

High Pressure Ignition Chemistry of Alternative Fuels

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**Abstract**

High Pressure Ignition Chemistry of Alternative Fuels

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High Pressure Ignition Chemistry of Alternative Fuels

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So long, and thanks for all the fish.

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# 1 Introduction

## 1.1 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 traditional 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 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 Bielefeld et al. [18] and Naik et al. [19]. Recent work on MCH combustion will also be highlighted in the following sections.

## 1.2 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 C<sub>4</sub> alcohols, and *i*-pentanol, a C<sub>5</sub> 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.

One of the most common biofuels currently in use is ethanol ( $C_2H_6O$ ). Although ethanol is ubiquitous at gasoline pumps, it suffers from several disadvantages that suggest it needs to be replaced [21]. 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 [22].

*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 [23, 24]. 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 [24, 25], 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 [26–28] fundamental combustion measurements have been made using many different systems. These include laminar flame speeds [29], jet-stirred reactor chemistry [30], low-pressure flame structure [31, 32], atmospheric pressure flame structure [33], pyrolysis [34–36], flow reactors [37, 38], 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 [39–47], HO<sub>2</sub> [48–50], and CH<sub>3</sub> [51, 52].

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. [53], Black et al. [54], Noorani et al. [55], Zhang et al. [56], Stranic et al. [57], Yasunaga et al. [58], Heufer et al. [59], Vranckx et al. [60], and Zhu et al. [61] and work in RCMs by Weber et al. [62], Weber and Sung [63], Weber et al. [64], and Karwat et al. [65]. 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. [53] 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. [54] 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 percents of 0.6, 0.75, and 3.5 %. Noorani et al. [55] investigated the ignition delays of the primary alcohols from C<sub>1</sub>–C<sub>4</sub> 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. [56] 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. [57] 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. [57] found that their ignition delays for the other isomers of butanol were shorter than the ignition delays measured by Moss et al. [53]. Stranic et al. [57] were unable to determine the reason for the discrepancy.

Yasunaga et al. [58] measured ignition delays of *s*-, *t*-, and *i*-butanol at pressures at 3.5 atm and temperatures between 1250–1800 K. In addition, Yasunaga et al. [58] 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. Several researchers have measured species profiles during the pyrolysis of butanol isomers in a shock tube by optical techniques, including Cook et al. [66], Stranic et al. [67, 68], and Rosado-Reyes and Tsang [69, 70]. At Stanford University, researchers measured the time-histories of the fuel, OH, H<sub>2</sub>O, C<sub>2</sub>H<sub>4</sub>, CO, and CH<sub>4</sub> were measured behind reflected shock waves for *n*-, *s*-, and *i*-butanol [66–68]. Rosado-Reyes and Tsang [69, 70] 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. [59] 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.

Specifically, the results of Heufer et al. [59] 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. [60] 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. [61] 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. [61] 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. [61] demonstrated that one recent kinetic model is 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. [62] 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. [62] found no evidence of two-stage ignition or non-Arrhenius behavior in their results. Weber et al. [62] also found that models available until the time of their work 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 [63] 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 [63] are presented in ???. In summary, Weber and Sung [63] 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 [63] 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. [64] 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<sub>2</sub>:N<sub>2</sub> ratio in the oxidizer was changed while the fuel mole fraction was held constant to change the equivalence ratio. Weber et al. [64] found that a newly developed kinetic model for *i*-butanol combustion was able to predict the stoichiometric (from the work of Weber and Sung [63]) 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. [61] and Weber et al. [62] noted similar effects for *n*-butanol for several different kinetic mechanisms.

Karwat et al. [65] studied the ignition delays of *n*-butanol for stoichiometric mixtures over temperatures from 920–1040 K and pressures near 3 atm. Karwat et al. [65] found good agreement of the ignition delays with the kinetic model developed in the study of Black et al. [54]. In addition, Karwat et al. [65] 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<sub>4</sub>, CO, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>O, C<sub>4</sub>H<sub>8</sub>O, 1-C<sub>4</sub>H<sub>8</sub>, 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. [54] 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<sub>2</sub>H<sub>4</sub>. 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 [71–73], low-pressure

flow reactors [74], counterflow flame experiments [73], shock tubes [73, 75, 76], and RCMs [73, 75]. Other studies have investigated the efficacy of using *i*-pentanol in an HCCI engine [77–79]. Finally, studies described in this work have been conducted to determine the ignition properties of *i*-pentanol. Both the works by Sarathy et al. [73] and Tsujimura et al. [75] 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. [73] 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.

### 1.3 Recent Work on the Combustion 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 are discussed here. Ignition delays of MCH have been measured in shock tubes [80–85] and RCMs [14, 86, 87] 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. [84].

The study of Rotavera and Petersen [80] 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. [85] 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. [85] compared their measurements with three mechanisms from the literature, including those by Pitz et al. [14] and Orme et al. [84] 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 [87] measured the ignition delays of MCH/O<sub>2</sub>/N<sub>2</sub>/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 [87]. Moreover, studies conducted in shock tubes by Vasu et al. [81] and Vanderover and Oehlschlaeger [82] came to similar conclusions in their studies, which collectively considered conditions between 795–1560 K and 1–70 atm.

## 1.4 Summary

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 models.

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. [65] to measure species profiles in their RCF using gas sampling; the work by Das et al. [88] and Uddi et al. [89] 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. [68] to perform simultaneous concentration measurements

of multiple species in their shock tube.

Moreover, fuels often exhibit substantially different ignition behavior at engine-relevant, high-pressure, low- to intermediate-temperature conditions. Thus 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

## 1.5 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 following sections are organized by the fuel studied: ?? considers the butanol isomers, ?? considers *i*-pentanol, and Sec. 13 considers methylcyclohexane. Finally, ?? presents conclusions based on this work and recommendations for future directions.

## 2 Rapid Compression Machine

### 2.1 Experimental Procedure

The studies in this dissertation were conducted using the Rapid Compression Machine (RCM) constructed by Mittal around 2005 and described in the work of Mittal and Sung [90] and Mittal [91]. This RCM has been used to study the autoignition behavior of a number of fuels, including *n*-decane, methylcyclohexane, hydrogen, syngas, dimethyl ether, methanol, toluene, benzene, di-isobutylene, iso-octane, jet fuel, and gasoline [12, 87, 88, 92–104], in addition to the studies presented in this work.

A modern RCM operates by rapidly compressing (hence the name) a test gas mixture to targeted pressure and temperature conditions. The compression is effected by either a single piston or dual, opposed pistons. Upon reaching the targeted state, the piston (or pistons) is stopped and fixed in place so that the reactions proceed in a constant volume reactor. When studying autoignition with an RCM, the primary data are the measured pressure traces during and after the compression stroke. These pressure traces are processed to derive information such as the pressure and temperature at the end of compression (EOC) and the ignition delay. It is also possible to employ laser diagnostics or extract gas samples from the reactor to examine reaction pathways in more detail.

The present RCM is a pneumatically-driven/hydraulically-stopped single-piston arrangement. A schematic of the RCM is shown in Fig. 1 and an image is shown in Fig. 2. The RCM consists of four chambers and three pistons that are used to control machine. The chambers are called the reaction chamber, the hydraulic chamber, the pneumatic chamber, and the driving tank; similarly, the pistons are called the reactor, hydraulic, and pneumatic pistons and are each installed in the chamber of the same name. The rear of the reaction chamber is bolted to the front of the hydraulic chamber; seals in the face of the hydraulic chamber prevent oil from leaking and contaminating the reaction chamber. The driving tank and the rear of the pneumatic chamber are connected by a union; a seal around the circumference of the pneumatic piston seals gas in the driving tank from the front of the pneumatic chamber. Thus, the pneumatic piston can be driven by pressure from the

driving tank on its rear and pressure from the pneumatic chamber on its front. The three pistons are connected by a rod running from the front of the pneumatic piston to the rear of the reactor piston so that they move as one; this will be referred to as the piston assembly.

At the start of an experimental run, with the piston in the EOC position, the reaction chamber is vacuumed to less than 1 Torr. Next, the piston assembly is retracted by pressurizing the front face of the piston in the pneumatic chamber. For safety, and to prevent damage to the RCM, the driving tank should be filled to limit the acceleration of the piston assembly during the retraction. The pressure on the front of the pneumatic piston pulls the piston assembly rearward and seats the rear of the hydraulic piston onto an O-ring in the rear of the hydraulic chamber. The hydraulic chamber is filled with oil to a pressure of approximately 800 psi, providing a rearward force on the front face of the hydraulic piston. Then, the air pressure is released from the front of the pneumatic chamber and the driving tank is filled to the desired driving pressure. The force on the hydraulic piston opposes the force on the pneumatic piston from the driving tank and the piston assembly remains at rest. Then, the reaction chamber is filled with the required initial pressure of test gas mixture from the mixing tank. Finally, compression is triggered by releasing the hydraulic pressure through an electrically-operated solenoid valve. The piston assembly is driven forward by the unbalanced force from the pressure in the driving tank on the pneumatic piston. The gases in the reaction chamber are brought to the compressed pressure ( $P_C$ ) and compressed temperature ( $T_C$ ) conditions in approximately 30–50 ms.

The required driving pressure for a given EOC pressure can be estimated from a force balance between the force on the pneumatic piston from the driving tank and the force on the reactor piston from the test gases, as shown in Eq. (1c).

$$P_{d,\min} \cdot A_p = P_{r,\text{EOC}} \cdot A_r \quad (1a)$$

$$P_{d,\min} \cdot \frac{\pi d_p^2}{4} = P_{r,\text{EOC}} \cdot \frac{\pi d_r^2}{4} \quad (1b)$$

$$P_{d,\min} = P_{r,\text{EOC}} \cdot \frac{d_r^2}{d_p^2} \quad (1c)$$

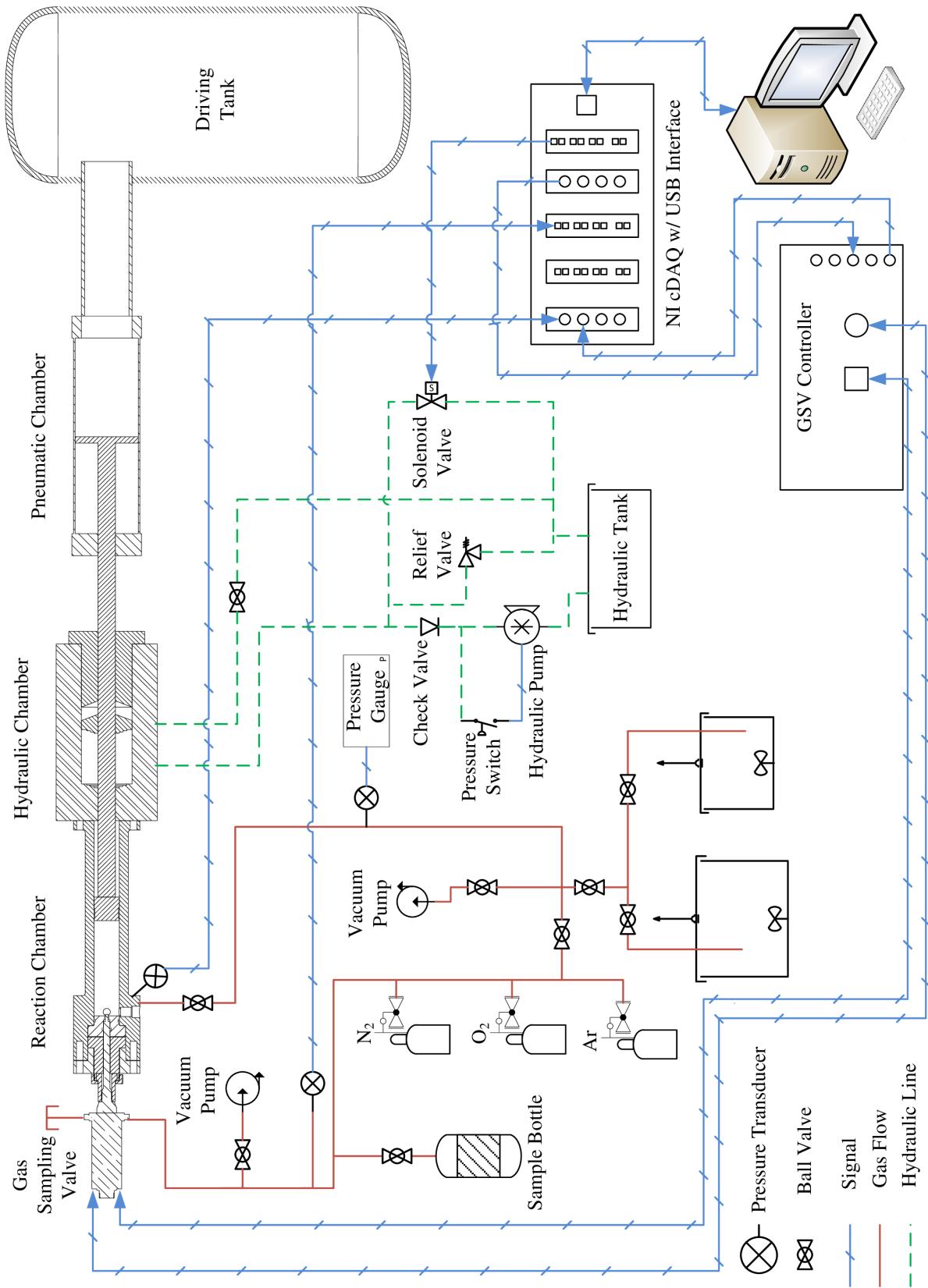
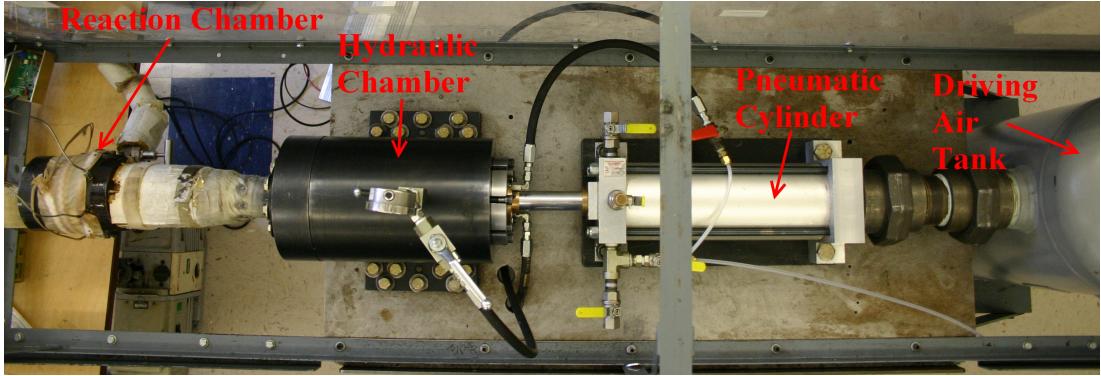


Figure 1: Schematic of the RCM. Not to scale



**Figure 2:** Photograph of the RCM.

In Eq. (1),  $P_{d,\min}$  is the minimum driving pressure,  $A_p$  is the cross-sectional area of the pneumatic piston,  $P_{r,EOC}$  is the pressure in the reactor at the EOC (i.e.  $P_C$ ),  $A_r$  is the cross-sectional area of the reactor piston,  $d_p$  is the diameter of the pneumatic piston, and  $d_r$  is the diameter of the reactor piston.

The minimum driving pressure is such that the piston does not rebound at the EOC due to pressure on the reactor piston. So that the driving pressure can be much lower than the EOC pressure, the diameter ratio of the reactor piston to the driver piston is 2/5, allowing a factor of 6.25 lower driving pressure than EOC pressure. The actual driving pressure should exceed the minimum by some safety margin so that the reactor remains at constant volume even if there is some pressure rise due to heat release in the reaction chamber prior to the main ignition.

There is not a theoretical upper limit on the driving pressure. It is desired that the piston should reach the EOC conditions in as short a time as possible to minimize heat loss from the reactants to the reactor walls and minimize the time for reactions to occur during the compression stroke. This implies that the driving pressure should be made as high as possible so that the highest piston velocity is achieved. However, higher piston velocities require a higher deceleration at the EOC. In the present RCM, the deceleration is provided by venting the hydraulic oil between steps on the hydraulic piston and matched steps on the front of the hydraulic chamber. If the piston is overdriven—that is, the driving pressure is too high—the piston will not be sufficiently decelerated by the oil venting and will impact the front of the hydraulic chamber at high velocity. This can

damage the RCM and cause the piston to rebound elastically. It also generates substantial noise in the pressure trace and should be avoided.

Typical driving gas pressures are between 50 psi for  $P_C = 15$  bar experiments to 125 psi for  $P_C = 50$  bar experiments. These driving pressures represent a good compromise between the minimum required for no rebound at EOC due to pressure and no rebound at EOC due to elastic reaction. Nonetheless, a small amount of piston rebound can be expected during/after the main ignition event. This small rebound may have an effect on the computation of ignition delay if it reduces the pressure rise rate during the ignition; it is expected that this effect will be very small relative to the typical random uncertainty in ignition delay experiments. Moreover, the driving pressures required to balance the full pressure rise during ignition are more likely cause elastic rebound, especially for high  $P_C$  when the post-ignition pressure rise is greater.

The EOC conditions ( $P_C$  and  $T_C$ ) can be independently varied. This is made possible by independent variation of the compression ratio, initial pressure and initial temperature, and the specific heat ratio of the test gases. The compression ratio can be increased by adding spacers onto the rear of the hydraulic chamber, increasing the stroke, and can be reduced by adding split shims onto the rear of the reaction chamber, increasing the EOC clearance length.

## 2.2 Test Gas Mixture Preparation

Fuel/oxidizer pre-mixtures are prepared in two mixing tanks, one approximately 17 L and the other approximately 15 L in volume. These large volumes allow many runs to be conducted from one mixture preparation. The mixing tanks are connected to the reaction chamber by flexible stainless steel manifold tubing. The tanks, reaction chamber, and connecting manifold are wrapped in heating tape and insulation to control the initial temperature of the mixture. Temperature controllers from Omega Engineering use thermocouples placed on the lid of each mixing tank, approximately in the center of each mixing tank, embedded in the wall of the reaction chamber, and near the inlet valve of the reaction chamber to control the preheat temperature of the mixture. A static pressure transducer measures the pressure in the manifold and mixing tanks. This transducer is used during

mixture preparation and to measure the initial pressure of a given experiment. Two transducers are for various experiments in this work, as described below in Sec. 2.8.

