Measurements and interpretation of shock tube ignition delay times in highly CO₂ diluted mixtures using multiple diagnostics

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Abstract

Common definitions for ignition delay time are often hard to determine due to the issue of bifurcation and other non-idealities that result from high levels of CO₂ addition. Using high-speed camera imagery in comparison with more standard methods (e.g., pressure, emission, and laser absorption spectroscopy) to measure the ignition delay time, the effect of bifurcation has been examined in this study. Experiments were performed at pressures between 0.6 and 1.2 atm for temperatures between 1650 and 2040 K. The equivalence ratio for all experiments was kept at a constant value of 1 with methane as the fuel. The CO₂ mole fraction was varied between a value of $X_{\text{CO}_2} = 0.00$ to 0.895. The ignition delay time was determined from three different measurements at the sidewall: broadband chemiluminescent emission captured via a photodetector, CH₄ concentrations determined using a distributed feedback interband cascade laser centered at 3403.4 nm, and pressure recorded via a dynamic Kistler type transducer. All methods for the ignition delay time were compared to high-speed camera images taken of the axial cross-section during combustion. Methane time-histories and the methane decay times were also measured using the laser. It was determined that the flame could be correlated to the ignition delay time measured at the side wall but that the flame as captured by the camera was not homogeneous as assumed in typical shock tube experiments. The bifurcation of the shock wave resulted in smaller flames with large boundary layers and that the flame could be as small as 30% of the cross-sectional area of the shock tube at the highest levels of CO₂ dilution. Comparisons between the camera images and the different ignition delay time methods show that care must be taken in interpreting traditional ignition delay data for experiments with large

bifurcation effects as different methods in measuring the ignition delay time could result in different interpretations of kinetic mechanisms and impede the development of future mechanisms.

1 Introduction

For nearly 50 years, shock tubes have been an integral part of combustion research and have provided useful kinetics data in various reaction systems which helped advance our state of the knowledge [1-30]. Shock tubes are nearly ideal devices for studying gas-phase high-temperature pyrolysis and oxidation kinetics as they provide well-controlled step changes in temperature and pressure, a well-defined time zero, and for large diameter tubes, are generally not significantly affected by surface or transport phenomena [31-36]. The shock tube is a long tube separated into two sections of different pressure. When the barrier is removed between the two sections, the gases strive for equilibrium resulting in a normal shock wave. The shock wave eventually hits the end wall of the tube and causes a stagnation point as the wave reflects. This stagnation point is the test location. The entire heating process happens within micro-second time-scales resulting in negligible heat loss from the system which holds the temperature constant until the arrival of waves from the driver side at the test location the system holds test pressures and temperatures. The process can be repeated for different test conditions with excellent reproducibility. A heated mixing facility attached to the shock tube enables accurate preparation of gas-phase mixtures for kinetics studies. Absorption-based diagnostic studies are non-intrusive, provide in-situ measurements (e.g., concentration of individual species including trace species, temperature) and have fast-time response. The combination of shock-heating and non-intrusive laser detection provides a state-of-the-art test platform for high-temperature kinetics of various hydrocarbons and oxygenates [32, 37-40].

The ideal shock tube theory assumes the following: diaphragm breaks instantly forming a constant speed shock wave; thermodynamic conditions and the flow velocity remain constant between the shock and the contact front; and, reflection from end wall produces uniform conditions behind reflected shock wave [41]. Actual shock tubes slightly deviate from ideal behavior: there is a finite diaphragm breaking and shock formation time; a boundary layer builds up due to viscous effects behind moving incident shock waves which affects the shock velocity described in the boundary layer models developed by the pioneering work of Mirels and co-

workers [42-46]; interaction of the reflected shock wave with the boundary layer produces bifurcation [47], and non-uniform test conditions and affects the shock velocity; and contact-surface/reflected-shock interaction affects the available test times [48]. Bifurcation has the potential to create fluid structures in the system due to the separation of the boundary layer which may result in turbulence and non-stagnant flow. Turbulence often results in greater uncertainty in the system and may limit test times due to rising uncertainties. Figure 1 shows the bifurcation process during a typical shock tube experiment.

Figure 1: Schematic for the bifurcation of reflected shock wave. As a result of the bifurcation, the fluid behind the reflected shock wave is no longer quiescent.

Bifurcation occurs because the boundary layer is not able to negotiate the pressure rise across the reflected shock when brought to rest relative to it, and is therefore trapped and carried along at the foot of the shock [49, 50]. Bifurcation features normally appear in diatomic and polyatomic gases (such as fuel/air mixtures, mixtures with CO₂) but not in argon diluted mixtures and its features have been well-known through experimental visualization utilizing color schlieren [51] and side-wall pressure measurements [52, 53]. Bifurcation has been modeled in many computational studies [54-58]. It has been shown that bifurcation causes large fluid fluctuations behind the reflected shock wave with large vorticity and an unstable shear layer. Bifurcation affects determination of time zero because of the uncertainty in determining the arrival of the normal shock wave at the sidewall location and its effects are severe as one moves away from the end wall and also for short ignition delay times (<100 μ s). However, it is commonly assumed that bifurcation should not affect the core portion of the post-shock region, which comprises most of the flow area [52]. However, a comprehensive study using multiple diagnostics to verify the influence of bifurcation and inhomogeneity on chemical kinetics is lacking in the literature though similar studies in rapid compression machines have been carried out by Walton et al. [59]. It was determined, through imaging that two ignition regimes (mild and strong) were present for iso-octane mixtures and that there was good agreement between the simulations and experimental results.

