A Rapid Compression Study of the Butanol Isomers at Elevated Pressure

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Introduction

- Butanols – 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

Previous Work

- Since 2010, there have been nearly 30 butanol combustion studies
- A number of these studies have been applications based, covering such devices as diesel engines, SI engines, and turbines
- Although fundamental work has also expanded, there are still only limited data available for many conditions, especially high pressure/low temperature

Previous Work

- Black et al.[1] have measured ignition delays of *n*-butanol in a shock tube at low pressure and high temperature (< 8 bar, 1100-1800 K)
- Moss et al.[2] have measured ignition delays of all four isomers of butanol in a shock tube at low pressure and high temperature (< 4 bar, 1200-1800 K)
- Grana et al.[3] have measured flame speeds of the isomers of butanol
- Hansen et al.[4] have studied three low pressure premixed flames of *n*-butanol and identified isomer-resolved intermediate species
- Heufer et al.[5], Vranckx et al.[6], and Stranic et al.[7] have investigated high pressure ignition delays of *n*-butanol in a shock tube (up to 90 bar, 795-1200 K)

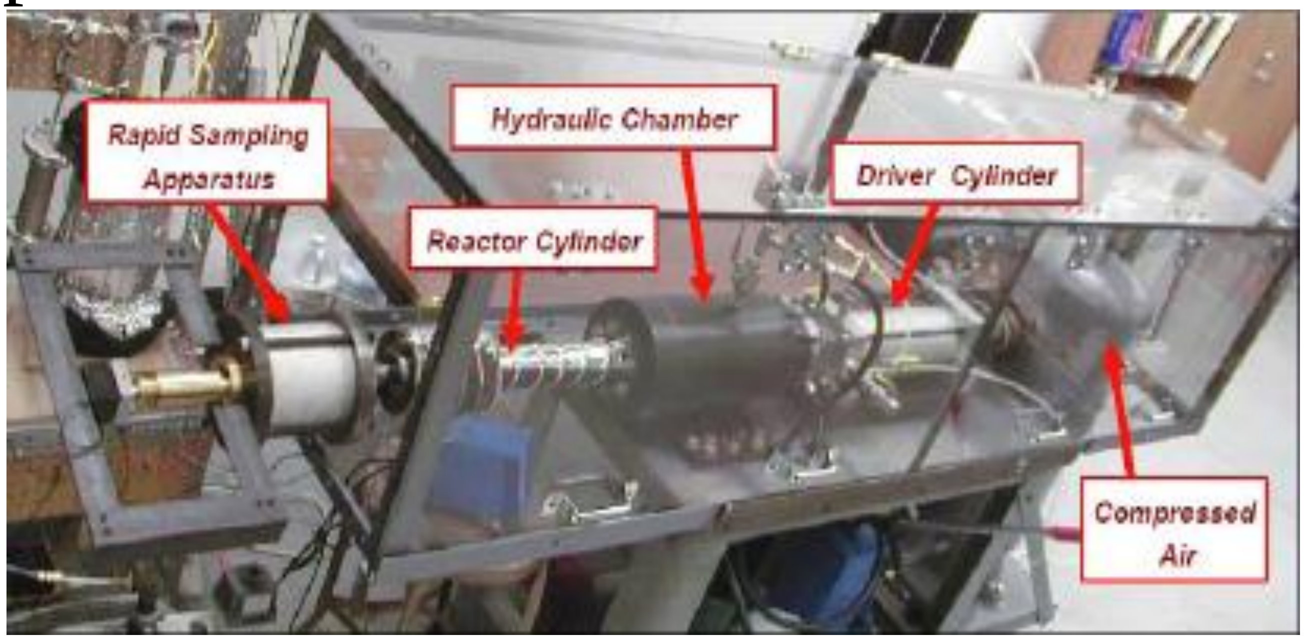
1. Black, G., Curran, H., Pichon, S., Simmie, J. M., and Zhukov, V., *Combustion and Flame,* Vol. 157, No. 2, 2010, pp. 363-373.
2. Moss, J. T., Berkowitz, A. M., Oehlschlaeger, M. A., Biet, J., Warth, V., Glaude, P., and Battin-Leclerc, F., *The Journal of Physical Chemistry. A,* Vol. 112, No. 43, 2008, pp. 10843-10855.
3. Grana, R., Frassoldati, A., Faravelli, T., Niemann, U., Ranzi, E., Seiser, R., Cattolica, R., and Seshadri, K., *Combustion and Flame*, Vol. 157, 2010, pp. 2137-2154.
4. Hansen, N., Harper, M.R., and Green, W.H., *7th US National Combustion Meeting*, Georgia Institute of Technology, Atlanta, GA, March 20-23, 2011, paper 1B09
5. Heufer, K.A., Fernandes, R. X., Olivier, H., Beeckmann, J., and Peters, N., *Proceedings of the Combustion Institute*, Vol. 33, 2011, pp.359-366.
6. Vranckx, S., Heufer, K.A., Lee, C., Olivier, H., Schill, L., Kopp, W.A., Leonhard, K., Taatjes, C.A., Fernandes, R.X., *Combustion and Flame,* 2011, Article in Press, doi:10.1016/j.combustflame.2010.12.028
7. Stranic, I., Chase, D., Harmon, J., Yang, S., Davidson, D.F., and Hanson, R.K., *7th US National Combustion Meeting*, Georgia Institute of Technology, Atlanta, GA, March 20-23, 2011, paper 1B11

