Speciation studies of methyl butanoate ignition

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\begin{abstract}
The current work presents the results of an experimental study of the intermediates formed during ignition of methyl butanoate (C\textsubscript{5}H\textsubscript{10}O\textsubscript{2}) and air mixtures. A rapid-sampling system and the University of Michigan rapid compression facility were used to acquire gas samples at conditions of P = 10.2 atm and T = 985 K using mixtures of \(x_{\text{air}} = 0.96\), \(x_{\text{C5H10O2}} = 0.04\), and \(x_{\text{O2}} = 25.25\%\) (mole fraction, percent basis); corresponding to \(\phi = 0.30\) and an inert gas to \(\text{O}_2\) molar ratio of 3.76. The samples were analyzed using gas chromatography. Quantitative measurements of mole fraction time-histories of methane, ethane, propane, ethene, propene, and 1-butene are compared with model predictions based on a reaction mechanism developed in previous work. The methane and ethene time-histories are in excellent agreement (within \(\pm 20\%\)), while propene and ethane are underpredicted by the model. Sensitivity analysis shows ignition is controlled primarily by competition between \(\text{H}_2\text{O}_2\) and \(\text{HO}_2\) kinetics at these conditions. Reaction path analysis shows the methyl butanoate fuel consumption is dominated by H-atom abstraction by OH.
\end{abstract}

1. Introduction

The increased use of biofuels presents an opportunity to improve combustion performance while simultaneously reducing greenhouse gases and pollutant emissions. Realization of this potential, however, requires a more complete understanding of the fundamental reaction chemistry at conditions relevant to advanced combustion systems, i.e. moderate temperatures and elevated pressures. Ignition studies that yield quantitative data on intermediate species provide new and rigorous benchmarks to determine reaction pathways important during combustion of ester compounds.

This work presents the results of high-speed gas sampling of intermediate species during auto-ignition of methyl butanoate (C\textsubscript{5}H\textsubscript{10}O\textsubscript{2}). Methyl butanoate was selected for investigation as an oxygenated reference compound because it has a structure that is common to larger esters and real biofuels derived from plant oils, and methyl butanoate chemistry has become a reference for comparison to longer chain esters. Note that methyl butanoate does not exhibit the negative temperature coefficient behavior expected of longer chain esters at low temperatures (where real biodiesel components can have alkyl chains from C\textsubscript{12} to C\textsubscript{22} in length with both saturated and unsaturated characteristics). While much important progress has been made representing the detailed chemistry of such long chain esters, see for example the recent works by Bax et al. on methyl oleate [1] and by Westbrook et al. on reaction mechanisms for soy and rapeseed biodiesel fuels [2], large comprehensive kinetic models are challenging to create and computationally costly to apply to engine simulations. Alternatively, methyl butanoate chemistry blended with n-heptane has been successfully developed as a surrogate for biodiesel fuel for engine combustion modeling [3,4].