In this work we focus on measuring ignition delay times under the influence of bifurcation in heavily CO₂ diluted mixtures that are applicable to the supercritical carbon dioxide (sCO₂) [60-

64], which has seen a growth in research in the last decade as society moves to reduce the effects of emissions and improve the efficiency of current turbine technology. In direct-fired sCO_2 systems, CO_2 is used as a diluent (up to 95% by volume) during combustion, and the product CO_2 may then be separated and captured for sequestration providing near zero CO_2 emissions, thus reducing global warming effects [65, 66]. Despite the recent focus on CO_2 diluted cycles, there is a lack of fundamental chemical kinetics for such cycles.

Comparisons between the flame speeds of nitrogen diluted mixtures to CO_2 mixtures have been studied [67-70]. It has been determined that the addition of CO_2 reduces the flame speeds compared to air. The reason for the reduction in flame speeds is due to the role of the third body collision efficiency compared to N_2 [26, 71]. Another reason CO_2 affects the flame speeds is the competition between CO_2 and O_2 for H radicals reducing the radical pools and inhibiting the overall reaction rate [72-74]. There are four different studies that have looked at the effects of CO_2 as a diluent on the ignition delay times of a mixture. The first two looked at low levels of carbon dioxide as would be found in exhaust gases. Holton et al. examined mixtures with up to 10% carbon dioxide in the mixture and determined that the addition of carbon dioxide in the mixture reduced the reactivity of the mixture and thus caused an increase in the ignition delay time for a given condition [73]. The other study by Vasu et al. examined syngas mixtures between 1 and 2.5 atm with up to 24% carbon dioxide in the mixture [28]. Koroglu et al. investigated CO_2 diluted methane mixtures up to 60% carbon dioxide and compared the ignition delay times and methane time-histories to the GRI-3.0 and the Aramco Mech 1.3 mechanisms [26, 75, 76]. Another study by Hargis and Petersen examined oxy-methane ignition delay times with large amounts of CO_2 in a nitrogen bath and was also compared to the Aramco Mech 1.3 [77]. Both of these studies determined that for pressures up to 10 atm which the research covered, the mechanisms that have been created for methane and validated for non- CO_2 mixtures predicted the ignition delay times within the margin of error for the experiments. One of the concerns that is detailed in Hargis and Petersen is the bifurcation of the shock wave that results from large amounts of carbon dioxide in the mixture [77]. Bifurcation becomes increasingly prevalent with increasing amounts of CO_2 in the mixture and it causes turbulence and other non-idealities that may result in issues with the constant-volume assumption that is made in a shock tube.

Conventionally, shock tube experimental measurements are compared to kinetic simulations which assume homogenous ignition at constant internal energy-volume [78, 79]. Although the conditions between the experimentation and modeling are comparable for these low pressure, CO₂ diluted mixtures, the non-idealities that have been investigated in this study could cause the ignition process to differ greatly compared to the current models at conditions which are more relevant to gas turbine and sCO₂ cycles (pressures up to 300 atm). This difference can be seen at pressures far below the CO₂ critical pressure and continues the trend beyond it when the Aramco Mech 1.3 deviates from its linear trend while the GRI 3.0 mechanism remains linear. These trends can be seen at both 10 atm and 100 atm in Fig. 2. This difference between mechanisms shows that the understanding of this combustion process is significant and that more research needs to be done to understand the combustion of high CO₂ diluted mixtures and how to interpret the data that is created behind reflected shock waves.

Figure 2: Comparison of ignition delay times at different pressures and CO₂ concentrations for both the GRI 3.0 and Aramco Mech 1.3 mechanisms. (a): Simulations conducted at a pressure of 10 atm. (b): Simulations conducted at a pressure of 300 atm. All simulations conducted for mixtures of $X_{CH_4} = 0.035$, $X_{O_2} = 0.070$, $X_{CO_2} = 0.00 - 0.895$ in an argon bath. Simulations done with the Chemkin-Pro [80] constant-internal energy, and constant-volume assumption (constant U , V).

Specifically, this paper looks at how CO₂ affects ignition and the development of the flame in the axial direction and compares the flame to common measurement techniques of the ignition delay time and time-resolved methane concentrations. Experiments were performed for temperatures between 1672 and 2038 K with pressures ranging from 0.625 to 1.093 atm. The equivalence ratio was kept at a constant value of 1 for all mixtures. Different methods of measuring the ignition delay time are compared and the advantages and disadvantages of each method are discussed. The methane time-histories are measured for all experiments as well as high-speed camera images being taken of the axial cross-section. The ignition delay times and methane concentrations were then compared to two mechanisms, the GRI 3.0 and the Aramco Mech 1.3 [75, 76].

2 Experimental Procedure

The procedure and instrumentation for the shock tube experiments have been described in detail in our recent paper [26] thus only a brief description is provided here. Experiments were performed for four different mixtures with varying amounts of carbon dioxide as the diluent. All experiments were performed for an equivalence ratio of 1. Temperatures for the experiments ranged from 1650 to 2050 K. Pressures for the experiments ranged from 0.6 to 1.1 atm. Table 1 shows the conditions for all of the experiments.

