Mid-Infrared Laser Absorption Spectroscopy and Ignition Delay Time Measurements of Advanced Renewable Fuels at High Pressure in a Shock Tube

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MID-INFRARED LASER ABSORPTION SPECTROSCOPY AND IGNITION DELAY TIME MEASUREMENTS OF ADVANCED RENEWABLE FUELS AT HIGH PRESSURE IN A SHOCK TUBE

by

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A dissertation submitted in partial fulfillment of the requirements for the degree Doctor of Philosophy in the Department of Mechanical and Aerospace Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Spring Term
2021

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ABSTRACT

The United States government has set 2050 as the target for net-zero greenhouse gas emissions due to their increasing levels and the subsequent rise in global temperatures. To meet this target, there has been renewed interest in the combustion of high-energy biofuels that could combat these issues. Thus, the Department of Energy started the Co-Optimization of Fuels and Engines program to find bioderived blendstocks that can harmonize with current and future generation engines to increase power and efficiency, all while reducing overall emissions. As part of this program, it is crucial to understand the combustion of these fuels at the temperatures and pressures internal combustion engines operate at. Therefore, the oxidation and pyrolysis of several advanced biofuels—cyclopentanone, prenol, 1-pentene and trans-2 pentene, and methyl propyl ether—have been studied in a shock tube reactor to quantify some of their fundamental combustion properties. Measurements include ignition delay times and time-resolved species concentrations, including that of fuel decomposition and formation of intermediate species such as carbon monoxide and ethylene. These measurements are useful for validating and updating chemical kinetic mechanisms that provide the chemistry input into computational fluid dynamic codes. This study's measured data are compared to the predictions of the most recent literature chemical kinetic mechanisms for each fuel. When appropriate, sensitivity analyses were conducted to highlight reactions sensitive to the conducted measurements, and some reaction rate modifications were made.
ACKNOWLEDGMENTS

Above all, I would like to thank my wife, Amy Ninnemann, for her unwavering support in my pursuit of this degree. Without your love, reassurance, and affection I never would have made it where I am today.

I would also like to thank my advisor, Dr. Subith Vasu, for his commitment to my success and all of the knowledge and skills that he has passed to me over the years. I would also like to thank all of my lab colleagues for their help in the various experiments and discussions that led to the collection of the data presented in this study. In particular, I would like to thank Joseph Lopez, Andrew Laich, Samuel Barak, and Ramees Rahman for the training, guidance, and discussions that led me to this point.
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CHAPTER ONE: INTRODUCTION

Internal combustion engines have been an integral part of our transportation infrastructure for decades and will continue to be prevalent for many more. The U.S. Energy Information Administration does not predict a significant shift away from petroleum-based fuels to other cleaner sources, Figure 42A, within the next 30 years which is likely due to the well-established infrastructure for these fuels and the quantity of internal combustion engines used by society. It is well understood that the burning of these fossil fuels produces greenhouse gases, Figure 42B, which have a negative impact on the Earth.

![Figure 1. (A) Transportation sector consumption by fuel, (B) energy related carbon dioxide emission by fuel. Data from the 2021 annual energy outlook from the U.S. energy information administration [1].](image)

In addition to carbon dioxide, other greenhouse gases are produced through the combustion of these fossil fuels, including methane and nitric oxides. Since the Mauna Loa observatory in Hawaii has started quantifying atmospheric greenhouse gas levels, CO₂ concentrations have risen
by 100 ppm [2], CH$_4$ by 200 ppb [3], and N$_2$O by about 20 ppb [4]. These greenhouse gases rise high into the atmosphere and trap excess heat from escaping the planet, effectively acting as a blanket for the Earth. While many other technologies, such as battery electric vehicles, are advancing, the demand and infrastructure for these technologies is still low, facilitating a need for cleaner, more efficient internal combustion engines.

The United States Department of Energy recognized these problems and created a multi-year project to co-optimize—design in tandem to maximize vehicle performance and carbon efficiency—previously independent research on biofuels, combustion, and engines. This initiative has brought together universities and national labs to harmonize fuel-engine combinations and create a cleaner and more sustainable transportation infrastructure. This is done in a 3-tier approach. First (1), the list of potential blend stocks is reduced and ordered based upon a fuel merit function [5]. This merit function factors in fuel properties such as RON sensitivity, heat of vaporization, laminar flame speed, low speed pre-ignition, particulate matter index, and catalytic light-off temperature. This merit function provides weight to each one of the mentioned properties to rank the potential biofuels for boosted internal spark ignition (SI) engines. In tier 1, the number of potential biofuels candidates is reduced from hundreds to 10 (Figure 2). In the second tier, (2) the chemical kinetics, environmental impact, and scalable infrastructure are considered for the fuels, and in the final tier (3) engine tests of the selected compounds are done.
The biofuels with the highest merit function scores have the greatest potential to increase efficiency and performance of SI engines. However, just because a fuel has made it through the merit function does not make it ready for engine tests. The detailed combustion chemistry of these molecules must be explored and captured in a comprehensive chemical kinetic mechanism. These mechanisms contain the reactions and the reaction rates that dictate how a fuel will react in an environment of different molecules at various temperatures and pressures. Having a robust and validated chemical kinetic mechanism is necessary because the fuel chemistry dictates the heat release rate, temperature, and emissions of a combusting system. For simple fuel-oxidizer combinations, there are only a few species and reactions that can govern the entire chemical process. For example, in the hydrogen-oxygen reaction, only 8 species and 19 reactions must be
accounted for [6]. However, as the complexity of the fuel increases, so does the mechanism necessary to capture its detailed chemistry—the recent mechanism from De Bruycker et al.[7] to describe prenol and isoprenol oxidation and pyrolysis contains 824 species and 3740 reactions. These chemical kinetic mechanisms are typically generated through quantum calculations and molecular theories and thus must have experimental validation measurements at combustion relevant conditions to test their performance.

Useful measurements that can validate these mechanisms include a fuel’s ignition delay time and time-resolved intermediate species concentrations. The former is a measure of the global reactivity of a fuel and is an important parameter in engine design. The latter can help validate chemical pathways by tracking time-resolved species concentrations during a fuel’s decomposition. Acquiring these measurements at conditions relevant to internal combustion engines is no easy task. To do so, a researcher needs a device to bring a fuel to these conditions nearly instantaneously, so that no low temperature chemistry can progress, and fast diagnostics to non-intrusively probe the reacting flow. A shock tube can accomplish this first task by bringing a gaseous mixture to extreme temperatures and pressures (900-3000 K and 0.1-100 atm, depending on the tube’s capabilities) within nanoseconds through shock wave compression. Optical access located in the tube’s test section provides access for high-speed diagnostics, such as lasers and emission detectors, to non-intrusively probe the reacting flow.

Without validation measurements at these engine relevant conditions, confidence in a kinetic mechanism can be eroded and have consequences when new engine designs are made. Large power generation and car companies couple reaction mechanisms with computational fluid dynamic codes to prototype new engine designs. If the chemistry of one of these fuels is not
validated, fuel-engine timing can be off and result in poor performance and efficiency of the engine.

In this investigation of Co-Optima biofuels, a novel diagnostic for carbon monoxide monitoring was developed. This diagnostic outputs monochromatic light at 2046.30 cm$^{-1}$ which is resonant with the P(23) transition of CO and allows for ppm level quantification of CO in harsh environments. Spectral characterizations of this line were done at 8.6-10.3 atm and 1085-1456 K. This diagnostic was utilized to measure time-resolved concentrations of carbon monoxide during the oxidation or pyrolysis or several biofuels, including: cyclopentanone, isoprenol, prenol, 1-pentene, 2-pentene, and methyl propyl ether. In addition, absorption-based diagnostics were developed for ethylene and cyclopentanone monitoring at wavelengths of 949.49 and 1749.84 cm$^{-1}$, respectively and were applied to cyclopentanone pyrolysis for time-resolved measurements of these molecules. Complementary to the absorption diagnostics, emission spectroscopy of OH$^*$ at 310 nm was used to quantify the ignition delay times of several of these fuels. A more detailed introduction of each fuel and the measurements performed are provided in their respective sections below.
CHAPTER TWO: SHOCK TUBE OPERATION

I. Shock Tube Theory

Shock tubes are long tubes that use shock wave compression to bring gaseous mixtures to elevated temperatures and pressures. Because a shockwave is used to compress and heat a mixture, nearly instantaneous changes in environmental conditions occur. This unique property of shock tubes provides an excellent testing platform for fuel research, as a fuel mixture can instantaneously be brought to engine-relevant conditions so that its chemistry may be explored [8-11]. The testing time scales of shock tubes are short and the test region is in a stagnated test fluid, thus, this fuel chemistry can be measured with negligible influence from heat transfer and fluid dynamic effects.

The standard shock tube operation is the same. The tube is sectioned off into two regions, driver and driven, by a diaphragm which is typically Lexan, but metal can be used as well. Both the driver and driven sections are vacuumed down to low pressure, ~10^{-6} Torr, before the driven side is filled with the test mixture to be investigated. Once the desired fill pressure is reached in the driven side, the driver is flooded with an inert gas to generate a large pressure differential across the diaphragm. Before rupture of the diaphragm, the gases in both the driver and driven sections are unperturbed by any shockwaves, and are designated as region 4 and region 1, respectively. This can be viewed in the x-t diagram of Figure 3. Upon continual filling of inert gas into the driver, the diaphragm will eventually rupture. At this time, an instantaneous discontinuity in pressure within the system exists and a shock wave is formed to equilibrate the system. The shock front travels from the driver through the driven gas, increasing the gas’ temperature and
pressure. The Mach number of the generated shockwave is a direct function of the pressure differential across the diaphragm, equation (1). As the shock front passes, region 1 turns into region 3. At the time of diaphragm rupture, an expansion fan also forms to help equilibrate pressure within the system, this wave travels into the driver and transforms region 4 into region 2.

