The detailed conclusions relevant to each of the experimental works considered in this study are presented in their respective chapters. The following gives a general summary of the previous works and provides recommendations for future work, including descriptions of ongoing investigations using a new sampling system.

0.1 Conclusions

The studies reported in this work are the first experiments exploring the low-to-intermediate temperature autoignition of the butanol isomers. These data provide a unique look into the behavior of these fuels under engine-relevant conditions. For the stoichiometric condition at two pressures, n-butanol is the most reactive of the isomers. However, the order of the reactivity of the other isomers depends on the prevailing pressure conditions during the induction period. t-butanol becomes the second most reactive isomer at the higher pressure condition and shows unique behavior during the induction period. Analysis of a detailed kinetic model for combustion of the butanol isomers is conducted to elucidate the controlling chemistry during the autoignition of the four isomers, and this analysis indicates that the different behavior of t-butanol is due to a unique set of controlling reactions for t-butanol.

New experimental autoignition data collected for i-butanol are used to compare the important pathways of butanol combustion predicted by two recent chemical kinetic mechanisms. The reactivity of each mechanism is controlled by a different radical (hydroxyl vs. hydroperoxyl) because the main fuel reaction pathways are also different. However, neither model is able to predict properly the dependence of the ignition delay on initial oxygen concentration. Overall, the importance of peroxy chemistry is highlighted in this work and further computational and experimental studies are needed to better understand the role of peroxy species in the autoignition of alcohols.

An existing model for the combustion of i-pentanol is updated with newly calculated rate coefficient estimates and newly discovered reaction pathways. The model is compared to new and existing experimental data from RCMs and STs and predicts the high-temperature ignition delays fairly

well. In addition, the model qualitatively predicts the slow pressure rise noted during the induction period of low-temperature autoignition. However, the model is not able to predict quantitatively the ignition delay for off-stoichiometric mixtures of i-pentanol and air at low temperatures.

0.2 Fast Sampling System

The fast sampling system (FSS) used in this work is a commercial system supplied by SME-Tec Gmbh. from Germany. The FSS is composed of two parts, the gas sampling valve (GSV) and the Controller. A schematic of the GSV is shown in **??**. Gases are admitted from the reaction chamber into the heated carrying tubes through the poppet-style valve on the left of the GSV. The sampled gases are then conducted through the GSV outlet into the 15 mL sampling bottle.

A schematic of the GSV assembly is shown in **??**. The GSV is mounted to the RCM by a custom-made end plug. The reaction chamber is sealed by an O-ring on the small- and large-diameter portions of the GSV. The depth that the GSV is inserted into the reaction chamber is adjustable by adding or removing shims in the end plug assembly. The insertion depth is chosen so that the tip of the GSV is outside the boundary layer on the end wall.

The portion of the GSV protruding into the reaction chamber has minimal effect on the homogeneity of the reaction chamber. Moreover, the removal of samples has minimal effect on the measured ignition delay. This has been verified experimentally by measuring the ignition delay with and without the GSV present, and with and without sampling occurring. In both cases, the difference in ignition delay was statistically insignificant for $\alpha = 0.05$.

The close-open-close (COC) cycle of the GSV is controlled by a mass-spring system. The poppet face is connected to a rod running the length of the GSV and connected to the mass at the rear of the valve. To open the poppet, the mass is accelerated forward by passing current through the coil around the mass. The rod is also connected to a spring that is used to restore the poppet to its original position after being extended.

The GSV has an adjustable COC time, by adjusting the distance the plate is allowed to move.

Furthermore, the GSV has the ability to measure the displacement of the mass, allowing the direct measurement of the COC time and the absolute time of opening.

The GSV controller is triggered by a 5 V signal from the cDAQ. The timing of the trigger signal is controlled by the LabView VI. The pressure signal from the reaction chamber is read from the cDAQ in 1 ms chunks in a loop. On each loop iteration, the maximum pressure is checked against a desired trigger pressure; when the reaction chamber pressure exceeds the trigger pressure, the cDAQ sends the trigger to the GSV controller. The GSV controller has an adjustable delay (4.5 ms to 70 ms) that is used to control the timing of the opening of the GSV during the induction period. The absolute opening time of the GSV is thus dependent on three parameters:

1. The cable delays from the PC to the cDAQ; from the cDAQ to the GSV controller; and from the GSV controller to the GSV itself

2. The processing time of the LabView VI

3. The delay set in the GSV controller.

However, since the absolute opening time of the GSV can be measured by the signal sent from the GSV to the controller (and thence to the cDAQ), the uncertainty in the opening time is actually quite small, and is related to the cable delay in sending the COC signal from the GSV to the cDAQ and the precision of the A/D conversion in the cDAQ. The uncertainty of the absolute opening time is thus estimated as $\pm 1\,\mu$s.

Verify this number

Furthermore, the correspondence of the COC signal from the valve with the physical valve movements has been experimentally verified by high speed video. Frames from these videos are shown in **??**. The frames show that the opening and closing times of the valve face correspond closely with repeatable points in the peak of the voltage.

GSV Video

0.2.1   Experimental Procedure

Prior to an experiment, the GSV and sampling bottle are vacuumed to less than 1 torr. The reaction chamber is vacuumed and filled in the same procedure as described previously, and the compression is triggered. For a given trigger pressure and controller delay, the GSV opens at some time after the EOC and removes a gas sample from the reaction chamber. The sample is diluted by high purity helium. Then the sample bottle is disconnected from the GSV and transported to the Gas Chromatograph/Mass Spectrometer, where the sample undergoes analysis.