Table 1: Summary of Experimental Conditions

2.1 Shock Tube Facility

The shock tube has a driven length of 8.54 m, a driver length of 4.88 m, an inside diameter of 14.17 cm, and is capable of using both metal and plastic diaphragms. A four-blade cutter located on the driven side was used to rupture the 5 mil Lexan sheets at a known pressure in this study. Two Agilent DS 102 rotary vane pumps lowered the pressure on either side of the diaphragm. An Agilent V301 turbo-molecular vacuum pump was used to lower the driven pressure to below 50 μ torr before each experiment. The vacuum pressure for each experiment was measured using a combination of a convection gauge and an ionization gauge (Lesker KJL275804LL and Lesker KJLC354401YF). This allowed for a range of pressures to be measured between 10^{-9} torr and 1000 torr. The velocity of the shock wave was measured using five PCB 113B26 piezoelectric pressure transducers attached to four Agilent 53220A timer-counters. The velocity of the shock wave is then extrapolated to the end wall to calculate the temperature and pressure at the test

location. The average uncertainty of the temperature and pressure has been measured to be around 2% for both the reflected temperature and reflected pressure leading to typical uncertainties of around 20% for shock tube ignition delay times measurements [26].

2.2 Mixture Preparation

All mixtures were prepared in a 33L mixing tank made of Teflon coated stainless steel. The mixing tank was vacuumed before each mixture overnight in order to ensure the most accurate mixture possible. The mixing tank utilized a magnetically driven stirrer to ensure homogeneity of the mixture. All gasses for the experiments were purchased from Praxair and were of research quality ($\geq 99.99\%$). The mixtures were made using a partial pressure method through a gas manifold. The pressure was measured using two manometers with full scale ranges of 100 and 10,000 torr baratrons (MKS E27D and MKS 628D). Mixtures were allowed to sit for a minimum of 6 hours before being inserted into the shock tube through the gas manifold. The initial pressure for each experiment was measured using the baratrons attached to the gas manifold.

2.3 Conventional Shock Tube Diagnostics

2.3.1 Pressure and Emission Measurements

Diagnostics for these experiments consisted of pressure measurements, emission detection, laser absorption and high-speed imaging all located at the test location of 2 cm from the end wall. The reflected pressure was measured using a Kistler 603B1 pressure transducer with an RTV coating. The chemiluminescent emission was recorded to determine the ignition delay time using a GaP transimpedance amplified detector from Thorlabs (PDA25K).

2.3.2 Laser Absorption Diagnostics for Methane Time-histories

Methane time-histories were measured using a continuous wave distributed feedback interband cascade laser from Nanoplus. Two HgCdTe (MCT) detectors (Vigo Systems PVI-2TE-3.4) were used to measure the laser intensity to obtain the absorbance of the laser beam during the experiment. Using this laser, absorption due to P(8) rovibrational transition line located in the ν_3 vibrational band of methane was measured and compared to the initial strength of the laser when the shock tube was under vacuum [81]. This line corresponds to 3403.4 nm and has been described as a good choice for time-resolved measurements of methane concentrations [26, 82-88]. The methane concentration was determined using the Beer-Lambert Law and converting the absorbance into the mole fraction from the following equation.

$$\alpha = -\ln\left(\frac{I_{tr}}{I_{ref}}\right)_v = \sigma(\nu, T, P) \frac{P_{tot}}{RT} \chi L \quad (1)$$

where α is the absorbance, I_{tr} is the intensity of light that passes through the shock tube, I_{ref} is the reference intensity in a vacuum, σ is the absorption cross-section, P_{tot} is the pressure behind the reflected shock wave, R is the specific gas constant, T is the temperature behind the reflected shock wave, X is the mole fraction of methane, and L is the diameter of the shock tube. Using the absorption cross-sections that were measured in Koroglu et al. [26], the methane mole fraction was measured over time for each experiment with typical uncertainties around 6%.

2.4 End Wall Imaging using High-Speed Camera

High-speed camera images were taken to compare with other measurements for all experiments based on a similar method performed by Troutman et al [89]. A Phantom V710 camera was used to record the combustion process with a 256 x 256 resolution at a rate of 67,065 frames per second corresponding to a time resolution of 14.91 μ s. The camera was positioned perpendicular to the shock tube so that the entire axial cross-section could be captured by the camera. The camera was focused at the plane corresponding to 2 cm from the end-wall to match the location of the pressure, laser and emission diagnostics. The camera was triggered on the voltage rise of the Kistler pressure transducer. It triggered after the voltage read 2 V for 5 μ s. Once triggered, 5,000 frames were then taken before and after frame 0 in order to ensure that the entire process was captured with a total time span of 150 ms. Figure 3a shows the schematic of the camera system and the post-processed output. Figure 3b shows the processed data that is displayed comparing different methods for measuring the ignition delay time.

Figure 3: (a) Schematic for the high-speed imaging and post-processed output (not drawn to scale). (b) Comparison of measured pressure and sidewall emission of chemiluminescence with camera emission.