The shock front reaches the end wall of the driven side and reflects toward the diaphragm. As the shock front passes through the region 3 gas, the thermodynamic properties are raised again and become region 5. Region 5 contains the test mixture at the highest temperature (T₅) and pressure (P₅) within the system, these are given by equations (2) and (3), respectively. Equations (1-3) are ideal shock relations and are reported here to demonstrate the dependence of Mach number on the pressure and temperature ratios in each state. The temperatures and pressure reported in this document are calculated through the FROzen Shock (FROSH) routine [12]. The primary difference between the ideal and FROSH temperatures and pressures is that the specific heat ratio of the test mixture is assumed constant in the ideal relations. For the most accurate calculation of temperature and pressure, a temperature dependance must be assumed on the specific heat ratio. The vibrational relaxation times of all mixtures in this document were short enough to report equilibrium-equilibrium values from the FROSH output.
Figure 3. X-t diagram depicting shock tube operation.

\[ \frac{P_4}{P_1} = \frac{2\gamma_1 M_s^2 - (\gamma_1 - 1)}{\gamma_1 - 1} \left[ 1 - \frac{\gamma_4 - 1}{\gamma_1 + 1} a_4 \left( M_s - \frac{1}{M_s} \right) \right]^{-\frac{2\gamma_4}{\gamma_4 - 1}} \]  

(1)

\[ \frac{P_5}{P_1} = \left[ \frac{2\gamma M_s^2 - (\gamma - 1)}{\gamma + 1} \right] \left[ \frac{(3\gamma - 1)M_s^2 - 2(\gamma - 1)}{(\gamma - 1)M_s^2 + 2} \right] \]  

(2)

\[ \frac{T_5}{T_1} = \frac{(2(\gamma - 1)M_s^2 + (3 - \gamma))(3\gamma - 1)M_s^2 - 2(\gamma - 1)}{(\gamma + 1)^2 M_s^2} \]  

(3)

II. University of Central Florida Shock Tube

The shock tube facility at the University of Central Florida is a heated, variable length driver, double-diaphragm shock tube. The interior of the tube was honed to 14.17 cm and
electropolished. The driven and driver lengths are 8.54m and 4.88m, respectively. Located 2.00cm from the driven end wall are 8 equally spaced diagnostic ports around the circumference of the tube. The diagnostic ports allow for window plugs to be inserted and can either house pressure transducers or windows for line-of-sight measurements. Two pressure transducers, Kistler 6031 and PCB 113B26 occupy two of the diagnostic locations in opposing positions. Throughout this document, pressure is reported using the Kistler 6031 transducer located at the top port location of the tube.

The speed of the incident shockwave is calculated through five piezoelectric pressure transducers (PCB 113B26) that are located along the last 1.50 m of the driven side of the tube and are wired to four Agilent 53220A time interval counters. The combination of these devices allows for the incident shock velocity to be extrapolated to the end wall position. The measured shock velocity is used to calculate the incident Mach number which is fed into equations 1-3 to obtain the reflected shock conditions.

Mixtures are prepared manometrically with 100 Torr and 10,000 Torr capacitance manometers (MKS E27, error 0.1% of reading and MKS 628D, error 0.25% of reading, respectively) and are kept in a magnetically stirred 33L Teflon-coated, stainless-steel mixing tank. Mixtures are permitted to mix for a minimum of 2 hours before introduced into the shock tube.
CHAPTER THREE: EXPERIMENTAL TECHNIQUE

I. Ignition Delay Time

Ignition delay time (IDT) is a measure of the global reactivity of a fuel-oxidizer system and is an important design parameter for any engine that relies on chemical combustion. In any combustion engine, the fuel and oxidizer spend a finite time inside the combustor of that engine, this is known as the residence time. If the IDT of the fuel-oxidizer is longer than the residence time of the engine, ignition will occur outside of the combustor causing serious damage to parts that are not meant to withstand such energy release, or the fuel will not ignite at all. On the contrary, if the IDT is shorter than the residence time, engine damage can also occur. For example, in an internal combustion engine, if the IDT of the mixture is too short the mixture may ignite while the piston is mid-compression stroke. The energy release from the chemical reaction can be enough to reverse the direction of the piston before it reaches top-dead-center and can cause engine knock.

In this study, the IDTs are measured at the diagnostic ports located 2.00cm from the driven end wall through a 3mm thick uncoated sapphire window (Thorlabs WG30530) epoxied (Epotek 353nd) to one of the window plugs. IDTs are defined from time-zero (minimum of Schlieren spike due to reflected shock passage) of the experiment to the max OH* signal captured with a Thorlabs PDA25K GaP detector and a 310nm CWL, 10nm FWHM bandpass filter (Edmund Optics 67-819).
II. **Absorption Spectroscopy**

When a molecule interacts with light, the light can be scattered, transmitted, or absorbed. Absorption of light occurs when the wavelength of light is resonant with the discrete energy spacing within the molecule. In other words, a molecule in its ground state absorbs a photon with energy equal to the difference of a higher quantum state and the ground state. Within the infrared portion of the electromagnetic spectrum, it is a molecules’ vibration and rotation that determine this energy spacing. The basis of quantitative absorption spectroscopy is the Beer-Lambert relation, equation (4) where $\alpha$ is the absorbance, $I$ is the transmitted laser intensity through the absorbing medium, $I_0$ is the transmitted laser intensity through the same path length in vacuum, $n$ is the number density of the absorbing molecule, $\sigma$ is the absorption cross-section, and $L$ is the absorbing path length. To write the Beer-Lambert relation into a more usable format, the number density can be substituted with the ideal gas equation of equation (5) where $P$ is the pressure, $R_u$ is the universal gas constant, $X$ is the mole fraction of absorbing species, and $T$ is the temperature.

\[
\ln(\alpha) = \frac{I}{I_0} = \exp(-n\sigma L) \quad \text{(4)}
\]

\[
\ln(\alpha) = \frac{I}{I_0} = \exp \left[ -\left( \frac{XP}{R_u T} \right) \sigma L \right] \quad \text{(5)}
\]

Equation (5) provides a useful means for quantifying the mole fraction of absorbing medium, $X$, through geometric, thermodynamic, and spectroscopic parameters. When the incident and reflected shock waves produced from the shock tube interact with the fuel mixture inside, the fuel will begin to thermally decompose or oxidize depending on the mixture. The temperature and pressure behind the shock wave are well known through the FROSH routine [12], the attenuation of light due to the presence of an absorbing gas is measured over the course of the experiment, and
L is known from the diameter of the shock tube. Therefore, the mole fraction of absorbing gas can be quantified with accurate knowledge of the molecules’ absorption cross-section. The process for quantifying this absorption cross-section is provided in the following section.

Figure 4. Experimental laser setup on the UCF shock tube.

III. Absorption Cross-Sections

To provide accurate information on the quantity of combustion intermediates, the absorption cross-sections of the intermediates must be known with temperature, pressure, and wavelength (Equations 4 and 5). The absorption cross-section is a measure of the effective area a photon must traverse in order to be absorbed and higher cross-sections translate to more light being absorbed by the molecule.
Measurements of absorption cross-section are quite trivial in a shock tube. If equation 5 is rearranged to solve for $\sigma$, then the parameters that must be known include the absorbance, temperature, pressure, and concentration of analyte. By preparing a mixture with a known concentration of analyte and shock-heating this mixture to known thermodynamic states (governed by equations 1-3), the absorbance in each state can be measured and thus the absorption cross section can be calculated. Figure 5 shows this process and the step change in absorbance due to the change in thermodynamic properties from the passage of the incident and reflected shockwaves.

Figure 5. Clear change in absorbance of 1% CO/12% He/Ar mixture, measured at a wavelength of 2046.30 cm$^{-1}$. State (1) $T=296K$ $P=451$ Torr; (2) $T=652$ K $P=3.12$ atm; (5) $T=1104$ K $P=10.31$ atm. Shaded region denote time interval in each state where the mean absorbance is taken and used to calculate spectral properties from the Beer-Lambert Law.
Carbon monoxide time-histories were collected in the manner described above. A 1% mixture of carbon monoxide, balanced with 12% helium and 86% argon, was used for these measurements. Carbon monoxide has a notoriously long vibrational relaxation time [13] and must be accounted for when doing such absorption cross section measurements. The vibrational relaxation time refers to the time required for an excited molecule (one that has taken in energy and jumped to an excited vibration energy state) to dissipate energy back to the environment and return to the ground state. Helium was added in this characterization mixture to decrease the vibrational relaxation time of carbon monoxide and ensure that all measurements were made on ground state species. A closer examination of Figure 5 in the post-reflected shock region shows the relaxation of the mixture, indicated by the ramp-like decrease in absorbance before a steady signal is achieved. All absorbance values in state 5 are averaged after this relaxation time when calculating absorption cross-section. The cross-section of CO was quantified at 2046.30 cm⁻¹ over the pressures of 8.6-10.3 atm and 1085-1456 K and can be represented with the empirical relation of equation (6) with pressure in units of Pascal and temperature in Kelvin. The equation fits the data well in both dimensions with an R² of 0.979. These results compared to HITRAN 2012 [14] are displayed in Figure 6. The max uncertainty in temperature and pressure for this characterization were 0.87% and 1.61%, respectively. An RMS uncertainty estimation for the absorption cross-section was made using Eq. (5) and was found to have an average uncertainty of 1.87% with a maximum uncertainty of 2.59%.

\[
\sigma_{CO}(2046.30 \text{cm}^{-1}) = 9.112 \times 10^6 P^{-1.132} T^{0.316}
\]  

(6)
Figure 6. Experimental characterization of CO absorption cross-sections at 2046.30 cm$^{-1}$. Measurements were performed on a 1% CO/12% He/86% Ar mixture. (A) cross-section with pressure, and (B) cross-section with temperature.
CHAPTER FOUR: RESULTS AND DISCUSSION

I. Cyclopentanone

Cyclopentanone, Figure 7, is a cyclic ketone with a high ring strain (41 kJ/mol [15]) and research octane number (RON) (101 [16]) making it a promising aviation biofuel and blending agent in boosted internal spark ignition engines. In addition to its favorable chemical properties, cyclopentanone is easily produced through bioprocesses, namely the breakdown of cellulose by fungi [17] and the pyrolysis of biomass [18]. The ease of cyclopentanone synthesis through sustainable means and its favorable chemical properties has attracted several researchers to study its oxidation and pyrolysis.

