

# 1 Experimental Procedure

The reactants used in this study, along with their purities, are shown in Table 1. To determine the relative proportions of each reactant in the mixture, the absolute mass of fuel, the equivalence ratio ( $\phi$ ), and the oxidizer ratio ( $X_{O_2} : X_{\text{inert}}$ , where  $X$  indicates mole fraction) are specified. *s*- and *i*-Butanol are liquid at room temperature and have relatively low vapor pressure; therefore, each is measured gravimetrically in a syringe to within 0.01 g of the specified value. *t*-Butanol is solid at room temperature (melting point: 25° C), and is melted before being handled in the same procedure as the other fuels. The 17 L mixing tank is vacuumed to an ultimate pressure less than 5 Torr prior to the injection of the liquid fuel through a septum. Proportions of O<sub>2</sub> and N<sub>2</sub> are added manometrically at room temperature. The preheat temperature of the RCM is set above the saturation point for each fuel to ensure complete vaporization. A magnetic stirrer mixes the reactants. The temperature inside the mixing tank is allowed to equilibrate for approximately 1.5 hours.

This approach to mixture preparation has been validated in several previous studies by withdrawing gas samples from the mixing tank and analyzing the contents by GC/MS, GC-FID, and GC-TCD.<sup>16,29,30</sup> These studies have verified the concentration of *n*-butanol, water, and *n*-decane, respectively. In addition, both the work by Kumar et al. [1] on *n*-decane and the study of Weber et al. [2] on *n*-butanol confirmed that there was no fuel decomposition over the course of a typical set of experiments. Furthermore, within this study, each new mixture preparation is checked against previously tested conditions to ensure reproducibility.

Table 1 shows the experimental conditions considered in this study. The compressed pressure conditions have been chosen to match the previous *n*-butanol study [2], but also to provide data in regions not covered extensively in previous work. In addition, the fuel loading conditions have been chosen to complement previous work; the studies by Stranic et al. [3] and Moss et al. [4] used relatively dilute mixtures, so we have included higher fuel loading conditions. Furthermore, the compressed temperature conditions we have studied ( $T_C = 715 - 910$  K) have not been examined in any other study, to our knowledge.

Table 1: Experimental Conditions and Reactant Purities

Reactant (Purity)					Equivalence Ratio $\phi$	Compressed Pressure $P_C$ (bar)
<i>s</i> -butanol (99.99%)	<i>i</i> -butanol (99.99%)	<i>t</i> -butanol (99.99%)	O <sub>2</sub> (99.999%)	N <sub>2</sub> (99.995%)		
Mole Percentage						
3.38			20.30	76.32	1.0	15
3.38			20.30	76.32	1.0	30
	3.38		20.30	76.32	1.0	15
	3.38		20.30	76.32	1.0	30
		3.38	20.30	76.32	1.0	15
		3.38	20.30	76.32	1.0	30
		1.72	20.65	77.63	0.5	30
		6.54	19.63	73.83	2.0	30

Each compressed pressure and temperature condition is repeated at least six times to ensure repeatability. The mean and standard deviation of the ignition delay for all runs at each condition are calculated. As an indication of repeatability, the standard deviation is less than 10% of the mean in every case. Representative experimental pressure traces for simulations and presentation are then chosen as the closest to the mean.

## 2 Experimental Results

Fig. 1 shows the ignition delays of the four isomers of butanol measured in the RCM, at compressed pressure of  $P_C = 15$  bar for stoichiometric mixture in air. The dashed line for each isomer is a least squares fit to the data. The vertical error bars are two standard deviations of the measurements of the ignition delay. The standard deviation is computed based on all the runs at a particular compressed temperature and pressure condition. A conservative estimate of the uncertainty in  $T_C$  was calculated in our previous work to be approximately 0.7–1.7%. Due to the similar nature of these experiments, and the similar properties of the fuels, this estimate is considered to be valid for this study as well.

