

0.1 Background

The world relies heavily on combustion to provide energy in useful forms for human consumption; combustion currently represents over 80% of the world energy production [1] and is predicted to decrease in importance only slightly by 2040 [2]. In particular, the transportation sector accounts for nearly 40% of the energy use in the United States and of that, more than 90% is supplied by combustion of fossil fuels [3]. Unfortunately, emissions from the combustion of traditional fossil fuels have been implicated in a host of deleterious effects on human health and the environment [4] and fluctuations in the price of traditional fuels can have a negative impact on the economy [5].

Despite its shortcomings, combustion is currently the only energy conversion mechanism that offers the immediate capability to generate the sheer amount of energy required to run the modern world. Since we cannot eliminate combustion as an important energy conversion method, we must instead ameliorate the shortcomings of a primarily combustion-based energy economy. A two-pronged approach has developed to achieve the necessary improvements. These prongs include: 1) development of new fuel sources and 2) development of new combustion technologies. First, using new sources of fuel for combustion-based energy conversion can reduce the economic impact of swings in the price of current fuels, in addition to potentially reducing emissions. Second, using new combustion technologies can reduce harmful emissions while simultaneously increasing the efficiency of combustion processes, thereby reducing fuel consumption.

Many new sources of fuels have been investigated recently. The most promising of these in the long term are renewable biological sources, which are used to produce fuels known as biofuels. The advantage of biofuels over traditional fuels lies in their feedstocks. Whereas traditional fuel feedstocks generally require millions of years to be produced, biofuel feedstocks are replenished on an annual basis. Furthermore, biofuels offer the potential to offset carbon emissions created from their combustion by reusing the emitted carbon to grow the plants from which the fuels are produced.

However, the combustion properties of biofuels may be substantially different from the tra-

ditional fuels they are intended to replace. This makes it difficult to quickly switch the energy economy to biofuels and necessitates medium-term investigation of alternative sources for traditional fuels. These sources include shale oil and liquefied coal, which have different chemical compositions than traditional fuel sources and therefore fuels made from these alternative sources have different combustion properties. Collectively, all of these fuels created from non-traditional sources are known as alternative fuels.

In addition to new fuel sources, new engine technologies are rapidly being developed. These include engines capable of operating in favorable combustion regimes, such as so-called Low Temperature Combustion (LTC) engines and Homogeneous Charge Compression Ignition (HCCI) engines. These devices avoid regions in the temperature-equivalence ratio space where combustion generates a large amount of emissions and operate in regions where efficiency is maximized and emissions are reduced. Other devices, such as the well-known catalytic converter, operate on the exhaust after it leaves the cylinder to improve emissions characteristics.

Neither of these approaches is able to mitigate all of the negative impacts of combustion by itself. By switching to biofuels but retaining the same engines, the efficiency and emissions targets may not be met; by only developing new engines, our sources of fuel will continue to cause economic distress, turmoil, and negative effects on the environment. It will take a concerted effort to bring these two pathways of innovation together.

Unfortunately, there are many roadblocks on the way to combining new fuels in new engines. For instance, one can imagine the design and testing process of new engines and fuels becoming circular: the “best” alternative fuel should be tested in the “best” engine, but the “best” engine depends on which is selected as the “best” alternative fuel. One way to cut this circle short is by employing computer-aided design and modeling of new engines with new fuels to design engines to be fuel-flexible. Accurate and predictive models of combustion processes can be used to computationally test the efficacy of new technologies and fuels before they undergo expensive real-world testing. The key to this process is the development of accurate and predictive combustion models.

Substantial work has been put forth recently to develop and validate predictive combustion

models for several alternative fuels. These studies include calculation and measurement of reaction rate coefficients, measurement of global and local combustion properties, and development of model construction methodologies. Nevertheless, much of the work is still ongoing, and there is substantial room for extending the state-of-the-art knowledge, especially at high-pressure conditions relevant to combustion in engines.

A combustion model for the combustion of a given fuel in a given device must necessarily accurately model the complete interaction of the operating elements of the device. This includes sub-models for the chemical reactions that the fuel and oxidizer undergo as well as the interaction of the fuel/oxidizer mixture with the operation of the device. The first of these is known as a chemical kinetic model or reaction mechanism; the second typically includes such effects as turbulence interaction, heat transfer, liquid spray dynamics, fluid mechanics, etc., each of which are typically modeled independently.

