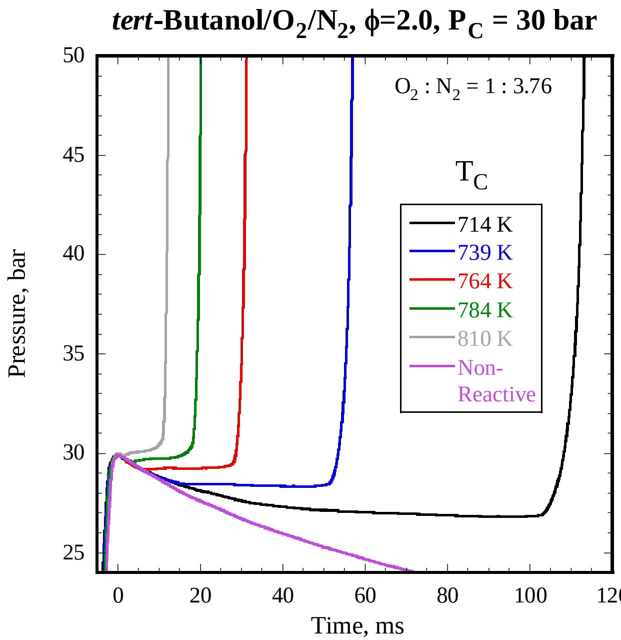


- Ignition delays at two other equivalence ratios ($\phi = 0.5$ and 2.0) in air are measured at 30 bar
- Fuel Mole Fractions:
  $\phi = 0.5 : X = 0.0172$
  $\phi = 1.0 : X = 0.0338$
  $\phi = 2.0 : X = 0.0654$
- Slopes of Arrhenius plots are similar, indicating a similar overall activation energy
- Overall reactivity is in the expected order (2.0 > 1.0 > 0.5)

Experimental Results (6)







- At lower and higher fuel concentrations, pre-ignition heat release is still evident
- Results for different equivalence ratios are qualitatively different

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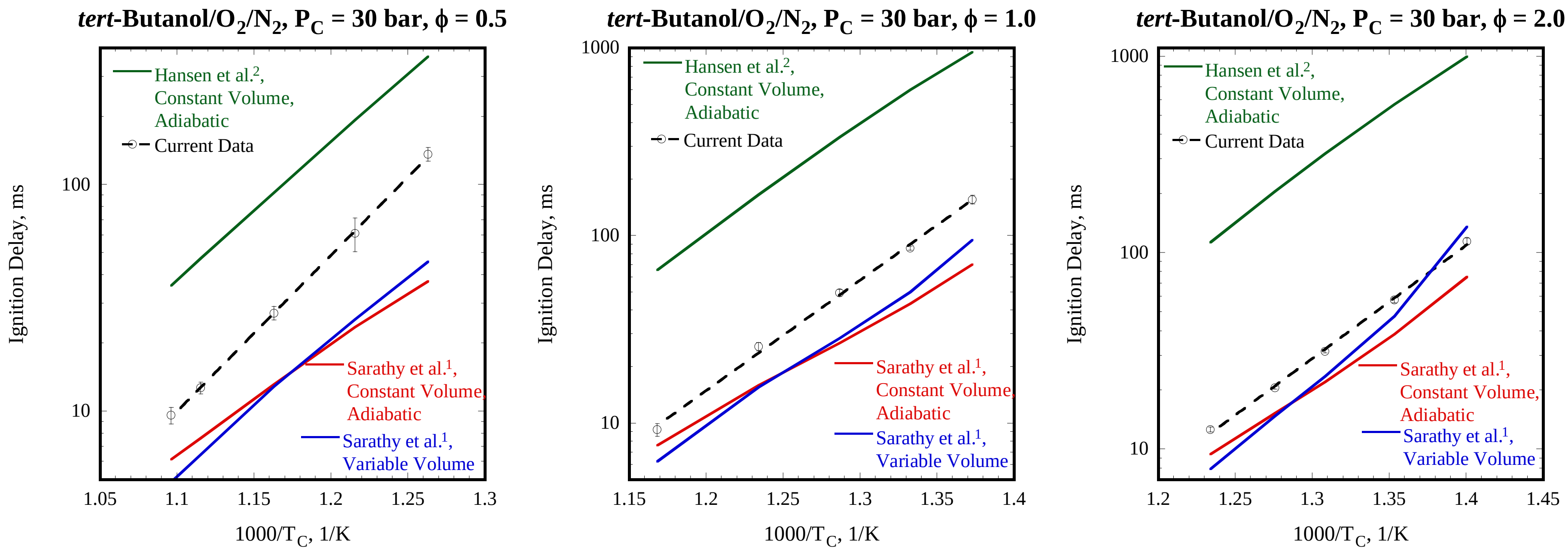
Comparison with Simulations (1)



- Simulations show that the mechanism from MIT (Hansen et al.[2]) consistently over-predicts the *tert*−butanol data, while the mechanism from LLNL (Sarathy et al.[1]) under-predicts the data
- Neither mechanism is validated for these experiments