Objectives

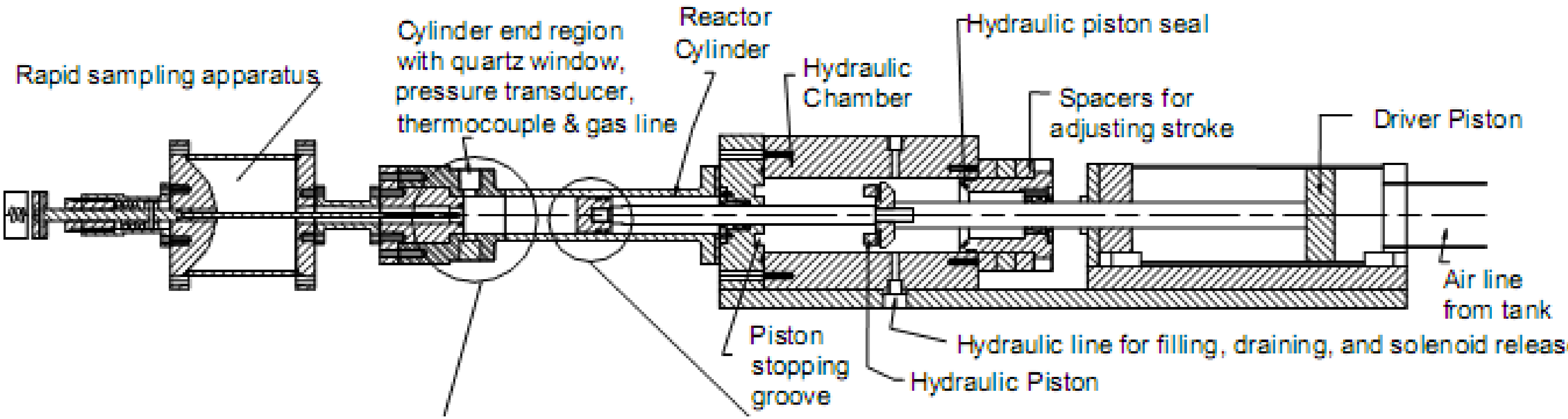
- Provide complementary data to the previous studies using a Rapid Compression Machine
  - Focus on high pressure and low to intermediate temperature conditions
- Provide validation studies for the existing reaction mechanisms
  - Cover many pressure ranges, equivalence ratios, and fuel loading conditions
- Experimental conditions for all four isomers:
  - P_C= 15 bar, T_C= 725-820 K, ϕ= 1.0, O_2/N_2 air

Rapid Compression Machine (1)

- Obtain experimental data for autoignition delays at elevated pressures and low-to-intermediate temperatures, using a heated rapid compression machine



Rapid Compression Machine (2)



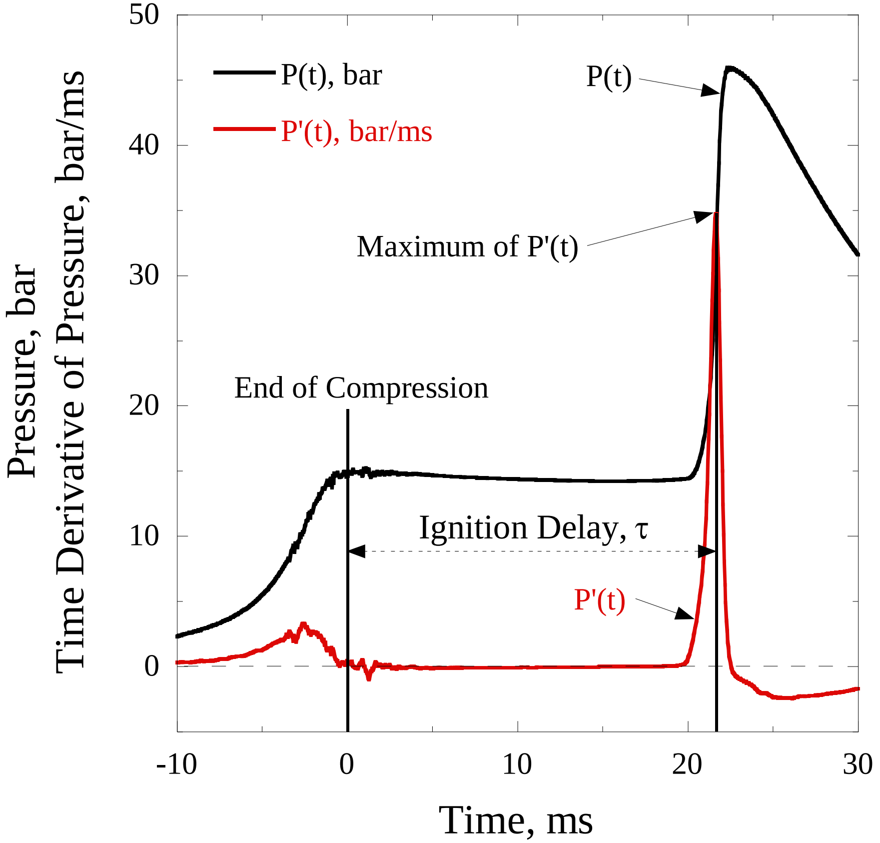
- Single, retractable piston
- Piston is pneumatically driven and hydraulically stopped, with compression time around 30 ms
- Piston is machined with crevices to contain roll-up vortex created by piston motion

Rapid Compression Machine (3)

- 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
- Fuel and oxidizer are preheated and mixed in a 15 L mixing tank to ensure homogeneity