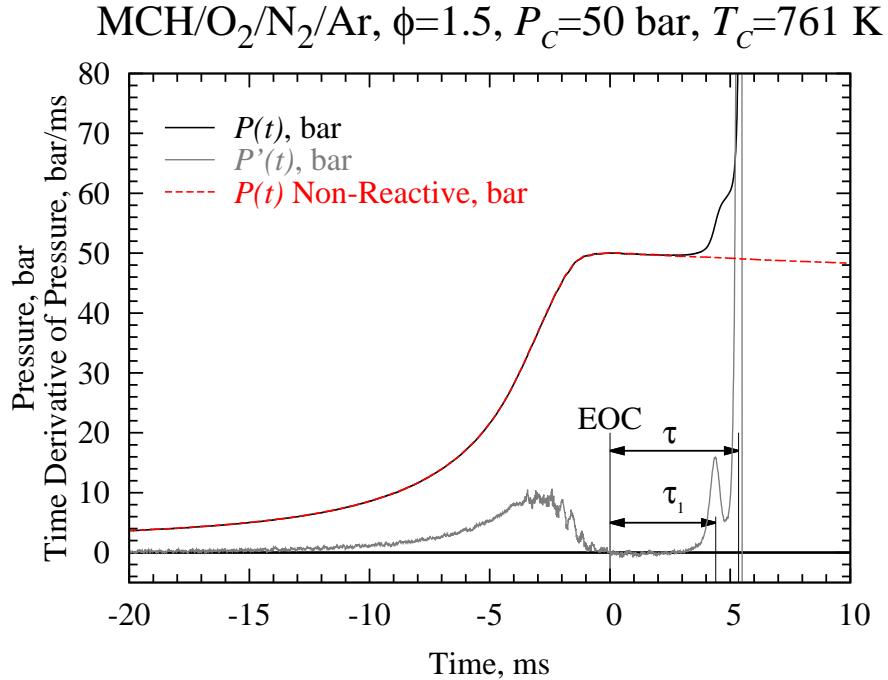
Most of the fuels studied in this work are liquids at room temperature and pressure and have relatively low vapor pressure. A similar procedure, outlined below, was used for all of the butanol isomers, *iso*-pentanol, and methylcyclohexane. First, the mixing tanks are vacuumed to an ultimate pressure less than 5 Torr. The liquid fuel is massed in a syringe to a precision of 0.01 g prior to injection through a septum. Proportions of O<sub>2</sub>, N<sub>2</sub>, and Ar 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. The vapor pressure as a function of temperature is calculated according to fits taken from Yaws [105]. A magnetic stirrer mixes the reactants. The temperature inside the mixing tank is allowed to equilibrate for approximately 1.5 h.

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 [62], GC-FID [92], and GC-TCD [88]. These studies have verified the concentration of *n*-butanol, *n*-decane, and water, respectively. In addition, both the work by Kumar et al. [92] on *n*-decane and the study of Weber et al. [62] 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.

## 2.3 Definition of Ignition Delay

The pressure in the reaction chamber during an experiment is monitored by a Kistler 6125B piezoelectric dynamic pressure transducer. The charge signal from the transducer is amplified and converted to a voltage by a Kistler 5010B charge amplifier. The voltage is sent to a National Instruments cDAQ equipped with the NI-9215 module. The signal is recorded by a LabView VirtualInstrument at 50 kHz.

Figure 3 shows a representative pressure trace from these experiments with methylcyclohexane (MCH) at  $P_C = 50$  bar,  $T_C = 761$  K, and  $\phi = 1.5$  (See Sec. 13). Note that Fig. 3 shows a case with



**Figure 3:** Representative pressure trace indicating the definition of the first stage and overall ignition delays and the corresponding non-reactive pressure trace. EOC stands for End of Compression.

two stages of ignition; not all of the fuels studied had conditions that showed two-stage ignition. Nonetheless, the ignition delay is consistently defined in all the work in this study. The definitions of the EOC and the ignition delays are indicated on the figure. The end of compression time is defined as the time when the pressure reaches its maximum before first stage ignition occurs, or for cases where there is no first stage ignition, the maximum pressure before the overall ignition occurs. The first stage ignition delay is the time from the end of compression until the first peak in the time derivative of the pressure. The overall ignition delay is the time from the end of compression until the largest peak in the time derivative of the pressure.

Each unique  $P_C$  and  $T_C$  condition is repeated at least 5 times to ensure repeatability of the experiments. The experiment closest to the mean of the runs at a particular condition is chosen for analysis and presentation. The standard deviation of all of the runs at a condition is less than 10% of the mean in all cases.

## 2.4 Non-Reactive Experiments

Figure 3 also shows a non-reactive pressure trace. Due to heat loss from the test mixture to the cold reactor walls, the pressure and temperature of the gas in the reaction chamber will decrease after the end of compression. A non-reactive pressure trace is measured that corresponds to each unique  $P_C$  and  $T_C$  condition studied to quantify the effect of the heat loss on the ignition process and to verify that no heat release has occurred during the compression stroke. The non-reactive pressure trace is acquired by replacing the oxygen in the oxidizer with nitrogen, so that the specific heat ratio of the initial mixture is maintained, but the heat release due to exothermic oxidation reactions is eliminated. Maintaining a similar specific heat ratio ensures that the non-reactive experiment faithfully reproduces the conditions of the reactive experiment. A representative non-reactive pressure trace is shown in Fig. 3 corresponding to the experimental conditions in the figure.

## 2.5 Reaction Chamber Homogeneity

An RCM to be used for studies of homogeneous chemistry—as in this study—must ensure that homogeneous conditions exist inside the reaction chamber for the duration of the experiment. Due to the high piston velocities required to minimize heat loss and reaction during the compression stroke, complex fluid mechanical effects can strongly affect the state of the reactants at the EOC. The most important of these effects is caused by the motion of the piston itself, where the piston pushes the wall boundary layer into a roll-up vortex [106]. This cold vortex mixes with the hotter gases near the center of the reaction chamber and causes large spatial inhomogeneities of temperature and species.

To facilitate spatially homogeneous conditions in the reactor and reduce the effect of the roll-up vortex, it is necessary to trap the boundary layer. This is accomplished on the present RCM by a crevice machined into the crown of the piston, shown in cross-section in ???. The boundary layer enters the crevice through the converging section as the piston moves forward and is trapped within the crevice. The dimensions of the crevice were optimized by Mittal [91] through CFD simulations for high-pressure conditions. Subsequently, Mittal and Sung [107] experimentally showed that the

optimized crevice design provides homogeneous conditions in the reaction chamber up to approximately 150 ms after the EOC. By using PLIF measurements of acetone-seeded mixtures, Mittal and Sung [107] showed that there was a core region of gases near the center of the reactor whose temperature remained spatially homogeneous.

## 2.6 Determination of Reactant Temperature

Two independent thermodynamic properties are required to fix the thermodynamic state of the reactants in the reaction chamber at a given time. The first property is the pressure, measured by the dynamic pressure transducer, as discussed previously; the second property is chosen to be the temperature.

In general, it is rather difficult to directly measure the temperature of the gases in the reaction chamber during and after compression. Intrusive methods such as thermocouples may introduce inhomogeneities into the reaction chamber and non-intrusive optical techniques are difficult to set up and require extensive calibration at the pressures of interest in RCM studies. Thus, the temperature is determined indirectly by applying an assumption called the “adiabatic core hypothesis” to the reaction chamber [90, 106].

If all of the gases in the reaction chamber were compressed isentropically, the temperature at the end of compression could be found by the following relations:

$$\ln(\text{CR}) = \int_{T_0}^{T_{ic}} \frac{1}{T(\gamma - 1)} dT \quad (2a)$$

$$\ln\left(\frac{P_{ic}}{P_0}\right) = \int_{T_0}^{T_{ic}} \frac{\gamma}{T(\gamma - 1)} dT \quad (2b)$$

where CR is the volumetric compression ratio,  $T_0$  is the initial temperature,  $T_{ic}$  is the temperature at the end of isentropic compression,  $\gamma$  is the temperature-dependent ratio of specific heats,  $P_{ic}$  is the pressure at the end of isentropic compression, and  $P_0$  is the initial pressure.

However, experiments show that the measured pressure in the reaction chamber does not reach the value of  $P_{ic}$  calculated by using the geometric compression ratio. The difference is due to finite

heat loss from the reactants to the reactor walls and the crevice volume during the compression. Under the adiabatic core hypothesis, it is assumed that the heat loss from the reactants only occurs in a thin boundary layer near the wall, and the central core region is unaffected by heat loss (i.e. the core is adiabatic) [108]. Thus, the heat loss is modeled as an effective reduction in the compression ratio, and the temperature during the compression stroke can be calculated by:

$$\ln\left(\frac{P_C}{P_0}\right) = \int_{T_0}^{T_C} \frac{\gamma}{T(\gamma - 1)} dT \quad (3)$$

where  $P_C$  is the measured pressure at the end of compression,  $T_C$  is the temperature at the end of compression, and the other variables are the same as in Eq. (2).

After the end of compression, the pressure in the reaction chamber decreases, as can be seen in Fig. 3. This pressure decrease is caused by heat loss from the reactants in the constant volume reaction chamber and is accompanied by a decrease in the temperature of the reactants. To model the thermodynamic state after the end of compression, the adiabatic core hypothesis is applied, and the heat loss is assumed to occur only in a thin boundary layer near the reactor walls. Thus, the core region is modeled as adiabatic, and the heat loss from the boundary layer can be modeled as an isentropic volume expansion.

## 2.7 Determination of Compressed Temperature

In general, the specific heat ratio used in Eqs. (2) and (3) is an unknown function of temperature and composition, so Eq. (3) cannot be integrated directly to find  $T_C$ . If the specific heats are parameterized with a linear fit and the composition is assumed to be fixed, it is possible to integrate Eq. (3) directly, but this process is quite tedious; nonetheless, it will be applied in Sec. 2.8 to determine the uncertainty of  $T_C$ . In general, the simplest method of calculating  $T_C$  is to use software to numerically integrate Eq. (3).

In this work, the CHEMKIN-Pro [109] software is used to perform the numerical integration and calculation of  $T_C$ . The CHEMKIN-Pro software provides the facility for a user-specified volume

as a function of time to be applied to a homogeneous, adiabatic reactor. Since the adiabatic core of the reaction chamber is modeled as undergoing an isentropic volumetric compression followed by an isentropic volumetric expansion, the user-specified volume functionality is used to compute the RCM reactor state as a function of time. A volume trace for simulation is computed from the measured pressure trace using the isentropic relation:

$$\frac{V_2}{V_1} = \left[ \frac{P_1}{P_2} \right]^{\frac{1}{\gamma}} \quad (4)$$

where  $V_1$  and  $V_2$  are the volumes at consecutive time points,  $P_1$  and  $P_2$  are the pressures at consecutive time points, and  $\gamma$  is the temperature dependent specific heat. This equation is applied during and after the compression stroke to calculate the volume trace. In Eq. (4) it is assumed that changes in composition of the reactants are negligible during the compression stroke.

For use in Eq. (4),  $\gamma$  is tabulated for each time point. Thus, the temperature at each time point must also be computed by using the isentropic relation for temperature:

$$\frac{T_2}{T_1} = \left[ \frac{P_2}{P_1} \right]^{\frac{\gamma-1}{\gamma}} \quad (5)$$

where  $T_2$  and  $T_1$  are the temperatures at consecutive time points. Since  $T_2$  depends on the value of  $\gamma$ , which in turn depends on  $T_2$ , Eq. (5) is iterated until the temperature changes by less than one tenth of one percent on consecutive iterations. Once again, it is assumed that changes in composition have a negligible influence on the ratio of specific heats. The temperature calculated by Eq. (5) is typically within 1K of the temperature calculated by CHEMKIN-Pro.

## 2.8 Uncertainty of Ignition Delay and Compressed Temperature

The uncertainty of the compressed temperature is an important parameter to report. Since  $T_C$  is not measured, we must perform an uncertainty propagation analysis on the equation used to calculate  $T_C$ , Eq. (3). First, we simplify the term involving  $\gamma$  in Eq. (3). By definition,  $\gamma$  is the ratio of the

specific heat at constant pressure to that at constant volume

$$\gamma \equiv \frac{C_p}{C_v} = \frac{C_p/R}{C_v/R} \quad (6)$$

where  $C_p$  and  $C_v$  are the specific heats in molar units at constant pressure and volume, respectively, and  $R$  is the universal gas constant, used to produce non-dimensional specific heats. Letting a hat denote the non-dimensional specific heats, the difference between the non-dimensional specific heats is one,  $\hat{C}_v = \hat{C}_p - 1$ . Then, it follows that

$$\frac{\gamma}{\gamma - 1} = \frac{\frac{\hat{C}_p}{\hat{C}_v}}{\frac{\hat{C}_p}{\hat{C}_v} - 1} = \frac{\frac{\hat{C}_p}{\hat{C}_p - 1}}{\frac{\hat{C}_p}{\hat{C}_p - 1} - 1} = \frac{\frac{\hat{C}_p}{\hat{C}_p - 1}}{\frac{1}{\hat{C}_p - 1}} = \hat{C}_p \quad (7)$$

In Eq. (3), the mean specific heat ratio for the mixture should be used; thus, the simplification as shown in Eq. (7) requires that the specific heat  $\hat{C}_p$  also be the mean specific heat. In the following, we assume that there is negligible change of the mean specific heat due to changes in reactant mole fractions. The mean specific heat is simply the sum of the product of the species mole fractions and their specific heats

$$C_{p,\text{total}} = \sum_i X_i C_{p,i} \quad (8a)$$

$$\hat{C}_{p,\text{total}} = \frac{\sum_i X_i C_{p,i}}{R} \quad (8b)$$

where  $i$  indicates the species and  $X_i$  is the species mole fraction. In the NASA polynomial formulation used by CHEMKIN, the non-dimensional specific heat at constant pressure as a function of temperature is represented by a fourth-order polynomial fit

$$\hat{C}_{p,i} = c_{1,i} + c_{2,i}T + c_{3,i}T^2 + c_{4,i}T^3 + c_{5,i}T^4 \quad (9)$$

In general, this means that the specific heat can be non-linear. However, since the mixtures prepared

in this study are composed primarily of O<sub>2</sub>, N<sub>2</sub> and Ar (i.e. no more than 7% of any mixture is the fuel), and since the specific heats of O<sub>2</sub>, N<sub>2</sub> and Ar are only weakly temperature dependent over the range of temperatures experienced during compression, we will approximate the total specific heat as a linear function of temperature.

$$\begin{aligned}\hat{C}_{p,\text{total}} &= \sum_i X_i \hat{C}_{p,i} \\ &= \sum_i X_i \left( \sum_{j=1}^5 c_{j,i} T^{j-1} \right) \\ &\approx a + bT\end{aligned}\tag{10}$$

$a$  and  $b$  are found by fitting the total non-dimensional specific heat over the temperature range from 300–1100 K, as discussed below in Sec. 2.8.4.

With this approximation of the specific heat, we can integrate Eq. (3) to find the compressed temperature

$$\ln \frac{P_C}{P_0} = \int_{T_0}^{T_C} \frac{\gamma}{T(\gamma - 1)} dT = \int_{T_0}^{T_C} \frac{\hat{C}_p}{T} dT\tag{11a}$$

$$= \int_{T_0}^{T_C} \frac{a + bT}{T} dT\tag{11b}$$

$$= [a \ln T + bT]_{T_0}^{T_C}\tag{11c}$$

$$\ln \frac{P_C}{P_0} = a \ln T_C + bT_C - (a \ln T_0 + bT_0)\tag{11d}$$

Solving Eq. (11d) for  $T_C$

$$T_C = \frac{a W\left(\frac{b}{a} \exp\left[\frac{bT_0}{a}\right] T_0 \left[\frac{P_C}{P_0}\right]^{\frac{1}{a}}\right)}{b}\tag{12}$$

where  $W(\dots)$  is Lambert's  $W$  function [110]. With an explicit function for  $T_C$ , we can estimate the uncertainty in  $T_C$  by the root square sum of the uncertainty in the parameters in Eq. (12) multiplied

by the partial derivative of Eq. (12) with respect to each of the parameters [111]. The parameters are  $P_C$ ,  $P_0$ ,  $T_0$ ,  $a$ , and  $b$ .

$$U_{T_C} = \sqrt{\left(\frac{\partial T_C}{\partial P_C} U_{P_C}\right)^2 + \left(\frac{\partial T_C}{\partial P_0} U_{P_0}\right)^2 + \left(\frac{\partial T_C}{\partial T_0} U_{T_0}\right)^2 + \left(\frac{\partial T_C}{\partial a} U_a\right)^2 + \left(\frac{\partial T_C}{\partial b} U_b\right)^2} \quad (13)$$

Then, letting

$$D = W \left( \frac{b}{a} \exp \left[ \frac{b T_0}{a} \right] T_0 \left[ \frac{P_C}{P_0} \right]^{\frac{1}{a}} \right)$$

the partial derivatives of Eq. (12) with respect to the parameters are

$$\frac{\partial T_C}{\partial P_C} = \frac{D}{b P_C (D + 1)} \quad (14a)$$

$$\frac{\partial T_C}{\partial P_0} = \frac{-D}{b P_0 (D + 1)} \quad (14b)$$

$$\frac{\partial T_C}{\partial T_0} = \frac{(a + b T_0) D}{b T_0 (D + 1)} \quad (14c)$$

$$\frac{\partial T_C}{\partial a} = \frac{-D [b T_0 + \ln(P_C/P_0) - a D]}{ab (D + 1)} \quad (14d)$$

$$\frac{\partial T_C}{\partial b} = \frac{D (b T_0 - a D)}{b^2 (D + 1)} \quad (14e)$$

The uncertainties of the parameters,  $U_j$  in Eq. (13), are in general found by their own root square sum procedure

$$U_j^2 = B_j^2 + R_j^2 \quad (15)$$

where the subscript  $j$  represents one of the parameters in Eq. (12). The total uncertainty of a particular parameter is composed of two parts, the systematic or bias uncertainty ( $B_j$ ) and the precision or random uncertainty ( $R_j$ ). In general, the bias uncertainty is contained in the measurement equipment and can be reduced, e.g. by using different equipment; the random uncertainty is inherent in any measured process and cannot be reduced by experimental techniques. The bias and precision

uncertainties for each parameter will be discussed in the following.

### 2.8.1 Uncertainty in Initial Temperature

The bias uncertainty in the initial temperature is due to the standard limits of error of the K-type thermocouple used to measure the initial temperature. According to the Omega Engineering specifications, this is "the greater of 2.2 °C or 0.75%". The largest initial temperature used in this work, 413 K, leads to an uncertainty of 3 K; thus,  $B_{T_0} = 3 \text{ K}$ . Bias uncertainty due to the A/D converter in the process meter is negligible compared to this uncertainty. The precision uncertainty is due to the limit of precision of the display on the Omega Engineering CNi3254 process meter used to control the process temperature. This is 0.05 K. The total uncertainty of the initial temperature is

$$U_{T_0} = \sqrt{(B_{T_0})^2 + (R_{T_0})^2} = \sqrt{(3 \text{ K})^2 + (0.05 \text{ K})^2} = 3 \text{ K} \quad (16)$$

### 2.8.2 Uncertainty in Initial Pressure

The bias uncertainty in the initial pressure is due to the standard error in the pressure transducer used to measure the initial pressure. Two different pressure transducers have been used in this study; the first, an Omega Engineering PX-303 (range: 0–50 psia), has a full scale uncertainty of 1.25%, or 0.625 psi (4309.2 Pa). The second transducer is an Omega Engineering MMA100V10T2D0T4A6 type (range: 0–5200 Torr) and was purchased because preliminary results of this uncertainty analysis indicated that the largest contributor to the uncertainty of  $T_C$  was the initial pressure measurement. The full scale uncertainty of the MMA type transducers is 0.05%, resulting in an uncertainty of 2.6 Torr (346.6 Pa), an order of magnitude lower than the PX-303 while also providing more than double the operating range. Total uncertainties using the appropriate pressure transducer are reported in each experimental section of this work; both transducers will be analyzed in this section. Bias uncertainty due to the signal acquisition equipment is negligible compared to the standard error in the pressure transducers.