2.5 Numerical Simulations

Numerical simulations were performed using Chemkin Pro [80] to compare with experimental data. Two methane mechanisms were used: 1) GRI 3.0 consisting of 325 reactions and 53 species [75], and 2) Aramco 1.3 containing 253 species and 1542 reactions [76]. The common method for modeling a shock tube is to consider the system as a closed-homogeneous batch

reactor [26]. This approach treats the entire system as a premixed system that has no mass or energy transfer across the boundary, but ignores any spatial differences in the system. Simulations were performed by constraining the volume and solving for the energy equation. The ignition delay times were calculated based on the temperature inflection point over the range of temperatures measured by the experiments. The temperature inflection point is the midpoint of the temperature rise during ignition which has shown good agreement with the simulated time-histories of the different radicals that are often used with emissions based measurements (OH^* , CH^*).

3 Results and Discussion

3.1 Ignition Delay Time Measurements

In previous experiments where the gas mixtures were diluted with CO_2 [26, 86], the ignition delay time for the system was measured by combining the pressure trace of the system with the sidewall emission trace. The pressure trace was used to measure the time-zero. As mentioned earlier, the problem with the gas mixtures containing CO_2 is the bifurcation of the system. For a mixture with diatomic and monoatomic compounds, such as the CO_2 diluted mixtures present in this system, the shock wave splits in the boundary layer into two oblique waves [52]. This results in a non-uniform pressure rise and time-zero was unable to be determined through the pressure trace. The time-zero was thus determined using the schlieren peak that occurs in the laser trace with the arrival of the reflected shock wave. Figure 4 shows an experiment with 89.5% CO_2 and the effect of bifurcation on the shock wave. Time-zero as defined by the pressure rise, $t_{0,p}$ was 34 μs after the schlieren peak created by the passing shock wave. The schlieren spike was used to determine the time-zero for all experiments in this study. The method of using a continuous wave laser to locate the time zero was first suggested in Petersen and Hanson [52].

Figure 4: Example of time-zero for a bifurcated shock wave. Time-zero as defined by the pressure rise, $t_{o,p}$ was $34\ \mu\text{s}$ after the schlieren peak created by the passing shock wave.

The second step in determining the ignition delay time is to find the time corresponding to the onset of ignition. This time location can be determined through various methods depending on the author's definition. In this study, we adopted six different techniques and compared the results to each other. The first two are based on a single location on the emission curve relative to the peak of the emission. These locations were at the peak location and at 50% of the value of the peak location. The third (or fourth) method was to trace the tangent line of the maximum rise in emission (or pressure) back to the baseline to determine the start of the ignition. The fifth method was based on the methane decay time determined from laser absorption measurements, which are explained in further detail in section 3.5. Therefore, the sidewall emission traces were used to obtain the ignition delay time in the first three methods, whereas pressure trace was used in the fourth method. The fifth method is contingent upon the laser absorption measurements only. The last method uses the camera images.

The different methods for ignition delay times resulted in various values for the parameter as expected. A comparison can be seen in Fig. 5 for Mixture 1 and Mixture 2 mentioned in Table 1. It is clear from Figs. 5 (a) and (b) that with 60% CO_2 , the average of the differences ($\Delta t_{\text{avg}} = 80\mu\text{s}$) is greater than without CO_2 ($\Delta t_{\text{avg}} = 50\mu\text{s}$). This sort of difference can be especially important for modeling of CO_2 diluted mixtures when the ignition delay time is short such as $100\ \mu\text{s}$, because different definitions can cause ambiguities that are outside the uncertainty limits of

the measurements. Table 2 shows the ignition delay times for all methods presented. The ignition delay times determined from laser absorption measurements and camera images are discussed in further detail in the following sections.

Figure 5: Comparison of different ignition delay time methods for two mixtures. (a) Mixture 1: $X_{CH_4} = 0.035$, $X_{O_2} = 0.07$, $X_{CO_2} = 0.00$, $X_{Ar} = 0.895$. (b) Mixture 2: $X_{CH_4} = 0.035$, $X_{O_2} = 0.07$, $X_{CO_2} = 0.60$, $X_{Ar} = 0.295$. (c) Comparison of results for both mixtures.

Table 2: Summary of ignition delay times based on different methods of evaluation. Ignition delay time based on the pressure rise could only be determined for mixture 1 due to the small pressure rise for the carbon dioxide diluted mixtures.

3.2 High-Speed Chemiluminescence Visualization and Image Processing

In order to understand how the bifurcation of the shock wave affects the ignition of CO_2 diluted mixtures, images were taken for each experiment at a rate of 67,065 fps. As a result, the ignition delay times were able to be compared to images of the flame at different times and the different values for the ignition delay time could be compared.

Several adjustments were made to the images in order to process the images. The first adjustment was to correlate the time-zero as determined by the laser to the first image recorded by the camera. This was done by triggering the camera off of the pressure signal, resulting in the first

image being recorded when the voltage of the Kistler reached 2 V for 5 μ s. As a result, each set of images could be accurately compared to the rest of the data with confidence. Another method to compare the images was to sum the intensity of each pixel and normalize each image to the image closest to the peak. This allowed for the rise of the camera emission to be plotted along with the sidewall emission for comparison. The last adjustment that was made was to convert the gray-scale images produced by the camera to color using a heat map. This correction was performed in order to more accurately compare the different images.

Figure 6: Comparison of images taken at the end wall to the pressure, sidewall emission and methane time-history. (a) Pressure and emission trace for Mixture 1 with the images from (c) seen are depicted as black lines. (b) Methane time-history and emission trace for Mixture 1 compared to high-speed camera images. (c) High-speed camera images of Mixture 1 at a temperature of 1687 K. Vertical black lines (in a, b) show time instances corresponding to images.