![Space filling model for cyclopentanone.](image)

Johnson and Walters [19] studied the thermal decomposition of cyclopentanone at 761-816 K and 0.130-0.413 atm in cylindrical Pyrex reaction vessels. Using infrared absorption spectroscopy, carbon monoxide, ethylene, 1-butene, hydrogen, and 2-cyclopenten-1-one were identified as intermediates or products of the decomposition. The authors also investigated the influence of temperature, pressure, and concentration of unsaturated hydrocarbons on the product
distribution and the decomposition rate. It was found that the decomposition process is autocatalytic, as the addition of 1-butene and propylene accelerated the decomposition. More recently, Zaras et al. [20] identified several unimolecular decomposition pathways of cyclopentanone using the G3B3 quantum chemistry method [21]. The three primary decomposition pathways identified include a concerted reaction leading to two ethylene and one carbon monoxide molecules, a step-wise decomposition resulting in the same products, and lastly a keto-enol tautomerism. Radical-involved decomposition pathways, including H abstraction reactions by H and CH₃ radicals at the α and β carbon sites, were also recently provided by Zhou et al. [22]. The low-temperature (550-700 K) oxidation of cyclopentanone as well as other cyclic ketones (cyclohexanone and 2-methyl-cyclopentanone) was studied with a multiplied photoionization time-of-flight mass spectrometer by Scheer et al. [23]. The prominence of chain-terminating pathways linked to HO₂ formation in the low-temperature oxidation of cyclic ketones was determined to yield low temperature reactivity at these conditions. The oxidation of cyclopentanone was investigated in a jet-stirred reactor at 1 and 10 atm and temperature of 730-1280 K by Thion et al. [24]. Using Fourier transform infrared spectroscopy and offline gas chromatography, a total of 16 intermediates and products were identified. A chemical kinetic mechanism was constructed and provided reasonable comparison to the experimental results.

a. Oxidation

Carbon monoxide time-histories and ignition delay times were collected during stoichiometric oxidation of cyclopentanone in the University of Central Florida shock tube. Measurements spanned temperatures of 1165-1327 K and 1-10 atm in a 0.1% C₅H₈O/0.7% O₂/Ar mixture. In contrast to the other carbon monoxide measurements reported in this document, the
CO measurements performed in cyclopentanone oxidation were done with a continuous wave distributed feedback quantum cascade laser (Thorlabs DFB QCL) at 2183.22 cm\(^{-1}\). Cross section data for CO was obtained from the HITRAN 2012 database [14] at each test’s given initial test temperature and pressure (\(T_5\) and \(P_5\), respectively). The mechanism of Zhang et al. [25] was used to simulate the top intermediates in the oxidation of cyclopentanone. According to the mechanism, \(\text{H}_2\text{O}, \text{CO}_2\), and \(\text{C}_2\text{H}_4\), are the top formed products, none of which absorb at the chosen wavelength to measure CO absorption at low pressure. However, at 10 atm, the pressure broadening of the CO absorption feature becomes on the same order of that as \(\text{CO}_2\). Therefore, for the 10atm data reported, the CO time-histories are truncated just prior to ignition where the absorbance due to \(\text{CO}_2\) is no longer negligible.

Due to the longer ignition delay times experienced at lower temperatures, driver gas tailoring was implemented to extend test time to observe CO formation during combustion at these lower temperatures. Driver gas tailoring mitigates the interaction between the reflected shock wave and the contact surface, which is the region produced between the driver and driven gases when the diaphragm ruptures. To prepare each tailored mixture, two Teledyne-Hastings HFC-D-303A mass flow controllers were used to regulate the flow of helium and nitrogen into the driver section according to the equations presented by Palmer and Knox [26], Mackay and Trass [27], and Ben-Dor et al. [28]. For these experiments, the mole fraction of helium ranged from \(X_{\text{He}}=0.643\) to \(X_{\text{He}}=1.000\).

Simulations were conducted in Chemkin Pro using a closed homogeneous batch reactor model with adiabatic and constant volume assumptions. Several of the experiments performed in the UCF shock tube showed evidence of a constant linear pressure rise, \(dP_5/dt\), prior to ignition.
For these individual experiments the linear pressure rise was quantified in terms of %/ms to obtain pressure profiles for input into Chemkin. All simulations were performed under the initial test temperature ($T_5$) and the calculated pressure profile, with an origin at the initial test pressure ($P_5$). For each pressure set (1 atm, 6 atm, 10 atm) the run with the highest uncertainty in temperature within each set was identified from the incident shock velocity and initial test conditions and was found to be ±1% for all three sets. This temperature uncertainty was then input into the model for each simulated mechanism and is displayed as a shaded region in the corresponding graphs. In order to compare the predicted ignition delay times to experimentally obtained ignition delay times, the peak of the modeled time dependent OH profile was used.

*Experimental and modeling collaboration*

The experimental data collected for CPO oxidation was part of a large effort to create a comprehensive chemical kinetic mechanism for this fuel under combustion conditions. The data provided here, and complementary ignition delay time data collected in an RCM, provided necessary validation targets for the constructed mechanism [25]. Overall, the mechanism showed great performance against experimental CO concentrations collected between 1156-1415 K and 1-10 atm and IDT data collected in an RCM between 794-1368 K at 15 and 30 bar.

*Results*

Figure 8 displays experimental and model CO concentrations during the combustion reaction of cyclopentanone with argon at three different pressures, 1, 6 and 8 atm. The 1 atm data (blue) shows that the initial rate of formation of CO is captured well by the current mechanism, with a slightly longer induction time than is seen in the experiment. The 6 atm data (red) and 8 atm
data (black) shows that CO yield from the mechanism agrees with the experimental data within its uncertainty. The deviation in the 6 atm data in the early and intermediate stages of CO formation can be attributed to beam steering from the density change of the reactive gas. After the laser signal becomes more stable, great agreement is seen with the mechanism prediction.

Figure 8. CO time histories in comparison with the Zhang et al. [25] mechanism at (Blue) 1 atm, (Red) 6 atm, (Black) 8 atm.
The reactivity of CPO can be assessed with the ignition delay time of the mixture. The experimental values along with mechanisms predictions from the current mechanism and a literature mechanism from Thion et al. [24] are reported in Figure 9. The experimental data suggest that at these high temperatures, there is little pressure dependence on its reactivity—the measured IDT at each pressure are within the experimental uncertainty of the other conditions. Both the Thion and Zhang mechanisms (LLNL in figure) predict similar reactivity to the experiments across the entire temperature range for the elevated pressure conditions. At 1 atm, both mechanisms predict a lower reactivity of the fuel, suggesting that reactions with pressure dependance may need to be updated to accurately captures the fuel’s global chemistry at these conditions. Because the CO time histories and ignition delay times at the higher pressures agree with the mechanism
(engine relevant conditions) no improvements were made to the current mechanism to increase performance at lower pressures.

All data comparisons with mechanisms, 1 atm

Figure 10. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1165 K and 1.67 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).
Figure 11. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1170 K and 1.09 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).

Figure 12. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1175 K and 1.08 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).
Figure 13. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1192 K and 1.08 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).

Figure 14. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1202 K and 1.05 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).
Figure 15. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1203 K and 1.07 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).

Figure 16. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1227 K and 1.66 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).
Figure 17. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1253 K and 1.58 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).

Figure 18. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1258 K and 1.65 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).
Figure 19. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1313 K and 1.72 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).

All data comparisons with mechanisms, 6 atm

Figure 20. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1168 K and 5.69 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).
Figure 21. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1170 K and 5.71 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).

Figure 22. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1215 K and 5.53 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).
Figure 23. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1235 K and 5.49 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).

Figure 24. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1280 K and 6.81 atm. The linear pressure rise in the experiment is captured in the model simulation (teal).
All data comparisons with mechanisms, 9 atm

Figure 25. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1190 K and 8.86 atm. The linear pressure rise in the experiment is captured in the model simulation (teal). CO traces are truncated at ignition due to interference with CO₂.
Figure 26. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1249 K and 8.89 atm. The linear pressure rise in the experiment is captured in the model simulation (teal). CO traces are truncated at ignition due to interference with CO₂.

Figure 27. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1250 K and 8.51 atm. The linear pressure rise in the experiment is captured in the model simulation (teal). CO traces are truncated at ignition due to interference with CO₂.
Figure 28. Experimental CO time-histories (red) and pressure (blue) compared against the performance of the Zhang et al. [25] (orange) and Thion et al. [24] (green) mechanisms at 1250 K and 8.51 atm. The linear pressure rise in the experiment is captured in the model simulation (teal). CO traces are truncated at ignition due to interference with CO₂.

b. Pyrolysis

Experimental and modeling collaboration

As discussed in the introduction on cyclopentanone (CPO), several researchers have identified unimolecular decomposition pathways of this chemical, specifically that of Zaras et al. [20]. The authors identified three primary decomposition pathways of cyclopentanone, shown in Figure 29. Reaction (1) is a concerted reaction leading directly to ethylene and carbon monoxide, (2) is a stepwise decomposition process that again results in ethylene and carbon monoxide, and reaction (3) is a keto-enol tautomerism. If cyclopentanone decomposes in the preceding manner
(with reactions 1&2 being dominate) then the ratio of C₂H₄/CO should remain fairly constant at 2 during the decomposition of the parent molecule.

\[ \text{(1) } 2 \text{C}_2\text{H}_4 + \text{CO} \]
\[ \text{(2) } \text{H}_2\text{C} - \text{CH}_2\text{C} = \text{O} \rightarrow 2 \text{C}_2\text{H}_4 + \text{CO} \]

\[ \text{(3) } \text{C}_2\text{H}_4 \text{OH} \]

\[ \text{Figure 29. Primary unimolecular decomposition pathways identified by Zaras et al. [20].} \]

However, our early measurements of carbon monoxide during cyclopentanone pyrolysis between 1173-1416 K and 8.97-9.69 atm [29] revealed that the rate of formation of CO was underestimated by the mechanisms of Thion et al. [24] and Zhang et al. [25], both of which include parameters from Zaras et al. [20]. Rather than adjusting reaction rates to match experimental data, we hypothesize that the discrepancy is caused by missing or underestimating other decomposition pathways, specifically radical-involved breakdown of cyclopentanone. One method for testing this hypothesis is to measure the concentration of radical intermediates; however, this is experimentally challenging as radicals are extremely short-lived species. Rather, the ratio of stable intermediates (C₂H₄ and CO) can be measured to highlight the missing or underestimated reactions.

\[ \text{Results} \]

Time-history measurements of cyclopentanone, ethylene, and carbon monoxide were made during cyclopentanone pyrolysis. Two different lasers, used in two separate experimental campaigns, were used for CPO quantification. In the first measurement campaign, a DFB ICL from Nanoplus was tuned to 2929.50cm⁻¹ and 2938.25cm⁻¹ in an attempt to measure CH₄ with a
two-color subtraction scheme to rid the measurement of interfering species; although, this scheme was not fruitful due to initial concentration variance. However, CPO absorbances could be extracted from these measurements instead, and the cross-sections of CPO from FTIR data were used to quantify the concentration. In these measurements, other hydrocarbon intermediates and products could interfere with CPO quantification in the intermediate and late stages of the reaction. Therefore, for some figures displayed, CPO time-histories and C$_2$H$_4$ time-histories (due to the dependence of CPO on C$_2$H$_4$ discussed in the next section) are truncated to remove the data strongly perturbed by the interference. To determine the time where the interference became significant, we used the current mechanism [30] to simulate when interfering species contributed 2% to the total simulated absorbance; the CPO trace is then truncated at 90% of this time. Likewise, because CPO interferes with the C$_2$H$_4$ measurement, C$_2$H$_4$ absorbances are not shown until 110% of the simulated time where CPO is fully depleted.