Fig. 2 demonstrates the differences in reactivity between the isomers for stoichiometric fuel/air

mixtures at compressed pressure  $P_C = 15$  bar. *n*-Butanol is clearly the most reactive, followed by *s*- and *i*-butanol, which have very similar reactivities in this temperature and pressure range. *t*-Butanol is the least reactive.

The order of reactivity found in the RCM at 15 bar agrees with the shock tube study at higher temperatures (approximately 1275–1667 K) and lower pressure (1.5 atm) by Stranic et al. [3] but differs slightly from the studies of Moss et al. [4] who measured ignition delays in a shock tube near 1.5 atm and between 1275–1400 K, and Veloo and Egolfopoulos [5] who measured atmospheric-pressure laminar flame speeds. In particular, Moss et al. [4] and Veloo and Egolfopoulos [5] found distinct differences in reactivity between *s*- and *i*-butanol, but the present study and the study by Stranic et al. [3] found that they were nearly indistinguishable in terms of reactivity under the conditions investigated. In addition, Stranic et al. [3] noted some disagreement between their shock tube ignition data and the data of Moss et al. [4] but their attempts to isolate the cause could not discern what the difference might be caused by.

Further, the order of the reactivity of the butanol isomers also shows complex temperature and pressure dependence. This is corroborated by the results shown in ???. In ??, the order of reactivity is different than in ??, where the only variation between the plots is the compressed pressure; in ?? the compressed pressure is  $P_C = 30$  bar. ?? shows *i*-butanol to be the least reactive, *s*-butanol to be less reactive than *t*-butanol (but similar), and *n*-butanol to be the most reactive. Interestingly, the results of the shock tube study by Stranic et al. [3] differ from those in the current study at higher pressure (despite the agreement at lower pressure). In their study, Stranic et al. [3] found *i*- and *n*-butanol to have similar reactivity near 43 atm. in the temperature range of 1020–1280 K, whereas in the present study we find *i*-butanol to be the least reactive of all four isomers at a pressure of 30 bar and over the temperature range (715–910 K) investigated.

The fact that *t*-butanol becomes relatively more reactive than *i*- and *s*-butanol as pressure increases is surprising at first glance, and the reasons are not immediately apparent. Closer examination of the pressure traces for each experiment gives one clue as to the cause of the increased reactivity. ?? shows the pressure traces for the *t*-butanol experiments at 15 bar for stoichiometric

mixtures in air. It is evident that there is some pre-ignition heat release, because the reactive pressure trace diverges from the non-reactive case prior to the ignition event. Of the other isomers of butanol, only *n*-butanol shows any visible heat release prior to the main ignition event at 15 bar.

?? shows the pressure traces for *t*-butanol experiments at 30 bar for stoichiometric mixtures in air. The effect of pre-ignition heat release is even more striking in this figure, with substantial changes in the slope of the pressure trace during the reactive runs. Comparing to the pressure traces of the other isomers once again shows that the magnitude of the pre-ignition heat release for *t*-butanol is much greater. Despite the appearance of early pressure rise, which is typically indicative of two-stage ignition and low temperature chain branching, we do not find a negative temperature coefficient region in terms of the ignition delay response for any *t*-butanol experiments. Therefore, we adopt the phrase "pre-ignition heat release" rather than "two-stage ignition" in this work.

In an effort to understand the reactions causing the pre-ignition heat release, further experiments are conducted for *t*-butanol at  $P_C = 30$  bar, for equivalence ratios of 0.5 and 2.0 in air. ?? shows Arrhenius plots of the ignition delays for the three equivalence ratios. As with the previous *n*-butanol experiments at 15 bar [2]  $\phi = 0.5$  is the least reactive and  $\phi = 2.0$  is the most reactive. The slopes are similar, indicating that the overall activation energies are similar for the conditions investigated.