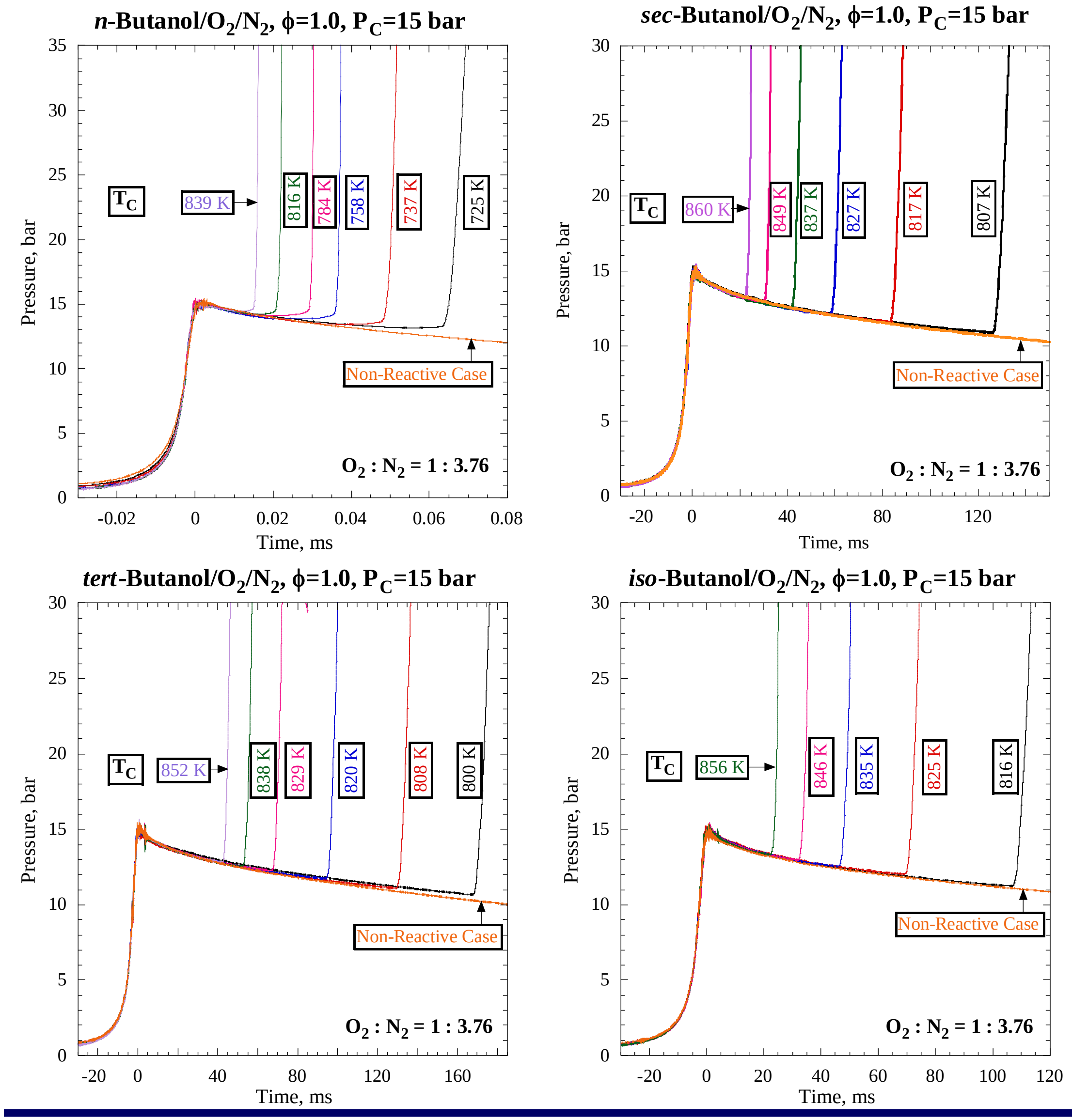
Definition of Ignition Delay

n-Butanol/O_2/N_2, ϕ=1.0, P_C=15 bar



- 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 6 times to ensure repeatability

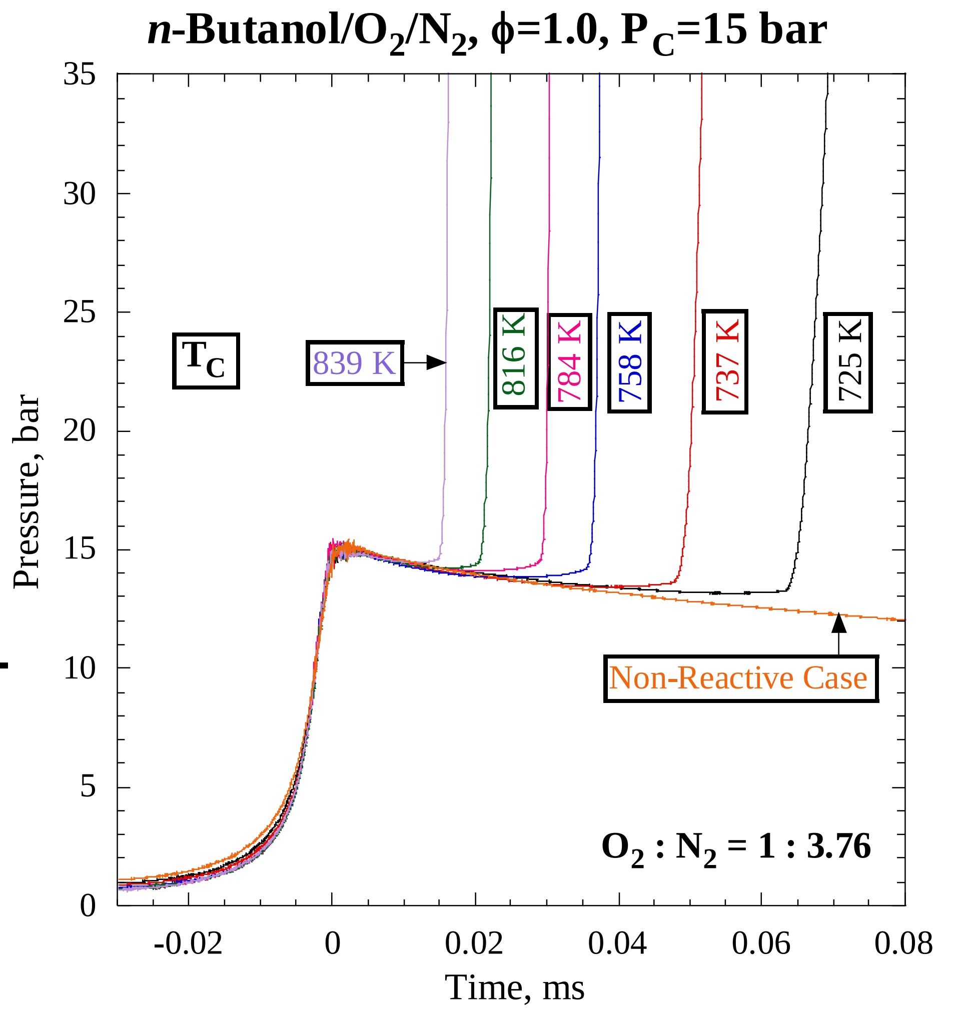
Experimental Results (1)