Due to the interference, the measuring strategy was adjusted in the second campaign. In the second campaign, we used a DFB QCL centered at 1749.84 cm$^{-1}$ from MIRSense for interference-free CPO quantification. For the initial CPO concentration measurement, the absorption cross-section of CPO was first measured by vaporizing the pure compound into the driven side of the tube and measuring the absorbance at 80 °C and different filling pressures. From the slope of the obtained absorbance-pressure curve the CPO cross-section at the specified wavelength and temperature was measured to be 20.24 m$^2$/mol. Then, this same stage-filling procedure was used prior to each experiment to extract the initial concentration of CPO, using the measured cross-section. The average initial concentration uncertainty was calculated to be ±8%.
From the measured initial concentration, the absorption cross-sections of CPO for all conditions were obtained from the absorbance plot immediately behind the reflected shockwave.

Ethylene absorbance was measured with a tunable CO$_2$ gas laser (Access Laser L4GS) centered at 949.49 cm$^{-1}$. Near this wavelength, CPO also has an absorption feature. Therefore, the contribution from CPO must be subtracted to obtain C$_2$H$_4$ time histories, and the derived formula for C$_2$H$_4$ absorbance is given in equation (7).

$$\alpha_{949,\text{C}_2\text{H}_4} = \alpha_{949,\text{total}} - \alpha_{\lambda_2,\text{CPO}} \frac{\sigma_{949,\text{CPO}}}{\sigma_{\lambda_2,\text{CPO}}}$$  \hspace{1cm} (7)

Where $\sigma_{949,\text{CPO}}$ is the cross-section of CPO at ethylene’s measured wavelength (949.49cm$^{-1}$), $\sigma_{\lambda_2,\text{CPO}}$ is the cross-section of CPO at the wavelength where CPO can be measured interference free ($\lambda_2 = 2938.25$cm$^{-1}$ or 2929.50cm$^{-1}$ in the first experimental campaign and $\lambda_2 = 1749.84$cm$^{-1}$ in the second experimental campaign), $\alpha_{949,\text{total}}$ is the total measured absorbance due to all absorbing species at 949.49cm$^{-1}$, $\alpha_{949,\text{C}_2\text{H}_4}$ is the absorbance at 949.49cm$^{-1}$ due only to C$_2$H$_4$, and $\alpha_{\lambda_2,\text{CPO}}$ is the absorbance of CPO at its separately measured wavelength. In the model validation, we still used the Beer-Lambert Law to convert C$_2$H$_4$ concentrations into C$_2$H$_4$ absorbances, and the C$_2$H$_4$ cross-section values were calculated according to the temperature and pressure correlation reported by Ren et al. [31].

Using the time history measurements discussed above, the new pyrolysis mechanism of cyclopentanone, with increased CPO decomposition pathways, can be validated [30]. For a more accurate comparison, the concentration outputs from the model are converted into absorbance through equation (5) and compared to the measured absorbance of each species. Comparison of
the absorbances is more accurate because the temperature and pressure are calculated throughout the reaction duration and can be seeded into the Beer-Lambert law. Converting experimental absorbance to concentration is generally less accurate due to the difficulty in measuring temperature. Figure 30 shows the absorbance time-histories of CO, one of the major CPO products, compared to several mechanisms. The current model [30] is in good agreement with the experimental results between 1217 and 1416 K. Further, according to the high temperature simulations where CO concentrations eventually plateaued, the predicted yields of CO (on CPO basis) are above 95%, which is consistent with the observation by Giri et al. [32]. Although comparing the CO concentration or absorbance time histories was a common strategy in the previous studies [29, 32] it cannot be regarded as a decisive metric for validating a mechanism or distinguishing it from another. In CPO pyrolysis, most of the carbonyl groups from cyclopentanone eventually convert to CO, one of the most stable oxygenated species in the pyrolysis system, via either concerted/stepwise decomposition pathways (1-2) or radical-involved pathways. Although branching ratios in the current model and Thion et al. model are quite different, the CO absorbance predictions from both models overlap with each other.
Figure 30. Time histories of CO absorbance at different temperatures. The green dotted lines are experimental results, the purple lines are predictions from the current model, while the blue and green dashed lines are predictions from the Thion et al. and Zhang et al. models. The temperature values in Kelvin are indicated at the top-right corner of each figure. The uncertainty of each curve is indicated by the translucent region with the same color as the curve.

More insights about the mechanisms can be unveiled by considering the time histories of C\textsubscript{2}H\textsubscript{4} absorbance, especially the absorbance ratio between C\textsubscript{2}H\textsubscript{4} and CO (\(\alpha_{\text{C}_2\text{H}_4}/\alpha_{\text{CO}}\)). \(\alpha_{\text{C}_2\text{H}_4}/\alpha_{\text{CO}}\) which can be regarded as a substitute for the mole fraction ratio between C\textsubscript{2}H\textsubscript{4} and CO (\(x_{\text{C}_2\text{H}_4}/x_{\text{CO}}\)), which is related to the branching ratio of the system. The transformation relation is

\[
\frac{\alpha_{\text{C}_2\text{H}_4}}{\alpha_{\text{CO}}} = \frac{\sigma_{\text{C}_2\text{H}_4}}{\sigma_{\text{CO}}} \frac{x_{\text{C}_2\text{H}_4}}{x_{\text{CO}}}
\]  

(8)
\( \sigma_x \) is the absorption cross-section of the absorbing species. According to Thion et al. and Giri et al., the concerted reaction (1) took up the most dominant flux, making most of the cyclopentanone convert to one CO molecule and two C\(_2\)H\(_4\) molecules, yielding a \( x_{C_2H_4}/x_{CO} \) ratio of approximately two. However, radical-involved decomposition pathways may be more dominant as shown in later sections. In such a scenario, CPO has a higher chance to be converted to other hydrocarbons, including butene and propene, which breaks the stoichiometry of the concerted reaction. Moreover, radicals also activate C\(_2\)H\(_4\) reaction channels and let C\(_2\)H\(_4\) be converted to other species. Thus, we expect to see a lower \( x_{C_2H_4}/x_{CO} \) (and thus a lower \( \alpha_{C_2H_4}/\alpha_{CO} \), according to Eq. (8)) under such a condition.

Also, from the experimental point of view, we find that \( \alpha_{C_2H_4}/\alpha_{CO} \) is much less sensitive to the uncertainties of initial conditions than species absorbances. The relative uncertainties of the predicted \( \alpha_{C_2H_4}/\alpha_{CO} \) is smaller than 3% in most cases regardless of the model being used, while the relative uncertainties of the predicted absorbances can be as large as 40% at increasing stage and typically larger than 15% during the whole process.
Figure 31. HPST experiments results at $T_5 = 1393K$, $P_5 = 0.977$ atm and $x_{CPO,0} = 4000$ ppm. (A) $\alpha_{C_2H_4}/\alpha_{CO}$; (B) pressure; (C) CO absorbances; (D) $C_2H_4$ absorbances. For (A), (C) and (D), the purple lines are the predictions from the current model, while the blue and green dashed lines are predictions from Thion et al. and Zhang et al. models, respectively, and the green dotted lines are experimental data. The uncertainty of each curve is indicated by the translucent region with the same color as the curve. For (B), the green dotted line is the measured pressure, while the purple line is the pressure fitted to the measurement used as the boundary condition for the ideal-gas adiabatic simulation.

Time histories of $\alpha_{C_2H_4}/\alpha_{CO}$ as well as the CPO, $C_2H_4$, and CO absorbances are shown in Figure 31, demonstrating our model is in good agreement with the experimental results, whereas the Thion et al. and Zhang et al. models show an overestimation of the $\alpha_{C_2H_4}/\alpha_{CO}$. Similar figures covering a temperature range of 1156 to 1416K are available in the supplemental
All data comparisons with mechanism

Figure 32. HPST experiment results at $T = 1196$ K, $P = 10.10$ atm and $X_{CPO} = 770$ ppm. (A) Absorbance ratio of CO/C$_2$H$_4$; (B) pressure; (C) CPO absorbance; (D) CO absorbance; (E) C2H4 absorbance.
Figure 33. HPST experiment results at $T = 1217$ K, $P = 10.07$ atm and $X_{CPO} = 4700$ ppm. (A) Absorbance ratio of CO/C$_2$H$_4$; (B) pressure; (C) CPO absorbance; (D) CO absorbance; (E) C$_2$H$_4$ absorbance.

Figure 34. HPST experiment results at $T = 1231$ K, $P = 8.81$ atm and $X_{CPO} = 1020$ ppm. (A) Absorbance ratio of CO/C$_2$H$_4$; (B) pressure; (C) CPO absorbance; (D) CO absorbance; (E) C$_2$H$_4$ absorbance.
Figure 35. HPST experiment results at $T = 1246$ K, $P = 9.95$ atm and $X_{CPO} = 980$ ppm. (A) Absorbance ratio of CO/C$_2$H$_4$; (B) pressure; (C) CPO absorbance; (D) CO absorbance; (E) C$_2$H$_4$ absorbance.

Figure 36. HPST experiment results at $T = 1247$ K, $P = 9.27$ atm and $X_{CPO} = 930$ ppm. (A) Absorbance ratio of CO/C$_2$H$_4$; (B) pressure; (C) CPO absorbance; (D) CO absorbance; (E) C$_2$H$_4$ absorbance.
Figure 37. HPST experiment results at $T = 1259$ K, $P = 9.32$ atm and $X_{CPO} = 7100$ ppm. (A) Absorbance ratio of CO/C$_2$H$_4$; (B) pressure; (C) CPO absorbance; (D) CO absorbance; (E) C2H4 absorbance.

