

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 been developed to achieve the necessary improvements. These approaches 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.

In the ideal case, biofuels could be used as drop-in replacements for traditional fuels, requiring

few changes in engine design. However, the combustion properties of biofuels may be substantially different from the fuels they are intended to replace. Moreover, finding sustainable large-scale production methods for biofuels may be challenging. These concerns make 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 advanced engines capable of operating in favorable combustion regimes such as so-called Low Temperature Combustion (LTC) engines, of which one type is the Homogeneous Charge Compression Ignition (HCCI) engine. 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, but do not necessarily improve fuel economy.

Neither of these approaches—new fuels and new engine technologies—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.

One important aspect of LTC engines is their control scheme. In traditional compression-ignition (CI) and spark-ignition (SI) engines, the phasing of the combustion is controlled by an external process—fuel injection and spark timing respectively. These control schemes are dictated by the fuel used in each engine and its state of mixture with the oxidizer upon entry into the cylinder. By contrast, LTC engines have no external process to control the combustion phasing, and because they use premixed fuel/air charges, the combustion phasing is controlled almost entirely by the chemical kinetics of the fuel and the oxidizer. This makes the use of predictive chemical models particularly important when designing LTC engines.

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.

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].

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 is naturally 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/or 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 alkyl-cycloalkane (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]. Moreover, MCH and other naphthenes make up a significant fraction of the hydrocarbon content in alternative “traditional” fuels, such as fuels derived from shale oil. 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 (C₂H₆O). 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(JSR) 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], HO₂ [50–52], and CH₃ [53, 54].

Several studies of ignition delay of the butanol isomers have been conducted in both shock tubes (STs) and rapid compression machines (RCMs), including work in STs 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 bar to 90 bar and 675 K to 1800 K.

Among the ST ignition studies, Moss et al. [55] have done measurements for all four isomers of butanol at 1 bar and 4 bar and 1200 K to 1800 K, over equivalence ratios of $\phi = 0.5$, 1.0, and 2.0 and fuel mole percentages of 0.25 %, 0.5 %, and 1.0 %. Black et al. [56] investigated autoignition for *n*-butanol from 1100 K to 1800 K and 1 atm, 2.6 atm, and 8 atm over equivalence ratios of $\phi = 0.5$, 1.0, and 2.0 and fuel mole percentages of 0.6 %, 0.75 %, and 3.5 %. Noorani et al. [57] investigated ignition of the primary alcohols from C₁–C₄ (methanol to butanol) at pressures of 2 atm, 10 atm, and 12 atm under dilute conditions for equivalence ratios $\phi = 0.5$, 1.0, and 2.0, and temperatures from 1070 K to 1760 K. Zhang et al. [58] measured ignition delays of *n*-butanol at pressures of 2 atm and 10 atm, temperatures in the range of 1200 K to 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 atm to 43 atm, temperature range 1050 K to 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 at a pressure of 3.5 atm and temperatures between 1250 K to 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 ST and analysis by gas chromatography. Other researchers have measured species profiles during the pyrolysis of butanol isomers in a ST 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-history of the concentration of the fuel, OH, H₂O, C₂H₄, CO, and CH₄ 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 ST 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 bar to 42 bar and 770 K to 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 appeared to change around 1000 K. Vranckx et al. [62] further developed the low-temperature oxidation mechanism of *n*-butanol by performing experiments between 61 bar to 92 bar and 795 K to 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 ST using a newly developed technique known as constrained reaction volume (CRV). In traditional ST experiments, it is difficult to measure ignition delays longer than approximately 1 ms to 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 ST 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 ST experiments. Zhu et al. [63] were thus able to measure ignition delays of *n*-butanol between temperatures of 716 K to 1121 K, pressures of 20 atm 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 accurately predict the ignition delay of *n*-butanol for most of the conditions they studied.