The precision uncertainty is due to the limit of precision of the display on the Omega Engineer-

ing DP41-B process meter used to monitor the initial pressure. This is 0.005 Torr (0.666 Pa). The total uncertainty of the initial pressure is

$$U_{P_0} = \sqrt{(B_{P_0})^2 + (R_{P_0})^2} = \sqrt{(4309.2 \text{ Pa})^2 + (0.666 \text{ Pa})^2} = 4309.2 \text{ Pa} \quad (17\text{a})$$

$$U_{P_0} = \sqrt{(B_{P_0})^2 + (R_{P_0})^2} = \sqrt{(346.6 \text{ Pa})^2 + (0.666 \text{ Pa})^2} = 346.6 \text{ Pa} \quad (17\text{b})$$

### 2.8.3 Uncertainty in Compressed Pressure

The bias uncertainty in the compressed pressure is due to the standard error in the piezoelectric pressure transducer. According to the manufacturer's calibration, the deviation of the full scale output from linearity is less than 0.2%, indicating that  $B_{T_C} = 0.5 \text{ bar}$ . The uncertainties in the signal acquisition equipment are negligible compared to this uncertainty. The precision uncertainty is due to the limit of precision of the output of the pressure, and is  $5 \times 10^{-7} \text{ bar}$ . This is negligible compared to the bias uncertainty, so the total uncertainty of the compressed pressure is

$$U_{P_C} = B_{T_C} = 0.5 \text{ bar} \quad (18)$$

### 2.8.4 Uncertainty in the Specific Heat

The uncertainty in the specific heat comes from two sources. First is the uncertainty in the mixture composition and second is the uncertainty in the linear fit to the total specific heat. The uncertainty in the mixture composition can be estimated by the same method as is used for  $T_C$ . The specific heat is given by Eq. (8), so we can take partial derivatives of that equation with respect to the mole fractions of the species to find the total uncertainty

$$\begin{aligned} (U_{\hat{C}_{p,\text{total}}})^2 &= \left( \frac{\partial \hat{C}_p}{\partial X_1} U_{X_1} \right)^2 + \dots + \left( \frac{\partial \hat{C}_p}{\partial X_n} U_{X_n} \right)^2 \\ &= (\hat{C}_{p,1} U_{X_1})^2 + \dots + (\hat{C}_{p,n} U_{X_n})^2 \end{aligned} \quad (19)$$

where  $n$  is the total number of species. In Eq. (19), it is assumed that the uncertainty in the specific heats of each species is negligible. This is considered an acceptable assumption for stable species such as the fuel molecules, oxygen, nitrogen, and argon. Experience with several kinetic mechanisms has shown that the typical variation in individual  $\hat{C}_p$  fits causes approximately 1 K changes in  $T_C$ .

The uncertainty of the mole fraction of the species is estimated differently depending on how the species was introduced to the mixing tank. For liquid fuel species, experiments with GC/MS have shown that there is approximately 5% variation in mole fraction from the expected value [62]; this value is adopted for the total uncertainty of all liquid fuels. The mole fraction of the gaseous species is determined by their partial pressures when filling; the mole fraction is related to the pressure by Dalton's Law of Partial Pressure [112, 113]

$$X_i = \frac{P_i}{P} \quad (20)$$

where  $P_i$  is the partial pressure of a species and  $P$  is the total pressure. It follows that

$$\begin{aligned} (U_{X_i})^2 &= \left( \frac{\partial X_i}{\partial P_i} U_{P_i} \right)^2 + \left( \frac{\partial X_i}{\partial P} U_P \right)^2 \\ &= \left( \frac{U_{P_i}}{P} \right)^2 + \left( \frac{-P_i}{P^2} U_P \right)^2 \end{aligned} \quad (21)$$

The uncertainties of the pressures  $P_i$  and  $P$  are equal and can be estimated by the same procedure as in Sec. 2.8.2 since the same pressure transducer is used to measure the pressure. The total pressure  $P$  will be different for each species as it is filled. The order followed in these experiments is liquid fuel injection, followed by oxygen, then nitrogen, then argon; for propene, the order is oxygen, nitrogen, argon, propene.

A typical total pressure after filling is approximately 1300 Torr ( $\approx 173,319$  Pa). The mixtures in Table 1 are the mixtures that will be analyzed in the following because they represent a worst case scenario in that the mole fraction of the fuel or oxygen is maximized in them.

**Table 1:** Mixtures studied in the uncertainty analysis.

Fuel	Mole Fraction			
	Fuel	Oxygen	Nitrogen	Ar
Methylcyclohexane	0.0107	0.2240	0.0000	0.7653
<i>n</i> -Butanol	0.0676	0.2030	0.7294	0.0000
<i>i</i> -Pentanol	0.0531	0.1989	0.7480	0.0000
Propene	0.0854	0.1921	0.7225	0.0000

Once the total specific heat has been calculated, a linear fit as a function of temperature is applied by least-squares estimation. Since there is an uncertainty in the specific heat, there is a corresponding uncertainty in the fit coefficients  $a$  and  $b$ . Following the methodology outlined by York et al. [114], the values and uncertainties of  $a$  and  $b$  are calculated iteratively. This procedure gives identical values of the slope, intercept, and standard errors as maximum likelihood estimation [114]. Equation 22 is reproduced from York et al. [114], and is presented as Eq. (13) in that work.

$$a = \bar{Y} - b\bar{X} \quad (22a)$$

$$b = \frac{\sum W_i \beta_i V_i}{\sum W_i \beta_i U_i} \quad (22b)$$

$$\sigma_a^2 = \frac{1}{\sum W_i} + \bar{x}^2 \sigma_b^2 \quad (22c)$$

$$\sigma_b^2 = \frac{1}{\sum W_i u_i^2} \quad (22d)$$

where the symbols in Eq. (22) are defined in Table 2. The general formulation is given here because it will be reused in ??; application to this section will be given below.

In this section,  $X_i$  are the temperatures at which Eq. (10) is evaluated and  $Y_i$  are the total specific heats evaluated from Eq. (10). The weighting of the specific heats— $\omega(Y_i)$ —is taken to be the reciprocal of the uncertainty as calculated by Eq. (19). Furthermore, there is no uncertainty in the abscissa (i.e. the temperature) and  $\omega(X_i) = 1$ . Finally, since there is no uncertainty in the temperature, there is no correlation between the uncertainties, i.e.  $r_i = 0$ .

First, the slope  $b$  is estimated by simple least-squares regression of the total specific heat on the temperature. Then, this slope is used to estimate the adjusted weighting of each point,  $W_i$ . Next,  $U_i$

**Table 2:** Symbols in Eq. (22). Reproduced from the work of York et al. [114].

Symbol	Meaning
$a, b$	$y$ intercept and slope of best line, $y = a + bx$
$\sigma_a, \sigma_b$	Standard errors of $a$ and $b$
$X_i, Y_i$	“Observed” data points
$r_i$	Correlation coefficient between uncertainty in $X_i$ and $Y_i$
$\omega(X_i), \omega(Y_i)$	Weights of $X_i$ and $Y_i$
$x_i, y_i$	Least squares adjusted points: $\bar{X} + \beta_i, \bar{Y} + b\beta_i$
$\alpha_i$	$\sqrt{\omega(X_i)\omega(Y_i)}$
$W_i$	$\frac{\omega(X_i)\omega(Y_i)}{\omega(X_i) + b^2\omega(Y_i) - 2r_i\alpha_i b}$
$\bar{X}, \bar{Y}$	$\frac{\sum W_i X_i}{\sum W_i}, \frac{\sum W_i Y_i}{\sum W_i}$
$U_i, V_i$	$X_i - \bar{X}, Y_i - \bar{Y}$
$\bar{x}$	$\frac{\sum W_i x_i}{\sum W_i}$
$\beta_i$	$W_i \left[ \frac{U_i}{\omega(Y_i)} + \frac{bV_i}{\omega(X_i)} - (bU_i + V_i) \frac{r_i}{\alpha_i} \right]$
$u_i$	$x_i - \bar{x}$

and  $V_i$  are calculated based on the adjusted weighting. Using  $U_i$ ,  $V_i$ , and  $\beta_i$ , a new value of the slope is calculated from Eq. (22b), and the process is repeated until the slope converges. Convergence is determined when the slope changes by less than 0.001 on successive iterations. Then, using Eq. (22a), the intercept  $a$  is calculated. Finally, the standard error of each parameter is calculated using the final values of the slope and intercept with Eqs. (22d) and (22c).

For the mixtures considered in this study, the correlation coefficient for the linear fits are greater than 0.99 (i.e.  $r^2 > 0.99$ ), indicating a good fit.

### 3 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 1 L sampling bottle.

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 is expected to have minimal effect on the homogeneity of the reaction chamber. This has been verified experimentally by measuring the ignition delay with and without the GSV present; little difference in the ignition delay was found. Moreover, it is expected that the removal of samples will also have minimal effect on the measured ignition delay, which has again been verified by testing with and without sampling.

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 measure the displacement of the mass, allowing the direct measurement of the COC time.

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 (4.5–50 ms) that is used to control the timing of the opening of the GSV during the induction period.

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 nitrogen so that the fuel has a mole fraction of approximately 0.001. Then the sample bottle is disconnected from the GSV and transported to the Gas Chromatograph/Mass Spectrometer, where the sample undergoes analysis.

## 4 Gas Chromatograph/Mass Spectrometer

### 4.1 Theory of Gas Chromatography/Mass Spectrometry

#### 4.1.1 Gas Chromatography

A gas chromatograph (GC) is a device that physically separates components of a gas sample by means of a tube—known as a *column*—lined or filled with a substance that interacts with the components in the sample. The sample is transported the length of the column by a flow of carrier gas,

usually helium or hydrogen, also known as the *mobile phase*. A detector is placed at the outlet of the column to measure the amount and type of components eluted from the column.

The separation of the gaseous components in the sample is effected by the interaction of the sample with the lining of the column, known as the *stationary phase*. Gaseous species that have little interaction with the stationary phase and spend most of their time in the mobile phase are eluted from the column before species that interact strongly with the stationary phase and spend little time in the mobile phase [115].

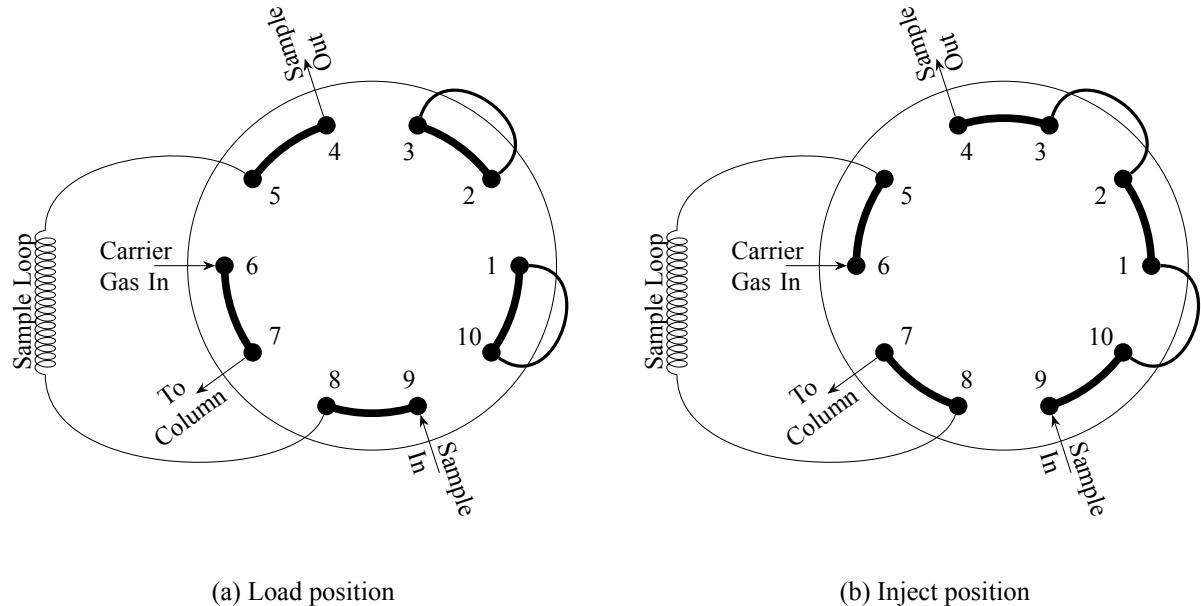
The column is placed in an insulated oven so that its temperature may be controlled. The column temperature in a given analysis may be constant or may be controlled as a function of time. Since the time that a given component takes to move through the column is a function of temperature, this facility allows optimization of the elution time of the various components in the sample.

The injector of the GC is also temperature controlled; the temperature of the injector is set high enough so that all components (including the solvent, if any) are vaporized but not so high that the sample starts to degrade. On the present GC, a split/splitless injector is installed. This allows for operation in the split mode, where a percentage of the injected sample is removed from the injector prior to injection into the column, or in the splitless mode, where nearly all of the sample is injected into the column. The split mode is used in this work. The amount of sample removed is controlled by a valve in the injector. The split ratio is calculated according to Eq. (23)

$$\text{Split Ratio} = \frac{\text{Column Flow} + \text{Vent Flow}}{\text{Column Flow}} \quad (23)$$

where the column flow is the carrier gas flow rate at the head of the column and the vent flow is the flow out of the splitter vent [115].

A GC may also be equipped with a gas sample injection valve, in addition to the split/splitless injector. The present GC is equipped with a 10-port Valco sample injection valve, shown schematically in Fig. 4. Each port is numbered, and curved lines indicate connections between ports. The sample injection valve is used to inject a consistent mass of sample into the column with each in-



**Figure 4:** GC/MS sample injection valve.

jection. This permits reliable quantification of the components in the sample. First, the sample is loaded into the sample loop when the valve is in the “load” position, as in Fig. 4a. Then, the valve is electrically actuated at the start of the GC temperature program to rotate the connections into the “inject” position. This allows carrier gas to flow through the sample loop and push the sample from the sample loop into the column (Fig. 4b). The valve is actuated again after 0.1 min to remove the sample loop from the carrier gas path (Fig. 4a) and restore the “load” position.

The sample injection valve is equipped with a heater to maintain the valve body at a constant temperature and the entire assembly is installed in an insulated box. However, this heater is insufficient to heat the tubes attached to the valve, so an additional heater rope is installed in the insulated box. To measure the temperature of the sample loop directly, a thermocouple is fixed to the sample loop by ceramic cement. The temperature of the sample loop is used to control the power provided to the rope heater, while a built-in thermocouple is used to control the power provided to the valve body heater.

### 4.1.2 Mass Spectrometry

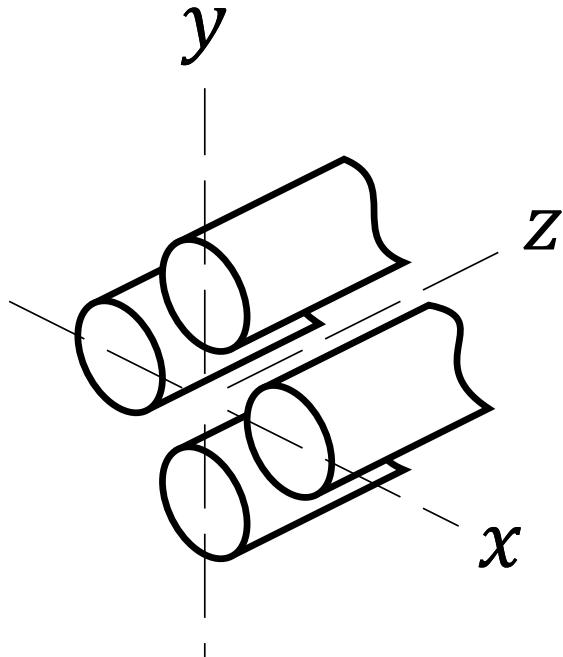
Many types of detectors are available for GC analyses. These commonly include flame ionization detectors, thermal conductivity detectors, and mass spectrometers. In this work, a mass spectrometer is used to identify and quantify the species eluted from the column.

The fundamental operation of a mass spectrometer (MS) is to separate ions with different mass-to-charge ( $m/z$ ) ratios from each other. Ions are generated from the effluent of the column—including sample components, mobile phase, and column bleed, collectively called *analytes*—by an ionization source, typically either electronic or chemical in nature. Nearly all of the ions generated will have a single charge,  $z = 1$  [116]; thus, the  $m/z$  value of the ions is also considered to be the mass.

In this work, electron ionization (EI) is used to generate the ions for analysis. The effluent from the column is passed in front of an electron source so that the electrons impact the analytes molecules and remove an electron, generating a positive ion. EI is a *hard ionization* technique, in that the electron impact transfers a significant amount of energy to the analyte molecule [116]. The additional energy causes the ion to fragment into two or more pieces; the spectrum of these fragments is characteristic for a given molecule and can be used as a “fingerprint” to identify the source molecule for a given spectrum.

After ionization, the fragments are accelerated out of the ionization chamber towards the detector. Several detectors are available, including time-of-flight and transmission quadrupole. All of these detectors require high vacuum to avoid impact of ions of interest with extraneous species prior to their reaching the detector. The vacuum is achieved in the present MS by a two-stage design, using a rotary vane pump in series with a turbomolecular pump to achieve ultimate pressures of approximately 2 Pa.

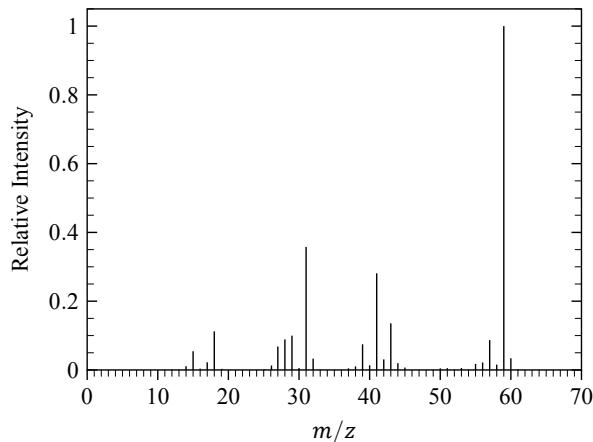
The MS used in this study is a transmission quadrupole type, shown schematically in Fig. 5. The transmission quadrupole separates specific ions from the flow of all of the ions from the ion source by means of a time-varying electric field. Conceptually, the quadrupole can be imagined as four round rods, arranged in a cross pattern, with their long axes aligned parallel to the ion flow.



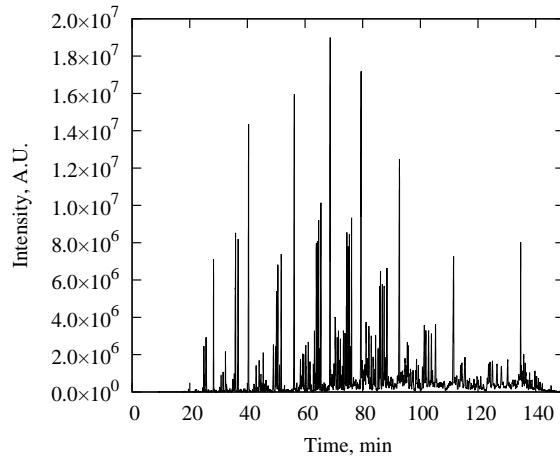
**Figure 5:** Schematic of the transmission quadrupole in an MS.

The ions are admitted to the rods at one end (e.g. at the origin in Fig. 5) and the detector is placed perpendicular to the long axes of the rods at the other end (not shown in Fig. 5). A positive DC voltage is applied to one pair of the rods, while a negative DC voltage is applied to the other pair of rods; in addition, an AC voltage is applied simultaneously to all four rods. Assuming a specific ratio of AC amplitude to DC amplitude, ions of a certain  $m/z$  will remain in the ion beam in the center of the rods and reach the detector. Then, holding the AD:DC amplitude ratio fixed, the amplitudes are increased or decreased together. This varies the particular  $m/z$  that will remain in the ion beam and reach the detector as a function of time [116]. The voltage amplitude is ramped to measure the desired  $m/z$  range over a time  $s$ , the sample time. The inverse of  $s$  is known as the *scan rate*.

This process of scanning the voltage amplitudes generates a mass spectrum. For a given scan from the lowest to the highest voltage, the number of ions of a particular  $m/z$  is measured at the detector. This information is typically presented in the form of a relative intensity plot. The abscissa is the (integer)  $m/z$  while the ordinate is the intensity of a particular  $m/z$  scaled by the maximum intensity of all the  $m/z$  in a given scan. It is not required that the  $m/z$  be integers, although they



**Figure 6:** Example mass spectrum for a given scan during a GC/MS analysis



**Figure 7:** Example TIC for a GC/MS analysis

are usually presented as such for simplicity. An example of a mass spectrum for a given time in a GC/MS analysis is shown in Fig. 6.