Figure 38. HPST experiment results at $T = 1275$ K, $P = 9.49$ atm and $X_{CPO} = 5200$ ppm. (A) Absorbance ratio of CO/C$_2$H$_4$; (B) pressure; (C) CPO absorbance; (D) CO absorbance; (E) C2H4 absorbance.
Figure 39. HPST experiment results at $T = 1275$ K, $P = 9.49$ atm and $X_{CPO} = 5200$ ppm. (A) CPO absorbance; (B) C2H4 absorbance, (C) pressure.

Figure 40. HPST experiment results at $T = 1310$ K, $P = 8.66$ atm and $X_{CPO} = 8600$ ppm. (A) Absorbance ratio of CO/C2H4; (B) pressure; (C) CPO absorbance; (D) CO absorbance; (E) C2H4 absorbance.
II. Prenol and Isoprenol

a. Introduction

Prenol is an unsaturated alcohol that displays promise as a next generation biofuel or additive. Prenol has a significantly higher heating value than ethanol, 29.6 MJ/L [33] which is only 7% lower than that of gasoline. Furthermore, unlike other fuels that have a linear/nonlinear blending behavior of octane rating, prenol boosts RON above that of the base fuels and prenol [34]. This is an attractive feature for turbocharged spark ignition engines that require high RON in order to prevent autoignition and maintain high thermal efficiency. Furthermore, both prenol and isoprenol are stable at STP conditions, they have a higher lower flammability limit (LFL), higher flash point, and higher autoignition temperature than gasoline [35] making for easy storage and
transportation. For these reasons, prenol is a considered candidate fuel under the Department of Energy’s Co-Optimization of Fuels and Engines (Co-Optima) initiative [36] that aims to simultaneously optimize new fuels and engine designs. However, despite its promise as a next generation fuel there is a scarcity of literature on both prenol and isoprenol. Figure 42 presents a space filling structural model of prenol and isoprenol where gray, white, and red correspond to atoms of carbon (C), hydrogen (H), and oxygen (O), respectively.

![Prenol and Isoprenol Models](image)

**III.**

Zheng et al. [37] and George et al. [38] have recently discovered metabolic pathways for the high-specificity production of prenol and isoprenol from *Escherichia coli*. However, additional synthesis routes will be necessary for the long-term use of these prenols. Monroe et al. [34] found that when added to a gasoline blend, prenol can induce octane hyperboosting in which the RON of the blend is above the neat RON value of the base fuels and prenol. This is distinct from typical blending rules that exhibit a linear relationship for RON based on the constituents’ mole fractions which limits the RON between that of the neat fuels. This novel octane hyperboosting was observed in five different gasoline blendstocks with varying volume fractions of prenol, with the effect first being observed with addition of just 10% of prenol [34] into a gasoline surrogate and the author’s blendstock #2. Prenol’s isomer, isoprenol, was also investigated for the same property
and did not exhibit the same behavior as its counterpart. De Bruycker et al. [7] studied the oxidation ($\phi=0.5, 1.0$) and pyrolysis of prenol and isoprenol in a jet stirred reactor from 500-1100 K at 0.107 MPa. The authors found that more than 99% of isoprenol consumption proceeds through a unimolecular reaction yielding formaldehyde and isobutene. Prenol, on the other hand, was found to be dominated by radical chemistry. The presence of a hydroxyl functional group in prenol near the C=C bond enables low temperature chemistry, yielding aldehydes and ketones [7]. The authors used the experimental data to validate a chemical kinetic mechanism for both fuel isomers. In general, the mechanism predictions agreed well with obtained data over the conditions studied. However, discrepancies were observed for several species during isoprenol decomposition, which the authors attributed to the isobutene submechanism, given the high sensitivity towards isobutene. To the authors’ knowledge no other studies in the literature are available on the combustion of these two fuels.

This study seeks to improve the understanding of ignition and combustion behavior of prenol and isoprenol isomers. Measurements of laminar burning velocity (LBV) which are essential for turbulent combustion modeling, predicting explosions, engine design, and kinetic mechanism validation are examined explicitly over equivalence ratios of 0.75-1.50 and are compared to that of ethanol over the same conditions. Carbon monoxide time-histories and ignition delay times using a shock tube and laser absorption technique, are also reported for these compounds. Measured shock tube data are compared to predictions of a chemical kinetic mechanism developed by De Bruycker et al. [7] (comparison of measured LBVs to the mechanism is not possible due to the lack of transport data available). To the best of our knowledge, the current measurements provide the first LBV and shock tube data for these fuels which can be used to
highlight the differences in combustion chemistry between the two isomers and lead to an understanding of the mechanism for octane hyperboosting in prenol.

\[ \textit{b. Results} \]

Carbon monoxide time-histories are reported behind reflected shockwaves during the oxidation of prenol and isoprenol, with a mixture composition of 0.05% fuel / 0.35% O\(_2\) / 99.6% Ar. To ensure that the measured CO concentrations are accurate, the measured absorbance must only be due to CO. This can be easily verified by examining the top formed species during the exothermic reaction and investigating the absorption from these species. Figure 43 displays the top 10 intermediates during the oxidation of prenol and isoprenol using the De Bruycker [7] mechanism and each molecules’ expected absorbance at 2046.30 cm\(^{-1}\) (absorption cross-sections obtained from the HITRAN 2016 [39] and HITEMP 2012 [40] databases). Although Figure 43 (A, C) shows high concentrations of H\(_2\)O, CO\(_2\), and other species, their absorption cross-sections are almost zero. Therefore, CO can be measured confidently without interference from any other species.

Figure 44A shows quick formation for CO with a peak yield of ~1500 ppm at 1.10 ms, followed by its depletion which continues until it has fully decayed at 3.0 ms. In contrast, the model prediction shows a slower formation of CO with a peak yield of ~1900 ppm at 2.02 ms. Although, quantitatively, the model overpredicts key features of the CO trace, the general profile is captured quite well. A lower temperature case is shown in Figure 44B up to the end of the test time around 3.5 ms. In the first millisecond, the model captures the CO formation very well;
however, beyond this point, the model underpredicts the rate of CO formation with an ~85% difference in CO yield at the end of the test time.

Figure 43. (A) Top intermediates during oxidation of 0.05% \text{C}_5\text{H}_{10}\text{O} / 0.35\% \text{O}_2 / 99.6\% \text{Ar}. (B) Theoretical absorbance of top prenol intermediates. (C) Top intermediates during oxidation of 0.05% \text{iC}_5\text{H}_{10}\text{O} / 0.35\% \text{O}_2 / 99.6\% \text{Ar}. (D) Theoretical absorbance of top isoprenol intermediates. Simulations conducted at 1325 K and 9.4 atm. Spectroscopic parameters taken from HITRAN 2012 [14]

Figure 45 displays the CO and pressure profiles during the oxidation of isoprenol. Similar to what was observed in prenol oxidation, the CO yield and ignition time is over predicted by the model with a percent difference of 39% and 73%, respectively. However, in the first 1.1 ms, the model captures the initial formation of CO very well before the traces begin to diverge from one
Comparison of CO profiles from isoprenol and prenol oxidation is presented in Figure 46 at different test temperatures. Large overlap in the traces is noticeable in the early stages of CO formation, this is particularly evident in the 1320 K case which shows great agreement between the two isomers for the duration of the test time. After this initial formation, the CO profiles between the isomers begin to deviate from one another, which is clearly seen in the 1395 K case. After 0.5 ms, the CO profile during prenol oxidation displays a concave shape while for isoprenol the CO profile is convex, this suggests different pathways for CO formation after this initial formation period.
Figure 44. Carbon monoxide and pressure histories during the stoichiometric oxidation of 0.05% $\text{C}_5\text{H}_{10}\text{O}$ / 0.35% $\text{O}_2$/ 99.6% Ar at (A) 1434 K and 9.76 atm and (B) 1315 K and 9.56 atm. Model comparisons are given with the De Bruycker [7] mechanism. Uncertainty in measurement shown by lightly shaded region.

Ignition delay times were measured (and tabulated in Table 1) for both isomers and are compared to model predictions in Figure 47. Ignition delay times are defined up to the peak of the measured OH* profile and are compared to the peak time of OH from the model. It is clear that the model overpredicts ignition delay times of both fuels, thus improvements are suggested in the following section.
Figure 45. Carbon monoxide and pressure histories during the stoichiometric oxidation of 0.05% iC₅H₁₀O / 0.35% O₂ / 99.6% Ar at 1427 K. Uncertainty in measurement shown by lightly shaded region.
Table 1. Experimental conditions of shock tube data. Runs where ignition occurs outside of the test time are denoted with ‘- -‘.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Temperature (K)</th>
<th>Pressure (atm)</th>
<th>Ignition Delay (ms)</th>
<th>dP/dt (%/ms)</th>
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<td>--</td>
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Figure 46. Comparison of CO profiles between prenol and isoprenol at various temperatures. (*) denotes temperatures for prenol experiments. Experimental conditions can be viewed in Table 1.

Figure 47. Ignition delay time of prenol and isoprenol with comparison to simulations from the De Bruycker [7] mechanism; simulations conducted at the average test pressure of 9.40 atm. Uncertainty in ignition delay estimated to be 20%.
c. Sensitivity Analysis

A sensitivity analysis was conducted for CO with a mixture of 0.05% fuel / 0.35% O\textsubscript{2} / 99.6% Ar for both prenol and isoprenol at conditions of 1434 K and 9.76 atm and 1427 K and 9.73 atm, respectively. Equation (9) gives the sensitivity coefficient (S) for the \textsuperscript{i}th reaction rate (k\textsubscript{i}) and Figure 48A displays the top 12 reactions that are most sensitive to CO formation or depletion during prenol oxidation, represented by positive and negative values, respectively. In the first 0.3 ms, CO formation is most sensitive to reactions 2, 4, 6, 8, and #9. In this initial formation, model and experimental results agree well and suggest no reaction rate modifications. However, after its initial formation, the experimental CO trace deviates from the simulation. Examining the sensitivity results show that this is the time when reactions #1 and #2 start becoming the most sensitive reactions for carbon monoxide formation.

\[ S(X_{\text{species}}, k_i, t) = \left( \frac{dX_{\text{species}(t)}}{dk_i} \right) \left( \frac{k_i}{X_{\text{species}(t)}} \right) \]

(9)
Figure 48. (A) CO sensitivity for a 0.05% prenol / 0.35% O\textsubscript{2} / 99.6% Ar mixture at 1434 K and 9.76 atm. (B) CO sensitivity for a 0.05% isoprenol / 0.35% O\textsubscript{2} / 99.6% Ar mixture at 1427 K and 9.73 atm. Sensitivity carried out in Chemkin-Pro [41] using the De Bruycker [7] mechanism.