Ignition delay experiments of the butanol isomers have also been performed in RCMs. Weber et al. [64] studied the ignition delays of *n*-butanol for low- to intermediate-temperature conditions between 675 K to 925 K, pressures of 15 bar 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 K to 910 K, pressures of 15 bar 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 changed when the pressure was 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 K to 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 was able to predict the ignition delay well, it was 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], STs [75, 77, 78], and RCMs [75, 77]. Other studies have investigated the efficacy of using *i*-pentanol in a homogeneous charge compression ignition (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 STs and RCMs in concert, these studies were able to provide ignition delays for temperatures, pressures, and equivalence ratios of 650 K to 1450 K, 7 bar to 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] 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 STs [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 K to 2100 K and 1 atm to 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 atm 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 K to 1480 K, pressures of 1.5 atm 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 bar and 25.5 bar, for three equivalence ratios of $\phi = 0.5, 1.0$, and 1.5 , and over the temperature range of 680 K to 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 substantially over-predicted both the first stage and overall ignition delay [89]. Moreover, studies conducted in STs by Vasu et al. [83] and Vanderover and Oehlschlaeger [84] came to similar conclusions, which collectively considered conditions between 795 K to 1560 K and 1 atm to 70 atm. Further studies described in ?? and published in the work of Weber et al. [90] have expanded the validation range of MCH ignition data and substantially improved the predictive ability of kinetic models of MCH combustion.

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 STs 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.

Optical methods can offer non-intrusive in-situ measurements of species and temperature during homogeneous ignition events—c.f. the work by Das et al. [91] and Uddi et al. [92] to directly measure the temperature and water number density 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 ST. However, these methods can detect only a limited set of species and require extensive calibration at engine-relevant pressure conditions.

Another avenue to improve the rigor of validation targets is to remove samples from the reacting gas and analyze them ex-situ. Work on this avenue began in the early part of the 20th century, to help explain the phenomenon of “knock” in engines. Several researchers developed techniques to remove gas samples from the cylinder of spark-ignition engines. According to Withrow et al. [93], Brooks [94] was the first to develop a system to withdraw samples from the cylinder of an oil-injection engine around 1922. Subsequently, Withrow et al. [93], Callendar [95], Egerton and Gates [96], Lovell et al. [97], Ricardo and Thornycroft [98], Steele [99], Egerton et al. [100], Downs et al. [101], and Pahnke et al. [102] further developed these systems for sampling from the cylinder of spark-ignition engines.

In 1961, Roblee [103] adapted a sampling device to an RCM 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 [103] used this apparatus to study the decomposition of benzene during the induction period. Roblee [103] 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. [104] measured the products of the decomposition of *i*-octane and *n*-octane at temperatures ranging from 600 K to 700 K and pressures between 15 atm to 20 atm. Martinengo et al. [104] 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 [105] 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 [105] 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. [106] 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 des Sciences et Technologies de Lille in France has conducted a number of studies using a sampling apparatus fitted to their RCM [107–119]. These studies have measured the concentration of intermediate species during the ignition of *n*-butane, *n*-heptane, *i*-octane, *n*-pentane, 1-pentene, *o*-xylene, *o*-ethyltoluene, *n*-butylbenzene, 1-hexene, *n*-propylcyclohexane,

toluene, cyclohexane, cyclohexene, and cyclohexa-1,3-diene. The sampling system used in these studies was similar to that developed by Roblee [103] in that it used an expansion chamber separated from the reaction chamber by a diaphragm that was punctured by a knife at the appointed time.

Using a gas chromatograph coupled to a mass spectrometer to analyze their samples, Minetti et al. [108] were able to identify approximately 25 species produced during the autoignition of *n*-butane. These species included several cyclic ethers produced during the low-temperature oxidation process through peroxy species. Minetti et al. [108] noted that a kinetic model for the combustion of *n*-butane was able to accurately reproduce the major species profiles, but was unable to predict the mole fractions of several minor species.