In addition to the mass spectrum, the MS reports the total ion current (TIC), also known as the total ion chromatogram. This is the sum of all of the mass intensities for a given scan. A sample TIC is plotted in Fig. 7 where the abscissa is time in min and the ordinate is an arbitrary unit. Finally, the MS can also report the mass chromatogram (MC), which is the chromatogram for a specific  $m/z$  as a function of time.

#### 4.1.3 Identification and Quantification of Species using GC/MS

Species are identified using a GC/MS system by their unique mass spectra. For each peak in the TIC, the set of mass intensities over the peak are averaged; these intensities are compared to a database supplied by the National Institute of Standards and Technologies (NIST).

In this work, the external standard method of quantification is used. This requires that calibration curves for each of the species of interest be created, relating the area of the peak in the TIC to the number of moles of analyte reaching the detector. The number of moles of analyte can in turn be related to the number of moles of sample in the gas sample injection valve sample loop. Once the calibration curve is generated, it is used to relate the measured area of the peak of particular

component to its mole fraction. Detailed methods for the construction of calibration curves will be given in Sec. 4.2.

## 4.2 Experimental Procedure

The GC/MS used in this study is a Shimadzu model QP-2010S, equipped with a 10-port Valco sample injection valve and split/splitless injector, as mentioned previously. The column used is a Phenomenex model ZB-5MS capillary column with length 30 m, inner diameter 0.25  $\mu\text{m}$ , and film thickness of 0.25  $\mu\text{m}$ . The operating parameters of the GC/MS (known as the “method”) are shown in ??.

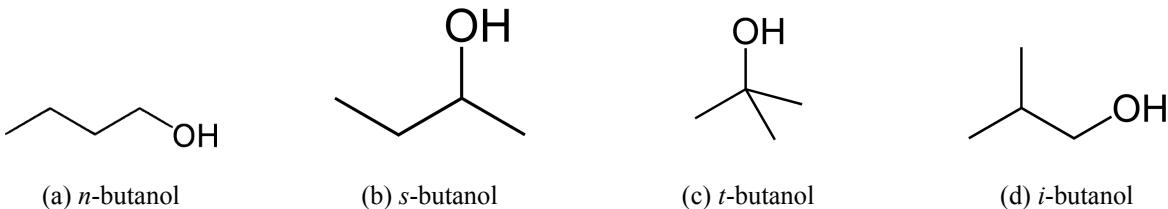
The pressure in the gas injection valve sample loop is monitored by an MMA type pressure transducer, the same model as used in Sec. 2.8.2. The sample outlet in Fig. 4 is open to the atmosphere so that a consistent pressure is maintained in the sample loop. The volume of the sample loop is 10  $\mu\text{L}$ . With the temperature, pressure, and volume of the sample loop known, the number of moles of sample can be calculated by the ideal gas law.

A calibration curve is built for the major species by the following procedure. First, the sample bottle is vacuumed to less than 1 Torr. Mixtures of the species of interest in the liquid state are prepared by massing each component on a high-accuracy AND-201 scale. A small mass of this mixture is drawn into a syringe and massed on the same scale. The mixture is injected through a septum into the sample bottle. Then the sample bottle is filled with high-purity nitrogen so that the largest mole fraction of a species of interest is approximately 0.001. The sample bottle is connected to the sample injection valve on the GC/MS and the valve on the sample bottle is opened and quickly closed. The pressure is allowed to equalize and the GC/MS is started.

After the completion of the GC/MS method, the total ion chromatogram (TIC) is analyzed by the Shimadzu GCMS Post-run Analysis software (version XXXX). Each peak is automatically integrated by the software so that its area can be found. The peak area is then related to the number of moles of sample sent to the detector by linear least-squares regression. This calibration curve is used to compute the mole fraction of any given peak area for that species.

**Table 3:** HHV of Ethanol, Butanol Isomers, and Gasoline

Compound	Ethanol [117]	Butanol Isomers [117]	Gasoline [118]
HHV [MJ/kg]	29.67	$\approx 36$	48.46



**Figure 8:** Skeletal structures of the butanol isomers

## 5 The Butanol Isomers

Butanol is the four carbon alcohol, and has four isomers: *n*-butanol (1-butanol); *s*-butanol (2-butanol); *t*-butanol (2-methyl-2-propanol); and *i*-butanol (2-methyl-1-propanol). The skeletal structures of the four isomers are shown in Fig. 8. Three of the butanol isomers can be produced by biological pathways (*n*-, *s*-, and *i*-butanol) [24, 25], making them candidates for the “second-generation” of biofuels [23, 24]. Although *t*-butanol does not have an identified biological production pathway, it has commercial significance as an octane enhancer. In addition, the four isomers of butanol represent the smallest alcohol system with all four types of branching in the skeleton. This makes them an excellent candidate to build kinetic models that can be extended to larger alcohols with similar structures.

Table 3 shows a comparison of the higher heating value of the butanol isomers with ethanol and gasoline. The higher energy density of the butanol isomers allows them to be blended in gasoline in higher proportions and reduces the volumetric fuel economy (e.g. mpg) impact of replacing gasoline with biofuels.

## 6 Experimental Procedure

The reactants used in this study, along with their purities, are shown in Table 4. 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 h.

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 [62], GC-FID [92], and GC-TCD [88]. These studies have verified the concentration of *n*-butanol, water, and *n*-decane, respectively. In addition, both the work by Kumar et al. [92] on *n*-decane and the study of Weber et al. [62] 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 4 shows the experimental conditions considered in this study. The compressed pressure conditions have been chosen to match the previous *n*-butanol study [62], 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. [57] and Moss et al. [53] used relatively dilute mixtures, so we have included higher fuel loading conditions. Furthermore, the compressed temperature conditions we have studied ( $T_C = 715\text{--}910\text{ K}$ ) have not been examined in any other study, to our knowledge.

Each compressed pressure and temperature condition is repeated at least six times to ensure

**Table 4:** Experimental Conditions and Reactant Purities

Reactant (Purity)					Equivalence Ratio $\phi$	Compressed Pressure $P_C$ (bar)
s-butanol (99.99%)	i-butanol (99.99%)	t-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

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.

## 7 Experimental Results

Figure 9 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.

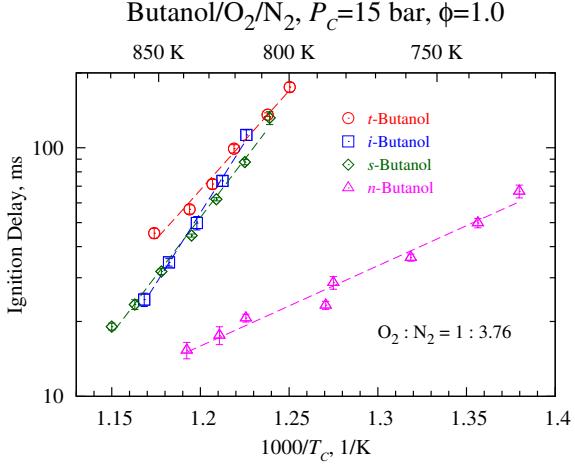
Figure 9 demonstrates the differences in reactivity between the isomers for stoichiometric fuel/air mixtures at compressed pressure  $P_C = 15$  bar. *n*-Butanol is clearly the most reactive, followed by *s*-

and *i*-butanol, which have very similar reactivities in this temperature and pressure range. *t*-Butanol is the least reactive.

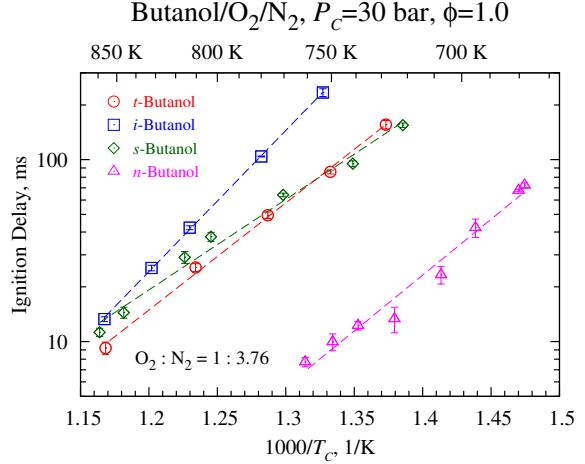
The order of reactivity found in the RCM at 15 bar agrees with the shock tube study at higher temperatures (approximately 1275–1667 K) and lower pressure (1.5 atm) by Stranic et al. [57] but differs slightly from the studies of Moss et al. [53] who measured ignition delays in a shock tube near 1.5 atm and between 1275–1400 K, and Veloo and Egolfopoulos [29] who measured atmospheric-pressure laminar flame speeds. In particular, Moss et al. [53] and Veloo and Egolfopoulos [29] found distinct differences in reactivity between *s*- and *i*-butanol, but the present study and the study by Stranic et al. [57] found that they were nearly indistinguishable in terms of reactivity under the conditions investigated. In addition, Stranic et al. [57] noted some disagreement between their shock tube ignition data and the data of Moss et al. [53] 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 Fig. 10. In Fig. 10, the order of reactivity is different than in Fig. 9, where the only variation between the plots is the compressed pressure; in Fig. 10 the compressed pressure is  $P_C = 30$  bar. Fig. 10 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. [57] differ from those in the current study at higher pressure (despite the agreement at lower pressure). In their study, Stranic et al. [57] 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. Figure 11 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



**Figure 9:** Ignition delays of the four isomers of butanol at compressed pressure  $P_C = 15$  bar. Dashed lines are least squares fits to the data.



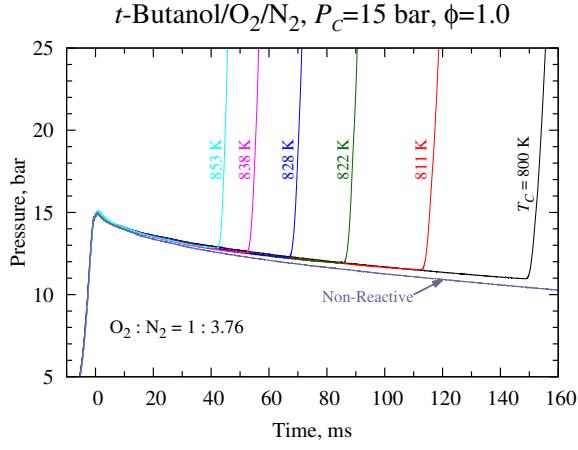
**Figure 10:** Ignition delays of the four isomers of butanol at compressed pressure  $P_C = 30$  bar. Dashed lines are least squares fits to the data.

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.

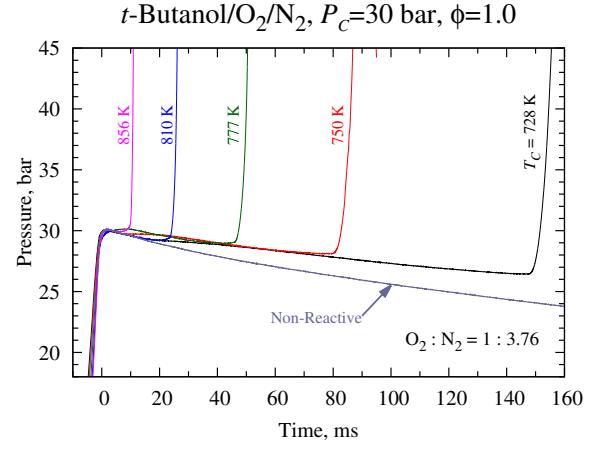
Figure 12 shows the pressure traces for *t*-butanol experiments at 30 bar for stoichiometric mixtures in air. The effect of pre-ignition heat release is even more striking in this figure, with substantial changes in the slope of the pressure trace during the reactive runs. Comparing to the pressure traces 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. Figure 13 shows Arrhenius plots of the ignition delays for the three equivalence ratios. As with the previous *n*-butanol experiments at 15 bar [62]  $\phi = 0.5$  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.

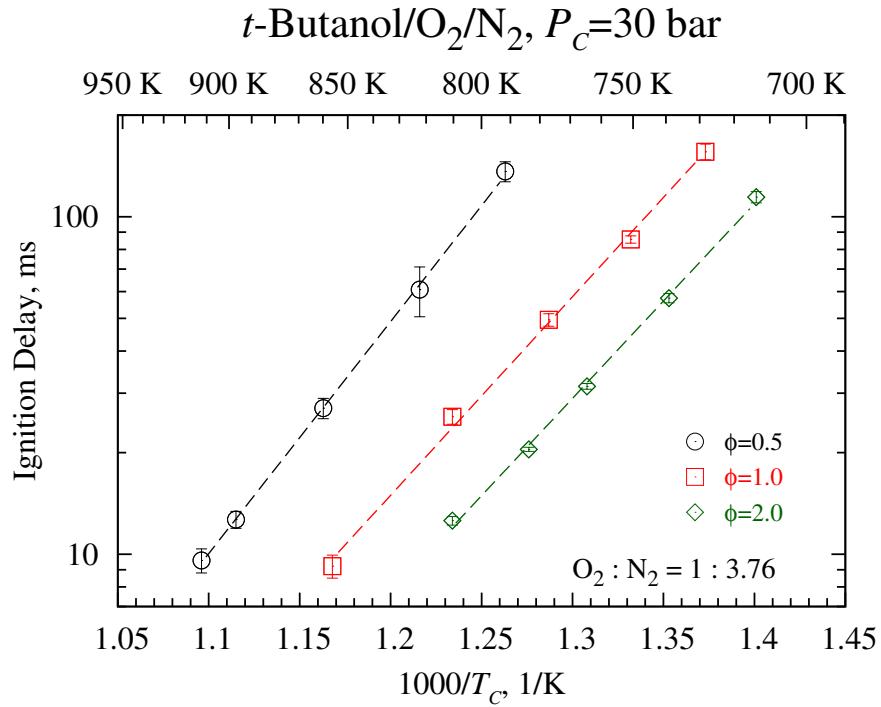
A more interesting comparison is of the pressure traces of the three equivalence ratios. It is



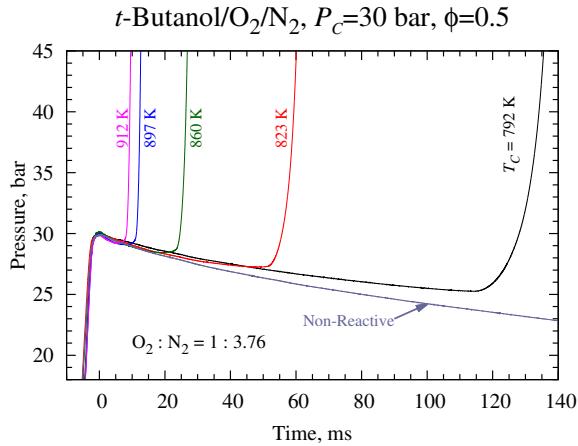
**Figure 11:** Pressure traces of the 15 bar *t*-butanol experiments, in stoichiometric air.



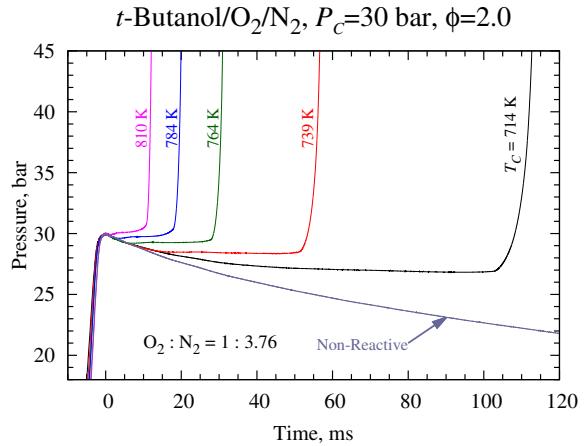
**Figure 12:** Pressure traces of the 30 bar *t*-butanol experiments, in stoichiometric air.



**Figure 13:** Ignition delays of three equivalence ratios of *t*-butanol in air, for  $P_c = 30$  bar. Lines represent least squares fits to the data.



**Figure 14:** Pressure traces of the 30 bar *t*-butanol experiments,  $\phi = 0.5$  in air.

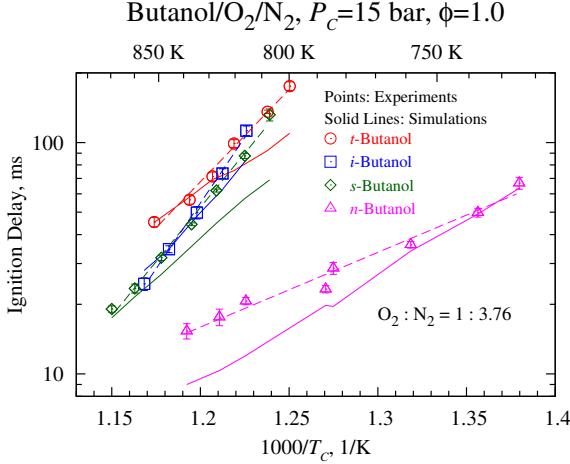


**Figure 15:** Pressure traces of the 30 bar *t*-butanol experiments,  $\phi = 2.0$  in air.

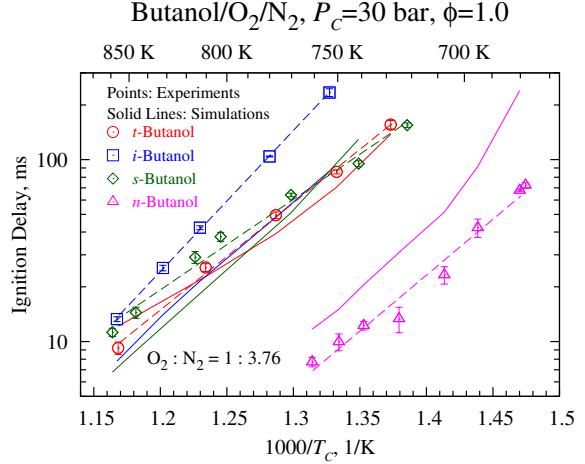
clear from Figures 12, 14, and 15 that there are qualitative differences in the pre-ignition heat release between the three equivalence ratios. This is most likely due to the effect of the increased (reduced) fuel mole fraction in the  $\phi = 2.0$  ( $\phi = 0.5$ ) case, since the mole fraction of fuel 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 4. 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.

## 8 Simulation Results

Simulations are performed with the kinetic mechanism from Sarathy et al. [119] and a recent mechanism discussed in Hansen et al. [32] and Merchant et al. [120] that is denoted as the MIT mechanism hereafter. Other recent mechanisms, such as the mechanism from Frassoldati et al. [121] 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. [119] 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. [57] up to 48 atm, our previous study on *n*-butanol [62], and the data being published in this study at 15 bar. Importantly, the mechanism of Sarathy et al. [119] was validated



**Figure 16:**  $P_c = 15$  bar, stoichiometric mixtures in air. Comparison of VPRO simulations using the kinetic mechanism of Sarathy et al. [119] with experimental ignition delays.



**Figure 17:**  $P_c = 30$  bar, stoichiometric mixtures in air. Comparison of VPRO simulations using the kinetic mechanism of Sarathy et al. [119] with experimental ignition delays.

only for the 15 bar RCM data for all four isomers, but not the 30 bar data also being published here. The MIT mechanism [32, 120] 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 16 and 17 show comparison of the VPRO simulations with the experimental data using the mechanism of Sarathy et al. [119]. As Sarathy et al. [119] showed in their work (and as we show here in Fig. 16), they found good agreement of the model predictions with the present RCM data at 15 bar. At  $P_c = 30$  bar (Fig. 17), 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. [119] 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.