Reaction #1, H+O\textsubscript{2}=O+OH, is a well-studied reaction and the current mechanism in question uses the reaction rate provided by Hong et al. [42] who reports a 4.6% uncertainty in the reaction rate at temperatures relevant to the present study. Changing the rate of this reaction within its uncertainty bounds will unlikely be able to account for the large deviation between experiment and model. Therefore, multiplicative modifications are made to the estimated reaction
rate of reaction #2, C$_3$H$_3$ + O$_2$→CH$_2$CO +HCO, to improve the mechanism’s performance. Figure 49 shows a reaction rate change of $k_{new} = 10k_{old}$ for a run at 1397 K and 9.32 atm. The modification to this reaction results in significant improvement to the predictive capabilities of the mechanism for CO time-histories as well as for ignition delay times, shown in Figure 47. It should be noted that changes to the reaction rate greater than 10× do not have a significant change in the time of max CO yield, suggesting that there may be a reaction pathway that is missing in the later stages of CO formation for prenol oxidation.

Figure 48B displays the CO sensitivity for stoichiometric isoprenol oxidation. Similar to prenol, reactions #1 and #2 are most sensitive to forming carbon monoxide after the initial formation stage. Reaction #1 is left untouched for the reason mentioned above, so the modification that was applied to reaction #2 in the case for prenol is tested for isoprenol as well. Figure 49B shows how this modification improves the predictive capabilities for CO formation during isoprenol combustion as well. While the peak time of the simulated CO trace matches better with the experiments, the simulation is shifted to a higher CO yield over the entire experiment. This suggests that CO formation may take another pathway that is either not present in the mechanism or is present but not considered as a very sensitive reaction in the time following the initial CO formation. While these modifications do provide some guidance to prenol isomers combustion chemical kinetics, new high temperature mechanisms will need to be created using current data as validation targets.
Figure 49. (A) Model performance before and after a modification of 10x to the rate of reaction #2. 0.05% prenol / 0.35% O₂ / 99.6% Ar oxidation at 1397 K and 9.32 atm. (B) Model performance before and after a modification of 10x to the rate of reaction #2. 0.05% isoprenol / 0.35% O₂ / 99.6% Ar oxidation at 1427 K and 9.73 atm.
b. *Uncertainty Analysis*

The relative uncertainty in the measured concentrations of CO is calculated as a time varying quantity by the root mean square of the relative uncertainties of the parameters in Beer’s Law, eq. 1. The time dependence in uncertainty arises from four factors: absorbance, pressure, temperature, and absorption cross-section. Because absorbance is a function of only the transmitted and reference laser signals, the uncertainty in this quantity is $1.5 \times$ the standard deviation of each laser signal divided by the signal value at each time step. To calculate the uncertainty in pressure, first the error in $P_5$ and then the noise of the signal are computed. The time dependent pressure uncertainty is then obtained from the $P_5$ uncertainty plus the uncertainty due to noise at each time step.

Accounting for the uncertainty in temperature and absorption cross-section is more difficult since temperature is not measured during the course of an experiment and since the absorption cross-section is a function of the experimental temperature. To account for the temperature change throughout these exothermic reactions, an isentropic compression is assumed during the linear pressure rise portion in each experiment, as has been done previously [43, 44] with great accuracy. From this point up to the end of the test time, a similarity argument between the experimental and model results is used. The pressure increase due to combustion from the experiment is compared to the same pressure increase in the simulation, using a constant U-V model and no added pressure $(dP_5/dt)$ trace. If the percent change in pressure from combustion between the two systems is similar, then the temperature jump due to combustion is also assumed to be similar. This temperature jump is then added to the last calculated temperature via the isentropic assumption to obtain a temperature profile over the entire test time. A graphical representation of the similarity
argument is provided in Figure 50. In this example, the pressure rise due to combustion according to the model, under a constant U-V assumption and no seeded in pressure trace, is about 5.6% and the measured pressure rise is 4.4%. Because the pressure rise in the model is greater than the observed pressure rise, the predicted temperature jump overpredicts the experimental temperature rise but also ensures that the calculated uncertainty band will encompass the true mole fraction of carbon monoxide. This temperature rise of 7.8% is applied to the last calculated temperature of the isentropic profile and assumed constant over the remainder of the test time.

Using this similarity analysis, the uncertainty in temperature is calculated as the percent difference from the calculated temperature described above and $T_5$, which is the value used throughout all calculations to obtain the CO mole fractions. This calculated temperature profile, and the measured pressure profile, are seeded into eq. 1 to obtain a time varying absorption cross-section. The percent difference of this profile and the cross-section using a scalar $T_5$ and vector $P(t)$ plus the uncertainty in measured CO absorption cross-section values constitutes the uncertainty in this parameter over the entire test time. In summary, uncertainties in CO concentrations remained <9% prior to ignition and <15% post ignition.
Figure 50. Temperature profile determination for uncertainty analysis of CO time-histories. Experiment shown is for a mixture of 0.05% iC$_5$H$_{10}$O / 0.35% O$_2$ / 99.6% Ar at $T=1427$ K and $P=9.73$ atm.
All data compared with mechanism, prenol

Figure 51. Experimental CO time-histories (solid red) and pressure (solid blue) compared to the output of the De Bruycker et al. [7] mechanism for the oxidation of prenol at 1266 K and 8.94 atm. Experimental pressure rise is captured in the simulation (dotted cyan).
Figure 52. Experimental CO time-histories (sold red) and pressure (solid blue) compared to the output of the De Bruycker et al. [7] mechanism for the oxidation of prenol at 1275 K and 9.09 atm. Experimental pressure rise is captured in the simulation (dotted cyan).

Figure 53. Experimental CO time-histories (sold red) and pressure (solid blue) compared to the output of the De Bruycker et al. [7] mechanism for the oxidation of prenol at 1296 K and 9.34 atm. Experimental pressure rise is captured in the simulation (dotted cyan).
Figure 54. Experimental CO time-histories (solid red) and pressure (solid blue) compared to the output of the De Bruycker et al. [7] mechanism for the oxidation of prenol at 1342 K and 9.82 atm. Experimental pressure rise is captured in the simulation (dotted cyan).

Figure 55. Experimental CO time-histories (solid red) and pressure (solid blue) compared to the output of the De Bruycker et al. [7] mechanism for the oxidation of prenol at 1353 K and 9.96 atm. Experimental pressure rise is captured in the simulation (dotted cyan).
Figure 56. Experimental CO time-histories (solid red) and pressure (solid blue) compared to the output of the De Bruycker et al. [7] mechanism for the oxidation of prenol at 1360 K and 8.79 atm. Experimental pressure rise is captured in the simulation (dotted cyan).

Figure 57. Experimental CO time-histories (solid red) and pressure (solid blue) compared to the output of the De Bruycker et al. [7] mechanism for the oxidation of prenol at 1408 K and 9.33 atm. Experimental pressure rise is captured in the simulation (dotted cyan).
Figure 58. Experimental CO time-histories (solid red) and pressure (solid blue) compared to the output of the De Bruycker et al. [7] mechanism for the oxidation of prenol at 1434 K and 9.76 atm. Experimental pressure rise is captured in the simulation (dotted cyan).

Figure 59. Experimental CO time-histories (solid red) and pressure (solid blue) compared to the output of the De Bruycker et al. [7] mechanism for the oxidation of prenol at 1443 K and 9.25 atm. Experimental pressure rise is captured in the simulation (dotted cyan).
All data compared with mechanism, isoprenol

Figure 60. Experimental CO time-histories (sold red) and pressure (solid blue) compared to the output of the De Bruycker et al. [7] mechanism for the oxidation of isoprenol at 1233 K and 8.60 atm. Experimental pressure rise is captured in the simulation (dotted cyan).
Figure 61. Experimental CO time-histories (sold red) and pressure (solid blue) compared to the output of the De Bruycker et al. [7] mechanism for the oxidation of isoprenol at 1269 K and 9.00 atm. Experimental pressure rise is captured in the simulation (dotted cyan).

Figure 62. Experimental CO time-histories (sold red) and pressure (solid blue) compared to the output of the De Bruycker et al. [7] mechanism for the oxidation of isoprenol at 1323 K and 8.98 atm. Experimental pressure rise is captured in the simulation (dotted cyan).
IV. Methyl Propyl Ether

a. Introduction

It is well known that blending oxygenated fuels with diesel decreases soot formation, even in fuel-rich conditions [45-47]. Ethers decrease the soot formation in this manner while also enhancing cetane numbers, generally resulting in less expensive diesel [48]. However, ether cetane numbers can vary considerably depending on length and structure [48], and the understanding of ether combustion is not advanced enough to know the impact particular ethers might have on diesel combustion and a blend’s cetane number.
Smaller ethers, such as dimethyl ether, have been well studied in the literature across a wide temperature range [49-54]. However, the chemistry of larger ethers is much less understood. Only a few previous investigations have looked at larger chain ethers, specifically: ethyl methyl ether, methyl tertiary butyl ether, ethyl tertiary butyl ether, and diethyl ether [55-58] but these studies have been constrained to high temperatures. Methyl propyl ether is an ideal candidate for mechanism construction because it has a long enough alkyl chain to undergo radical feedback loops typical of low temperature alkane combustion but is also small enough to construct a highly detailed chemical kinetic mechanism.

b. Experimental and modeling collaboration

The data presented in this section is part of a large effort to create a comprehensive chemical kinetic mechanism for methyl propyl ether combustion and pyrolysis. Complementary data include product concentrations in a flow tube and ignition delay times in a rapid compression machine. The acquired results (spanning a range of 1-20 bar and 600-1500 K) were used to validate a chemical kinetic mechanism for MPE constructed through the Reaction Mechanism Generator software [59].

c. Results

Carbon monoxide time histories were measured during the oxidation and pyrolysis of methyl propyl ether (MPE). The oxidation mixture consisted of 0.1% MPE at an equivalence ratio of 1 in oxygen, and the pyrolysis mixture consisted of 0.5% MPE, both mixtures balanced in argon. The time history measurements were performed over reflected shock conditions of 1205-1511 K and 8.41-9.69 atm.
The time-history measurements with temperature are plotted for the oxidation and pyrolysis mixture in Figure 64. Both mixtures show very consistent CO yields across the investigated temperatures and an increase in CO rate for formation with increasing temperature. In the oxidation case, the CO yield/fuel molecule is 2.35, indicating that for every molecule of fuel in the initial mixture 2.35 molecules of CO are formed. For the pyrolysis case, the CO yield/fuel molecule is 0.81. It is reasonable that the CO yield in the oxidation reaction is more because there is a larger pool of oxygen molecules to form CO, with the carbon contained within MPE being the limiting agent in CO formation. On the contrary, the oxygen is the limiting agent for CO formation for the pyrolysis mixture. This is because there is no outside oxygen to react with MPE or its intermediates and all the oxygen comes from the oxygen bound within MPE. Approximately 81% of all oxygen atoms in MPE pyrolysis go to CO formation.
The presence of O$_2$ does not change the initial decomposition pathways of MPE [59]. In both oxidation and pyrolysis conditions, the dominant decomposition pathway of MPE is the elimination reaction to methanol and propene. Scission of the O-propyl bond and hydrogen abstraction from the central carbon account for the next most dominant loss pathways. The products of these reactions undergo further pyrolysis to produce formaldehyde and propanal, the
main pathways to CO formation. These aldehydes form CO through hydrogen abstraction at the carbonyl group. The main difference in CO yield in the oxidation reaction comes from the presence of HO₂ and OH radicals produced through reaction with O₂. These two radicals form H₂O₂ and H₂O that are not major products of pyrolysis that lead to increased CO levels at later times.