There have been several experimental and computational research efforts to understand the combustion chemistry of methyl butanoate. The experimental studies provide data over a broad range of conditions to quantify methyl butanoate oxidation rates and fuel decomposition pathways. Based on these experimental data sets, several chemical reaction mechanisms have been developed; many of which are based on the pioneering work of Fisher et al. [5]. The reaction mechanism initially proposed by Fisher et al. was developed and validated using low pressure (P = 0.13–0.54 atm) and low temperature (T = 520–740 K) isothermal reactor results from Parsons and Hinshelwood [6] and Hoare et al. [7]. Gail et al. [8,9] and Sarathy et al. [10] extended the experimental data available on methyl butanoate to higher temperatures and pressures in further reactor studies (P = 1 atm, T = 800–1350 K; P = 12.5 atm, T = 500–900 K) and flame studies (P = 1 atm, and T\textsubscript{max} = 1218 K). Metalcalfe et al. [11] expanded the experimental data for methyl butanoate combustion to include the results of shock tube studies of methyl butanoate ignition at P = 1 and 4 atm, T = 1100–1670 K, and the shock tube studies by Farooq et al. [12]
provided new quantitative time resolved data on CO$_2$ formation during methyl butanoate pyrolysis at approximately atmospheric pressures and high temperatures ($P = 1.4–1.7$ atm, $T = 1260–1653$ K). Dooley et al. [13] report complementary shock tube data ($P = 1$ and 4 atm, $T = 1100–1670$ K) and made great strides in extending experimental results to very high pressures and moderate temperatures using a rapid compression machine (RCM, $P = 10$, 20 and 40 atm, $T = 640–949$ K). More recent shock tube studies by Hakka et al. [14] have further extended the ignition delay time data for methyl butanoate to even higher temperatures (to 1915 K, $P = 8$ atm), and the recent shock tube studies by Akih-Kumge and Berghorston [15] extensively compare the ignition behavior of methyl butanoate with n-heptane. At lower temperatures (approximately 800–850 K for methyl butanoate), Hadjali et al. [16] compared the reactivity of methyl butanoate with a progression of linear methyl esters from C$_4$ to C$_6$ in RCM experiments ($P \geq 17–21$ atm for methyl butanoate). They found methyl butanoate to be the most resistant to auto-ignition, due to its very short alkyl chain length, which is not representative of the long chain esters found in biodiesel fuels. Recent computational studies [17–21] have used ab initio and quantized estimates for key methyl butanoate data including important thermochemical parameters (e.g., enthalpies of reaction and formation at 298 K [17,18]), and high temperature reaction pathways (e.g., elementary rate coefficients for 300–2500 K [19,20] and 800–1000 K [21]). These studies have led to additional insights into dominant reaction pathways for fuel consumption and pollutant formation.

In Walton et al. [22], the University of Michigan rapid compression facility (UM RCF) was used to study the ignition behavior of the two esters methyl butanoate and ethyl propanoate at high pressures and moderate temperatures ($P = 4.7–19.6$ atm, $T = 935–1117$ K). A modified version of the Fisher et al. [5] mechanism yielded excellent agreement in ignition delay times for conditions spanning the UM RCF data and shock tube data by Metcalfe et al. [11].

The current work builds on the previous experimental studies of methyl butanoate to quantify the intermediate species formed during ignition, and to identify the reaction pathways important to methyl butanoate ignition at high pressures and moderate temperatures. While there is generally good agreement between the experimental and computational studies of ignition delay time, speciation data provide even more rigorous targets for understanding fuel decomposition and oxidation, and ensure that these reaction pathways are captured accurately. Specifically, high-speed gas sampling allows for the qualitative and quantitative determination of stable intermediate species time-histories during each UM RCF experiment. The determination of these concentrations gives insight into the reaction pathways important at these conditions.

## 2. Experimental approach

### 2.1. UM RCF ignition studies

The UM RCF is a unique apparatus that has been used to investigate a broad range of fuel chemistries and conditions, including previous studies of ester ignition [22] and hydrocarbon combustion intermediates [23]. A summary of the key dimensions of the UM RCF are provided in Table 1. More details on the dimensions, components and performance characterization of the UM RCF can be found in Donovan et al. [24]. Briefly, during ignition studies, a fuel/air mixture is rapidly compressed by a free piston in the UM RCF. At the end of compression, the nose cone of the piston seals the test gas mixture in the test section at elevated temperatures and pressures. The mixture auto-ignites after a period of time defined as the ignition delay time ($\tau_{\text{ign}}$). The fuel/air mixture is prepared external to the RCF nanometrically, to ensure homogeneous composition of the test gas mixtures. The pressure in the test section is monitored using a piezoelectric transducer (Kistler 6041AX4) and charge amplifier (Kistler 5010B) with less than 10 µs time response. The pressure-time history is used to quantify $\tau_{\text{ign}}$ for each experiment. A transparent end wall and/or transparent cylindrical section provide optical access for end-view and side-view imaging using a high-speed CMOS camera. For these experiments, the side-view imaging was used to confirm uniform ignition in the test section, and the transparent end wall was replaced with the gas-sampling system.