An example of the images compared to the different traces is shown in Fig. 6. Vertical black lines displayed in Figs. 6 (a) and (b) correspond to the six camera images demonstrated in Fig. 6 (c). The curve denoted by normalized camera emission in Fig. 6 (a) was also obtained using the six images shown. It can be seen that the camera images correlate extremely well with the emission trace and that the camera captures both the start of emission ($t=837.1 \mu$ s) as shown in the second image and the peak emission ($t=896.8 \mu$ s) where the majority of the shock tube is illuminated by the flame. A circle has been drawn for the sidewall of the shock tube.

3.3 Experiments without CO₂ Dilution

The experiments that were performed without CO₂ showed that the difference between various methods for defining ignition times is much smaller (despite the ignition delay times for these conditions being longer than most of the other experiments). Even at the fastest ignition delay time tested, the difference was only 10% of the average of all methods which implies that the numerous methods are all well within the normal uncertainty of ignition delay times ($\sim 20\%$) measured in shock tubes [90]. Therefore, any of the methods that are commonly used to measure the ignition delay time in shock tubes would make for a good method to measure this value. The ignition delay time predictions by both mechanisms also showed good agreement with both falling within the bounds of uncertainty of 25% (Fig. 7).

Figure 7: Ignition delay times for Mixture 1. Both mechanisms predict the ignition delay time within the uncertainty of 20%.

Figure 7 displays images of the ignition process for the four runs of Mixture 1. For the imaging of this mixture it can be seen that most of the runs start around where the window plugs sit before rapidly combusting homogeneously as has been discussed in other papers [89]. It can also be noted that the flame fills the entire cross-section of the shock tube by the location of peak sidewall emission with small voids located around a circle just inside of the wall. By comparing different experiments at the same time at the same points of ignition, several interesting similarities are capable of being drawn. First each of the images show that the flame takes approximately the same amount of time to propagate from the top left corner to the rest of the shock tube, occurring in approximately $75\text{ }\mu\text{s}$ from the first image when there is very little flame. It can also be noted that although each of the runs have small voids around the edge of the flame that most likely correspond to the positions where the plugs used for the different diagnostics are located. At the conditions present for Mixture 1, it is clear that the flame propagates across the entire shock tube and remains there until the arrival of the contact surface or expansion waves that quench the experiment.

Figure 8: Comparison of high-speed camera images for different temperatures of Mixture 1. All intensities were normalized to the highest pixel intensity of the last image for each individual run.

3.4 Experiments with CO₂ Dilution

The ignition delay times and images for the mixtures with CO₂ are presented in this section. CO₂ had a dramatic effect on all of the diagnostics as expected. With the addition of CO₂, the overall signal of the emission is reduced, increasing the noise compared to the overall signal. The ignition delay times are in fact well represented by the sidewall emission within a standard margin of error as shown in Fig. 9.

Figure 9: Experimental pressure and emission trace compared to the high-speed camera images. Black vertical lines represent the time location for each of the images. (a) Pressure and emission trace for Mixture 4 with the images from (c) seen are depicted as black lines. (b) Methane time-history and emission trace for Mixture 4 compared to high-speed camera images. (c) High-speed camera images of Mixture 4 at a temperature of 1839 K. Vertical black lines (in a, b) show time instances corresponding to images.

The camera images for CO₂ diluted mixtures are shown to accurately match the ignition delay times within the larger error shown between the different methods but the flame no longer ignites the entire cross-section of the system. The flame was much smaller when compared to the cross-sectional area when CO₂ was added to the system. The ratio of the visible flame to the cross-sectional area was calculated and presented in Table 3. The area ratio was determined by estimating the flame using a circle and then comparing the area of the flame circle to the area of the circle of the highlighted wall. It was determined that the flame became smaller with increasing CO₂ mole fraction. This heterogeneous behavior of the flame becomes more apparent with large amounts of CO₂ and this shows that non-idealities such as the bifurcation of the shock

wave affects the flame in measurable ways. At the highest levels of CO₂ (Mixture 4), the area ratio of the flame to the reactor cross-section was only 46% on average. Another difference between the area ratios could be a result of the different temperature ranges between the mixtures. Mixture 1 was performed at lower temperatures while others were performed between 1724 and 2038 K. This difference is a result of the lowered test time that results from bifurcation and CO₂ dilution. As bifurcation causes large fluid structures in the system, techniques that could be applied to extend the test time (tailoring) were not utilized.

Table 3: Ratio of the flame area to the cross-sectional area of the shock tube. Flame area was assumed to be circular and be the maximum extent of the flame as determined by the high-speed imaging. The ratio of the visible flame to the cross-sectional area was calculated (Flame Area Ratio).