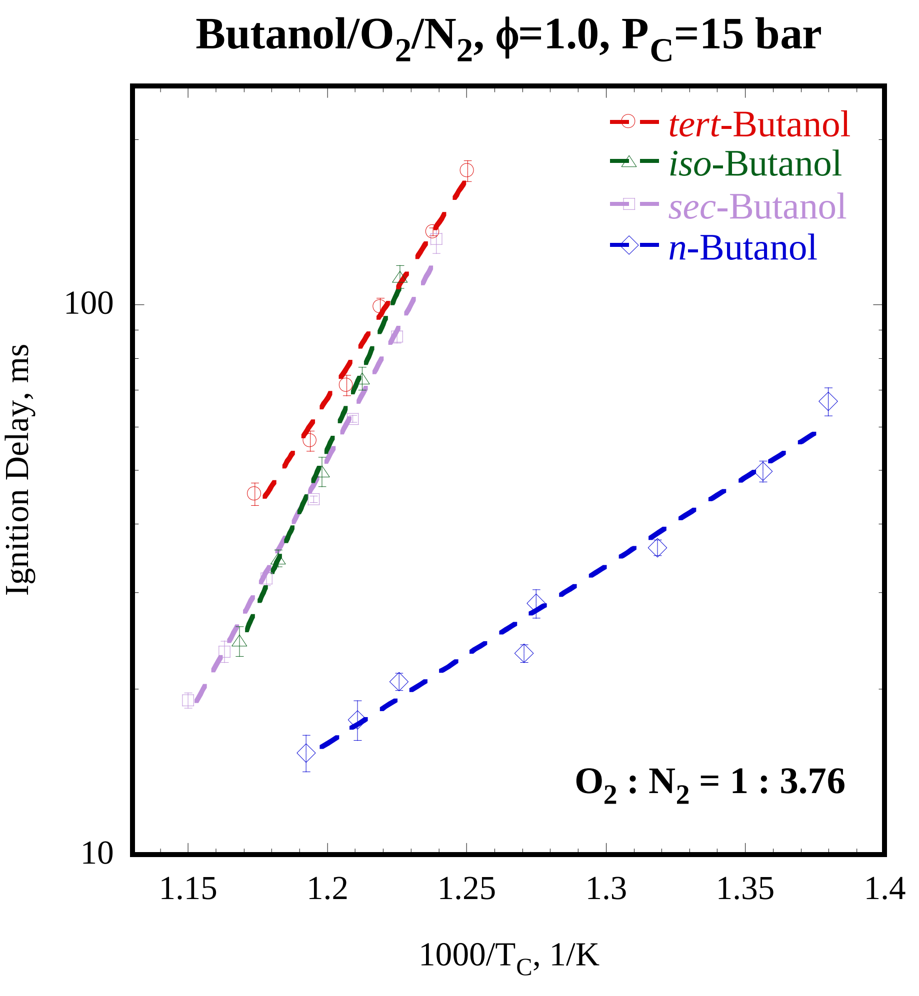
- No two-stage ignition or NTC region for any of the fuels under these conditions
- *sec*-, *tert*- and *iso*-butanol do not deviate significantly from the non-reactive pressure trace

Experimental Results (2)

- Non-reactive case replaces oxygen with nitrogen to eliminate oxidation reactions but maintain the specific heat ratio
- Pressure traces for *n*-butanol deviate from non-reactive case
- Indicates minor pre-ignition heat release