### 2.2. High-speed gas-sampling system

We have conducted previous studies using rapid gas sampling from UM RCF experiments to investigate the intermediates formed during iso-octane ignition [23]. For this work, the same sampling approach was used, but a new gas-sampling system was created to improve the time response (via custom modified valves) and decrease the level of dilution of the sample gases (via decreased dead volume in the sampling system and with the potential to acquire larger gas samples in the same sampling time). These modifications reduce the uncertainty in the species measurements. The new sampling system also allows higher pressure experiments (up to approximately 10 atm).

### Table 1: Key dimensions of the UM RCF.

<table>
<thead>
<tr>
<th>Component</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Driven section length</td>
<td>2740 mm</td>
</tr>
<tr>
<td>Driven section inner</td>
<td>101.2 mm</td>
</tr>
<tr>
<td>Driver section length</td>
<td>5540 mm</td>
</tr>
<tr>
<td>Driver section diameter</td>
<td>154 mm</td>
</tr>
<tr>
<td>Globe valve inner diameter</td>
<td>101.6 mm</td>
</tr>
<tr>
<td>Convergent section length</td>
<td>101.6</td>
</tr>
<tr>
<td>Convergent section diameter</td>
<td>126 mm</td>
</tr>
<tr>
<td>Instrumented test section length</td>
<td>50.8 mm</td>
</tr>
<tr>
<td>Instrumented test section length</td>
<td>50.8 mm</td>
</tr>
<tr>
<td>Extension section length (multiple available)</td>
<td>126 mm</td>
</tr>
<tr>
<td>Overall compression time</td>
<td>Typically &gt;80 ms</td>
</tr>
</tbody>
</table>

$\text{a}$ Varies based on the extension section equipment used and where the nose cone of the free piston seats at the end of compression.

$\text{b}$ For typical operating conditions, the majority of the pressure rise (80%) and the temperature rise (50%) in the test section occur in less than 10 ms [24].
The major components of the sampling system are the sample chamber, pressure transducer, septum, and four vacuum isolation valves. For the current work, the gas sample was acquired by triggering only one of the last acting valves (modified Festo MHE3 valves with a stock response time of 3 ms, 3 mm orifice) mounted on the wall of the RCF. The sampling tube connected to the valve extends approximately 10 mm from the wall into the test section. The valves isolate the sample chamber (18 mL) from the test section during an experiment. Before each RCF experiment, the sample chamber is evacuated using a vacuum pump. A single gas sample is then acquired for each RCF experiment at a targeted time interval during the ignition delay period. Triggering circuits are used to open and close the gas-sampling valves and result in a gas-sampling time of ~1.3–1.4 ms. During the sampling event, the gases are quickly quenched as they expand into the vacuum of the sample chamber. Once the sample is acquired, the gases are drawn into a syringe (Vici, Pressure-Lok, 5 mL) through the syringe port on the sampling chamber for delivery to the gas chromatographs (GCs).

### 2.3. Gas chromatography

The gas analysis system consists of three gas chromatographs (PE Autosystem GCs). A summary of the GC equipment and operating conditions is presented in Table 2. Permanent gases, oxygenates and small hydrocarbons were targeted for this study. The intermediates species were identified from the gas chromatograms. The GCs each used helium as the carrier gas and were calibrated to allow quantitative measurements from the chromatograms for species where calibration standards could be established. The calibration methods were the same as used in He et al. [23], where individual species and custom mixtures of calibration gases were used.

### 3. Results

The experimental conditions were optimized for gas sampling. The key features include ignition delay times which allow several discrete sampling events in approximately 2 ms increments, spatially uniform ignition (confirmed through high-speed imaging), and good experimental repeatability (as indicated by low variability in the maximum pressure at the end of compression, \( P_{\text{max}} \)). Additionally, low initial fuel concentration (\( \phi = 0.97 \)) and low water concentration (\( X_{\text{H}_2} \leq 10,000 \text{ppm} \)) at 95% of the ignition delay time during the sampling times were targeted to minimize concerns regarding condensation of these species as well as key intermediates. Applying these criteria, a lean mixture with a level of dilution comparable to air was selected. The target mixture and experimental conditions were \( \phi = 0.30, P = 10.2 \text{ atm}, \) and \( T = 985 \text{ K} \) with an inert gas to \( \text{O}_2 \) ratio of 3.76.