Chemical kinetic models for the combustion of large molecules are typically built in a hierarchical fashion, as described by Westbrook and Dryer [6]. That is, the model for the combustion of heptane contains the model for the combustion of hexane added to the model of combustion for pentane, and so on down to the models for hydrogen and carbon monoxide combustion. Therefore, it is important to thoroughly validate the models for smaller species while building models of higher hydrocarbons and other molecular types. Work has been ongoing to explore the chemistry of small molecules for decades. Notable recent kinetic mechanisms to emerge from this work include the GRI-Mech series of mechanisms (most recently, version 3.0 [7]), USC-Mech v2 [8], and the AramcoMech series of mechanisms, most recently version 1.3 [9].

In addition, validation of kinetic models for the combustion of larger fuels has proceeded in parallel with the small molecule chemistry. Given their projected importance to combustion, one focus of the larger molecule work has naturally been on biofuels. These biofuels typically include chemical species such as alcohols and esters – neat alcohols can be used as fuels, while esters are typically found as components of biodiesel fuels. A review by Kohse-Höinghaus et al. [10] covers much of the experimental data available until 2010. Since then an enormous amount of data has

been produced for both alcohols and esters. Since the focus of this study is on alcohols, I will highlight alcohols in the following sections.

Model construction and validation has also been focused on alternative “traditional” fuels, that is, fuels that are chemically similar to traditional fuels but produced from alternative sources such as shale oil or coal liquefaction. Traditional fuels and alternative “traditional” fuels typically contain hundreds or thousands of chemical components. This makes building and using models containing every species present in the fuel intractable on current computer hardware. Therefore, a more useful approach to building models for these fuels is to define a surrogate fuel. Surrogate fuels are made of a limited number of chemical components to ensure that model building and use are tractable, but the components are chosen so that the surrogate fuel faithfully reproduces the physical and chemical properties of the real fuel.

Much progress has been made recently to construct surrogates for typical transportation fuels. For instance, work on diesel surrogate formulation has recently been reviewed by Pitz and Mueller [11], work on gas turbine fuel surrogates has been briefly summarized by Dooley et al. [12], and work on gasoline surrogates has been summarized in the work of Anand et al. [13] and Pitz et al. [14]. One typical component class in the surrogate formulations is a cycloalkane or alkylcycloalkane (collectively known as naphthenes), due to this class’ presence in nearly all transportation fuels [14–17]. One particular cycloalkane, methylcyclohexane (MCH), has been suggested in several surrogate formulations, including those by Bieleveld et al. [18] and Naik et al. [19]. Recent work on MCH combustion will also be highlighted in the following sections.

0.2 Recent Work on the Combustion of Alcohols

Among the alcohols being considered as biofuels, two criteria are typically used to judge the suitability of a species: 1) its ease of production and 2) its potential as a “drop-in” replacement for current fuels. Because of these criteria (among others), much research recently has focused on the isomers of butanol, the C₄ alcohols, and *i*-pentanol, a C₅ alcohol. This is because these fuels are

easy to produce by a number of biological pathways [20] and offer similar properties as gasoline for use in typical automotive transportation applications [21, 22].

One of the most common biofuels currently in use is ethanol ($\text{C}_2\text{H}_6\text{O}$). Although ethanol is ubiquitous at gasoline pumps, it suffers from several disadvantages that suggest it needs to be replaced [23]. In particular, ethanol has a much lower energy density than gasoline, reducing volumetric fuel economy, and ethanol is typically produced from crops that would otherwise be used as food sources [24].

n-Butanol has recently been identified as one of a suite of so called “second generation” biofuels intended to supplement or replace the “first generation” biofuels currently in use, such as ethanol [25, 26]. The second generation biofuels will help alleviate some of the problems identified with the first generation biofuels, including concerns about feedstocks. In addition to the normal (*n*) isomer, there are three other isomers of butanol—*s*-, *i*-, and *t*-butanol. Biological production pathways have been identified for *n*-, *s*-, and *i*-butanol [26, 27], but *t*-butanol is a petroleum derived product. Nevertheless, *t*-butanol is currently used as an octane enhancer in gasoline.