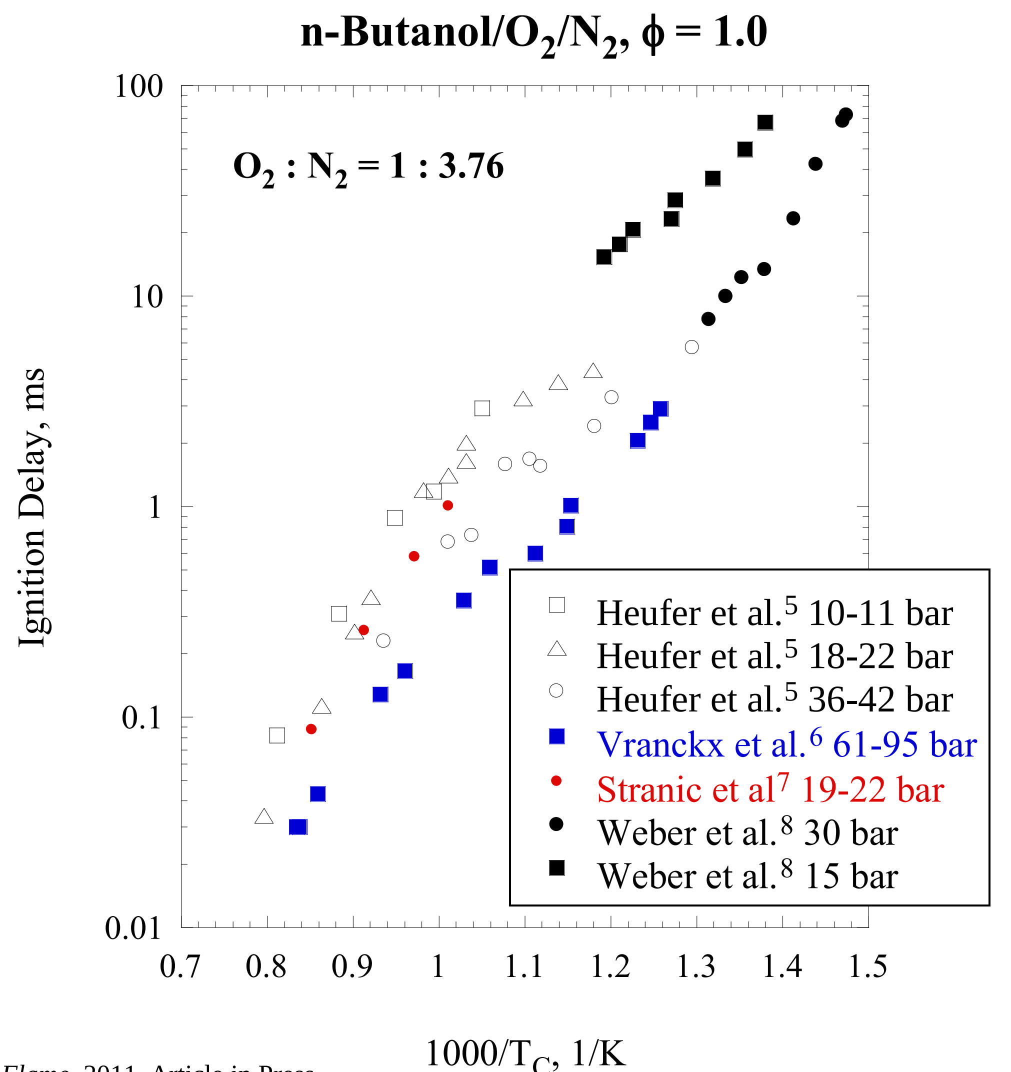
Experimental Results (3)



- *n*-Butanol is more reactive than *iso*-butanol and *sec*-butanol, which are more reactive than *tert*-butanol
- As the temperature goes down, *iso*-butanol and *sec*-butanol appear to become less reactive than *tert*-butanol

Experimental Comparisons

- Comparison of the data for *n*-butanol from this work and the work by Heufer et al.[5], Vranckx et al.[6], and Stranic et al.[7]
- More complete sets in the neighborhood of 800 K are necessary to "connect the dots"



8. Weber, B.W., Kumar, K., Zhang, Y., and Sung, C.J., *Combustion and Flame*, 2011, Article in Press doi:10.1016/j.combustflame.2011.02.005

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Types of Simulations

- Simulations of ignition delay are performed in CHEMKIN-PRO[9] using four mechanisms available in the literature
- Constant Volume, Adiabatic simulations have initial conditions set to the pressure and temperature conditions at TDC, and neglect heat loss to the reactor walls
- Variable Volume simulations have the reactor volume as a controlled function of time
  - Used to compute T_C by matching the experimental pressure trace during compression
  - Include effects of heat loss after compression by including parameters deduced from non-reactive experimental cases

9. CHEMKIN-PRO, Software Package, Ver. 15092, Reaction Design, San Diego, CA, 2008.

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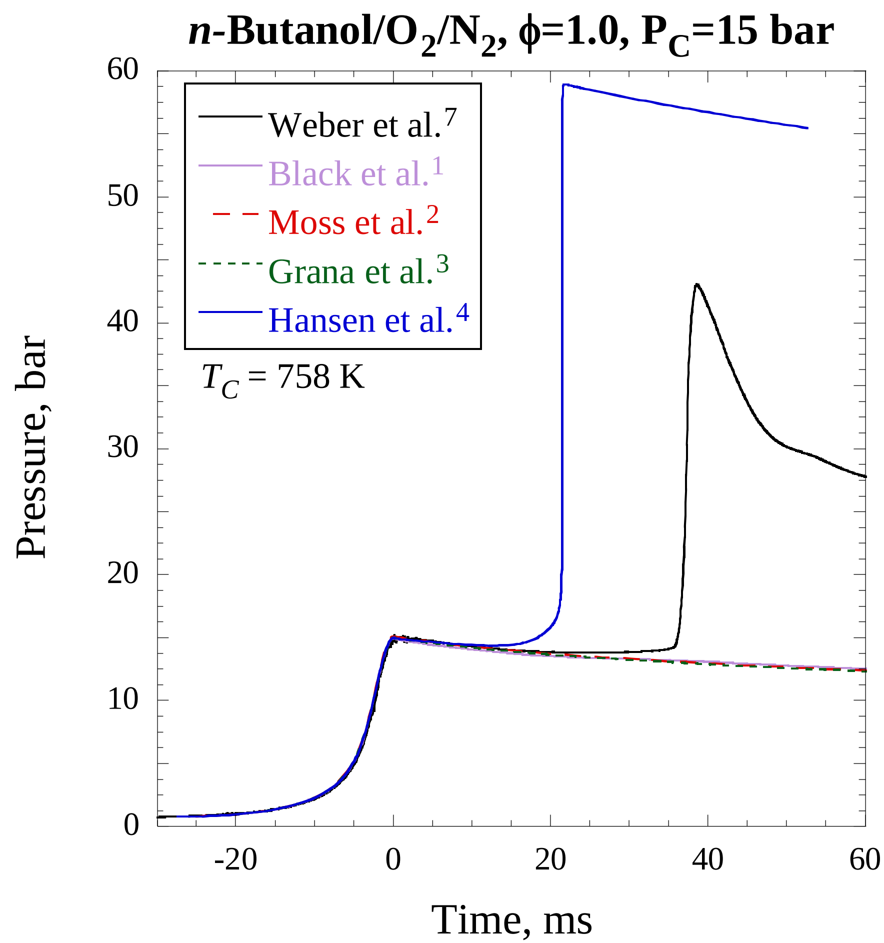
Variable Volume Simulations