Minetti et al. [109] studied the species produced during autoignition of *n*-heptane and found that, although a detailed kinetic model was able to correctly predict the ignition delays, it was unable to capture the concentration profiles of the major species, including *n*-heptane and its oxidation products. Minetti et al. [110] compared the oxidation products of *n*-heptane with *i*-octane under conditions of similar ignition delay. The authors noted that the kinetic scheme for two-stage ignition for the two fuels was similar in the sense that the important reaction classes were the same; however, the species produced by the two fuels were largely different. Moreover, Minetti et al. [110] emphasized the importance of oxygenated species such as cyclic ethers and unsaturated hydrocarbons in the low-temperature chain branching pathways.

Ribaucour et al. [111] and Minetti et al. [112] studied the autoignition of *n*-pentane and 1-pentene by analyzing the intermediate species formed during the induction period. They further emphasized the importance of cyclic ether and ketone formation in the low-temperature ignition process. Ribaucour et al. [111] and Minetti et al. [112] also noted that the presence of the double bond in 1-pentene causes marked differences in the selectivity of the intermediate species compared to *n*-pentane, although the overall oxidation scheme of the fuels can be described by similar reaction types.

Ribaucour et al. [113] and Roubaud et al. [114] studied the autoignition of alkylated aromatics including *n*-butylbenzene, *o*-xylene, and *o*-ethyltoluene. The authors found that a detailed oxidation mechanism was able to well reproduce the ignition delays and intermediate species profiles of those

fuels. Moreover, similar intermediate products as for alkane species were noted for the aromatic species with ortho-alkyl groups. These species are able to undergo the critical hydrogen-transfer reactions in the low-temperature chain branching pathways due to the position of the alkyl group. Other aromatic species such as toluene, *m*-xylene, and *p*-xylene react through different low-temperature chain branching pathways and do not have the typical two-stage ignition and NTC region that alkanes and ortho-alkyl aromatics have.

Lemaire et al. [115] and Ribaucour et al. [116] studied the concentration of intermediate species during autoignition of cyclohexane, cyclohexene, and cyclohexa-1,3-diene. Lemaire et al. [115] noted that cyclohexane was prone to the same autoignition phenomena as acyclic alkanes, namely two-stage ignition at low temperatures, followed by a region of negative temperature dependence of the ignition delay as the temperature increases, and finally, single stage ignition at high temperatures. They further observed that cyclohexa-1,3-diene did not exhibit such behavior. Lemaire et al. [115] also compared the species present during the autoignition and found that cyclohexane showed many of the same species as acyclic alkane ignition, whereas cyclohexa-1,3-diene did not have such species. Cyclohexene showed behavior intermediate between cyclohexane and cyclohexa-1,3-diene, both in terms of the ignition behavior and the species concentrations.

Ribaucour et al. [116] studied the autoignition of cyclohexene and constructed a detailed model for its oxidation. They found two primary reaction pathways, one involving the double bond and the other involving peroxy radicals, during the induction period and also noted that effects from the ring structure and the double bond combined to produce the observed chemistry.

Vanhove et al. [117, 118] studied binary blends of 1-hexene and toluene with the primary reference fuels, *n*-heptane and *i*-octane, and one ternary blend of *i*-octane/1-hexene/toluene. The authors found that each fuel primarily propagated through its own pathways, without much direct interaction between the fuels in the mixture. However, the fuels competed for the chain-branching radicals and the addition of unsaturated species tended to have a stronger effect on the reactivity in the NTC regime, where the saturated hydrocarbon reactivity is limited by the NTC reactions but the unsaturated species can still react by adding radicals to the double bond.

Crochet et al. [119] investigated autoignition of *n*-propylcyclohexane. They found that the fuel forms several bicyclic ethers and conjugated alkenes during the induction period. These species are formed through low temperature chain branching pathways by reactions with both the alkyl chain and the cyclohexyl ring in *n*-propylcyclohexane.