Typical test section and sampling chamber pressure time-histories for the test section for a methyl butanoate sampling experiment are shown in Fig. 1. The corresponding triggering signals used to actuate the sampling valve are included in Fig. 1, as well as the pressure derivative for the test section data. The initial pressure rise in the RCF test section data is due to compression of the test gas mixture ahead of the free piston. At the end of compression, the pressure in the test section reaches the first maximum. This time is set as \( t = 0 \text{ s} \) and is labeled \( P_{\text{max}} \) in the figure. The pressure then decreases slightly due to cooling losses to the test volume walls. After a delay period, the mixture auto-ignites resulting in a rapid increase in pressure in the test section. The pressure in the sampling chamber shows a rapid rise after the sampling pulse triggers the sample valve to open and close, yielding sampling times of 1.3–1.4 ms.

Side view images corresponding to the experiment of Fig. 1 are shown in Fig. 2. The side-view imaging window allows optical access not previously available during UM RCF sampling experiments. The images confirm homogeneous ignition inside the test volume for each of the sampling experiments conducted. Note the location of a sampling tube in the upper right hand corner of the last panel of Fig. 2.

The effective test conditions were determined using the same methods applied in previous UM RCF experiments, and are based on the pressure time-history from each experiment. The effective pressure (\( P_{\text{eff}} \)) is defined as the time-integrated average pressure from the maximum pressure (\( P_{\text{max}} \)) at the end of compression to the point of maximum rate of pressure rise (\( \text{d}P/\text{d}t_{\text{max}} \)). The effective temperature for each experiment is determined using the effective pressure and by numerical integration of the isentropic relation

\[
\int_{T_\text{s}}^{T_{\text{max}}} \frac{\gamma}{\gamma-1} \, \text{d}T = \ln \left( \frac{P_{\text{eff}}}{P_\text{s}} \right)
\]

### Table 2

Summary of GC equipment and operating conditions used.

<table>
<thead>
<tr>
<th>Designation</th>
<th>GC1</th>
<th>GC2</th>
<th>GC3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column(s) (source, model)</td>
<td>CP-Molsieve 5 Å (Varian, CP7518)</td>
<td>CP PLOT LowOx FS (Varian, CP8587)</td>
<td>CP-Al₂O₃/Na₂SO₄ FS (Varian, CP7568)</td>
</tr>
<tr>
<td>Species targeted</td>
<td>Permanent gases (e.g. ( \text{N}_2, \text{O}_2, \text{Ar}, \text{CO} ))</td>
<td>Oxygenates</td>
<td>Small hydrocarbons</td>
</tr>
<tr>
<td>Flow rate</td>
<td>26 cm/s</td>
<td>34 cm/s</td>
<td>36 cm/s</td>
</tr>
<tr>
<td>Detector</td>
<td>TCD (150 °C)</td>
<td>FID (150 °C)</td>
<td>FID (150 °C)</td>
</tr>
<tr>
<td>Temperature program</td>
<td>30 °C (55 min) → 10 °C</td>
<td>80 °C (10 min) → 10 °C/min → 150 °C</td>
<td>40 °C (10 min) → 10 °C/min → 140 °C (34 min) → 10 °C/min → 200 °C</td>
</tr>
</tbody>
</table>
where $P_0$ is the initial charge pressure, $T_0$ is the initial temperature (typically 298 K), and $\gamma$ is the temperature-dependent ratio of the specific heats of the unreacted test gas mixture (determined using the NASA thermodynamic data base [25] and the thermodynamic specific heats of the unreacted test gas mixture (determined using $P_{eff}$)

Comparison of ignition delay time data for methyl butanoate ignition by Walton et al. [22] as a function of equivalence ratio ($\phi$) and inert/O2 ratio of 3.76 and $\phi = 0.3$. Here, the equivalence ratio ($\phi$) is defined as the fuel to oxygen (O2) ratio in the test mixture divided by the stoichiometric fuel to oxygen (O2) ratio.