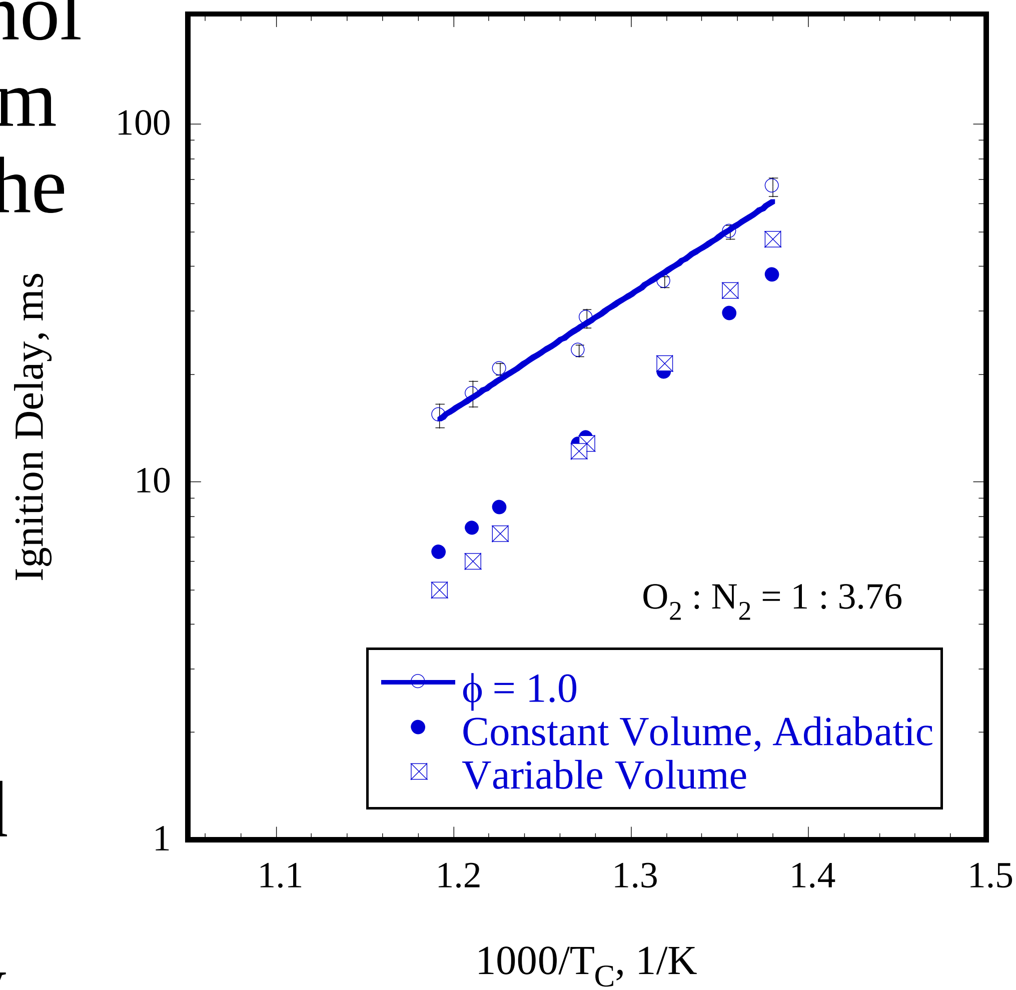
- Most of the reaction mechanisms do not have ignition near the experimental value despite matching the compression stroke quite well
- This is due to the fact that these do not include low temperature chemistry of butanol, the lack of which causes over-prediction of the ignition delay in this temperature range