In the last five years, research into the combustion characteristics of the isomers of butanol has exploded, so exemplary references are provided here except for the articles of particular interest to this work. In addition to applied engine research [28–30], fundamental combustion measurements have been made using many different systems. These include laminar flame speeds [31], jet-stirred reactor chemistry [32], low-pressure flame structure [33, 34], atmospheric pressure flame structure [35], pyrolysis [36–38], flow reactors [39, 40], and ignition delays, which will be discussed in more detail shortly. Other researchers have measured or calculated the reaction rate constants of reactions of butanol with various radicals, including OH [41–49], HO_2 [50–52], and CH_3 [53, 54].

Several studies of ignition delay of the butanol isomers have been conducted in both shock tubes and RCMs, including work in shock tubes by Moss et al. [55], Black et al. [56], Noorani et al. [57], Zhang et al. [58], Stranic et al. [59], Yasunaga et al. [60], Heufer et al. [61], Vranckx et al. [62], and Zhu et al. [63] and work in RCMs by Weber et al. [64], Weber and Sung [65], Weber et al. [66], and Karwat et al. [67]. These studies have covered a wide range of temperature-pressure regimes,

from 1–90 bar and 675–1800 K.

Among the shock tube ignition studies, Moss et al. [55] have done measurements for all four isomers of butanol at 1 and 4 bar and 1200–1800 K, over equivalence ratios of $\phi = 0.5$, 1.0, and 2.0 and fuel mole percents of 0.25, 0.5, and 1.0 %. Black et al. [56] investigated autoignition for *n*-butanol from 1100–1800 K and 1, 2.6, and 8 atm over $\phi = 0.5$, 1.0, and 2.0 and fuel mole percentages of 0.6, 0.75, and 3.5 %. Noorani et al. [57] investigated the ignition delays of the primary alcohols from C₁–C₄ at pressures of 2, 10, and 12 atm under dilute conditions for equivalence ratio $\phi = 0.5$, 1.0, and 2.0, and temperatures from 1070–1760 K. Zhang et al. [58] measured ignition delays of *n*-butanol at pressures of 2 and 10 atm, temperatures in the range of 1200–1650 K, and for equivalence ratios of 0.5, 1.0, and 2.0. Stranic et al. [59] measured ignition delays of all four isomers of butanol over the pressure range 1.5–43 atm, temperature range 1050–1600 K, and equivalence ratios of 0.5 and 1.0. These studies showed generally good agreement of the ignition delays for *n*-butanol, but Stranic et al. [59] found that their ignition delays for the other isomers of butanol were shorter than the ignition delays measured by Moss et al. [55]. Stranic et al. [59] were unable to determine the reason for the discrepancy.

Yasunaga et al. [60] measured ignition delays of *s*-, *t*-, and *i*-butanol a pressure of 3.5 atm and temperatures between 1250–1800 K. In addition, Yasunaga et al. [60] measured reactant, intermediate, and product species during pyrolysis of all four butanol isomers by sample extraction from their shock tube and analysis by gas chromatography. Other researchers have measured species profiles during the pyrolysis of butanol isomers in a shock tube by optical techniques, including Cook et al. [68], Stranic et al. [69, 70], and Rosado-Reyes and Tsang [71, 72]. At Stanford University, researchers measured the time-histories of the fuel, OH, H₂O, C₂H₄, CO, and CH₄ were measured behind reflected shock waves for *n*-, *s*-, and *i*-butanol [68–70]. Rosado-Reyes and Tsang [71, 72] measured the thermal decomposition of *n*- and *s*-butanol in a single-pulse shock tube and derived rate expressions for the decomposition reactions.

Heufer et al. [61] reported high pressure ignition delay results of stoichiometric *n*-butanol/air mixtures under the conditions behind the reflected shock of approximately 10–42 bar and 770–1250 K.

The results of Heufer et al. [61] showed an interesting non-Arrhenius behavior at temperatures lower than about 1000 K for the pressure range studied. They found that the rate of increase of ignition delay with decreasing temperature appears to change around 1000 K. Vranckx et al. [62] further developed the low-temperature oxidation mechanism of *n*-butanol by performing experiments between 61–92 bar and 795–1200 K and updating a kinetic model with a butyl-peroxy sub-mechanism. They showed improved agreement with predictions of low-temperature butanol ignition delays, but incorrectly predicted the existence of two-stage ignition phenomena.