The results for the ignition delay times measured in these experiments are compared with the data from our previous study of methyl butanoate ignition by Walton et al. [22] as a function of the inverse effective temperature in Fig. 3. Data for $\phi = 0.3$ and $\phi = 0.4$ at pressures of ~10 atm are presented. The results of the current work are in good agreement with the earlier data, particularly given the slight differences in the experimental conditions. In the previous study by Walton et al. [22], a range of pressures (4.7–19.6 atm), temperatures (935–1109 K) and mixture compositions ($\phi = 0.3–0.4$) were investigated. Regression analysis of the data from Walton et al. [22] yields the following empirical expression for $\tau_{ign}$ for methyl butanoate with an $R^2$ value of 0.97 [27].

$$
\tau_{ign} \; [ms] = 0.0032P_0^{-1.21}O_2^{0.77}N_2^{0.12} \\
\times \exp(30.300/R \; [cal/mol/K/\tau_{eff}])
$$

In Eq. (2), $P_{eff}$ has units of [atm]; $\phi$ is the fuel/O2 equivalence ratio; $X_{O2}$ is the mole percentage of O2 in the mixture [%], $R$ is the universal gas constant, and $\tau_{eff}$ has units of [K]. The form of the expression was selected for consistency and comparison with ignition studies of other reference fuels, e.g. iso-octane [28]. Eq. (2) allows us to account for differences in experimental conditions and compare summaries of the data sets. For example, Fig. 4 presents the data from the Walton et al. [22] and the current work where the data have been normalized to the conditions of $\phi = 0.3$, $P = 10$ atm, and $X_{O2} = 21%$ using Eq. (2). The data are in excellent agreement; well within the experimental uncertainty of ±16% cited in [22]. The data are also compared in Fig. 4 with the results of the study by Akih-Kumgeh and Berghorson [15]. They derived the following correlation based on their experimental shock tube data on methyl butanoate ignition delay times.

$$
\tau_{ign} \; [ms] = 2.46 \times 10^{-3}P_0^{0.6}O_2^{-0.04}D^{0.4} \\
\times \exp(38.100/R \; [cal/mol/K/\tau_{eff}])
$$

In Eq. (3), $P_{eff}$ has units of [atm]; $\phi$ is the fuel/O2 equivalence ratio; $X_{O2}$ is the mole percentage of O2 in the mixture [%], $R$ is the universal gas constant, and $\tau_{eff}$ has units of [K]. The form of the expression was selected for consistency and comparison with ignition studies of other reference fuels, e.g. iso-octane [28].
where $D$ is the molar ratio of inert diluent to $O_2$ in the mixture. Note that the correlation by Akih-Kumgeh and Berghorson was extended in Fig. 4 to temperatures below the range for which it was derived ($T = 1090–1600 K$) as well as to a lower equivalence ratio of $\phi = 0.3$ than what they considered in the shock tube studies ($\phi > 0.5$). Within these limitations, the two correlations are in good agreement (within a little more than a factor of 2 for $t_{\text{ign}}$) with similar activation energies (within 20%). Differences in the other fit parameters are not attributed to specific effects of methyl butanoate chemistry due to the limited range of experimental conditions considered.

The UM RCF data are also compared in Fig. 4 with the model predictions of Westbrook et al. [2], where the authors developed detailed reaction mechanisms to represent the combustion and ignition properties of both soy and rapeseed biodiesel fuels, also called soy methyl ester (SME) and rapeseed methyl ester (RME). The model calculations considered slightly higher initial pressures (13.3 atm) and equivalence ratios ($\phi = 1.0$) compared to the current work, which both serve to decrease ignition delay times. Indeed, the biofuel predictions are a little less than an order of magnitude faster than the UM RCF results for methyl butanoate. It is also worth noting the model predictions by Westbrook et al. [2] reproduce the negative temperature coefficient (NTC) behavior expected of biofuels and long chain esters, and the NTC behavior starts at approximately 910 K for the SME and RME fuels at 13.3 atm.