Simulations of *n*-Butanol

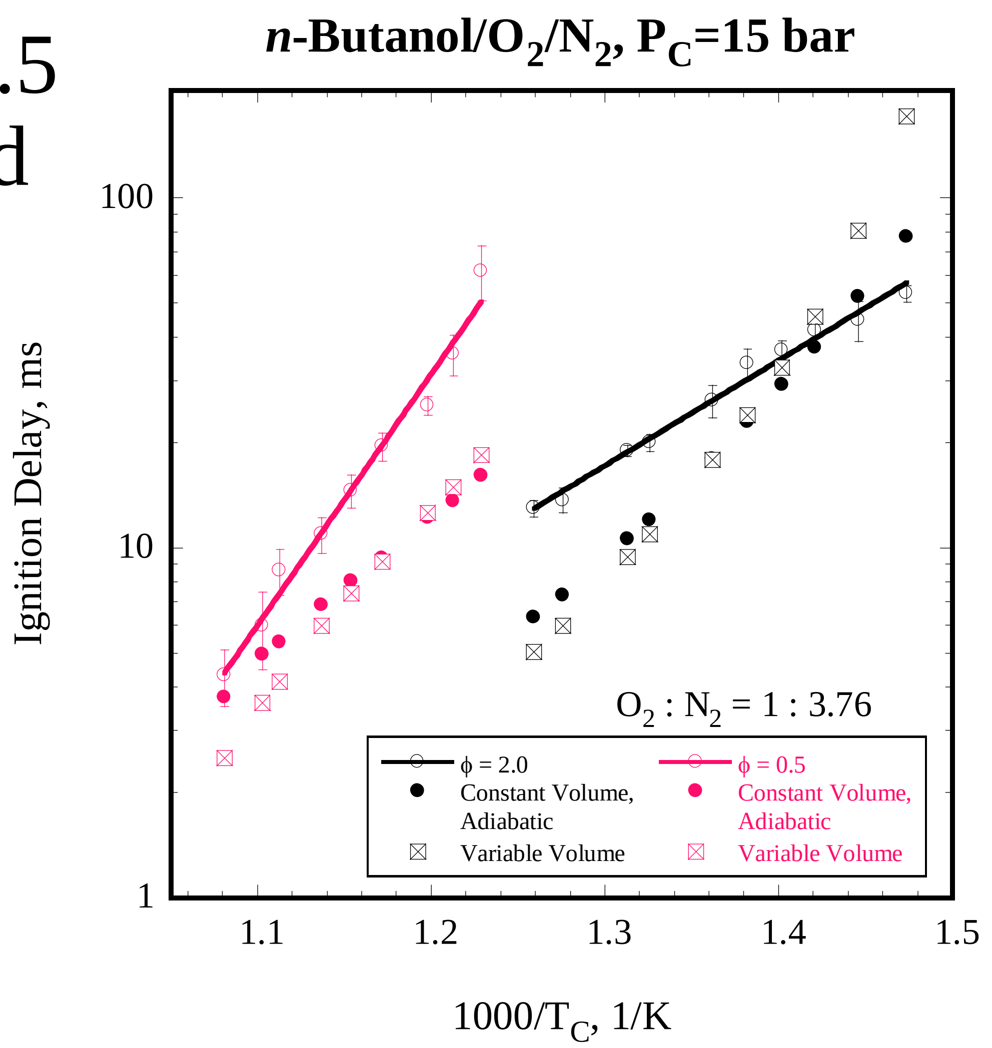
- Simulations for *n*-butanol with a newer mechanism (Hansen et al.[4]) agree the best of any tested mechanism
- Crossover point of constant volume, adiabatic simulations and variable volume simulations determined by balance of heat loss and chemical reactivity

n-Butanol/O_2/N_2, P_C=15 bar



Simulations of *n*-Butanol

- Agreement with $\phi = 0.5$ in air is reasonable and variable volume simulations improve the slope of the simulations
- Agreement with $\phi = 2.0$ experiments is somewhat worse, especially for variable volume cases



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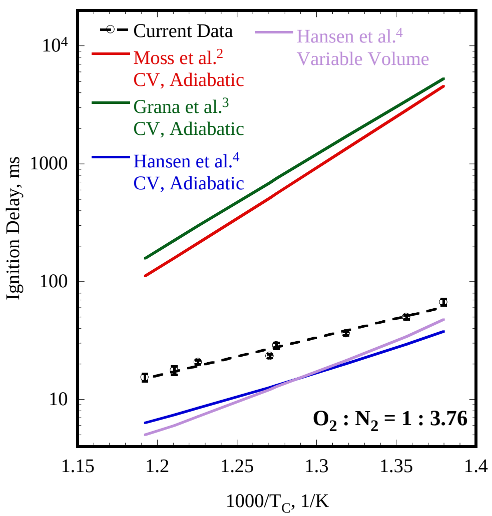
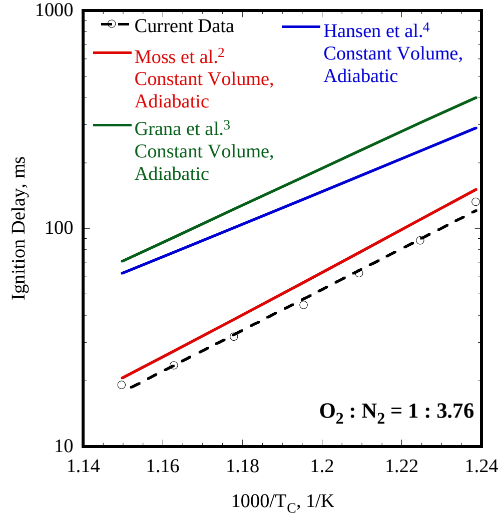
Simulations of Isomer Autoignition

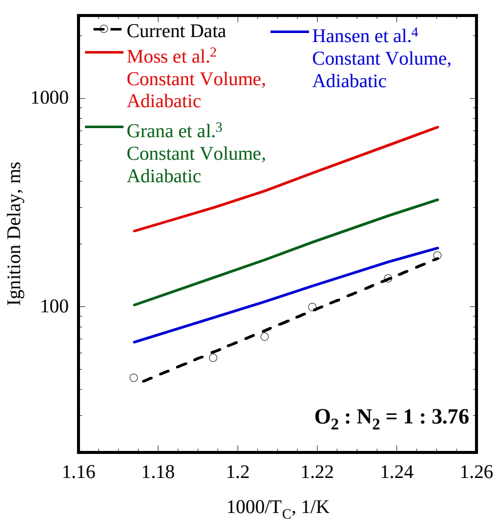
***n*-Butanol/O_2/N_2, ϕ=1.0, P_C=15 bar**