The experimental CO traces compared to the mechanism output are given in Figure 65. The measurements and predictions agree reasonably well. CO peak times agree within a factor of 1.5 for all experiments. Predicted peak heights are within about 34% of experiments.

Figure 65. CO time-histories during the oxidation of 0.1% MPE, φ=1, balanced in argon. Model simulations are done with [59].

A similar comparison for data measured at pyrolysis conditions is presented in Figure 66. The model very closely emulates the experimental data, generally within the uncertainties of the experiment and the model. Because the model agreed so well with data, no refinements were made to kinetic mechanism.
At these high temperatures, particularly in the pyrolysis case, the various competing unimolecular reactions of MPE are very important, and strongly affect the formation of CO and other products. These reactions are listed in Table 2. At lower temperatures reaction 18 dominates, while above 1300 K reaction 17 dominates. All of these reactions are barrierless in the bimolecular direction and were estimated using the Reaction Mechanism Generator (RMG) described in [59]. Due to approximations made in the RMG’s pressure dependent rate coefficient calculations, there is uncertainty in these reactions rates by about a factor of 2 or 3 [60]. When combined with uncertainties in the thermochemistry, there is factor of 5 uncertainty in the absolute decay rate of MPE and uncertainty in the branching ratio between these different decomposition channels. These uncertainties in the model, combined with the experimental uncertainties are more than enough to describe the differences in Figure 65 and Figure 66.
Figure 66. CO time-histories during the pyrolysis of 0.5% MPE in argon. Model simulations done with [59]

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>$\text{O} \rightarrow \text{CH}_4 + \text{O}_2$</td>
</tr>
<tr>
<td>18</td>
<td>$\text{O} \rightarrow \text{H}_2\text{O} + \text{H}^+$</td>
</tr>
<tr>
<td>19</td>
<td>$\text{O} \rightarrow \text{H}_2\text{O} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>20</td>
<td>$\text{O} \rightarrow \text{CH}_4 + \text{O}_2$</td>
</tr>
</tbody>
</table>
All data compared with mechanism, oxidation

Figure 67. Experimental CO time-histories (solid red) and pressure (solid blue) during MPE oxidation at 1313 K and 9.01 atm. Model pressure is shown with the dotted cyan line and simulated CO time-histories simulated with the Johnson et al. [59] mechanism.
Figure 68. Experimental CO time-histories (solid red) and pressure (solid blue) during MPE oxidation at 1369 K and 8.93 atm. Model pressure is shown with the dotted cyan line and simulated CO time-histories simulated with the Johnson et al. [59] mechanism.

Figure 69. Experimental CO time-histories (solid red) and pressure (solid blue) during MPE oxidation at 1373 K and 9.69 atm. Model pressure is shown with the dotted cyan line and simulated CO time-histories simulated with the Johnson et al. [59] mechanism.
Figure 70. Experimental CO time-histories (solid red) and pressure (solid blue) during MPE oxidation at 1426 K and 8.86 atm. Model pressure is shown with the dotted cyan line and simulated CO time-histories simulated with the Johnson et al. [59] mechanism.

Figure 71. Experimental CO time-histories (solid red) and pressure (solid blue) during MPE oxidation at 1511 K and 9.36 atm. Model pressure is shown with the dotted cyan line and simulated CO time-histories simulated with the Johnson et al. [59] mechanism.
All data compared with mechanism, pyrolysis

Figure 72. Experimental CO time-histories (solid red) and pressure (solid blue) during MPE pyrolysis at 1205 K and 8.41 atm. Model pressure is shown with the dotted cyan line and simulated CO time-histories simulated with the Johnson et al. [59] mechanism.
Figure 73. Experimental CO time-histories (solid red) and pressure (solid blue) during MPE pyrolysis at 1311 K and 9.69 atm. Model pressure is shown with the dotted cyan line and simulated CO time-histories simulated with the Johnson et al. [59] mechanism.

Figure 74. Experimental CO time-histories (solid red) and pressure (solid blue) during MPE pyrolysis at 1394 K and 8.72 atm. Model pressure is shown with the dotted cyan line and simulated CO time-histories simulated with the Johnson et al. [59] mechanism.
Figure 75. Experimental CO time-histories (solid red) and pressure (solid blue) during MPE pyrolysis at 1472 K and 9.56 atm. Model pressure is shown with the dotted cyan line and simulated CO time-histories simulated with the Johnson et al. [59] mechanism.

V.  1 & 2 Pentene

a. Introduction

Petroleum fuels can be comprised of hundreds of different hydrocarbon species [61], making it difficult and impractical to construct a detailed chemical kinetic mechanism for these fuels. However, gasoline is composed of only a few chemical classes, namely: alkanes, alkenes, iso-alkanes, cycloalkanes, cycloalkenes, and aromatics [61]. Therefore, an alternative method for mechanism construction of a detailed fuel, such as gasoline, is to create a mechanism for a surrogate fuel. A surrogate fuel is one that has similar physical and chemical properties to the real fuel. In the development of gasoline surrogate mechanisms, one or two species are generally used to represent each chemical class in the real fuel. While alkenes comprise roughly 2-5% by volume
of a typical gasoline, alkenes show higher research octane number (RON) compared to alkanes and thus may play an equivalent role in autoignition behavior. Furthermore, the unsaturated double bond in alkenes can also contribute to soot formation [62] so it is important to include alkenes within a surrogate mechanism. Many previous researchers have used 1- and 2-pentene to represent the alkene components in their surrogate mechanisms [61-65], because of this it is important to have experimental measurements of fundamental combustion properties to validate these mechanisms.

There have been a few experimental studies on the combustion of 1- and 2-pentene in the past. Ribaucour et al. [66] measured the IDT of 1-pentene at 8 atm between 700-900 K in an RCM and created a kinetic model which was validated over these conditions. Touchard et al. [67] extended experimental ignition delay times of 1-pentene to higher temperatures (1130-1620 K) at 8.5 atm in a shock tube reactor and created a kinetic model for these high temperature ignition times. Mehl et al. [68] studied the ignition delay time of 1 and 2-pentene between 1100-1950 K at 1 and 10 atm, minimal difference and the ignition delay times of the two isomers was observed. Cheng et al. [69] measured the ignition delay times of 1-pentene and n-pentane in the temperature range of 1040-1880 K at 1 and 10 atm. 1-petene was found to have a shorter IDT than n-pentane in the low temperature region due to the abundant H atom production channels and the fast unimolecular decomposition of the parent compound. At higher temperatures, the IDT of 1-pentene was found to be longer than n-pentane which was attributed to the higher amount of allyl radicals and lower concentration of oxygen at these conditions. There is scarce combustion data on 2-pentene and the data published on 1-pentene is focused on ignition delay times. To validate branching ratios and intermediate concentrations, time-resolved concentrations of intermediate
species are necessary. Therefore, carbon monoxide time-histories are reported for the first time for the oxidation of both 1 and 2-pentene.

b. *Experimental and modeling collaboration*

The data presented in this section is part of a collaborative effort to create a comprehensive chemical kinetic mechanism for 1 and 2-pentene oxidation. The carbon monoxide time histories and ignition delay times provided here are complemented by ignition delay times collected in an RCM between 600-1330 K, equivalence ratios of 0.5, 1.0, and 2.0 in air and at pressures of 15 and 30 atm. Moreover, species versus temperature profiles were collected in a jet stirred reactor at an equivalence ratio of 1.0, pressure of 1 atm, and temperatures of 700-1100 K. All of this data has been used to validate the kinetic mechanism for 1 and 2-pentene by Dong et al. [70].

c. *Results*

Carbon monoxide time histories were collected in the manner described in the Absorption Spectroscopy section. Measurements were collected over a temperature range of 1228-1372 K at a pressure of 9.5 atm in a stochiometric mixture of 0.25% fuel/ O\textsubscript{2}/ Ar. The CO time histories presented in Figure 76 show a very similar rate of CO formation between the two isomers (similar temperatures have been grouped by color). The CO concentrations are truncated near the ignition time due to the pressure and temperature rise experienced during ignition. Because the pressure rise was significant, even at 0.25% fuel loading, the associated temperature rise was likely also significant. Because temperature is not measured in the experiment, we could not be certain that the temperature after ignition was within the limits of equation (6).
The data point in yellow in this graph (1-pentene at 1228 K) has a slightly higher CO formation rate than does the next highest temperature (1243 K). This may be attributed to a deflagration to detonation transition that can occur when the derivative of ignition delay time with temperature is large [71]. There are always some small gradients in temperature that exist within a shock tube due to nonperfect reflection of the endwall and shock wave attenuation. These gradients may cause local ignition spots within the test region which can increase the temperature and pressure slightly of the unburned fuel, accelerating the ignition delay time. This can be observed in the pressure traces for the two individual tests (Figure 78 and Figure 79). The pressure trace in Figure 79, the data point at 1243 K, shows a nearly constant test pressure after ignition, which indicates that the reactor is following constant volume behavior and the ignition was uniform. On the contrary, Figure 78 shows a mild ramp in pressure just prior to ignition and pressure oscillations after ignition has occurred. This is a sign that inhomogeneous ignition has occurred, and a detonation type wave was formed. Typically, measurements that are done within an inhomogeneous ignition should not be used for mechanism validation; however, the ignition delay time for this this data point is within the uncertainty of the previous temperature and did not significantly affect the measurement.
Figure 76. Experimental CO time histories for 1-pentene (solid) and 2-pentene (dashed) oxidation.