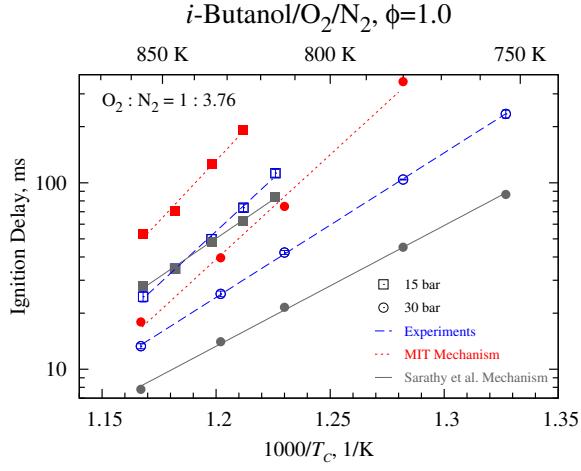
VPRO simulations for *n*- and *s*-butanol (and also some conditions for *t*-butanol) using the MIT mechanism [32, 120] do not ignite during the duration of the simulations (the same as the experimental duration), and therefore no simulations are shown for these fuels. In Fig. 18, VPRO

simulations at 15 and 30 bar using both mechanisms are shown for *i*-butanol. It is seen that the mechanism from Sarathy et al. [119] is in better agreement at 15 bar. However, at 30 bar the MIT mechanism [32, 120] over-predicts the ignition delay (as at 15 bar), while the Sarathy et al. [119] mechanism under-predicts the ignition delay. The reason for these diverging predictions will be explored and discussed below.

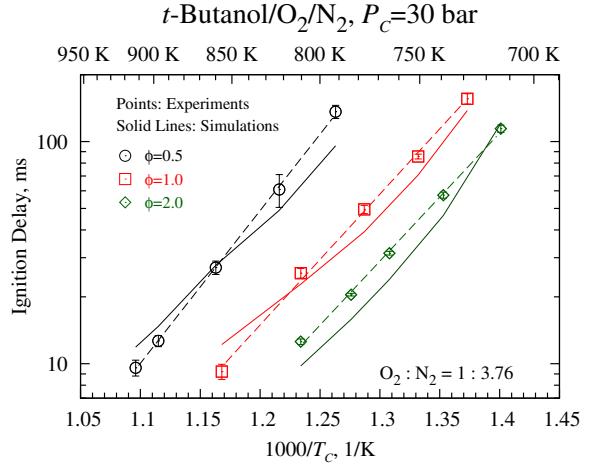
The agreement of the mechanism by Sarathy et al. [119] with the off-stoichiometric mixtures of *t*-butanol is also quite good, as shown in Fig. 19. Figures 20a – 20c show more detailed comparisons of the simulated pressure traces and the experimental results, for similar temperatures at the three equivalence 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.

## 9 Discussion

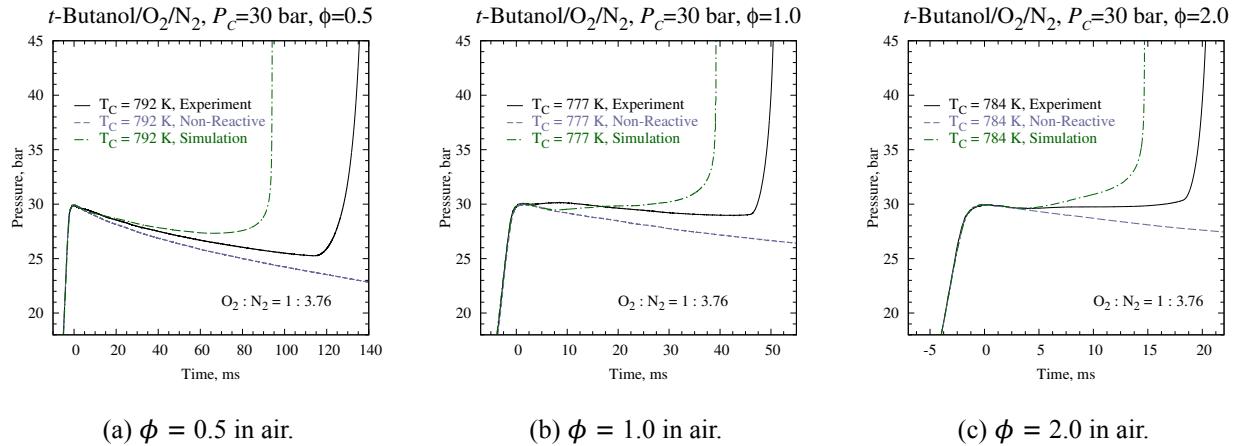
The relatively good agreement of the mechanism of Sarathy et al. [119] with the experimental data, even for conditions at which the mechanism has not been validated, suggests that using the mechanism to further interpret our experimental data is not a facile exercise. In particular, Figures 21–24 show the initial steps of the fuel breakdown process for each isomer. The percentages listed are the percent of the reactant that is consumed to produce the product shown, by all the reactions that can produce that product from the reactant (except where one particular reaction is noted). These numbers are determined by integrating the rate of production or consumption of each species by each reaction up to the point of 20% fuel consumption, and normalizing each reaction by the total produced or consumed of each species up to that point. The 20% fuel consumption point is chosen



**Figure 18:** Comparison of VPRO simulations using the kinetic mechanism of Sarathy et al. [119] (solid lines) and the MIT mechanism [32, 120] (dotted lines) with the experimental ignition delay results (dashed lines) for stoichiometric mixtures of *i*-butanol in air at  $P_C = 15$  bar (squares) and  $P_C = 30$  bar (circles).



**Figure 19:** Comparison of the simulations using the kinetic mechanism of Sarathy et al. [119] for three equivalence ratio mixtures of *t*-butanol in air at  $P_C = 30$  bar.



**Figure 20:** Pressure traces of selected *t*-butanol experiments compared with the corresponding non-reactive and simulated traces, using the mechanism of Sarathy et al. [119].

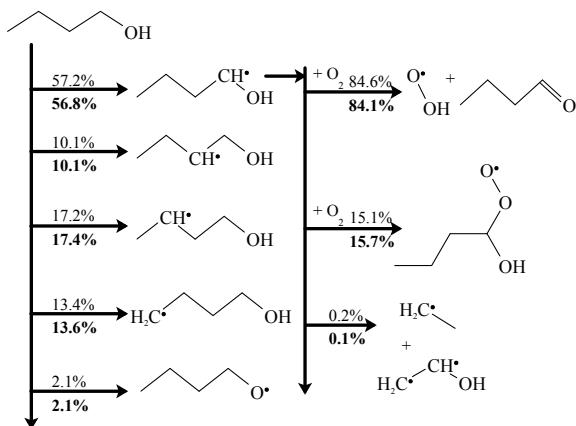
because it is before small molecule chemistry takes over to drive the ignition, and it has been used previously [62, 119]. The rates of production are taken from a CONV simulation, with initial conditions 750 K and 15 bar as well as 750 K and 30 bar. These conditions are representative of typical conditions after compression in the present RCM experiments. The plain text percentages on top of the arrows are the 15 bar case and the bold numbers underneath are for the 30 bar case.

In the following discussion, carbon-centered radicals are labeled according to their distance from the hydroxyl moiety in the fuel molecule. Therefore, the  $\alpha$  carbon is the closest to the hydroxyl, followed by  $\beta$ ,  $\gamma$ , and  $\delta$  carbons. Not all of the butanols have all of the types of carbons listed here, due to varying chain lengths. For instance, *t*-butanol has one  $\alpha$  carbon, three  $\beta$  carbons, and no  $\gamma$  or  $\delta$  carbons.

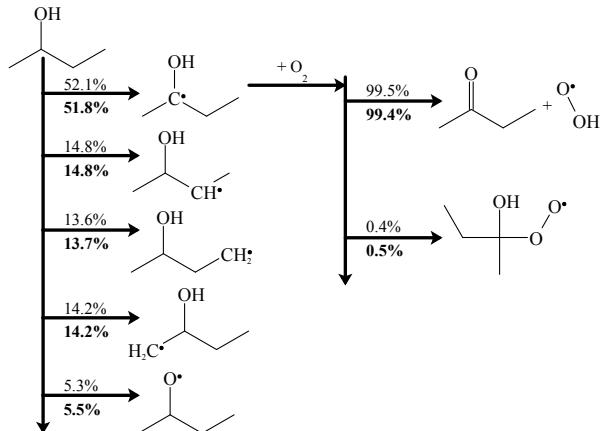
As expected at the relatively low temperature of this analysis, H-abstraction reactions dominate over unimolecular decomposition for all four isomers. It is also expected that *n*-, *s*-, and *i*-butanol react primarily to their respective  $\alpha$ -hydroxybutyl radicals, since the  $\alpha$  C-H bond has the lowest energy [119]. Due to its unique structure, *t*-butanol does not have an  $\alpha$ -hydroxybutyl radical that can be formed by H-abstraction, so *t*-butanol is primarily consumed to form the  $\beta$ -hydroxybutyl radical, because the O-H bond energy is much higher than  $\beta$  C-H bond energies.

The unique structure of *t*-butanol continues to affect the second level of reactions as well. In the temperature and pressure regime investigated, *t*-butanol tends to add to molecular oxygen at the carbon radical site, forming a hydroxybutylperoxy ( $\text{RO}_2$ ) species. That this pathway is dominant is due to the fact that *t*-butanol has no  $\alpha$ -hydroxybutyl radical. For the other three butanol isomers that do have an  $\alpha$ -hydroxybutyl radical, the second level of reactions primarily produces an aldehyde +  $\text{HO}_2$  by direct reaction — no hydroxybutylperoxy adduct is formed in this reaction, and there is no possibility for typical hydrocarbon low-temperature chain branching. Therefore, it is hypothesized that the pre-ignition heat release seen in *t*-butanol is caused by the oxygen addition to the fuel radical to form  $\beta$ -hydroxybutylperoxy, which is an exothermic reaction.

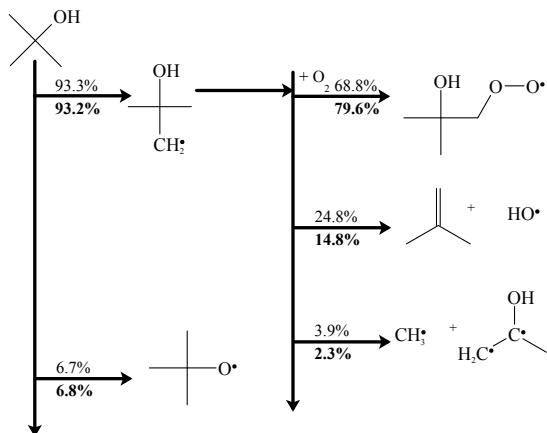
Figure 25 shows the total cumulative heat release of each isomer and the cumulative heat release of an important reaction for each of the isomers (inset), from a CONV simulation with initial



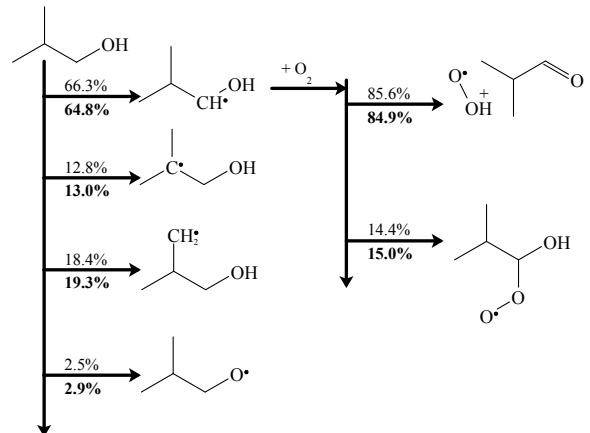
**Figure 21:** Pathway analysis for simulations of *n*-butanol at temperature of 750 K, in stoichiometric air, using the mechanism of Sarathy et al. [119]. Percentages in normal text represent an initial condition of 15 bar; bold text is for 30 bar.



**Figure 22:** Pathway analysis for simulations of *s*-butanol at temperature of 750 K, in stoichiometric air, using the mechanism of Sarathy et al. [119]. Percentages in normal text represent an initial condition of 15 bar; bold text is for 30 bar.



**Figure 23:** Pathway analysis for simulations of *t*-butanol at temperature of 750 K, in stoichiometric air, using the mechanism of Sarathy et al. [119]. Percentages in normal text represent an initial condition of 15 bar; bold text is for 30 bar.



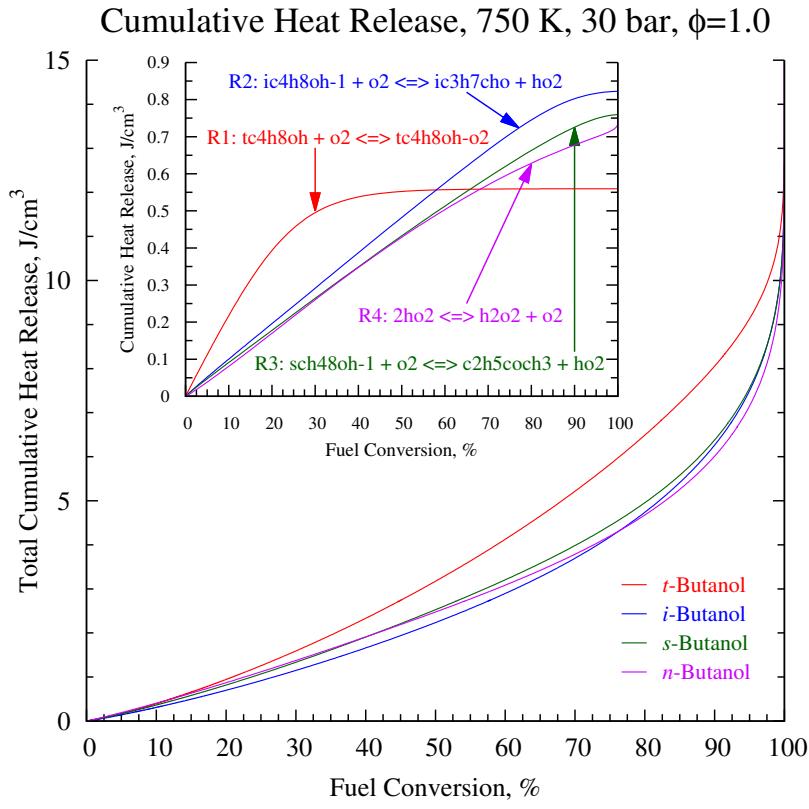
**Figure 24:** Pathway analysis for simulations of *i*-butanol at temperature of 750 K, in stoichiometric air, using the mechanism of Sarathy et al. [119]. Percentages in normal text represent an initial condition of 15 bar; bold text is for 30 bar.

conditions of 750 K and 30 bar; analysis of 15 bar results is substantially similar. The cumulative heat release in the inset is found by integrating the heat release by each reaction with respect to time, while the reactions shown are the respective reactions that have released the most heat up to the 20% fuel consumption point for each isomer. The abscissa of the plot is the fuel conversion, in percent. This choice of x-axis allows a fair comparison of the heat release, because the ignition delays of each isomer are markedly different, so comparing the heat release with a time axis is more difficult. In Fig. 25, exothermicity is represented by positive quantities.

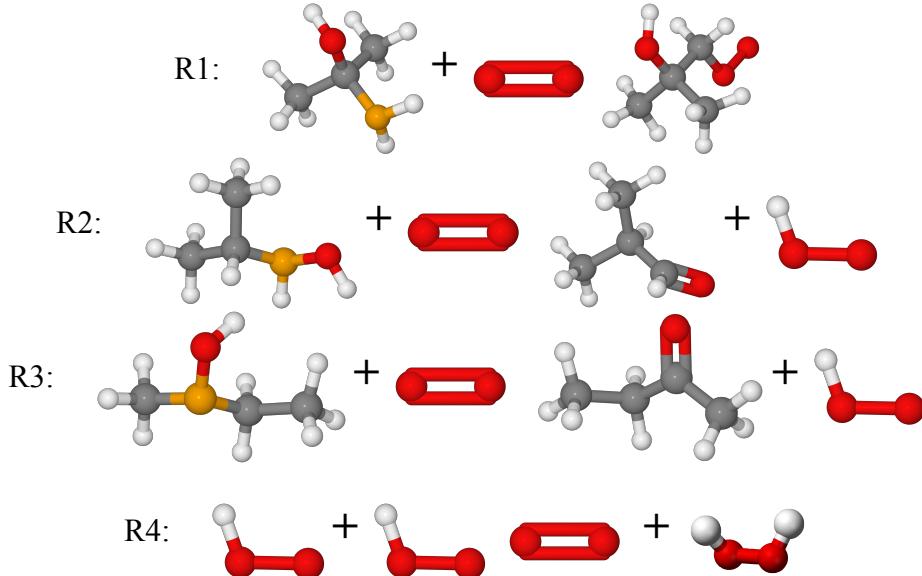
In Fig. 25, it is clear that *t*-butanol has higher heat release at low fuel consumption (during the induction period) than the other three isomers. In addition, the primary heat release reaction for *t*-butanol has created much more heat than the primary reactions of the other three isomers. As the reactions proceed, and the temperature increases, the reverse reaction in the *t*-butanol case becomes more important, and the heat release contribution of this oxygen-addition reaction levels off. The dominance of this reaction at early times is unique to *t*-butanol ignition, and appears to be driving the pre-ignition heat release.

Other researchers have also undertaken studies of the low to intermediate temperature combustion of *t*-butanol. Lefkowitz et al. [37] performed a study in the Variable Pressure Flow Reactor (VPFR) at Princeton University on the oxidation of *t*-butanol over the temperature range from 680–950 K, at 12.5 atm and stoichiometric mixture conditions. It is interesting to note that they found no evidence of traditional hydrocarbon low temperature chemistry. They did, however, find significant quantities of acetone, peaking at approximately 800 K. Lefkowitz et al. [37] concluded that the primary pathways of acetone formation are tautomerization of propen-2-ol and  $\beta$ -scission of the alkoxy radical, based on an analysis of the mechanism from Grana et al. [33]. Both of these pathways are dependent on unimolecular decomposition of the hydroxybutyl radicals. However, this mechanism has only been validated for flame studies; indeed, an updated version of this model (by Frassoldati et al. [121]) is unable to predict the low-temperature ignition delays measured in this study and hence is not considered for analysis.

In contrast to the study of Lefkowitz et al. [37] path analysis of the mechanism by Sarathy et al.



**Figure 25:** Total cumulative heat release and cumulative heat release by important reactions (inset) as a function of fuel consumption from a simulation using the mechanism of Sarathy et al. [119] with initial conditions of 750 K and 30 bar, in stoichiometric air. See Fig. 26 for definitions of reactions in the inset.



**Figure 26:** Reactions causing the most heat release in the ignition of the butanol isomers. The reaction number refers to Fig. 25.

[119] shows that unimolecular decomposition of the hydroxybutyl radicals is not the most important pathway; as mentioned earlier, the most important pathway is the formation of  $\beta$ -hydroxybutylperoxy. Further analysis shows that the primary pathway of reaction of the *t*-butanol  $\beta$ -hydroxybutylperoxy species is through the Waddington mechanism. The Waddington mechanism has been shown experimentally to be an important pathway for  $\beta$ -hydroxypentylperoxy radicals in the low temperature combustion of *i*-pentanol [74], as well as the  $\beta$ -hydroxybutylperoxy radicals of *i*- and *t*-butanol [122]. *t*-Butanol only produces  $\beta$ -hydroxybutyl radicals, and one of the products of the Waddington pathway in *t*-butanol is acetone (the others are formaldehyde and hydroxyl radical); over 88% of the acetone produced up to the 20% fuel consumption point is produced by the Waddington reaction. The study in the VPFR thus provides further evidence of the importance of low-temperature hydroxybutylperoxy chemistry in *t*-butanol, although it is not traditional hydrocarbon low-temperature chemistry.