A summary of the pressure time-histories of the gas-sampling experiments is presented in Fig. 5. Fig. 5 demonstrates the excellent level of repeatability of the sampling experiments. Note the nearly identical, smooth compression processes. The standard deviation of the end of compression pressures for the sample experiments is 0.24%. The slight decrease in pressure after the end of compression (due to heat losses to the test manifold walls, prior to the sampling event) is also extremely consistent between experiments. The primary cause of the variation in the pressure time-histories, and consequently $t_{\text{ign}}$, is the difference in the sampling times and sampling intervals. During sampling slightly different amounts of reacting gas are removed from the test volume in each experiment. Additionally, the sampling event slightly cools the test gas mixture slightly due to expansion, leading to a 5% standard deviation in ignition delay time observed in the experiments.

To compensate for these differences in the experimental time-histories, the time domain is normalized by the actual ignition delay time for each experiment, and $P_{\text{max}}$ is defined as $t = 0$, and $t = 1$ is the time of ignition. Fig. 6 includes the pressure time-histories for the same six sampling events presented in Fig. 5 after they have been normalized by the ignition delay time for each experiment. The normalized time scale is used for comparison between each experiment, and against the model predictions which are described below.

Fig. 7 presents typical chromatograms from a methyl butanoate ignition experiment. The chromatograms were used to determine the mole fraction for each species where an accurate calibration had been established. As seen in Fig. 7b), the light hydrocarbons elute quickly and do not interfere with the oxygenate peaks. However, the oxygenate species observed could not be quantified. This was due to interference from methanol and methyl butanoate in the experimental data and the calibration standards, and the non-linear detector response to these species. Specifically, the high...
signals and long tails to the methanol and methyl butanoate peaks (see Fig. 7b) interfere with each other and with the methyl acrylate, methyl 3-butenolate and methyl crotonate peaks observed. This interference limits closing the mass balance on carbon, as methyl butanoate measurements are vital to the C balance. However, the light hydrocarbon species were well isolated, and the GC3 data allowed for excellent identification and quantification of the smaller intermediate hydrocarbons (see Fig. 7c). Note that uncertainty due to repeatability of the sampled gases was much smaller than the uncertainty due to dilution and GC calibration discussed below, and Fig. 8 presents two typical gas chromatograms for repeat experiments at $t_{\text{norm}} = 0.36$ for the small hydrocarbons.

The mole fraction time-histories of the light hydrocarbon intermediates are presented in Fig. 9 as a function of $t_{\text{norm}}$. With respect to the carbon balance, the measurements of the light hydrocarbons account for a maximum of 13% (at $t_{\text{norm}} = 0.9$) of the carbon contained in the methyl butanoate fuel. A typical time-history of the test section pressure is included in Fig. 9 for reference. For species where data points are not presented at early times, the concentrations of those species were below the detectable limits. The error bars in the figure represent the uncertainties in the measurements. The horizontal error bars are the uncertainties in the sampling time which is primarily due to the duration of the sampling process. The vertical error bars are the uncertainties in the species measurements. The primary sources of uncertainty are the dilution of the sampling gases with gases trapped in the dead volume of the sampling system (e.g. the sampling tube and valve volume) and the uncertainty in the GC calibration. The dilution of the sample is calculated using the methods outlined in He et al. [23]. Briefly, the ratio of the pressure, volume and temperature ($PV/T$) of the gases in the dead volume (which are assumed to be the same composition as the initial mixture composition) and the gases in the sampling chamber after extraction from the test section is used to estimate the dilution of the sample gases.