Provided in Fig. 10 are the images of the ignition process at three temperatures for Mixture 2. By comparing the very last images (i.e. sixth image) taken at each temperature, one can realize the decrease of the flame area ratio as the temperature is reduced. In fact, the same trend was more clearly seen for experimental results taken with Mixture 4 (refer to the flame area ratios for Mixtures 2 and 4 in Table 3). The flame area ratio increases from 0.288 at 1724 K to 0.452 at 1951 K. The reason for this trend can be explained by the fact that bifurcation occurs when the boundary layer does not have sufficient momentum to pass through the normal shock wave. Therefore, anything decreasing the momentum such as the decrease of temperature or specific heat ratio (speed of sound is given by $a = \sqrt{\gamma RT}$) would escalate the severity of bifurcation. For example, increasing CO₂ percentage in the mixture from 60 to 85% causes the flame area ratio to decrease from 0.806 to 0.452 around 1900 K. This trend happens for the same reason. In other words, the mixture specific heat ratio decreases when X_{CO2} is increased, because $\gamma_{CO2} = 1.28$, whereas $\gamma_{Ar} = 1.66$. The comparison in the flame sizes is valid despite the different levels of luminosity due to the similar levels of total dilution present in each mixture. By keeping the exposure time constant, the size of the flame can be directly compared in these mixtures as shown in Table 3 above.

Figure 10: Comparison of high-speed camera images for different temperatures of Mixture 2. All intensities were normalized to the highest pixel intensity of the last image for each individual run.

3.4.1 Effect of Increasing CO₂ Dilution on Ignition Delay Times

Figure 10 shows ignition delay times as a function of temperature for Mixtures 2 and 4. The ignition delay times are not affected much by the addition of CO₂ reaching the same conclusion as previous literature [75, 76]. The ignition delay times are presented in Fig. 11 as both the slope of the sidewall emission and the peak of the emission. With the method of emission slope, the agreement between the GRI 3.0 predictions and measurements is good for Mixture 2, whereas both mechanisms under predict the results for Mixture 4. With the method of emission peak, both mechanisms always over predicted the results. Note that the discrepancy in results between the two methods gets larger with increasing CO₂ mixture as seen in Fig. 11 (b). This results in drastically different interpretations of the ignition delay time results compared to the model. Therefore, by changing the definition of the ignition delay times, the determination for how to improve mechanisms by adjusting the reaction rates could result in mechanisms with vastly different reaction rates for the same reactions.

Figure 11: Ignition Delay Times for methane with carbon dioxide dilution. (a): Mixture 2, $X_{CH_4} = 0.035$, $X_{O_2} = 0.07$, $X_{CO_2} = 0.60$, $X_{Ar} = 0.295$. (b): Mixture 4, $X_{CH_4} = 0.05$, $X_{O_2} = 0.10$, $X_{Ar} = 0.85$.

CO₂ has a large effect on the ignition delay times when high-speed imaging is added to the system. The global effect on the ignition delay time can be picked up by the current system but that the flame behaves completely differently when CO₂ is present in the mixture. When X_{CO_2} is increased to the maximum allowable for Mixtures 3 and 4, traditional diagnostics have an increasingly hard time measuring the ignition delay time. Experimental traces such as pressure rise during combustion or the sidewall emission have much smaller signal-to-noise ratios or do not change at all. This is a result of the decreasing size of the flame during combustion. As shown by the flame area ratio, the increase of CO₂ in the system reduces the size of the flame and thus the signal measured for traditional diagnostics would decrease as more CO₂ is added to the system.

An explanation for the increase in the ignition delay times may be found in the literature on MILD (Moderate or Intense Low-Oxygen Dilution) combustion. In such a system, the diluent makes up around 94% of the overall mole fraction of the system similar to the conditions presented in this study where the dilution ranges between 85.0% and 89.5%. It has been shown that with both the dilution of CO_2 and H_2O , the third body collision rate changes dramatically for the H_2/O_2 combustion [71, 91]. Also, it has been revealed that CO_2 plays a much larger role in the reactions than N_2 . Through competition with O_2 for H atoms, CO_2 reduces the radical pools that help propagate combustion reducing the overall speed at which the reaction takes place [72, 73, 92].

The heterogeneity of the system was also increased with the increase in CO_2 concentrations. Mixture 1 showed close to uniform flame formation but as shown in Fig. 12, with CO_2 mole fractions of 0.85, the flame does not behave in the uniform manner as before. This could lead to errors in simulating the shock tube experiments through chemical kinetics simulation programs such as Chemkin-Pro, because the models assume homogenous ignition within the reactor. The average flame ratio was reduced from 98% (Mixture 1) to a 43% (Mixture 4). This drop of over half the area shows that the non-ideal behavior of such mixtures is much greater than traditional experiments conducted without CO_2 . In addition, the run-to-run difference between the flame ratios was also much greater for the mixtures with high CO_2 diluted mixtures. The high CO_2 diluted mixtures had a difference of 20% between the largest flame and the smallest but Mixture 2, with only 60% CO_2 , had a difference of 10%. This shows that the homogeneity of the flame was decreased as the percent of CO_2 present in the system increased. The reason for the increase in the heterogeneity of the flame is most likely a result of the non-stagnant conditions present in the test section. Normally, the fluid behind the reflected shock wave is assumed to be quiescent and that it does not have any large structures that are commonly seen with bifurcation. With movement in the system that has been described by Grogan and Ihme, the homogeneity of the temperature and pressure can no longer be assumed and the heterogeneity of the flame is increased [58].

Flameless combustion is another theory that may explain the results presented. Flameless combustion has been seen to reduce the luminosity of the flame [91, 93]. This could explain the weaker flame event that has been pictured in the mixtures that contained CO_2 . The mixtures may

have ignited but emitted no light that the camera could record. Bifurcation is the more likely reason because flameless combustion has also been shown to have a consistent temperature and heat release distribution compared to conventional combustion [93-96]. If the temperature distribution had been uniform (as expected in a flameless combustion scenario), it most likely would have been uniform across the entire cross-section and not centered in the shock tube as has been shown for each of the CO₂ diluted mixtures. The difference in luminosity between the core region and the edge is another indication that it is most likely not flameless combustion.