Up to this point, the discussion has focused mainly on the importance of hydroxybutylperoxy chemistry in *t*-butanol. Nevertheless, the chemistry of the hydroxybutylperoxy species is important in the combustion of the other isomers of butanol as well. Using the high pressure shock tube at RWTH Aachen University, Vranckx et al. [60] showed the importance of peroxy chemistry pathways in the autoignition of *n*-butanol. By adding a lumped peroxy model to an existing kinetic model for *n*-butanol combustion, they were able to substantially improve agreement of the model with their experiments at high pressure and low temperature. In their mechanism, Sarathy et al. [119] included a semi-detailed peroxy chemistry model for all the isomers of butanol. In fact, one of the main differences between the mechanism from Sarathy et al. [119] and the MIT mechanism [32, 120] is their respective treatment of the peroxy mechanism. Specifically, oxygen-addition chemistry is not included in the MIT mechanism for *i*-butanol [32, 120]. In addition, the radical that primarily controls *i*-butanol decomposition is hydroxyl (OH) in the mechanism of Sarathy et al. [119] (generated by the peroxy chemistry sub-mechanism), but is hydroperoxyl ( $\text{HO}_2$ ) in the MIT mechanism [32, 120] (generated from the direct  $\alpha$ -hydroxybutyl +  $\text{O}_2 = \text{HO}_2 + \text{aldehyde}$  formation pathway).

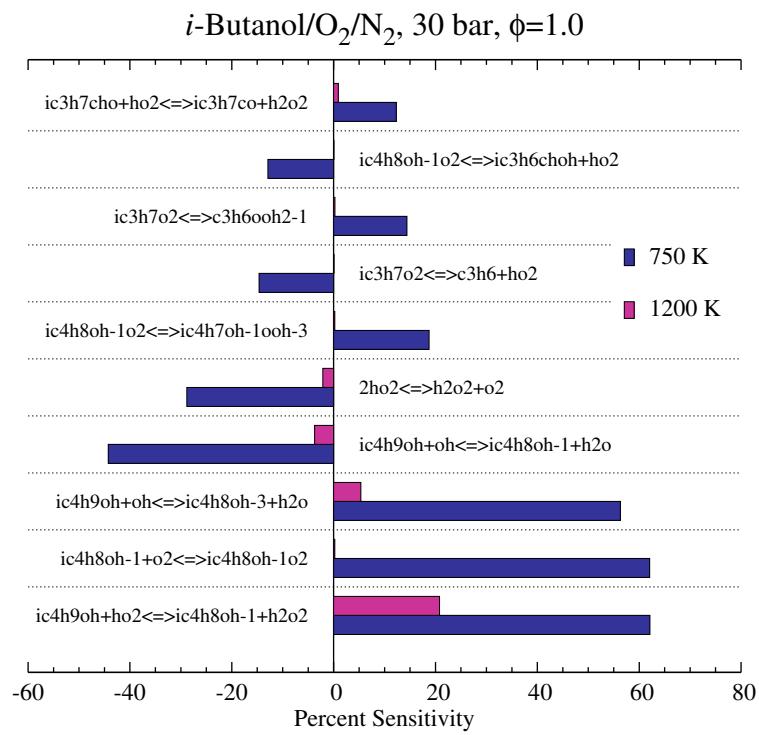
In their work, Sarathy et al. [119] used the reaction rates computed by Silva et al. [123] for the hydroxyethyl system (i.e. ethanol as the parent fuel) to determine the rate of direct reaction of  $\alpha$ -hydroxybutyl and oxygen to form aldehyde and HO<sub>2</sub>, and then set the rate of oxygen addition to the  $\alpha$ -hydroxybutyl radical (to form  $\alpha$ -hydroxybutylperoxy) so that the total rate was less than the collisional limit. The rates of oxygen addition for the other radicals were prescribed depending on the type of carbon (primary, secondary, or tertiary) based on studies of butane and *i*-octane [119]. Based on the well-known importance of hydroxyl in driving the reactivity of combustion systems, and the sources of the estimates for the reaction rates of oxygen addition to hydroxybutyl (i.e. the entry to the pathway that controls the rate of hydroxyl formation), it can be hypothesized that the rates of hydroxybutylperoxy formation are overestimated in the mechanism of Sarathy et al. [119], as the simulated results under-predict the experimental data of *i*-butanol.

This hypothesis is supported by the results shown in Fig. 27, which shows the linear brute force sensitivity of the ignition delay ( $\tau$ ) of *i*-butanol to changes in the A-factor of the rate coefficient, using the mechanism from Sarathy et al. [119]. The percent sensitivity is defined as the difference between the ignition delay when the A-factor of each reaction is halved and the nominal ignition delay, normalized by the nominal ignition delay, as shown below:

$$S_i = \frac{\tau(0.5A_i) - \tau(A_i)}{\tau(A_i)} \times 100\% \quad (24)$$

Therefore, negative sensitivity means that halving the A-factor of a reaction decreases the ignition delay, and positive sensitivity indicates the ignition delay increases. These results are for CONV simulations with initial conditions of 750 K and 30 bar as well as 1200 K and 30 bar.

The most sensitive reaction at the lower temperature is the initiation reaction of the fuel with hydroperoxyl radical to form the primary fuel radical and the second most sensitive reaction is the addition of oxygen to the primary radical. Both of these reactions have positive sensitivities, indicating that reducing the rate of these reactions would increase the ignition delay (increasing the computed ignition delay will improve the agreement of the simulations relative to the experiments in this case). It is apparent, then, that reducing the amount of fuel propagating into the low temper-



**Figure 27:** Linear brute force sensitivity analysis of the ignition delay with respect to the A-factors of the listed reactions in the mechanism from Sarathy et al. [119]. Positive quantities indicate the ignition delay is increased when the A-factor is halved.

ature chain branching pathway of oxygen addition to the primary  $\alpha$ -radical improves the simulated results. Interestingly, the *i*-butanol system is not sensitive to the rates of oxygen addition to the hydroxybutyl radicals other than the  $\alpha$ -radical. At the higher temperature of 1200 K, there is little sensitivity on the ignition delay by changing the rate of the oxygen-addition reaction, demonstrating its lack of influence at higher temperatures.

As a final comparison, we have modified this pathway in the mechanism from Sarathy et al. [119] so that the rate of oxygen addition to the primary fuel radical is arbitrarily set to zero; that is, the rate of the reaction  $\text{ic4h8oh-1+o2}=\text{ic4h8oh-1o2}$  is set to zero by zeroing the A-factor, while the rates of the other oxygen addition reactions were unchanged. This unphysical situation substantially changes the results of simulations for *i*-butanol — removing this pathway in the mechanism from Sarathy et al. [119] brings the simulations into close agreement with the ignition delay results from the MIT mechanism [32, 120], which does not consider this reaction for *i*-butanol. Since the other oxygen addition reactions were unchanged, it is apparent that the addition of oxygen to  $\alpha$ -hydroxybutyl is one of the controlling reactions for the high-pressure, low-temperature ignition of *i*-butanol using the mechanism of Sarathy et al. [119]. It is therefore concluded that a detailed examination of the rates of direct formation of aldehyde+ $\text{HO}_2$  and oxygen addition to the  $\alpha$ -hydroxybutyl radical are required to better predict the low-temperature ignition behavior of *i*-butanol. Furthermore, based on the other results of this study, a detailed analysis of the oxygen addition reactions to all the isomers of butanol is probably warranted.

## 10 Conclusions

In this work, ignition delays for all four isomers of butanol in stoichiometric mixture with air have been presented over the low to intermediate temperature range, and at two compressed pressures of 15 and 30 bar. The order of reactivity of the isomers goes *n*-butanol>*s*-butanol≈*i*-butanol>*t*-butanol at the lower pressure, but changes to *n*-butanol>*t*-butanol>*s*-butanol>*i*-butanol at the higher pressure. This unexpected result is partially explained by the fact that there is substan-

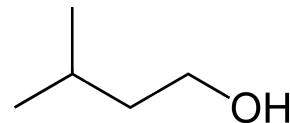
tial pre-ignition heat release present for *t*-butanol. To help understand the nature of the pre-ignition heat release of *t*-butanol, studies at off-stoichiometric conditions,  $\phi = 0.5$  and  $\phi = 2.0$  in air, are also conducted.

Comparisons of the experimentally measured ignition delays with two kinetic mechanisms show good agreement for certain isomers, but relatively poorer agreement for others. The kinetic mechanism of Sarathy et al. [119] is used to further elucidate the chemical processes controlling the autoignition of these butanol isomers. Pathway analysis of the fuel decomposition shows that *n*-, *s*-, and *i*-butanol primarily form  $\alpha$ -hydroxybutyl radicals, because the proximity of the  $\alpha$  carbon to the hydroxyl group reduces the C-H bond energy. The  $\alpha$ -hydroxybutyl radicals tend to form an aldehyde plus HO<sub>2</sub> directly, without forming a hydroxybutylperoxy complex. However, due to its unique structure, *t*-butanol can only form  $\beta$ -radicals; these radicals do not have the tendency to react with oxygen to directly form HO<sub>2</sub> and an aldehyde. Rather, *t*-butanol preferentially adds oxygen to the fuel radical site. It is hypothesized that this reaction, O<sub>2</sub> addition to form hydroxybutylperoxy, causes the pre-ignition heat release in *t*-butanol and leads to a chain propagation pathway through the Waddington mechanism. The fact that this oxygen-addition reaction is preferred is unique to *t*-butanol, although a detailed understanding of the peroxy chemistry of alcohols is still of vital importance to the other butanol isomers. This is further demonstrated in this work for the case of *i*-butanol, where the ignition delay is shown to be quite sensitive to both the rate of primary fuel radical formation and to the rate of oxygen addition to the primary fuel radical. It is also noted that *n*-butanol autoignition was shown to be quite sensitive to peroxy chemistry in the study of Vranckx et al. [60].

All together, these analyses show the importance of the peroxy chemistry pathways in the autoignition of the butanols. Further experimental studies, such as species profiles from the low temperature ignition of the butanol isomers, could help reduce uncertainty in the pathways of fuel breakdown. Finally, further understanding of the rates of the peroxy pathways is important and therefore further theoretical and quantum chemical studies are warranted.

**Table 5:** HHV of Ethanol, *i*-pentanol, and Gasoline

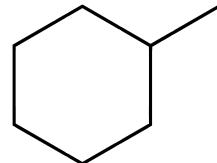
Compound	Ethanol [117]	<i>i</i> -pentanol[117]	Gasoline [118]
HHV [MJ/kg]	29.67	37.73	48.46



**Figure 28:** Skeletal structure of *i*-pentanol

**Table 6:** Molar Proportions of Reactants in MCH Experiments

Mix #	$\phi$	MCH	O <sub>2</sub>	N <sub>2</sub>	Ar
1	1.0	1	10.5	12.25	71.75
2	0.5	1	21.0	0.00	73.50
3	1.5	1	7.0	16.35	71.15



**Figure 29:** Skeletal structure of methylcyclohexane

## 11 Structure of *i*-pentanol

*i*-Pentanol (3-methyl-1-butanol) is a five-carbon alcohol whose skeletal structure is shown in Fig. 28. *i*-Pentanol can be produced biologically, and offers several similar advantages as the butanol isomers as compared to ethanol. Table 5 compares the HHV of ethanol, *i*-pentanol, and gasoline.

## 12 Structure of Methylcyclohexane

Methylcyclohexane (MCH) is the simplest branched cycloalkane, and as such, represents an excellent target to use as the base for models of larger branched cycloalkanes. MCH has the elemental composition C<sub>7</sub>H<sub>14</sub>, and its skeletal structure is shown in Fig. 29.

## 13 Procedures

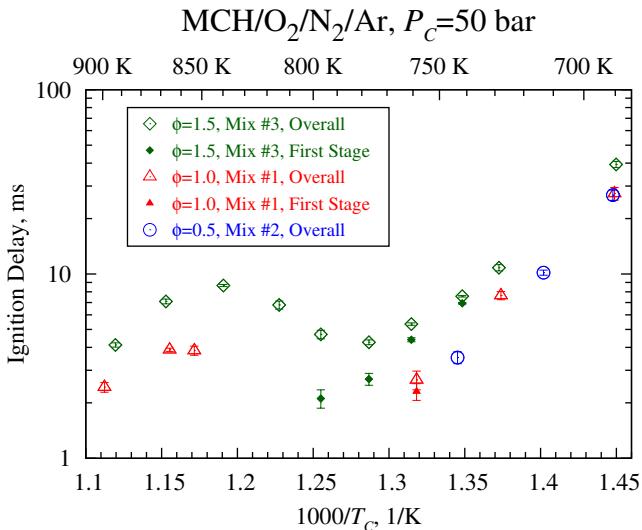
The liquid fuel (methyl-cyclohexane, 99.0% purity) is massed to a precision of 0.01 g in a syringe before being injected into the mixing tank through a septum. The proportions of oxygen (99.9999% purity), nitrogen (99.9995% purity), and argon (99.9999% purity) are determined by specifying the oxidizer composition, the equivalence ratio, and the total mass of fuel. The gases are added to the mixing tank manometrically at room temperature.

Three different mixtures of MCH/O<sub>2</sub>/N<sub>2</sub>/Ar are prepared in this study, as outlined in Table 6. These mixtures (denoted as Mix #1–3) match the mixtures prepared in our previous work with MCH in the RCM [87]. The equivalence ratios corresponding to Mix #1–3 are  $\phi = 1.0, 0.5$ , and  $1.5$ , respectively. As in the previous RCM experiments, the mole fraction of MCH is held constant and the mole fraction of O<sub>2</sub> is varied to adjust the equivalence ratio. This experimental design allows these data to be used to validate chemical kinetic models for changes in O<sub>2</sub> concentration, which is an important variable in internal combustion engines where exhaust gas recirculation is used to reduce the oxygen concentrations to avoid NO<sub>x</sub> formation. Few validation data for ignition are available for changing oxygen concentrations. In addition, the relative proportions of O<sub>2</sub>, N<sub>2</sub>, and Ar are adjusted so that the same specific heat ratio is maintained in the three mixtures. The utility of this experimental design will be discussed in due course.

## 14 Model Improvements

Through collaboration with researchers at Lawrence Livermore National Laboratories, many improvements to the chemical kinetic model for MCH were made. Some of the major improvements are highlighted below; see the article for more detail. It should be noted that the improvement relative to the model from 2007 by Pitz et al. [14] is substantial.

1. The base C<sub>1</sub>–C<sub>4</sub> chemistry has been updated with the AramcoMech version 1.3 [9]
2. The aromatics base chemistry was updated with the latest LLNL-NUIG model [124]
3. The cyclohexane sub-model was updated with a new version from Silke et al. [125]
4. Rates of abstraction reactions from MCH have been updated with recently measured experimental values [126] and standardized according to the LLNL reaction rate rules [127]
5. Products of MCH breakdown with unsaturated rings such as methylcyclohexene were previously lumped into one species for simplicity. In the new model, they have been unlumped and provide improved fidelity in modeling these species. [128]



**Figure 30:** Experimentally measured ignition delays at  $P_C = 50$  bar for the mixture conditions in Table 6

6. The reaction rates of some low-temperature specific reactions were updated using new quantum chemical calculations to compute the rate. Other reaction rates were updated from similar calculations performed by Fernandes et al. [129]
7. The activation energy of the ketohydroperoxide decomposition reactions was increased to bring it into closer agreement with the activation energy used by Metcalfe et al. [9]. This change has a dramatic effect on the low-temperature ignition delays, as shown in Sec. 16.

## 15 Experimental Results

The experimental ignition delays measured at the three equivalence ratios and compressed pressure of 50 bar are shown in Fig. 30. The open symbols are the overall ignition delays and the filled symbols are the first stage ignition delays. The vertical error bars on the experimental data represent twice the standard deviation of all of the experiments at that condition. Detailed uncertainty analysis of the deduced compressed temperature was conducted in Sec. 2.8 where the maximum uncertainty of the compressed temperature was found to be approximately 1%.

The negative temperature coefficient (NTC) region is an important feature of low temperature ignition where the ignition delay time increases with increasing temperature. The NTC region of

the overall ignition delay is evident in Fig. 30 for the  $\phi = 1.5$  case (Mix #3) and approximately includes the temperature range of  $T_C = 775\text{--}840\text{ K}$ . For  $\phi = 1.5$ , first stage ignition is evident for conditions in the range of  $T_C = 740\text{--}800\text{ K}$ .

For  $\phi = 1.0$  (Mix #1), the NTC region of the overall ignition delay could not be completely resolved. Only three conditions in the low temperature region and three conditions in the high temperature region are shown in Fig. 30. The experimental pressure traces during the compression stroke for intermediate temperature conditions were seen to deviate from their non-reactive counterparts, demonstrating appreciable reactivity therein. Hence, those data are not included in Fig. 30.

For the experiments at  $\phi = 0.5$  (Mix #2), only three data points in the low temperature region are reported and none of them exhibits two-stage ignition response. As the temperature is increased further, noticeable reactivity during the compression stroke is evident.

As stated earlier, the mole fraction of MCH is held constant in this study, while the mole fraction of the oxidizer is changed to modify the equivalence ratio. Figure 30 demonstrates that the  $\phi = 0.5$  case is the most reactive (as judged by the inverse of the ignition delay) and the  $\phi = 1.5$  case is the least reactive. As has been shown for other fuels, including *n*-butanol [62] and Jet-A [99], decreasing the equivalence ratio by increasing the oxygen mole fraction but holding the fuel mole fraction constant increases the reactivity.

## 16 Comparison to Model

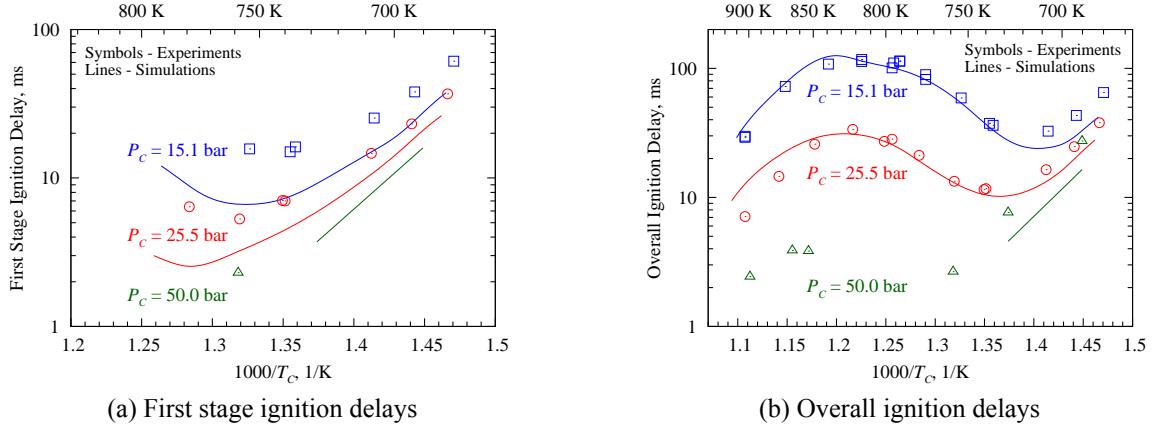
A comparison of the experimentally measured first stage ignition delays (open symbols) and the first stage ignition delays computed using the updated model (lines) is shown in Figs. 31a, 32a, and 33a for Mix #1, #2, and #3, respectively. In addition, a comparison of the experimentally measured overall ignition delays (open symbols) and the overall ignition delay computed by the updated model (lines) is shown in Figs. 31b, 32b, and 33b. The experiments include the new work being presented here at  $P_C = 50\text{ bar}$  in addition to the previous RCM experiments at  $P_C =$

15.1 and 25.5 bar [87]. The simulations are the VPRO type of simulations. For some computational cases, substantial heat release during the compression stroke caused the computed pressure to depart from the non-reactive profile prior to EOC. Therefore, these cases are not shown in Figs. 31–33. For these conditions, the experimental pressure trace did not exhibit significant heat release during the compression stroke and the experimental pressure at EOC for the reactive case matched that of the non-reactive counterpart.

