Validation of Kinetic Models of the Butanol Isomers at High Pressure using a Rapid Compression Machine

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Introduction and Objectives:

- Energy security and climate change are driving development of fuels from many new sources, particularly renewable bio-sources
- Accurate kinetic models are required to enable design of new engine technologies to optimize operation towards emerging non-petroleum derived fuels
- The butanol system is the smallest system with primary, secondary, and tertiary alcohols groups
- Goal is to provide validation data using a heated rapid compression machine (RCM) at high pressures and low to intermediate temperatures

Rapid Compression Machine:

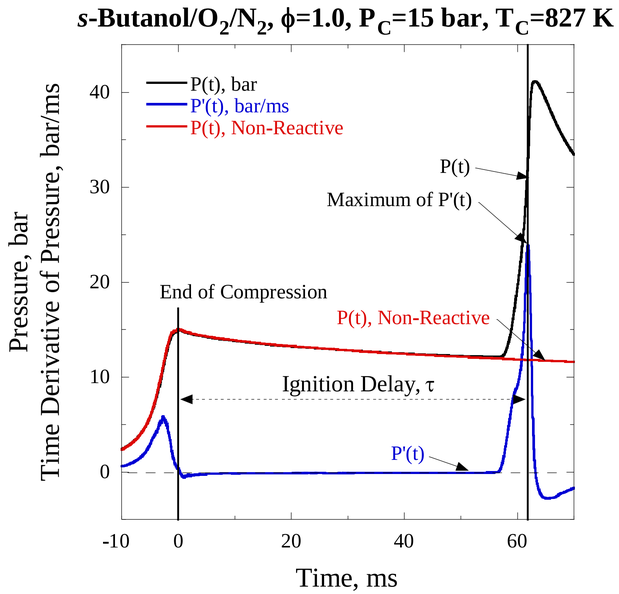
- Single, retractable, piston
- Piston is pneumatically driven and hydraulically stopped
- Piston is machined with crevices to control the roll-up vortex effect
- Pressure and temperature from TDC reported as compressed conditions
- The RCM has the ability to vary compressed temperature and compressed pressure independently

Experimental Conditions:

- Compressed Temperature Range: 680-860 K
- Compressed Pressure Range: 15 and 30 bar
- Equivalence Ratio: $\phi = 1.0, O_2 : N_2 = 1 : 3.76$

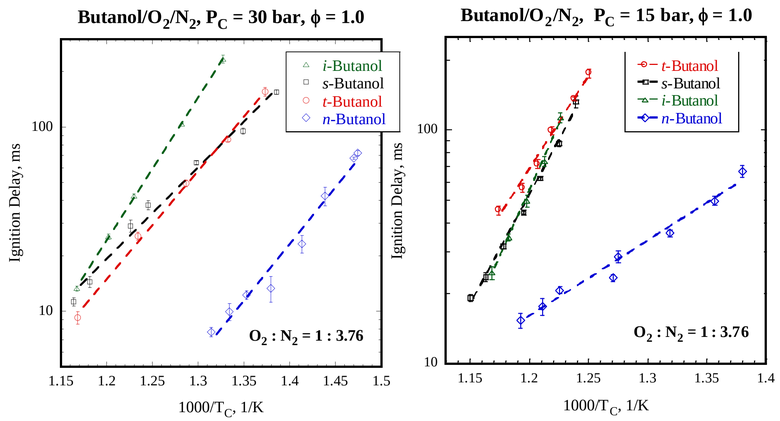
Experimental Analysis:

- Ignition is defined by the local maximum of the time derivative of the post-compression pressure
- Compressed temperature is computed using a non-reactive run, where oxygen in the mixture is replaced by nitrogen to eliminate reactions while maintaining a similar specific heat ratio