Figure 12: Experimental Images for Mixture 4. This mixture shows that the flame forms in the center of the shock tube and that the edges do not ignite during the combustion process as it did for Mixture 1.

3.4.2 Effect of CO₂ and Bifurcation of the Shock Wave on Emission

One of the possible sources of uncertainty and error for CO₂ containing mixtures is large fluid structures created by the bifurcation of the shock wave. Bifurcation occurs when the boundary layer of the fluid splits the shock wave upon reflection into two opposing oblique shocks known as a lambda wave. By splitting the shock wave, a separation bubble forms under this location and creates large fluid structures in the test area which is generally considered to be stagnant. Bifurcation occurs as a result of a momentum deficiency in the boundary layer splitting the normal shock wave near the end wall [47]. This momentum deficiency occurs due to the composition of gases, only occurring in diatomic and polyatomic molecules.

The effects of bifurcation have been a recurring issue with shock tube experiments for a long time [49-51, 57, 77, 97-100]. Hargis and Petersen described these effects for CO₂ diluted mixtures and how the temperature, pressure, and mixture composition may have altered the results. By examining the length of time of the bifurcated foot, Hargis and Petersen were able to observe that the increasing CO₂ mole fraction resulted in longer bifurcation times regardless of both pressure and temperature [77]. Nowak et al. also raise the issue of the formation of hot spots at the separation point [100]. Once the shock wave passes these spots, the pressure and temperature increase to the test conditions which could possibly result in early or heterogeneous ignition. Grogan and Ihme showed that higher Mach numbers increased both attenuation and

inhomogeneity. Since CO₂ mixture requires higher Mach Numbers to reach the reflected shock temperatures and pressures, this could be a reason why the inhomogeneity is so strong.

Bifurcation is the main theory for the variation between the different definitions of ignition delay time. The reduction in signal which leads to the large uncertainty in the experiments is most likely caused by the bifurcation and non-ideal flame structure that is present in the bifurcated shock waves. Based on the images, bifurcation does not cause the system to ignite early but does play a factor in the homogeneity of the combustion process. The system does not ignite on or around the edge where the boundary layer has formed. The boundary layer keeps the system cool enough that it remains unburnt despite the flame in the center of the system for every run tested with CO₂ dilution. This unburnt ring also grows in size with increasing concentrations of CO₂. At the smaller concentration, the ring was small and most of the cross-section burned during the combustion process but with 85% CO₂, the flame only filled about half the cross section, despite the fuel and oxidizer concentrations being increased for these experiments. One possible concern with the flame area ratio described earlier was that the bifurcation was creating cold spots and the flame denoted the size of the bifurcation region. Using a correlation developed by Petersen et al, it was determined that the size of the bifurcation was on a similar scale for the experiments and that it did not correspond to the difference in the average flame area ratio between the mixtures [52]. The flame area ratio deviated by up to 44% between Mixtures 2 – 4 but the bifurcation area only differed by approximately 7%.

3.5 Methane Decay Times Determined through Laser Absorption Measurements

Ignition is unable to occur unless the fuels present break down into radicals which initiate and propel chain branching reactions. Therefore, another parameter that was measured for the experiments was the methane decay time using the laser absorption diagnostics described in earlier studies [26]. The methane decay time (behind reflected shock waves) has been defined here as the time it takes for the methane concentration to reach to $1/3^{\text{rd}}$ of its initial value. Such a time definition was adopted to be consistent when comparing the results for various mixtures. Also, it was seen in the earlier studies [26] that a decay time defined in such a manner (i.e. a percentage of the initial concentration of the fuel) can be chosen such that the resultant time value is closest to the ignition delay time value determined through the sidewall emission measurements. In this case, such a similarity in the time value obtained from laser and emission

measurements was seen when the fraction was chosen as one-third. As mentioned earlier, the uncertainties in methane mole fraction measurements were much smaller than those of in ignition delay time measurements (since ignition time is a global phenomenon controlled by many species). Thus methane decay time provide additional validation targets for kinetic mechanisms.

Figure 13 shows an example of the methane time-history for each mixture compared to the predictions of both the GRI 3.0 and Aramco Mech 1.3 mechanisms [75, 76]. The methane time-history shows that although the noise in the laser was much greater with the addition of CO₂, the laser was still able to accurately predict the concentration of methane during the experiment. In experiments without CO₂, the Aramco Mech 1.3 showed better agreement with the experimental trace with the methane decay time only being off by 25 μ s while the GRI mechanism was off by 213 μ s. This is the same result that was determined in our previous work [26]. The addition of CO₂ resulted in greater uncertainty in the experimental measurement. However, both mechanisms were able to predict closer values for the last mixture with the GRI and Aramco Mech 1.3 being off 38 μ s and 45 μ s, respectively. This shows that the CO₂ harder on the diagnostic although the mechanisms still have approximately 20% disagreement with each other.