Zhu et al. [63] measured the ignition delays of *n*-butanol in a shock tube using a newly developed technique known as constrained reaction volume (CRV). In traditional shock tube experiments, it is difficult to measure ignition delays longer than approximately 1–10 ms because fluid-dynamic effects and other phenomena invalidate the assumptions typically used to calculate the thermodynamic state. In the CRV strategy, the reactants are effectively limited to a small region in the shock tube ensuring that the conditions under which ignition occurs are constant enthalpy/nearly constant pressure and are well characterized for longer time scales than in traditional shock tube experiments. Zhu et al. [63] were thus able to measure ignition delays of *n*-butanol between temperatures of 716–1121 K, pressures of 20 and 40 atm, and equivalence ratios of $\phi = 0.5, 1.0$, and 2.0. Using the CRV strategy and constant enthalpy/constant pressure modeling assumptions, Zhu et al. [63] demonstrated that one recent kinetic model was able to predict the ignition delay of *n*-butanol well for most of the conditions they studied.

Ignition delay experiments of the butanol isomers have also been performed in rapid compression machines (RCMs). Weber et al. [64] studied the ignition delays of *n*-butanol for low- to intermediate-temperature conditions between 675–925 K, pressures of 15 and 30 bar, and equivalence ratios of $\phi = 0.5, 1.0$, and 2.0. Weber et al. [64] found no evidence of two-stage ignition or non-Arrhenius behavior in their results. Weber et al. [64] also found that models available until the time of their work (2011) were unable to predict the ignition delays of *n*-butanol, over-predicting the ignition delay by approximately one order of magnitude. Subsequently, Weber and Sung [65] extended their study to the other isomers of butanol, covering temperatures between 715–910 K,

pressures of 15 and 30 bar, and the stoichiometric equivalence ratio. Results from the study by Weber and Sung [65] are presented in ???. In summary, Weber and Sung [65] found that the order of reactivity—in terms of the inverse of ignition delay—of the butanol isomers changes when the pressure is changed from 15 to 30 bar. Moreover, Weber and Sung [65] found unique pre-ignition heat release behavior during the ignition of *t*-butanol that was not present during the ignition of the other isomers.

Weber et al. [66] studied the autoignition of *i*-butanol at three mixture conditions, including $\phi = 0.5$ with air as the oxidizer and $\phi = 0.5$ and 2.0 where the $O_2:N_2$ ratio in the oxidizer was changed while the fuel mole fraction was held constant to change the equivalence ratio. Weber et al. [66] found that a newly developed kinetic model for *i*-butanol combustion was able to predict the stoichiometric (from the work of Weber and Sung [65]) and lean ignition delays in air, but was unable to capture the dependence of the ignition delays on the initial oxygen concentration. In addition, Zhu et al. [63] and Weber et al. [64] noted similar inability to predict the dependence of ignition delay on initial oxygen concentration for *n*-butanol for several different kinetic mechanisms.

Karwat et al. [67] studied the ignition delays of *n*-butanol for stoichiometric mixtures over temperatures from 920–1040 K and pressures near 3 atm. Karwat et al. [67] found good agreement of the ignition delays with the kinetic model developed in the study of Black et al. [56]. In addition, Karwat et al. [67] used a high-speed sampling valve to remove gas samples from the reaction chamber during the induction period of *n*-butanol ignition. They quantified mole fractions of CH_4 , CO , C_2H_4 , C_3H_6 , C_2H_4O , C_4H_8O , $1-C_4H_8$, and *n*-butanol at several times during the ignition. Comparison of the time histories of these species with predictions from the model by Black et al. [56] showed that, although the model is able to predict the ignition delay well, it is not able to reproduce the time history of species concentrations very well, particularly C_2H_4 . This result demonstrates the importance of rigorously validating a kinetic model over a wide range of conditions and for a wide range of validation targets.