1. Sarathy, S.M., Vranckx, S., Yasunaga, K., Mehl, M., Oßwald, P., Westbrook, C. K., Pitz, W.J., Kohse-Hoinghaus, K., Fernandes, R.X., and Curran, H.J. Submitted to *Combustion and Flame*, Sept. 2011
2. Hansen, N., Harper, M.R., and Green, W.H. Submitted to *Physical Chemistry Chemical Physics*, Aug. 2011

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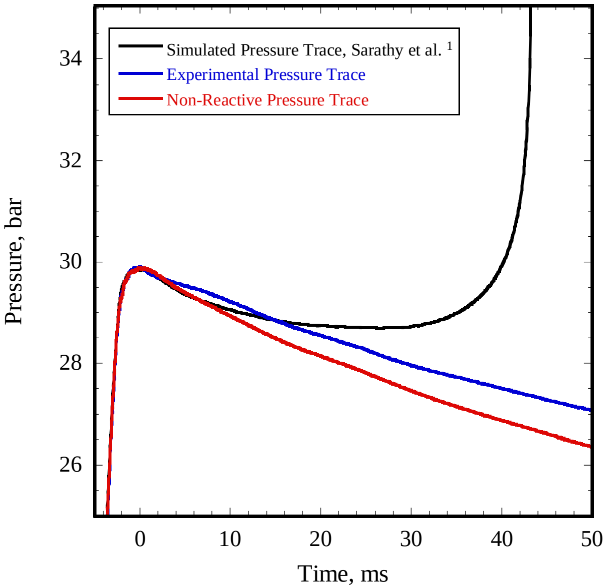
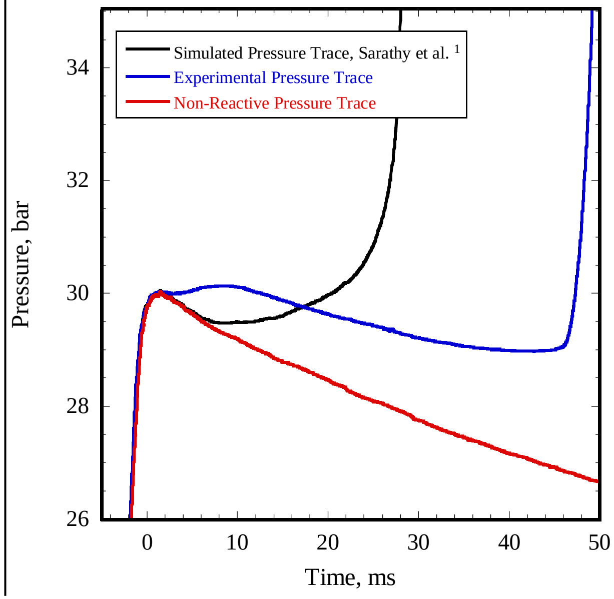
Comparison with Simulations (2)

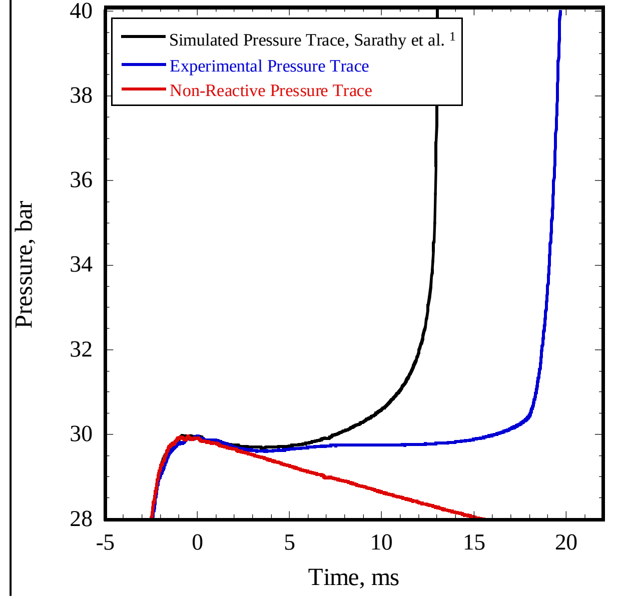
tert-Butanol/O_2/N_2, ϕ=0.5, P_C=30 bar, T_C=792 K



tert-Butanol/O_2/N_2, ϕ=1.0, P_C=30 bar, T_C=777 K



tert-Butanol/O_2/N_2, ϕ=2.0, P_C=30 bar, T_C=784 K



- Despite reasonable agreement in overall ignition delay, the pressure traces are not well reproduced by the mechanism from LLNL

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Summary (1)

- Autoignition delays of the isomers of butanol show unexpected behavior over the currently studied temperature and pressure ranges
- Pre-ignition heat release during $tert-$butanol autoignition delays were unable to be reproduced by mechanisms, so the chemistry causing this is unclear
- New autoignition delays for off-stoichiometric conditions of $tert-$butanol in air have been collected to help determine the cause of the pre-ignition heat release

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Summary (2)

- Although the overall activation energy of three equivalence ratios of $tert-$butanol ($\phi = 0.5, 1.0, 2.0$) are quite similar, they show markedly different pressure profiles
- One recent mechanism was able to reproduce the ignition delays within a factor of ~2-3, despite not being validated for these conditions
- Despite this relatively good agreement, the pressure profile is still unable to be reproduced

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Acknowledgements

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- Dr. Bill Green for providing his mechanism prior to publication, and for helpful discussions

Thank you!