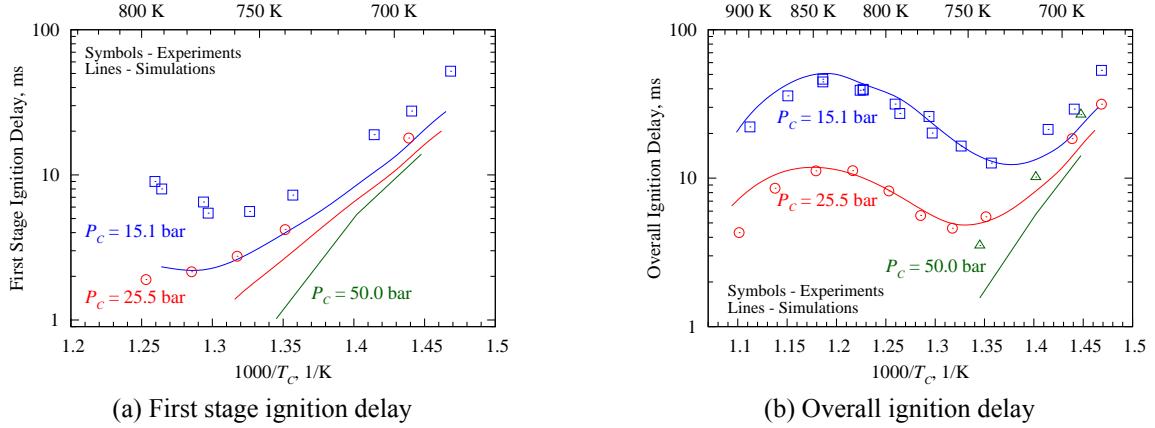
At 15.1 and 25.5 bar for Mix #1 and #2, the overall ignition delay is very well predicted for temperatures above approximately 715 K. For lower temperatures at these two equivalence ratios, the experimental ignition delays are under-predicted by the model, but the predictions are nevertheless within a factor of two of the data. For the rich case (Mix #3), the simulations under-predict the ignition delay over a wider temperature range but the results improve as temperature increases. Again, the experimental ignition delays are predicted to within approximately a factor of two. At 50 bar, the ignition delays are under-predicted for all of the equivalence ratios studied here, but the agreement is within a factor of two.

The first stage ignition delays for all of the pressure and equivalence ratios are under-predicted, but are within a factor of three of the experimental values. Furthermore, for all of the equivalence ratios tested at  $P_C = 50$  bar, it is of interest to note that there are several cases where simulated ignition delays show two-stage response where the experiment shows only a single stage ignition. Nevertheless, the present mechanism is a marked improvement from the comparison performed by Mittal and Sung [87] who found that the ignition delays were strongly and uniformly over-predicted by the previous LLNL mechanism by Pitz et al. [14].

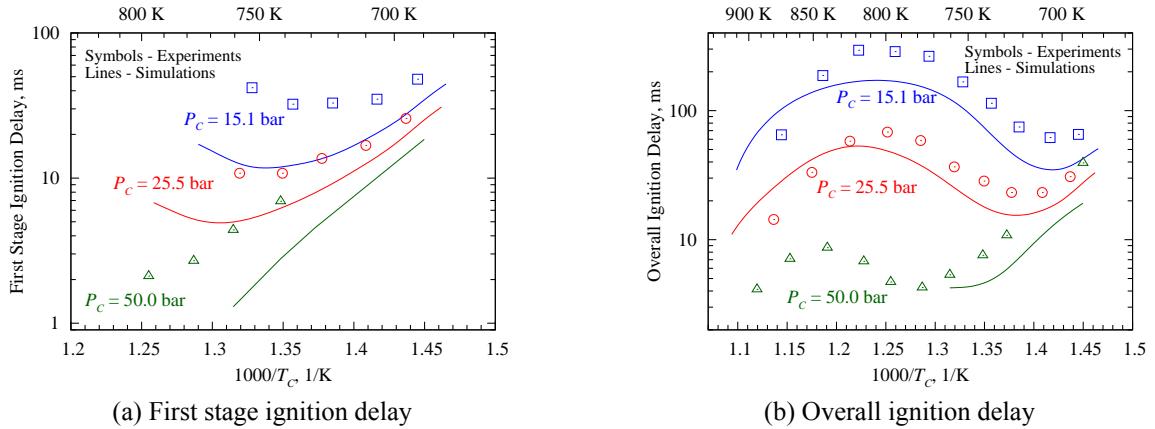
Figure 34 shows a comparison of selected simulated and experimentally measured pressure traces for Mix #1, #2, and #3, respectively, at  $P_C = 50$  bar. Also shown in Fig. 34 is the simulated non-reactive pressure trace corresponding to each experimental condition. Small differences in the heat loss profile for different temperatures are apparent in the non-reactive pressure traces. These differences arise from the changing surface area to volume ratio of the reaction chamber at the end of compression as the compression ratio is changed to vary the compressed temperature. This



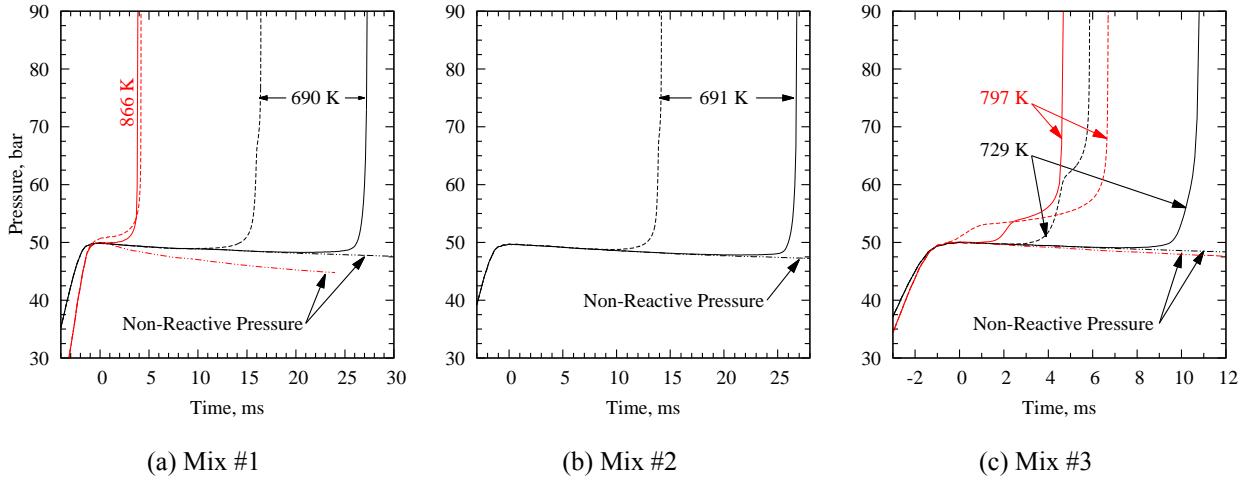
**Figure 31:** Comparison of experimental and simulated ignition delays for three pressures for Mix #1. The data at 15.1 and 25.5 bar are from the study of Mittal and Sung [87].



**Figure 32:** Comparison of experimental and simulated ignition delays for three pressures for Mix #2. The data at 15.1 and 25.5 bar are from the study of Mittal and Sung [87].



**Figure 33:** Comparison of experimental and simulated ignition delays for three pressures for Mix #3. The data at 15.1 and 25.5 bar are from the study of Mittal and Sung [87].



**Figure 34:** Comparison of selected simulated and experimental pressure traces at  $P_C = 50$  bar. Red lines indicate that the pressure profile of the reactive simulation deviates from the non-reactive case prior to EOC. Solid lines: experiment; dashed lines: reactive simulation; dot-dot-dashed lines: non-reactive simulation.

highlights the importance of using VPRO simulations to compare predictions of ignition delay with the experimental data.

For Mix #1, it is clear that the simulated reactive pressure trace in Fig. 34a at  $T_C = 866$  K (red dashed line) deviates from the non-reactive pressure trace (red dot-dot-dashed line) prior to the end of compression. The same is also true of the 797 K case shown for Mix #3 in Fig. 34c. Remarkably, the simulated case for Mix #1 at  $T_C = 866$  K predicts the overall ignition delay quite well. However, due to the heat release prior to EOC, this simulated result is not plotted in Fig. 31. The simulated case for Mix #3 at  $T_C = 797$  K is also not plotted on Fig. 33 due to the heat release prior to EOC; interestingly, this case under-predicts the first stage ignition delay but over-predicts the overall ignition delay. For the other simulated cases (black lines), the reactive pressure traces closely follow their non-reactive counterparts until the ignition event begins. The experimental ignition delays of these cases are under-predicted by the model. It is also seen in Fig. 34c for  $T_C = 729$  K that the model predicts two-stage ignition, although two-stage ignition is not observed experimentally.

The current mechanism is also compared to shock tube ignition delays from the studies of Vasu et al. [81] and Vanderover and Oehlschlaeger [82]. Those studies considered the autoignition of

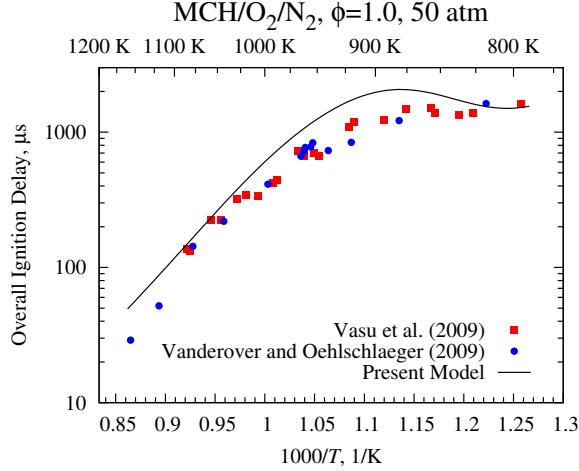
stoichiometric mixtures of MCH with O<sub>2</sub>/N<sub>2</sub> air. The comparison is shown in Fig. 35 for the near 50 atm data from those studies. Note that the experimental data shown are the raw data and are not scaled to a constant pressure, whereas the simulated ignition delays are at a constant initial pressure of 50 atm. It can be seen that the ignition delays are over-predicted over the nearly entire temperature range of 795–1160 K studied. Nevertheless, the predicted ignition delays are within approximately a factor of 1.5 of the experiments, indicating good agreement overall and a substantial improvement from the previous version of the model. Furthermore, the simulations shown here are of the CONV type and do not account for any facility dependent effects present in the experiments. Although the experimentalists noted in [81, 82] that the effect of such considerations is minimal in their studies, including facility dependent effects will tend to make the simulations ignite sooner and improve the agreement, especially for cases with ignition delays longer than approximately 1000  $\mu$ s.

As discussed in Sec. 16, one of the updates to the model was to increase the activation energy of ketohydroperoxide decomposition, from  $E_a = 39 \text{ kcal mol}^{-1}$  ( $163.2 \text{ kJ mol}^{-1}$ ) to  $41.6 \text{ kcal mol}^{-1}$  ( $174.1 \text{ kJ mol}^{-1}$ ). This update substantially improved the prediction of the low-temperature ignition delays, including the first stage and overall ignition delays. As mentioned by Curran et al. [130], "the high activation energy [of ketohydroperoxide decomposition] ensures an induction period during which the ketohydroperoxide concentration builds up." Furthermore, updating this activation energy does not affect the high-temperature ignition delays. A comparison of calculated ignition delays demonstrating the effect of this update is shown in Fig. 36.

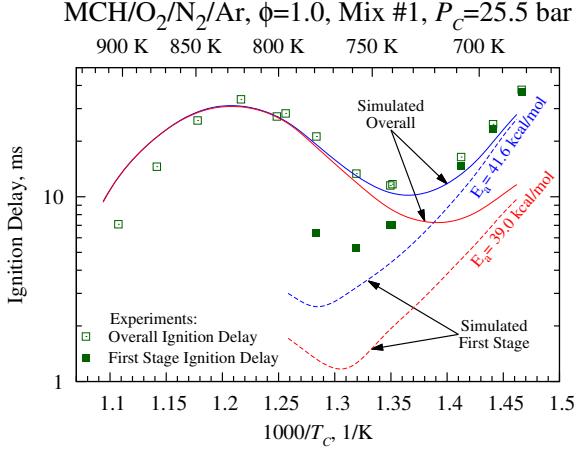
## 17 Discussion

### 17.1 Path Analysis

The relatively good agreement of the updated model with the experimental data suggests that a more detailed analysis of the mechanism is a worthwhile exercise and such analysis may point the way to further improvements to the mechanism. We begin with a reaction path analysis. The present



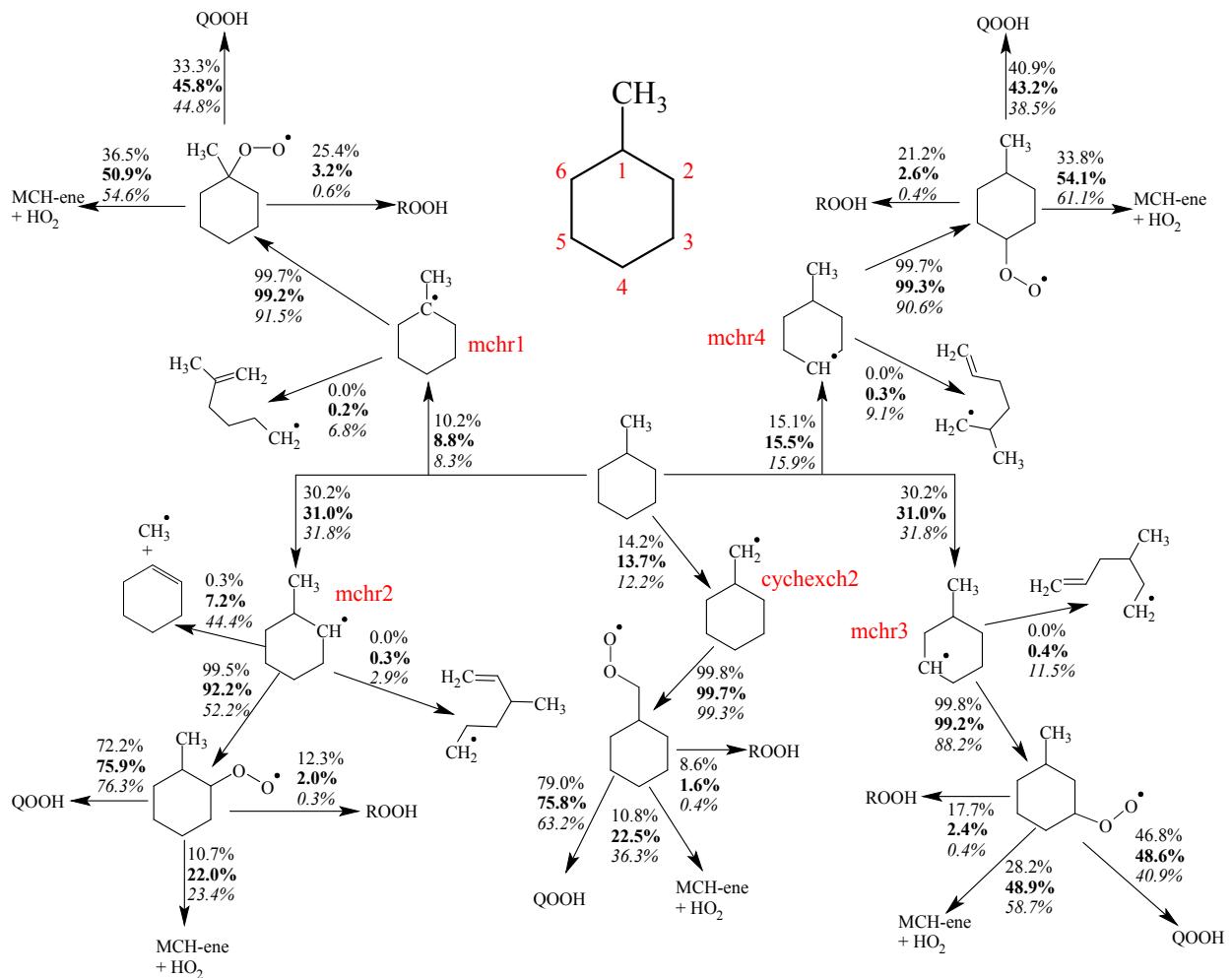
**Figure 35:** Comparison of the present model with the experiments from Vasu et al. [81] and Vanderover and Oehlschlaeger [82] near 50 atm and for stoichiometric mixtures in  $O_2/N_2$  air.



**Figure 36:** Comparison of mechanism performance with the activation energy of ketohydroperoxide decomposition set at  $41.6 \text{ kcal mol}^{-1}$  (blue) and  $39.0 \text{ kcal mol}^{-1}$  (red). Experimental ignition delays are shown in green symbols.

reaction path analysis is conducted using a CONV (adiabatic, constant-volume) type simulation for three initial temperatures (700, 800, and 900 K), at 25.5 bar and for Mix #1 (the stoichiometric case). For the other mixture conditions and pressures considered in this work, the absolute percentages for each channel change slightly. However, the analysis of the reaction pathways is the same for all of the equivalence ratios and pressures considered in the experiments presented previously. The three temperatures considered in this analysis correspond to the low-temperature, peak of the NTC, and high-temperature portions of the ignition delay curve illustrated in Fig. 36; their results are shown in Fig. 37 with plain text, bold text, and italic text, respectively.

The path analysis presented in Fig. 37 is an integrated analysis where the rate of production (ROP) of each species by each reaction has been integrated with respect to time up to 20% fuel consumption. The integrated ROPs from each reaction are normalized by the total production or destruction of that species up to 20% fuel decomposition, such that reactions that produce a species are normalized by the total production of the species and reactions that consume a species are normalized by the total consumption of that species. The percentages in Fig. 37 therefore represent the percent of the given reactant that is consumed to form the given product by all reactions that can form a particular product. Species such as hydroperoxyalkyl radicals (QOOH), alkyl hydroper-



**Figure 37:** Path analysis of MCH combustion. Initial conditions are 25.5 bar and Mix #1 ( $\phi = 1.0$ ) and 700 K (plain text), 800 K (bold text), 900 K (italic text). Note that not all possible reaction pathways are shown for each species.

oxides (ROOH), and methylcyclohexenes (MCH-ene) are shown as lumped on the path diagram; however, these species are unlumped in the mechanism and presented as a lumped sum for simplicity in this diagram. Note that not all of the pathways present in the mechanism for each species are presented in Fig. 37, again for simplicity; the pathways that are shown in Fig. 37 typically account for more than 95% of the consumption of each species.

The first step of fuel breakdown occurs by H-atom abstraction at these pressure and temperature conditions. None of the fuel is directly decomposed by unimolecular reactions. Each of the seven possible radicals are formed in comparable quantities; however, due to the symmetry of MCH, sites 2 and 3 are equivalent to sites 6 and 5, respectively, so mchr2 and mchr3 have close to double

the production rate compared to the other radicals. It is interesting to note that the production of mchr2, mchr3, and mchr4 increase as the initial temperature increases and the production of mchr1 and cychexch2 decrease to compensate. However, the change is small, no more than 2 percentage points for each radical.