Mittal [120] at Case Western Reserve University also developed a sampling system for their RCM. The design was similar to the design of Roblee [103]. Mittal and Sung [121] demonstrated the feasibility of their sampling apparatus by measuring the major species during the induction period of methane ignition. To date, no further results have been published from this sampling apparatus.

Finally, He [122] developed a unique sampling apparatus for the Rapid Compression Facility (RCF) at the University of Michigan. This sampling apparatus quenches only a small portion of the reactants from the reaction chamber instead of quenching the entire chamber, as in the design of Roblee [103] and similar designs. In the design of He [122], a small diameter tube protrudes into the reaction chamber through which samples are drawn into a large expansion chamber. The sampling time is controlled by a fast-acting solenoid valve located outside the reaction chamber that is triggered based on the position of the piston in the RCF and a delay timer.

The local sampling technique developed by He [122] has several important advantages compared to the global sampling techniques used in previous work. In particular, capturing the entire reaction chamber also captures the boundary layer near the chamber walls, potentially causing significant dilution of the test sample. By capturing only a small sample from the center of the reaction chamber, the boundary layer and attendant dilution can be avoided. In addition, the local sampling technique does not substantially disturb the ongoing reactions, meaning that the ignition process is allowed to proceed nearly unhindered.

Nonetheless, the local sampling technique has some disadvantages. Notably, the presence of dead volume in the sampling system can impact the quantification of species in a manner similar to the capture of the boundary layer in global sampling techniques. In particular, the dead volume will have a much lower temperature than the core gases due to the large surface-area-to-volume ratio, which prevents reactions from occurring in the dead volume.

He et al. [123] used this sampling system to study the oxidation products developed during the autoignition of *i*-octane and noted that comparison to a detailed kinetic model developed after the work of Minetti et al. [110] showed agreement within a factor of two for most species. For the species that showed larger disagreement, the authors were able to use their results to suggest several alternate oxidation pathways that were not included in the model.

Subsequently, Walton [124] upgraded the sampling system at the University of Michigan to reduce the dead volume and improve the response time. Walton et al. [125] used the upgraded system to study the intermediate species in the oxidation of methyl butanoate. The authors found that a kinetic model was able to well predict the concentration profiles of the several species, although larger disagreement was noted for propene.

Karwat et al. [67, 126, 127] used the upgraded sampling system to study the autoignition chemistry of *n*-butanol [67], *n*-heptane/*n*-butanol blends [126], and *n*-heptane [127] (the results for *n*-butanol have been described previously). Karwat et al. [126] demonstrated that the reactivity of *n*-heptane was reduced when blended with *n*-butanol, and moreover that the fundamental reaction pathways of *n*-heptane were changed by the addition of *n*-butanol. A kinetic model over-predicted the consumption of *n*-heptane during the first stage of ignition, and was thus unable to reproduce many of the species profiles for the duration of the induction period. Karwat et al. [127] further used species sampling measurements of pure *n*-heptane, combined with newly calculated reaction rate constants for alkylperoxy reactions from the literature, to improve a kinetic model of *n*-heptane combustion, although they did not compare the updated model to their blending results.

0.5 Summary

The works presented in the previous sections represent a large volume of validation data for kinetic models, and have greatly expanded our understanding of the combustion chemistry of alternative fuels. Nonetheless, gaps in the state of the art knowledge have been revealed through several experimental studies, gaps that prevent the development of truly predictive kinetic models—for

example, the inability of models to predict the oxygen concentration dependence of ignition delays of alcohols is still unexplained.

Thus, the major 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 a new experimental apparatus to enable ex-situ species measurements from the reaction chamber of the RCM during the ignition delay
3. Use the data acquired from ?? and ?? 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 bulk of what follows has been published in the archival literature, and includes a summary of some results from the following chapters. ?? presents an introduction to the RCM and other facilities used in the experiments described in subsequent chapters, including the rapid sampling apparatus that is newly upgraded for this work. Detailed uncertainty analyses are also considered for the appropriate apparatuses.