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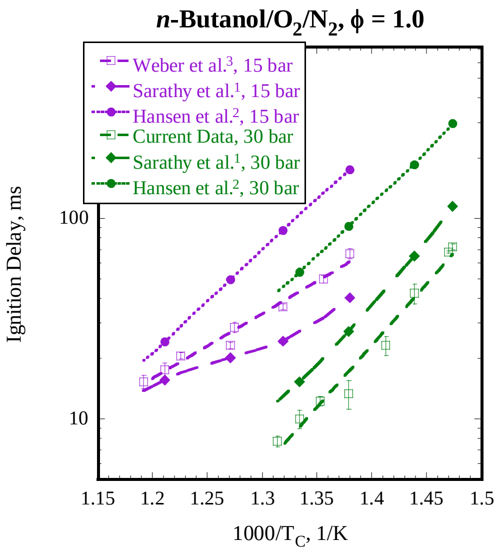
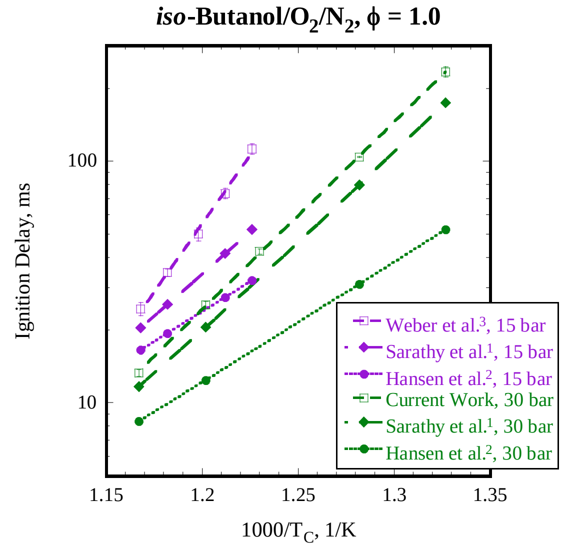
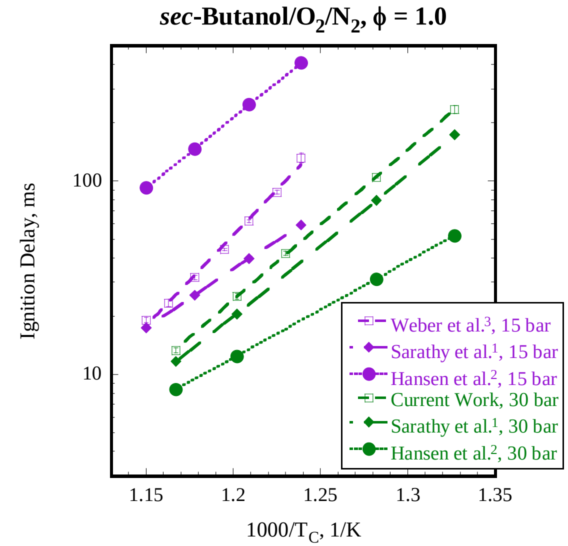
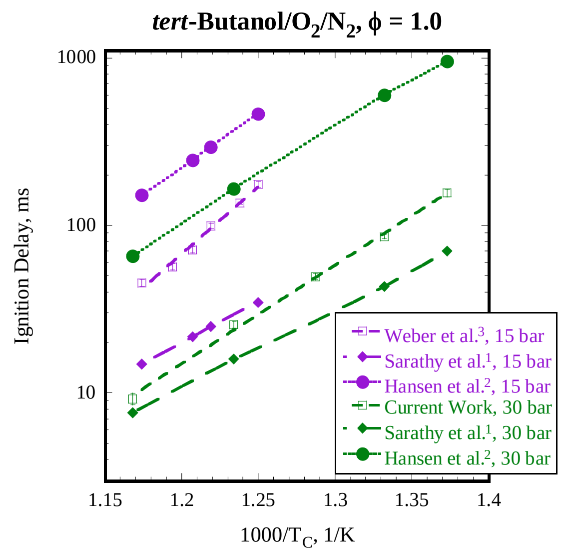
Comparison with Simulations









- Constant Volume, Adiabatic Simulations
- Mechanisms are NOT validated for 30 bar cases
- Agreement for 15 bar cases is reasonable – agreement for 30 bar cases is luck of the draw

1. Sarathy, S.M., Vranckx, S., Yasunaga, K., Mehl, M., Oßwald, P., Westbrook, C. K., Pitz, W.J., Kohse-Hoinghaus, K., Fernandes, R.X., and Curran, H.J. Submitted to *Combustion and Flame*, Sept. 2011
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3. Weber, B.W., and Sung, C.J. National Combustion Meeting.

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