In comparison to the butanol isomers, *i*-pentanol has received significantly less focus in the literature. Studies of the combustion of *i*-pentanol have been conducted in JSRs [73–75], low-

pressure flow reactors [76], counterflow flame experiments [75], shock tubes [75, 77, 78], and RCMs [75, 77]. Other studies have investigated the efficacy of using *i*-pentanol in an HCCI engine [79–81]. Finally, studies described in this work have been conducted to determine the ignition properties of *i*-pentanol (see ??). Both the works by Sarathy et al. [75] and Tsujimura et al. [77] developed detailed kinetic models for the combustion of *i*-pentanol whose validation was based, in part, on ignition delay experiments. Using shock tubes and RCMs in concert, these studies were able to provide ignition delays for temperatures, pressures, and equivalence ratios of 650–1450 K, 7–60 bar, and $\phi = 0.5, 1.0$, and 2.0 , respectively. These studies generally found good agreement of their models with their validation data sets, although Sarathy et al. [75] found that their model had difficulty predicting rich ignition delays. In addition, substantial pre-ignition heat release was observed for all of the equivalence ratios at 40 bar in the RCM measurements, similar to *t*-butanol.

0.3 Recent Work on Ignition of Methylcyclohexane

Several studies have suggested the use of methylcyclohexane (MCH) as a component in surrogate formulations [18, 19], as discussed previously. Furthermore, MCH is the simplest branched or substituted cycloalkane, and can therefore provide a base from which to build models of the combustion of other, larger, naphthenes.

Substantial experimental and modeling work has been conducted for naphthenes in general, and MCH in particular. Pitz and Mueller [11] has conducted an extensive review of the work on naphthenes, so only studies involving homogeneous ignition of MCH are discussed here. Ignition delays of MCH have been measured in shock tubes [82–87] and RCMs [14, 88, 89] by a number of researchers. These studies collectively cover the temperature-pressure space in the range of 700–2100 K and 1–70 atm. To complement this experimental work, a number of kinetic models for MCH combustion have been constructed, notably by Pitz et al. [14] and Orme et al. [86].

The study of Rotavera and Petersen [82] measured ignition delays of MCH behind reflected shock waves near 1 and 10 atm for equivalence ratios of $\phi = 0.5, 1.0$, and 2.0 . They compared

their measured ignition delays with predictions from the model of Pitz et al. [14] and found generally good agreement. Hong et al. [87] measured ignition delays for conditions of temperature between 1280–1480 K, pressures of 1.5 and 3 atm, and equivalence ratios of $\phi = 1.0$ and 0.5. Hong et al. [87] compared their measurements with three mechanisms from the literature, including those by Pitz et al. [14] and Orme et al. [86] and found relatively good agreement for their conditions.

However, other studies have found that the existing models are not able to predict ignition delays at conditions for which they were not validated—that is, the models are not truly predictive. For instance, previous work conducted in an RCM by Mittal and Sung [89] measured the ignition delays of MCH/O₂/N₂/Ar mixtures at pressures of 15.1 and 25.5 bar, for three equivalence ratios of $\phi = 0.5$, 1.0, and 1.5, and over the temperature range of 680–840 K. They compared their measured ignition delays to simulated ignition delays computed using the mechanism of Pitz et al. [14] and found that the model over-predicted both the first stage and overall ignition delay substantially [89]. Moreover, studies conducted in shock tubes by Vasu et al. [83] and Vanderover and Oehlschlaeger [84] came to similar conclusions in their studies, which collectively considered conditions between 795–1560 K and 1–70 atm. Further studies conducted in this work have expanded the validation range of MCH ignition data and substantially improved the predictive ability of kinetic models of MCH combustion (see ??).

0.4 Gas Sampling in Rapid Compression Machines

Due to its relevance in predicting the performance of a fuel in existing and advanced engines, ignition delay is a very common measure of the global performance of a kinetic mechanism. Ignition delays for homogeneous systems are typically measured in shock tubes or RCMs, where the effects of fluid motion and turbulence are generally minimized. However, as demonstrated for the case of butanol isomers, *i*-pentanol, and methylcyclohexane, the validation target of ignition delays is necessary but not sufficient to develop truly predictive kinetic models.

The next sentence is terrible and super generic. It needs to be changed. It seems like sampling started in engines as a way to understand knock. Then Roblee1961 realized that engines have cycle-to-cycle variation, and an RCM would probably be better.