4. Discussion

The experimental data are evaluated by comparison with predictions based on the methyl butanoate reaction mechanism of
Walton et al. [22], which is a slight modification to the mechanism developed by Metcalfe et al. [11]. Specifically, Metcalfe et al. [11] expanded the methyl butanoate mechanism of Fisher et al. [5] and revised key H-atom abstraction rates from methyl butanoate (among other reaction rates they changed). In the work by Walton et al. [22], the rate coefficients for methyl butanoate + H = H2 + mb4j; methyl butanoate + H = H2 + mbmj were increased by a factor of two to improve agreement between the model predictions and ignition delay time data from the UofM RCF. Other reaction rates were also changed to improve the agreement between the UM RCF data and the Metcalfe et al. [11] shock tube data. A summary of the reactions affected and the revised rate coefficient expressions can be found in Walton et al. [22]. Note that all of the changes were within the uncertainty bounds for each of the reaction rate expressions.

The species predictions were generated using the CHEMKIN™ suite of programs and assuming a spatially-homogeneous, adiabatic constant volume system. The adiabatic model used here has been validated against more complicated models incorporating heat losses to the test section walls (see for example, He et al. [28]). While other rapid compression machines are often affected by significant heat losses that require both experimental and modeling calibration, the adiabatic 0D modeling approach is applicable for these UM RCF experiments for several reasons. The UM RCF has high ratios of volume to surface area of the test section (0.8–1 cm, depending on the length of the test section used). This ratio is a factor of 2–5 times higher than other rapid compression facilities. The large volume of the test section coupled with the unique design of the UM RCF free piston (which traps the cold boundary layer gases accumulated during compression outside the test section, see Donovan et al. [24] for details) minimizes the effects of heat losses. We have validated the heat losses to well within 5% of predicted adiabatic state conditions [24], and confirmed the size of the homogeneously reacting core region with high-speed imaging. Moreover, the small heat losses that are experienced early after the end of compression are well captured in both the experimental and modeling data by using the time integrated definitions for $P_{eff}$ and the $T_{eff}$ presented earlier. Walton et al. [26] discuss the merits of using these average values to define the state conditions for weak and strong (volumetric) ignition systems. The experiments presented in this study were each documented as volumetric ignition using the high-speed imaging data. These results both confirm these conditions were in the strong ignition regime for methyl butanoate and validate the use of gas sampling. Note that this quality standard of using high-speed imaging data to characterize and document each ignition experiment is unique to the UM RCF.

The input data to the CHEMKIN model were the target sampling conditions of $\phi = 0.30$, $P = 10.2$ atm, $T = 985$ K, and inert/O2 = 3.76. Ignition was defined computationally as the maximum rate of temperature rise of the reacting mixture. The model predicts $\tau_{avg} = 19.4$ ms which is in excellent agreement (within 10%) of the average measured ignition delay time of 21.6 ms. Note that the
compression process is not modeled, and reaction during compression is not considered a concern due to the lack of significant low temperature reactivity for methyl butanoate at the conditions considered [22] (which is one of the reasons methyl butanoate is not considered representative of real biodiesel fuels).

As seen in Fig. 8, there is excellent quantitative agreement between the experimental measurements and the model predictions for the methane and ethene time-histories (within $\pm 20\%$). The experimentally determined mole fractions for ethane, propane, and propene were each higher than the model predictions. However, in the case of propane this is an absolute difference of less than 5 ppm so the agreement is still considered excellent for this hydrocarbon. In the case of ethane, the difference in the experimental data and the model results is less than 100 ppm. Propene is observed experimentally at high levels (>200 ppm after $t_{\text{norm}} = 0.6$), whereas model predictions peak at ~400 ppm. 1-Butene was measured at 10–30 ppm during ignition, whereas the model predicts 1-butene in sub-ppm levels. Note that CH$_3$ is predicted to be present at levels less than 1 ppm for $t < 15$ ms. Thus, CH$_3$ recombination at the sampling probe is not expected to affect the measurements reported here.

As noted earlier, quantitative measurements could not be made for the oxygenated species identified in the chromatograms; however, a qualitative comparison was made with the model predictions. Methyl acrylate, methyl-3-butenolate, and methyl crotonate were each identified from the gas chromatograms (Fig. 7b). These species are involved in the major decomposition pathways and are predicted to exhibit peaks of approximately 1000 ppm (methyl-3-butenolate), 200 ppm (methyl crotonate) and 100 ppm (methyl acrylate) immediately prior to ignition ($t_{\text{norm}} = 0.85–0.9$) (see Fig. 10). Thus, their presence in the chromatograms is consistent with model predictions.