A more interesting comparison is of the pressure traces of the three equivalence ratios. It is clear from Figures ??, ??, and ?? that there are qualitative differences in the pre-ignition heat release between the three equivalence ratios. This is most likely due to the effect of the increased (reduced) fuel mole fraction in the  $\phi = 2.0$  ( $\phi = 0.5$ ) case, since the mole fraction of fuel is changed by +93% (-49%) compared to the  $\phi = 1.0$  case, while the mole fraction of oxygen changes by only -3% (+2%) compared to the  $\phi = 1.0$  case, as shown in Table 1. Therefore, it appears that the qualitative change in pre-ignition behavior is due to the change of fuel mole fraction, where higher fuel loading promotes pre-ignition heat release.

### 3 Simulation Results

Simulations are performed with the kinetic mechanism from Sarathy et al. [6] and a recent mechanism discussed in Hansen et al. [7] and Merchant et al. [8] that is denoted as the MIT mechanism hereafter. Other recent mechanisms, such as the mechanism from Frassoldati et al. [9] do not include low temperature chemistry and are therefore unable to reproduce the low-temperature ignition delays measured in this study. The study by Sarathy et al. [6] validated their model for a wide set of the existing experimental data. In terms of ignition delays, this included the data from the study of Stranic et al. [3] up to 48 atm, our previous study on *n*-butanol [2], and the data being published in this study at 15 bar. Importantly, the mechanism of Sarathy et al. [6] was validated only for the 15 bar RCM data for all four isomers, but not the 30 bar data also being published here. The MIT mechanism [7, 8] was validated for *i*-butanol experiments, including pyrolysis and low pressure premixed flames; although the model includes all four isomers of butanol as reactants, it has not been optimized for any of the isomers except *i*-butanol.

Figures ?? and ?? show comparison of the VPRO simulations with the experimental data using the mechanism of Sarathy et al. [6]. As Sarathy et al. [6] showed in their work (and as we show here in ??), they found good agreement of the model predictions with the present RCM data at 15 bar. At  $P_C = 30$  bar (??), similar degree of agreement is found for *t*-butanol and *s*-butanol compared to  $P_C = 15$  bar, although the *s*-butanol results are under-predicted at high temperature and over-predicted at low temperature. While the model of Sarathy et al. [6] is able to well capture the overall activation energy of *i*-butanol, it under-predicts the experimental data by about a factor of 2–3. The *n*-butanol data are over-predicted by about a factor of 1.5. Nevertheless, this agreement is quite good, especially considering that the model is not validated for these conditions.

VPRO simulations for *n*- and *s*-butanol (and also some conditions for *t*-butanol) using the MIT mechanism [7, 8] do not ignite during the duration of the simulations (the same as the experimental duration), and therefore no simulations are shown for these fuels. In ??, VPRO simulations at 15 and 30 bar using both mechanisms are shown for *i*-butanol. It is seen that the mechanism from Sarathy et al. [6] is in better agreement at 15 bar. However, at 30 bar the MIT mechanism [7, 8]

over-predicts the ignition delay (as at 15 bar), while the Sarathy et al. [6] mechanism under-predicts the ignition delay. The reason for these diverging predictions will be explored and discussed below.

The agreement of the mechanism by Sarathy et al. [6] with the off-stoichiometric mixtures of *t*-butanol is also quite good, as shown in ???. Figures ??--?? show more detailed comparisons of the simulated pressure traces and the experimental results, for similar temperatures at the three equivalence ratios, respectively. Clearly, the simulations also exhibit some pre-ignition heat release. In general, the simulations qualitatively predict the pre-ignition heat release behavior at all three equivalence ratios. The  $\phi = 0.5$  case has the least heat release and the  $\phi = 2.0$  case has the most. Although the simulations are unable to match the heat release behavior quantitatively, they match the experimental ignition delays quite well. Considering the model is not validated for this temperature, pressure, and equivalence ratio regime, the mismatch of the pre-ignition behavior may not be of critical importance, depending on the application.