

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.

Finally, new experimental data is collected for MCH at compressed pressure of  $P_C = 50$  bar. These data at three equivalence ratios showed that the lean case is the most reactive and the rich case is the least reactive (in terms of the inverse of ignition delay) because the equivalence ratio is changed by varying the initial oxygen concentration at constant initial fuel concentration. In addition, the data include the characteristic NTC region for the rich and stoichiometric case, but the ignition delay is too short to resolve the NTC for the lean case. Finally, a sampling system is upgraded and used to identify and quantify important intermediate species during the induction period of MCH ignition.

An existing model for MCH combustion was updated with new reaction rate coefficient estimates and new reaction pathways. The new model shows good agreement with the overall ignition delays of several datasets including the new experimental data collected in this work. However, the first stage ignition delay is uniformly under predicted. Pathway and sensitivity analysis are used to identify the important reactions in the model, including reactions of the primary fuel radicals and the peroxy radicals formed from the primary fuel radicals.

## 0.2 Future Work

The high-pressure autoignition chemistry of alternative fuels is similar in many ways to the chemistry of traditional fuels, but there are a number of subtle distinctions outlined through the course of this work. There remains much work to do to characterize these subtleties so that predictive chemical models can be constructed for alternative fuels. In particular, the low-temperature reactions of alternative fuel radicals with oxygen molecule are still poorly understood and further study is required to determine appropriate reaction rate coefficients and pathways.

These future studies include using the new rapid sampling system to investigate other alternative

fuels to measure the important species in the autoignition of those fuels. In addition, a local sampling system could provide further characterization information about the global sampling system developed in this work. A brief description of some preliminary characterization of the local sampling system is provided in ??.

The sampling system developed in this work is of course not restricted to studying alternative fuels, and speciation studies of other chemicals would be useful to improve the models of those fuels. The speciation studies conducted by removing gas samples could be compared to similar studies using optical techniques.