The subsequent chapters are organized by the fuel studied: ?? considers the butanol isomers and was published in *Energy & Fuels* [65] and the 8th U.S. National Combustion Meeting [66]; ?? considers *i*-pentanol and was published in *Combustion and Flame* [75]; ?? considers methylcyclohexane and was published in *Combustion and Flame* [90]. Finally, ?? presents conclusions based on these works and recommendations for future directions.

The appendices present additional information relevant to the studies presented here: ?? contains the species dictionary for the methylcyclohexane mechanism developed in collaboration with

Lawrence Livermore National Laboratory; ?? describes the partial characterization of an all-new sampling system for the RCM used in this study; ?? contains the documentation for a new software package for zero-dimensional chemical kinetic simulations based on the Cantera software package; and ?? contains the code of the PySens program, used for sensitivity analysis with the CHEMKIN-Pro software package.

Finally, ?? contains experimental results for the ignition delay of propene, a foundational fuel that was studied to improve the base of many reaction mechanisms. Moreover, the study is conducted in concert with collaborators at the National University of Ireland at Galway, Texas A&M University, the King Abdullah University of Science and Technology, Stanford University, and Rensselaer Polytechnic Institute. By involving the diverse group of researchers, a comprehensive comparison of experimental facilities is conducted for identical conditions. The experimental results presented in ?? are included in the last article noted below, submitted to *Combustion and Flame*.

The works published in or submitted to the archival literature during the course of this program are as follows:

Weber, B.W., Kumar, K., Zhang, Y., and Sung, C.-J. “Autoignition of *n*-butanol at elevated pressure and low-to-intermediate temperature.” *Combust. Flame*, vol. 158, no. 5 (Mar. 2011), pp. 809–819. DOI: doi:[10.1016/j.combustflame.2011.02.005](https://doi.org/10.1016/j.combustflame.2011.02.005).

Tsujimura, T., Pitz, W. J., Gillespie, F., Curran, H. J., Weber, B. W., Zhang, Y., and Sung, C.-J. “Development of Isopentanol Reaction Mechanism Reproducing Autoignition Character at High and Low Temperatures.” *Energy Fuel*, vol. 26, no. 8 (Aug. 2012), pp. 4871–4886. DOI: doi:[10.1021/ef300879k](https://doi.org/10.1021/ef300879k).

Weber, B. W. and Sung, C.-J. “Comparative Autoignition Trends in Butanol Isomers at Elevated Pressure.” *Energy Fuel*, vol. 27, no. 3 (Mar. 2013), pp. 1688–1698. DOI: doi:[10.1021/ef302195c](https://doi.org/10.1021/ef302195c).

Sarathy, S. M., Park, S., Weber, B. W., Wang, W., Veloo, P. S., Davis, A. C., Togbé, C., Westbrook, C. K., Park, O., Dayma, G., Luo, Z., Oehlschlaeger, M. A., Egolfopoulos, F. N.,

Lu, T., Pitz, W. J., Sung, C.-J., and Dagaut, P. “A comprehensive experimental and modeling study of iso-pentanol combustion.” *Combust. Flame*, vol. 160, no. 12 (Dec. 2013), pp. 2712–2728. DOI: doi:[10.1016/j.combustflame.2013.06.022](https://doi.org/10.1016/j.combustflame.2013.06.022).

Weber, B. W., Pitz, W. J., Mehl, M., Silke, E. J., Davis, A. C., and Sung, C.-J. “Experiments and modeling of the autoignition of methylcyclohexane at high pressure.” *Combust. Flame*, vol. 161, no. 8 (Aug. 2014), pp. 1972–1983. DOI: doi:[10.1016/j.combustflame.2014.01.018](https://doi.org/10.1016/j.combustflame.2014.01.018).

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