The most important second step is oxygen addition (i.e. formation of ROO) at all of the initial temperatures in this analysis. The importance of this reaction diminishes for each radical as the initial temperature increases due to the increasing importance of  $\beta$ -scission reactions. At 700 K, less than 0.05% of each of the fuel radicals is consumed via  $\beta$ -scission. Between 800 and 900 K, the percentages of mchr1, mchr2, mchr3, and mchr4 that are decomposed via  $\beta$ -scission increase by several thousand percent each; nevertheless, the absolute change is small and the consumption of these radicals still occurs mostly by oxygen addition. The mchr1, mchr3, and mchr4 radicals undergo scission of the cyclohexyl ring, whereas mchr2 primarily scissions at the methyl-cyclohexyl bond. This beta scission of mchr2 competes significantly with its consumption by O<sub>2</sub> at 900 K. Furthermore, the increasing importance of the ring opening reactions from 800 K to 900 K means that chain propagation pathways (instead of effective chain termination pathways forming methylcyclohexene and hydroperoxyl) are available, increasing the reactivity. Finally, even at the elevated initial temperature of 900 K, cychexch2 does not undergo significant ring opening. Instead, it will scission an H atom from site 1 or steal an oxygen atom from hydroperoxyl to form an alkoxy radical (RO) when it does not undergo oxygen addition (these pathways each only consume about 0.3% of cychexch2 and hence are not shown in Fig. 37).

Returning to the low temperature pathways, there are four important classes of reactions that consume the ROO radicals in the current mechanism. These classes are: C1) internal H-atom transfer (isomerization) to form QOOH; C2) direct elimination of hydroperoxyl and methylcyclohexene; C3) H-abstraction by ROO from either the fuel or hydroperoxyl to form ROOH; and, C4) reactions among the ROO radicals. Class C4 consumes less than 5% of each of the ROO radicals at 700 K and less than 0.1% for the other temperatures and this class is therefore not shown on the path diagram in Fig. 37. Of the other three classes, C1 (formation of QOOH) is the predominant pathway

in the low temperature ignition process. Nevertheless, the direct elimination of methylcyclohexene and hydroperoxyl and the formation of ROOH are important at low temperatures as well.

For all of the temperatures considered here, a majority of the ROOH is formed by reactions of ROO with hydroperoxyl to give ROOH and an oxygen molecule. At the initial temperature of 700 K, approximately 15% of the fuel reacts to form ROOH, indicating its importance in low-temperature MCH combustion. The primary route of ROOH formation in this mechanism (H-abstraction from hydroperoxyl by ROO) has not been well studied at combustion relevant temperatures [131] and is therefore a good candidate for further investigation given its importance in the model for MCH combustion.

As the temperature increases, the formation of ROOH becomes substantially less important while the direct HO<sub>2</sub> elimination reaction becomes more important. The increase in production of methylcyclohexene and hydroperoxyl plays a role in the NTC region of ignition delay because this is effectively a chain terminating channel until the temperature increases enough that the sequence MCH+HO<sub>2</sub>=R+H<sub>2</sub>O<sub>2</sub>; H<sub>2</sub>O<sub>2</sub>(+M)=2OH(+M) becomes important and drives the overall ignition.

Interestingly, for most of the ROO radicals, the change in the fraction of ROO consumed to form QOOH is non-monotonic as temperature increases. That is, for mch1oo, mch3oo, and mch4oo the production of QOOH increases in going from 700 K to 800 K, then decreases going from 800 K to 900 K due to the increasing importance of the HO<sub>2</sub> elimination channel (due to nuances in the various reaction paths, mch2oo and chxch2oo do not follow this trend). Furthermore, the branching ratios in the decomposition of the QOOH species change as the temperature is increased (not shown in Fig. 37). At the lowest temperature (700 K), the formation of hydroperoxyalkylperoxy radicals (OOQOOH) is favored, leading to low-temperature chain branching and the two-stage ignition phenomenon. However, at 800 K and 900 K, the QOOH tends to decompose into a heptenone and a hydroxyl radical, or one of two epoxide species. Due to the apparent importance of these species in the intermediate temperature decomposition of MCH, further investigation of their pathways is warranted.

## 17.2 Sensitivity Analysis

Our second type of analysis is a brute force, one-at-a-time sensitivity analysis. In this work, the sensitivity of the ignition delay to the reaction rates is considered. Due to the size of the mechanism, only the reactions of the fuel and the fuel radicals up to the OOQOOH species are considered. This approach is justified because many of the reactions of the C<sub>0</sub>–C<sub>4</sub> base mechanism are known to be important to the ignition process (e.g., H<sub>2</sub>O<sub>2</sub>(+M)=2OH(+M)), but we are more interested in the effect of updates to the fuel specific sub-mechanism. The sensitivity index is defined in Eq. (25),

$$S_i = \frac{\ln(\tau_{i,2}/\tau_{i,1})}{\ln(k_{i,2}/k_{i,1})} \quad (25)$$

where  $\tau$  is the ignition delay time, either first stage or overall,  $k$  is the reaction rate, and subscript  $i$  indicates the reaction number. The numbered subscripts in Eq. (25) indicate the type of modification that has been made to the rate of reaction  $i$  when computing the ignition delay, as discussed in the following.

The reaction rates are modified by multiplying and dividing the pre-exponential constant by a factor  $f$ . Thus, the forward and reverse rates are simultaneously modified. Special care is taken to properly modify reaction rates with pressure dependence and explicit reverse parameters. Each rate is modified sequentially and the ignition delay is computed; the pre-exponential constant is reset to its nominal value before modifying the next reaction. Finally, the nominal ignition delay with no rate modification is computed. Thus, each set of reactor input conditions requires  $2N + 1$  model evaluations, where  $N$  is the number of reactions considered in the sensitivity analysis and  $N$  may be less than or equal to the total number of reactions.

The  $2N + 1$  model evaluations result in  $4N + 2$  ignition delays if two-stage ignition is present and  $2N + 1$  ignition delays otherwise. These ignition delays are used to compute the sensitivity indices according to Eq. (25). In the case of bidirectional sensitivity indices, the subscript 2 in Eq. (25) is associated with multiplication by  $f$  and the subscript 1 is associated with division by  $f$ , resulting in  $2N$  sensitivity indices if two-stage ignition is present and  $N$  indices otherwise. In

the case of unidirectional sensitivity indices, the subscript 2 is associated with either multiplication or division by  $f$  and the subscript 1 is associated with the nominal ignition delay,  $\tau_{i,1} = \tau_1$ . For unidirectional sensitivity indices,  $4N$  indices are obtained if two-stage ignition is present and  $2N$  are obtained otherwise.

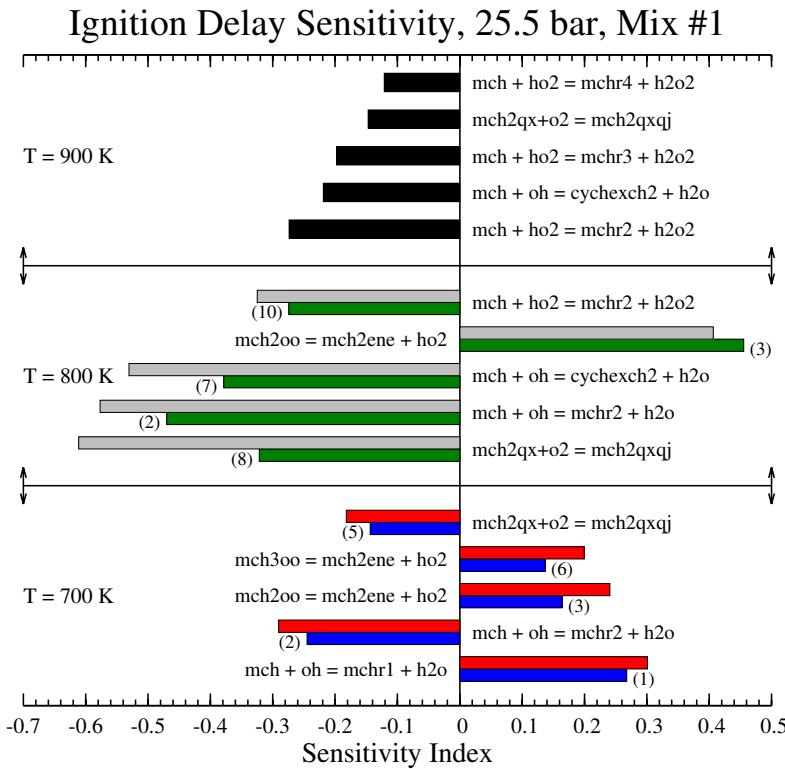
In this work, the bidirectional sensitivity is used with  $f = 10$ . For all of the reactions considered here, multiplying and dividing a given rate had opposite effects on the ignition delay. Thus, if the ignition delay increased (relative to the nominal case) when the rate of a certain reaction was multiplied, the ignition delay decreased (relative to the nominal case) when the rate of the same reaction was divided and vice versa. Since  $k_{i,2}$  is greater than  $k_{i,1}$  by definition, the sensitivity index  $S_i$  will be positive if  $\tau_{i,2} > \tau_{i,1}$  (i.e. increasing the rate increases the ignition delay) and negative if  $\tau_{i,2} < \tau_{i,1}$  (i.e. increasing the rate decreases the ignition delay). The sensitivity analysis is run at the same conditions of the path analysis: CONV simulation, initial temperatures of 700, 800, and 900 K, initial pressure of 25.5 bar, and Mix #1. As with the path analysis, similar results are obtained for other pressures and mixtures.

Figure 38 shows the sensitivity indices for the five reactions (among all the reactions considered in the present sensitivity analysis) to which the overall ignition delay is most sensitive for each temperature studied (700, 800, and 900 K). For the results at 700 and 800 K, the bidirectional sensitivity of the first stage ignition delay to the same reactions is also shown, except for two reactions at 800 K for which the unidirectional sensitivity is plotted. The reasons for this will be discussed in due course. It should be noted that the sensitivity indices of the first stage ignition delay have a slightly different ranking than the indices of the overall ignition delay. Therefore, the rank of the first stage sensitivity index of the reactions shown is given in parentheses next to the bar. At 700 K, the sensitivity of the overall ignition delay is in red and the sensitivity of the first stage ignition delay is in blue; at 800 K, the sensitivity of the overall ignition delay is in grey and the sensitivity of the first stage ignition delay is in green. The most sensitive reaction affecting the first stage ignition delay at 800 K is found to be  $\text{MCH}+\text{OH}=\text{mchr3}+\text{H}_2\text{O}$ , although it is not listed in Fig. 38. At 900 K, there is no first stage ignition, and thus no sensitivity of the first stage ignition delay.

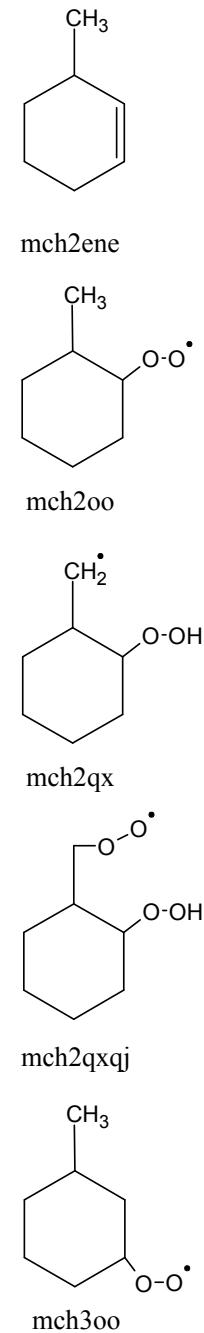
Under the pressure/stoichiometry conditions of the present simulations, 800 K is approximately the highest initial temperature at which distinct two-stage ignition (i.e. two inflection points in the temperature or pressure trace) is found for MCH with the current mechanism. As such, several reactions affect the ignition strongly enough to eliminate the first inflection point. These reactions are given in Table 7 for either multiplication or division of the rate by the factor  $f = 10$ . The naming convention of the species listed in Table 7 can be found in Fig. 37, Fig. 39, and ???. Two reactions shown in Table 7 also appear in Fig. 38, namely (R1)  $\text{mch2oo}=\text{mch2ene}+\text{ho2}$  and (R2)  $\text{mch2qx}+\text{o2}=\text{mch2qxqj}$ . For these reactions at 800 K, the unidirectional sensitivity index is shown in Fig. 38, where  $\tau_{i,2}$  in Eq. (25) is found by division of the rate for  $i = R1$  and by multiplication of the rate for  $i = R2$ .

The role of the  $\text{ROO}=\text{methylcyclohexene}+\text{HO}_2$  reactions in the left column of Table 7 in eliminating the first stage of ignition is clear—this set of reactions diverts ROO radicals from entering the low-temperature chain branching pathway via QOOH that leads to the two-stage ignition. Similarly, in the right column, decreasing the rate of the reaction of oxygen with QOOH to form OOQOOH reduces the rate of chain branching that leads to two-stage ignition. Concerning the reactions of the fuel with OH in the left column of Table 7, increasing these rates increases the formation of fuel radicals that are less reactive at low temperature than the cychexch2 and mchr2 radical. For example, the mchr2 radical adds to  $\text{O}_2$  and forms a peroxy radical (mch2oo) that has a fast  $\text{RO2}$  isomerization path to QOOH involving the abstraction of an H atom from the methyl group. This ROO isomerization is the path calculated and discussed in Section 4.1 of [132]. QOOH subsequently adds to  $\text{O}_2$  and leads to chain branching. The high reactivity of cychexch2 and mchr2 at low temperature is reflected by the high percentages at 800 K (>70%) leading to QOOH from cychexch2oo and mch2oo in Fig. 37.

In general, Fig. 38 shows that the ignition delay is sensitive to different sets of reactions at the three temperatures, although there is some overlap. The overlapping reactions confound simple recommendations for rate improvements. For instance, at 700 K, increasing the overall ignition delay will improve agreement with the experimental data, but at 800 K, the agreement is already



**Figure 38:** Sensitivity of the ignition delay to various reaction rates for Mix #1 ( $\phi = 1.0$ ), 25.5 bar and three temperatures (700, 800, and 900 K). At 700 K, the sensitivity of the overall ignition delay is in red and the sensitivity of the first stage ignition delay is in blue. At 800 K, the sensitivity of the overall ignition delay is in grey and the sensitivity of the first stage ignition delay is in green. At 900 K, the sensitivity of the overall ignition delay is in black. Numbers in parentheses represent the ranking of the first stage sensitivity indices.



**Figure 39:** Species mentioned in Fig. 38 or Table 7 and not included in Fig. 37.

**Table 7:** Reactions that eliminate the first inflection point for a nominal case with two-stage ignition.

Multiplication	Division
$mch2oo = mch2ene + ho2$	$mch2qx + o2 = mch2qxqj$
$mch3oo = mch2ene + ho2$	
$mch3oo = mch3ene + ho2$	
$mch + oh = mchr1 + h2o$	
$mch + oh = mchr4 + h2o$	
$mch + oh = mchr3 + h2o$	

quite good. Therefore, adjusting any of the rates to improve the agreement with the overall ignition delay at 700 K will probably make the agreement worse at 800 K. However, the first stage ignition delays at 700 K and 800 K are both under-predicted; furthermore, two-stage ignition is predicted at temperatures for which the experimental ignition is single stage. It should therefore be possible to adjust several rate constants simultaneously to improve agreement with the first stage ignition delay and not deteriorate agreement with the overall ignition delay. To accomplish the simultaneous improvement of agreement of first stage and overall ignition delays, the rate constants of reactions that control the second stage ignition delay may also need to be adjusted (where second stage ignition delay is the difference between the overall ignition delay and the first stage ignition delay).

Interestingly, the formation and destruction reactions of ROOH species do not appear in Fig. 38, despite their importance in the destruction of ROO radicals, particularly at 700 K (see Fig. 37). This may be due to the fact that formation of ROOH by reaction with HO<sub>2</sub> followed by consumption of ROOH is a chain propagation path through the reactions ROO+HO<sub>2</sub>=ROOH+O<sub>2</sub>; ROOH=RO+OH. In this sequence two radicals are formed (RO, OH) and two radicals are consumed (ROO, HO<sub>2</sub>). Thus, the formation of ROOH by reaction with HO<sub>2</sub> and its subsequent destruction has a somewhat neutral effect on the radical pool.

At 900 K, the overall ignition delay is particularly sensitive to reactions that form hydrogen peroxide, which decomposes to two hydroxyl radicals as the temperature increases during the induction period. Therefore, increasing the rate of formation of hydrogen peroxide will increase the formation of hydroxyl radical and decrease the overall ignition delay. At 900 K, the overall igni-

tion delay is over-predicted, so to improve the results the overall ignition delay should be reduced (i.e. increasing the rates of reactions with negative sensitivity will improve the comparison). In addition, many of the reactions that are important at 900 K are not important at 700 and 800 K, implying that changes made to the rates to improve the high-temperature agreement will not significantly change the agreement at lower temperature. In particular, the MCH+HO<sub>2</sub> rate constants have not been measured or calculated to our knowledge and are based on acyclic alkane rate constants [133]. They have uncertainties of at least a factor of 2 and as much as a factor of 10 based on the work of Aguilera-Iparraguirre et al. [133]. Increasing these rate constants would improve the agreement with the experimental ignition data at 900 K in the RCM and shock tube. Experimental measurements and theoretical calculations are needed for the fuel+HO<sub>2</sub> reaction class to reduce this uncertainty in the rate constants.

## 18 Conclusions

In this study, new experimental data are collected for methylcyclohexane autoignition in a heated rapid compression machine. Following the work of Mittal and Sung [87], three mixtures of MCH/O<sub>2</sub>/N<sub>2</sub>/Ar at equivalence ratios of  $\phi = 0.5, 1.0$ , and  $1.5$  are used and the ignition delays are measured at compressed pressure of 50 bar, for compressed temperatures in the range of 690–900 K. Two-stage ignition phenomena are reported for the stoichiometric and rich mixtures. However, substantial reactivity during the compression stroke limited the temperature range over which ignition delays could be reported, especially for the lean case. For these mixtures where the fuel concentration was kept constant, the order of reactivity, in terms of inverse overall ignition delay, is  $\phi = 0.5 > \phi = 1.0 > \phi = 1.5$ .

In addition, an existing model for the combustion of MCH developed by Pitz et al. [14] is updated with new reaction rates and pathways. The new model shows good agreement with the overall ignition delays measured in this study, as well as the overall ignition delays measured in the studies of Vasu et al. [81], Vanderover and Oehlschlaeger [82], and Mittal and Sung [87]. However,

the first stage ignition delays are uniformly under-predicted and in several cases, first stage ignition is predicted by the model where experimental ignition response shows no two-stage character. To help understand the fuel decomposition pathways and the reactions controlling the ignition, further analysis of the present mechanism is conducted.

First, reaction path analysis is conducted for low-, intermediate-, and high-temperature ignition considered in this study. The results show that MCH primarily decomposes by H-abstraction reactions involving OH and HO<sub>2</sub> radicals, followed by oxygen addition reactions. At low temperatures, the oxygen addition is followed by isomerization to QOOH species and second oxygen addition, leading to the low-temperature chain branching characteristic of two-stage ignition. At intermediate temperatures, the elimination of methylcyclohexene and HO<sub>2</sub> becomes competitive with the isomerization reaction, leading to the NTC region of the overall ignition delay. Finally, at high temperatures, MCH+HO<sub>2</sub> reactions form H<sub>2</sub>O<sub>2</sub> and end the NTC region.

Second, a brute force sensitivity analysis is conducted to identify the reactions of the fuel and primary fuel radicals that control the ignition process. The overall and first stage ignition events at low and intermediate temperatures are primarily controlled by the initial reactions to form fuel radicals, especially H-abstraction by OH. At high temperatures, the controlling reactions are still the fuel radical formation reactions, but now the ignition process is controlled by H-abstraction by hydroperoxyl instead of hydroxyl. Combined, these analyses suggest that further investigation of several of the low-temperature fuel decomposition pathways is required and more accurate rate constants for fuel+HO<sub>2</sub> reactions are needed.

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