Figure 77. Experimental and mechanism ignition delay times for 1 and 2-pentene. Experiments are shown as symbols and mechanism outputs are solid lines from Dong et al. [70].

Ignition delay times are reported against the mechanism predictions for both isomers. Within the temperature range of the experiments, there is no discernable difference in the reactivity.
of the fuels. However, the mechanism prediction shows a shift in reactivity of the isomers at high and low temperatures. This is attributed to a chain branching mechanism similar to that found in alkanes, that is responsible for the higher reactivity of 1-pentene at low temperatures. The over prediction of the reactivity from the mechanism compared to the experimental IDT values is likely due to the base mechanism being validated for higher fuel concentrations. It was necessary to have a low fuel loading for the current experiments to not saturate the laser signal used to monitor CO.

*All data compared with mechanism, 1-pentene*

![Graph](image)

*Figure 78. Pressure (blue) and carbon monoxide time-histories (red) during oxidation (φ=1) of 1-pentene at T=1228 K, P=10.03 atm. Simulations of CO concentrations performed with Dong et al. [70].*
Figure 79. Pressure (blue) and carbon monoxide time-histories (red) during oxidation ($\phi=1$) of 1-pentene at $T=1243$ K, $P=8.17$ atm. Simulations of CO concentrations performed with Dong et al. [70].

Figure 80. Pressure (blue) and carbon monoxide time-histories (red) during oxidation ($\phi=1$) of 1-pentene at $T=1287$ K, $P=9.26$ atm. Simulations of CO concentrations performed with Dong et al. [70].
Figure 81. Pressure (blue) and carbon monoxide time-histories (red) during oxidation ($\phi = 1$) of 1-pentene at $T = 1357 \text{ K, } P = 9.48 \text{ atm}$. Simulations of CO concentrations performed with Dong et al. [70].
All data compared with mechanism, 2-pentene

Figure 82. Pressure (blue) and carbon monoxide time-histories (red) during oxidation ($\varphi=1$) of 2-pentene at $T=1246$ K, $P=9.26$ atm. Simulations of CO concentrations performed with Dong et al. [70].
Figure 83. Pressure (blue) and carbon monoxide time-histories (red) during oxidation ($\phi=1$) of 2-pentene at $T=1305$ K, $P=9.31$ atm. Simulations of CO concentrations performed with Dong et al. [70].

Figure 84. Pressure (blue) and carbon monoxide time-histories (red) during oxidation ($\phi=1$) of 2-pentene at $T=1372$ K, $P=8.80$ atm. Simulations of CO concentrations performed with Dong et al. [70].
CHAPTER FIVE: CONCLUSIONS

A novel absorption-based diagnostic for carbon monoxide monitoring at 10 atm was developed as part of this project. This diagnostic, as well as emission-based sensors, were used to measure ignition delay times and time-resolved species concentrations for numerous promising biofuels. These measurements are imperative for validating chemical kinetic mechanisms that capture a fuel’s chemistry. The measurements taken in this document are useful for assessing decomposition pathways and global reactivity specified in these mechanisms. A detailed summary for each compound is provided below.

I. Cyclopentanone

The oxidation of cyclopentanone has been investigated experimentally by measuring ignition delay times and CO time-histories over a wide range of conditions. These results show little effect of low temperature chemistry. The reaction rates of olefin +HO˙2 elimination of fuel peroxyl radicals have been derived using quantum chemistry calculations and adopted in the kinetic model developed here [25]. The model predicts well, not only the ignition delay times but also the CO time-histories measured in the experiments. The reaction pathways based on rate of production analysis indicate that at low temperature the reactivity of cyclopentanone is largely inhibited by the competitive chain propagation processes, especially from the olefin +HO˙2 elimination. Therefore, HO˙2 related chain branching and chain terminating processes dominate the reactivity of cyclopentanone in this region. At higher temperature, ring opening reactions and subsequent decompositions become important, which contribute to the radical pool and enhance
its reaction with cyclopentanone. The experimental data and the kinetic model have provided further insight into the ignition related chemistry of cyclopentanone, yet the current model could be further improved by refining the reaction rates adopted and their pressure dependence. Meanwhile, more experimental data is needed for model validation.

We studied the pyrolysis of cyclopentanone and presented a kinetic model verified through shock tube experiments. We measured time histories of cyclopentanone, ethylene, and CO simultaneously over a wide range of conditions and used C<sub>2</sub>H<sub>4</sub>/CO time history to validate the models. Concurrently, we generated a comprehensive kinetic model using the Reaction Mechanism Generator (RMG) with refined parameters from literature and quantum calculations. The current model shows good agreement with the experimental time histories. According to ROP and sensitivity analysis, the model suggests that radical-involved pathways play essential roles in cyclopentanone decomposition. During the early stage, when H radicals are accumulating, the radical-involved decomposition pathways are activated and become as crucial as pathway (1) and (2), resulting in the C<sub>2</sub>H<sub>4</sub>/CO ratio decreasing swiftly. During the transition stage, radical-product reactions become as important as cyclopentanone-radical reactions due to product accumulation, resulting in decreasing H radical concentration. During the product pyrolysis stage, the decomposition of the mixture of ethylene and other products becomes dominant as CPO being depleted. Our finding in this study helps better understand the pyrolysis of cyclopentanone process and establish a more comprehensive combustion/pyrolysis model. Such understanding can also be helpful when proposing pyrolysis or combustion models for other biofuels.
II. (Iso)Prenol

The current investigation examines the combustion chemistry of prenol and isoprenol isomers through measurements of carbon monoxide time-histories, and ignition delay times. Carbon monoxide time-histories and ignition delay times were recorded behind reflected shockwaves in a double-diaphragm, heated shock tube over the temperature range 1269-1472 K near 9.4 atm with a mixture of 0.05% fuel / 0.35% O₂ / 99.6% Ar. To the best of our knowledge, we have provided the first shock tube laser-absorption measurements for these isomers.

Comparisons with predictions of a detailed chemical kinetic mechanism from the literature were provided. Current model predictions capture the qualitative profile of carbon monoxide formation and depletion but fall short for specific predictions such as CO yield and ignition delay time. A reaction rate change of a factor of 10 to the common reaction $C_3H_3 + O_2 = CH_2CO + HCO$ improves model performance for both prenol and isoprenol, suggesting this reaction may deserve further attention. However, other reactions may still play an important role in improving model development and could possibly be missing, as the process through which octane hyperboosting manifests is still unknown.

This study presents the next step in an ever-growing understanding of the reactivity of prenol and isoprenol. Future investigations include expanding the range of measured species to CH₂CO and C₂H₄ which are important species during intermediate chemistry. Also, measurements with blends of prenol isomers will be needed. Furthermore, validation over a wider range of experimental conditions, particularly at lower temperatures, is necessary to ensure model performance and compatibility with current and future engines.
III. Methyl Propyl Ether

This study presents a chemical kinetic mechanism for oxidation and pyrolysis of methyl propyl ether. This kinetic mechanism was constructed iteratively using RMG to generate the mechanism, flux and sensitivity analyses to identify important parameters, improving parameters with quantum chemistry calculations and literature values and then repeating the cycle. RMG was able to discover almost all of the chemistry on its own, however one important reaction involved an unexpected concerted H shift that would not have been discovered by RMG. We have validated this mechanism against shock tube data at about 10 bar and 1205-1511 K, RCM data at 10-20 bar and 600-900 K and flow tube data at 1 bar and 700-900 K. An analysis of the sensitivities, a list of stationary point geometries, tables of rate and thermochemistry parameters calculated in this study, the associated RMG input file and the full mechanism of 443 species and 26,108 reactions are available in the supporting information. Methyl propyl ether chemistry is characterized strongly by the reactions branching off and competition between the two main radical addition to O\textsubscript{2} pathways. The two radical pathways transition between addition to O\textsubscript{2}/pyrolysis pathways at significantly different temperatures. This leads to a very high sensitivity to the branching between the two radicals in the flow tube experiments. Low temperature reactivity at higher pressures made it key to simulate the compression stroke when modeling RCM experiments. Competition between the 2nd addition to O\textsubscript{2} and pyrolysis resulted in an abnormally large difference between ignition delay times in the 10 bar and 15 bar simulations at higher temperatures. Under IQT conditions, more representative of diesel engines, the chemistry is similar to that in the RCM except that bimolecular hydrogen abstractions from MPE by peroxy radicals are more important and the ignition timescale is shorter.
due to the higher MPE concentrations. This study provides a basis for improving our understanding of detailed ether chemistry across a wide range of temperatures and pressures. It suggests that the branching between pyrolysis and additions to \( \text{O}_2 \) in key pathways is very important for understanding how easily an ether will ignite.

IV. **1 & 2 Pentene**

Ignition delay times for 1- and 2-pentene oxidation in ‘air’ at various equivalence ratios, at 15 and 30 atm and over a wide temperature range were studied using both a high-pressure shock tube and a rapid compression machine. These new data together with species profiles measured in a JSR and CO time-histories measured in a HPST are used for model validation. The experimental results show that 1- and 2-pentene show similar fuel reactivities at high temperatures (> 900 K), while 1-pentene shows an NTC behavior and higher fuel reactivity compared to 2-pentene at intermediate temperatures (650–800 K). The newly developed chemical kinetic model can capture well the auto-ignition behavior of both 1- and 2-pentene at different temperatures and pressures. Flux and sensitivity analyses show that, at low temperatures, hydroxyl radicals add across the double bond, followed by addition to molecular oxygen producing hydroxy-alkylperoxy radicals. These radicals can further proceed via the Waddington mechanism or other alternate internal H-atom isomerization reactions in a chain branching mechanism similar to those for alkanes, and this chain branching reaction pathway is responsible for the higher fuel reactivity of 1-pentene relative to 2-pentene at low temperatures. To help further validate the chemical model, a robust evaluation of low-temperature oxidation products and high temperature pyrolysis products could be performed in the future.
LIST OF REFERENCES