In the early part of the 20th century, researchers realized the models available to explain the phenomenon of “knock” in engines were insufficient. Thus, several researchers endeavored to expand the models by removing gas samples from the cylinder of spark-ignition engines. According to Withrow et al. [90], Brooks [91] was the first to develop a system to withdraw samples from the cylinder of an oil-injection engine. Subsequently, Withrow et al. [90], Callendar [92], Egerton and Gates [93], Lovell et al. [94], Ricardo and Thornycroft [95], Steele [96], Egerton et al. [97], Downs et al. [98], and Pahnke et al. [99] further developed these systems for sampling from the cylinder of spark-ignition engines.

In 1961, Roblee [100] adapted a sampling device to a rapid compression machine for the first time. The design of this sampling apparatus was such that the entire reaction chamber could be quickly evacuated to an expansion chamber through a punctured diaphragm. The diaphragm was ruptured either by pressure difference between the reaction chamber and the expansion chamber, or by a spring-actuated knife. Upon diaphragm rupture, the gases in the reaction chamber rushed into the expansion chamber, generating a shock wave that propagated further into the expansion chamber. Simultaneously, a rarefaction wave was generated that propagated backwards into the combustion chamber, expanding the gases therein and quenching any ongoing reactions. After quenching, the products were transferred to a gas chromatograph for analysis.

Roblee [100] used this apparatus to study the decomposition of benzene during the induction period. Roblee [100] noted that minimal consumption of benzene and oxygen occurred during the induction period. Using a similar technique, but in a different RCM, Martinengo et al. [101] measured the products of the decomposition of *i*-octane and *n*-octane at temperatures ranging from 600–700 K and pressures between 15–20 atm. Martinengo et al. [101] noted that the main intermediate species they measured were alkenes and carbonyl compounds under these conditions, and that CO was produced nearly simultaneously with the final stage of ignition.

Affleck and Fish [102] used a wide-aperture, electronically-triggered valve to effect sampling from their RCM. The valve was triggered after the first stage of ignition of 2-methylpentane, and the sample was quenched by adiabatic cooling through expansion into a large sampling chamber. Affleck and Fish [102] also compared the composition of the samples from high-pressure experiments in the RCM with samples drawn from low-pressure ignition experiments conducted in Pyrex bulbs. The authors noted that the products were largely similar between the two experiments, despite the wide variation in pressure.

Beeley et al. [103] used the diaphragm-puncture method to analyze the reaction intermediates during the pyrolysis and combustion of isopropyl nitrate. The results from the pyrolysis indicated that the breakdown of the fuel did not lead to chain branching and thus ignition, whereas when oxygen was added, chain branching pathways were available and hot ignition was observed.

The group at the Université de Lille in France has conducted a number of studies using a sampling apparatus fitted to their RCM [104–106]. These studies have measured the concentration of intermediate species during the ignition of *n*-butane, *n*-heptane, and cyclohexane.

Work has begun to utilize homogeneous ignition experimental platforms to measure characteristics other than ignition delays—see, for instance, the work by Karwat et al. [67] to measure species profiles in their RCF using gas sampling; the work by Das et al. [107] and Uddi et al. [108] to directly measure the temperature in the reaction chamber of an RCM using mid-IR laser light absorption; and the work by Stranic et al. [70] to perform simultaneous concentration measurements of multiple species in their shock tube.

0.5 Summary

Moreover, fuels often exhibit substantially different ignition behavior at engine-relevant, high-pressure, low- to intermediate-temperature conditions. Therefore it is critically important to generate validation datasets at these conditions.

Thus, the objectives of this work can be stated succinctly as follows:

1. Generate ignition delay datasets for alternative fuels at high-pressure, low-temperature conditions that have not been studied extensively in previous work
2. Develop and characterize a new experimental apparatus to enable ex situ species measurements from the reaction chamber of the rapid compression machine during the ignition delay
3. Use the data acquired from Item 1 and Item 2 to extend the validation of new and existing chemical kinetic models for the combustion of alternative fuels
4. Analyze new and existing chemical kinetic models to help understand the cause of discrepancies and clarify the important reaction pathways in high-pressure alternative fuel ignition

0.6 Organization of this Work

The remainder of this work is structured as follows. ?? describes the experimental facilities used in this work, including the rapid compression machine and the newly-developed fast sampling system. Detailed uncertainty analyses are considered for the appropriate apparatuses. The subsequent sections are organized by the fuel studied: ?? considers the butanol isomers, ?? considers *i*-pentanol, and ?? considers methylcyclohexane. Finally, ?? presents conclusions based on this work and recommendations for future directions.