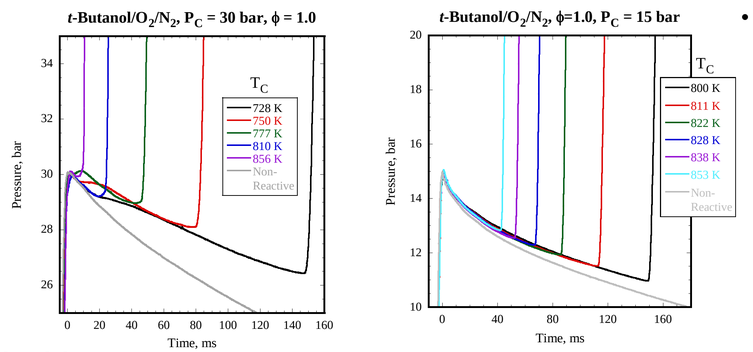


Experimental Results:

- Arrhenius plots of the ignition delay show a clear dependence on compressed pressure
- The order of reactivity of the isomers changes at higher pressure, from $n-$BuOH > $s-$BuOH ≈ $i-$BuOH > $t-$BuOH at 15 bar to $n-$BuOH > $t-$BuOH > $s-$BuOH > $i-$BuOH at 30 bar
- There does not appear to be a negative temperature dependence region in these data



- Pressure traces from the RCM do not show two-stage ignition for any of the isomers, in either pressure range
- However, there is significant pre-ignition heat release for $t-$butanol and $n-$butanol, but not as much for the other isomers



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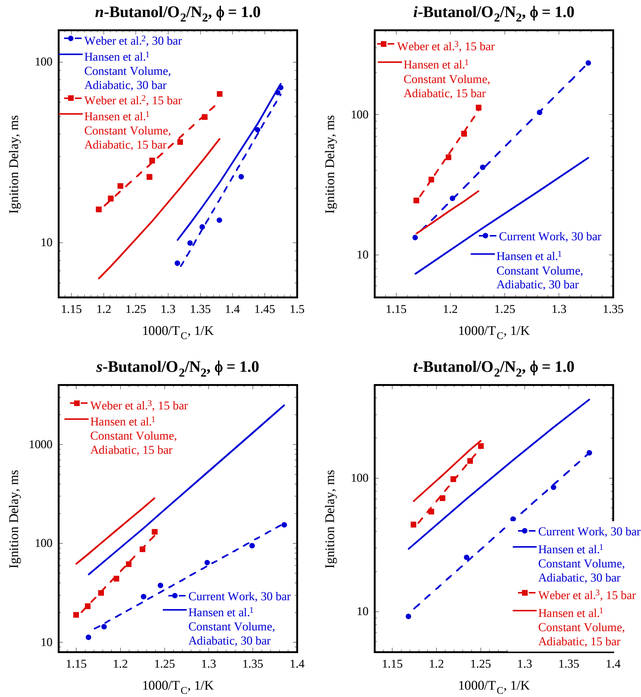
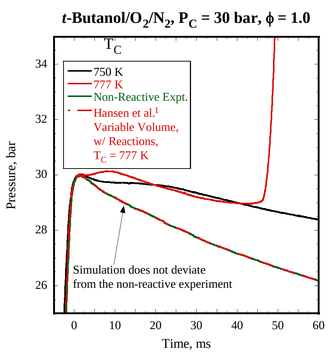
Modeling Results:

- Constant volume, adiabatic simulations were performed using one recent mechanism from Hansen et al.[1]
- Simulations do not capture the pressure dependence of $n-$butanol ignition delays, under predicting at lower pressure and over predicting at higher pressure
- The deviations from experiments for $i-$ and $s-$butanol are similar in both pressure ranges
- The discrepancy for t-butanol becomes worse at higher pressure – this may have to do with the effect of pre-ignition heat release



- The mechanism from Hansen et al.[1] is unable to reproduce the pre-ignition heat release behavior of $t-$butanol



References:
[1] 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
[2] Weber, B.W., Kumar, K., Zhang, Y., and Sung, C.J., *Combustion and Flame, Volume 158, Issue 5, Pages 809-819* doi:10.1016/j.combustflame.2011.02.005
[3] Weber, B.W. and Sung, C.J., *7th US National Combustion Meeting*, Georgia Institute of Technology, Atlanta, GA, March 20-23, 2011, paper RK13

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