Quantitative measurements of CO$_2$ can be made using GC1 (CO$_2$ elutes after approximately 2.2 min); however, no CO$_2$ was detected during any experiments. CO$_2$ is not predicted to be present at levels above 500 ppm until times after ~17 ms for the target conditions. Thus, the CO$_2$ is below our detectable limits for the entire time-history of the sampling data, and the results are completely consistent with model predictions.

Sensitivity and rate of production analyses demonstrate the significance of the OH/HO$_2$/H$_2$O$_2$ kinetics for methyl butanoate/air ignition at these conditions. Sensitivity analysis was conducted for key species, including OH, H and methyl butanoate. Each analysis yielded the same top reactions. The results for OH are presented in Fig. 11. The OH + OH (+M) = H$_2$O$_2$ (+M) reaction is the most critical to ignition, and the chain branching H + O$_2$ reaction plays a relatively smaller role. Reactions forming H$_2$O$_2$ accelerate ignition, and reactions forming HO$_2$ slow ignition. A reaction path diagram for methyl butanoate for the target conditions at Fig. 11. OH sensitivity analysis based on the reaction mechanism developed by Walton et al. [22]. The modeling conditions are $\phi = 0.30$, $T = 985$ K, $P = 10.2$ atm, and inert/O$_2 = 3.76.

![Fig. 12. Reaction path diagram for the initial steps in methyl butanoate (mb) oxidation, based on rate of production analysis at $t = 14.9$ ms ($t_{\text{norm}} = 0.77$), for the initial conditions of $\phi = 0.30$, $T = 985$ K, $P = 10.2$ atm, and inert/O$_2 = 3.76.](image-url)
\[ t = 14.9 \text{ ms} \] is presented in Fig. 12. In the figure, the values by the arrows are the rates of production for each path normalized by the net rate of production or net rate of consumption, depending on the direction of the reaction. Fuel consumption is dominated by H-atom abstraction from the 4 or 3 site on the methyl butanoate by OH (>60% of the total methyl butanoate removal rate). The mb4j and mbmj predominantly react with O$_2$ to form mbmoo and mb4oo, which then isomerizes and then undergo further reaction.

The reactions identified in the sensitivity analysis are consistent with the reactions identified as important by Dooley et al. [13] for sensitivity analysis performed on $\tau_{ign}$ for methyl butanoate ignition at 836 K, 20 atm, $\phi = 0.5$ and $\chi_{mb} = 3.13\%$ (in particular, HO$_2$ + HO$_2$ = H$_2$O$_2$ + O$_2$ and OH + OH = H$_2$O$_2$). Further, rate of production analysis by Dooley et al. also found methyl butanoate fuel consumption dominated by H-atom abstraction by OH (70%). A key difference in the two flux analyses is that the m and 4 sites are equally preferred and are the dominant reaction pathways for methyl butanoate reaction with OH in the current work. In the study by Dooley et al., the 2 site on methyl butanoate is preferred. Increasing the branching fraction for the H-atom abstraction from the 3 site in the mechanism used in this work would directly increase the model predictions for propene, as C$_3$H$_6$ is formed directly via scission of mb3j.

5. Conclusions

The results of this work provide new, more rigorous data for understanding the reaction pathways and species controlling the auto-ignition of methyl butanoate at moderate pressures and intermediate temperatures. Model predictions for species time-histories during methyl butanoate ignition are in excellent agreement for several stable molecules. Some oxygenated species (methyl 3-butanoate, methyl crotonate, and methyl acrylate) were identified in the gas chromatograms, but could not be quantified experimentally. These species were predicted to occur at high levels (in excess of 100 ppm at the maximum predicted levels). Model analyses indicate OH/HO$_2$/H$_2$O$_2$ kinetics dominate the methyl butanoate ignition behavior. Discrepancies observed for propene indicate the H-atom abstraction rate for the methyl butanoate 3 site may be slightly too low at the conditions studied here.

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References