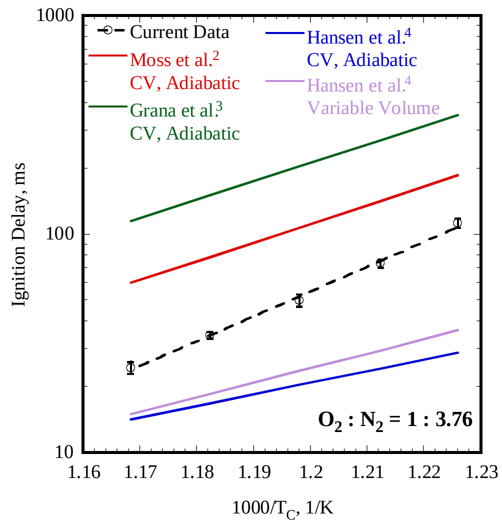
***sec*-Butanol/O_2/N_2, ϕ = 1.0, P_C=15 bar**



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

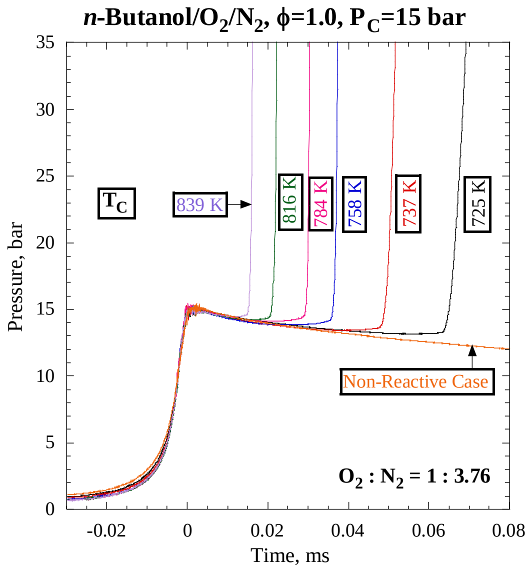


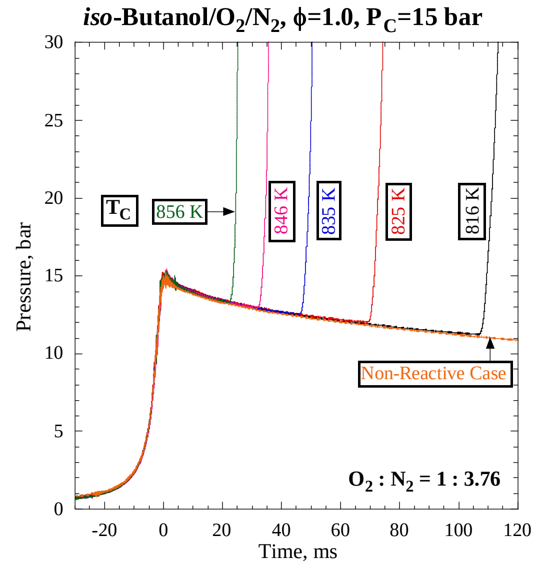
***iso*-Butanol/O_2/N_2, ϕ=1.0, P_C=15 bar**



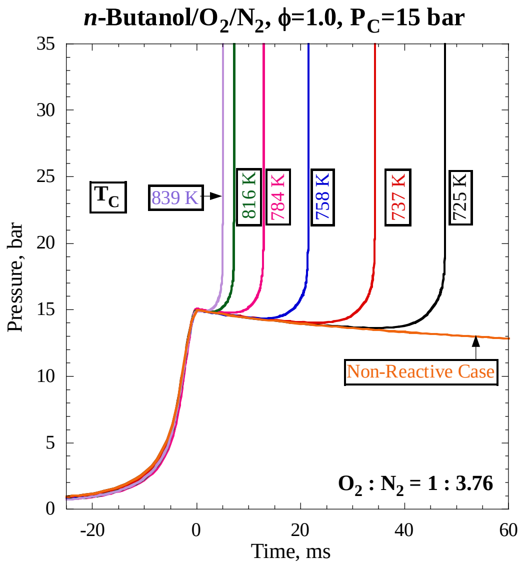
- Most mechanisms over predict the ignition delay of all the isomers, but the mechanisms by Moss et al.[2] and Grana et al.[3] do not include low temperature chemistry
- The mechanism by Hansen et al.[4] generally performs relatively better
- Variable Volume simulations improve results for *n*- and *iso*-butanol

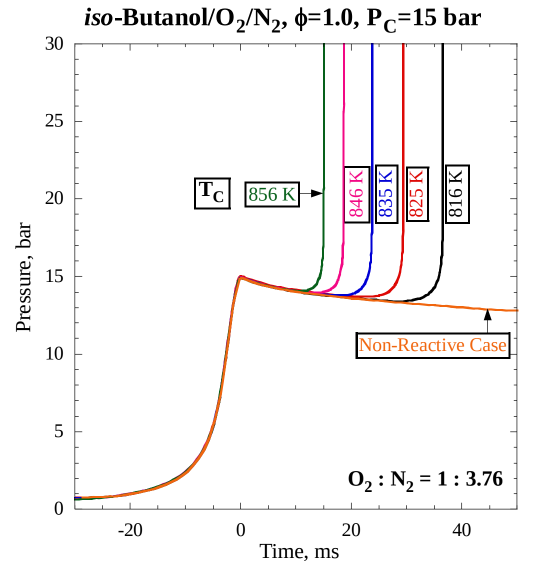
Simulations of Isomer Autoignition





Experiments





Simulations

Summary

- New autoignition delay data has been collected for all four isomers of butanol at elevated pressure and low to intermediate temperature conditions
- One (very recent) reaction mechanism predicts the ignition delay reasonably well for *n*-, *tert*- and *iso*-butanol, but gives somewhat poorer results for *sec*-butanol
- Future work will expand the pressure, temperature, and equivalence ratio range of the experiments

Acknowledgements

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