The increase in noise is most likely from one of two different sources both involving the non-quiescent flow behind the reflected shock wave. The bifurcation of the shockwave may be causing cold spots that have unburnt methane in them. As the fluid moves into the beam path, unburnt methane could cause the signal to instantaneously jump compared to the actual value as is measured in Mixture 1. The other explanation is that the fluid movement is causing density gradients in the fluid. Density gradients would cause the beam to refract slightly causing the beam to move in and out of the detector area. The combination of these two sources is most likely the reason for the increased noise that is seen at these higher CO₂ dilutions.

Plotted in Fig. 14 is the methane decay time as a function of the inverse of temperature. It is observed that the decay time increases as temperature decreases for all tested mixtures due to slower reactivity at lower temperatures. It should be noted that both GRI 3.0 and Aramco Mech 1.3 mechanisms [75, 76] are able to capture these trends for all mixtures tested. However, the predictions of Aramco Mech 1.3 are closer in magnitude to experimental values especially for

Mixtures 1 and 4. Current measurements will provide crucial validation data required for future development of methane kinetic mechanisms in the presence of excess CO₂ dilution.

Figure 13: Time-resolved methane concentrations for different levels of carbon dioxide dilution. (a) Methane time-history for Mixture 1. (b) Methane time-history for Mixture 2. (c): Methane time-history for Mixture 3. (d) Methane time-history for Mixture 4.

Figure 14: Methane Decay Times for all tested mixtures. Methane decay times were defined as the time it took for methane concentration to reach 1/3rd of its initial value. The solid lines are a linear fit of the data.

4 Conclusions

The ignition delay times and methane time-histories were measured with various amounts of CO_2 in stoichiometric methane/ O_2 /Ar mixtures. Experiments were performed for a pressure of approximately 1 atm for a range of temperatures between 1650 and 2040 K. It has been shown through a combination of diagnostics as well as high-speed camera imaging that the non-idealities play a major role in the ability to accurately measure the ignition delay time of methane behind bifurcated reflected shock waves.

It was shown that for mixtures with large amounts of CO_2 dilution the flame is no longer homogeneous and the bifurcation of the shock wave is extreme leading to increased uncertainty in the measurement. Comparing different methods of measuring ignition delay time, it has been shown that different methods such as the slope intercepting the baseline compared to the peak of the emission trace can lead to differences of over 100 μs and lead to completely different interpretations of the accuracy of different chemical kinetic models.

High-speed camera images were taken of the flame which showed that the bifurcation of the shock wave that occurs with the addition of carbon dioxide results in a smaller less homogeneous flame compared to the control mixture. While high-speed camera images show a smaller flame it showed that the ignition could be accurately captured and compared to traditional ignition delay measurements and provided another accurate method for measuring the ignition delay time of a fuel behind reflected shock waves.

Finally, the methane decay time was measured using a quantum cascade laser and it was determined that for mixtures without large amounts of CO_2 , the Aramco Mech 1.3 provided a more accurate representation of the decay, but that both mechanisms were within the uncertainty when CO_2 was added to the mixture.

We have provided the first comprehensive study on interpreting shock tube results when significant bifurcation is present using multiple diagnostic techniques with CO_2 dilution. Currently efforts are underway to extend this research to higher pressures to examine the effect of CO_2 on methane combustion at conditions more relevant to practical engine operations.

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a)

b)

a)

b)

b)

c)

a)

b)

c)

$T = 1672 \text{ K}$

$T = 1687 \text{ K}$

$T = 1749 \text{ K}$

$T = 1770 \text{ K}$

a)

b)

c)

$T = 1750 \text{ K}$

$T = 1797 \text{ K}$

$T = 1920 \text{ K}$

a)

b)

a)

b)

c)

d)

Table 4: Summary of Experimental Conditions

Mixture	P ₅ [atm]	T ₅ [K]	X _{CO2}	X _{CH4}	X _{O2}	X _{Ar}	Φ
1	0.780	1672	0.0	0.035	0.07	0.895	1.0
	0.756	1687					
	0.625	1749					
	0.737	1770					
2	0.944	1750	0.60	0.035	0.07	0.295	1.0
	0.866	1797					
	0.833	1920					
3	0.608	2038	0.895	0.035	0.07	0.0	1.0
4	1.093	1724	0.85	0.05	0.10	0.0	1.0
	1.043	1726					
	0.993	1839					
	0.946	1874					
	0.919	1951					

Table 2: Summary of ignition delay times based on different methods of evaluation. Ignition delay time based on the pressure rise could only be determined for mixture 1 due to the small pressure rise for the carbon dioxide diluted mixtures.

Mixture	T5 [K]	Emis. Peak [μ s]	Emis. $\frac{1}{2}$ Peak [μ s]	Emis. Slope [μ s]	Laser [μ s]	Pres. [μ s]	Camera [μ s]	Δt [μ s]
1	1672	1021.5	998.5	969.5	1022	1003	976.5	52.5
	1687	902.5	886.5	866.0	905.5	897.5	867.0	39.5
	1749	644.5	626.5	609.0	656.5	645.5	591.0	65.5
	1770	469.0	456.5	445.0	485.0	477.0	442.0	43.0
2	1750	504.0	455.0	409	516.0		461.5	107
	1797	309.0	265.0	212.5	301.0	n/a	254.0	96.5
	1920	172.5	155.0	135.0	166.5		166.0	37.5
3	2038	140.0	103.0	70.0	142.0	n/a	95.0	72.0
4	1724	503.0	448.0	396.0	536.5		440.0	140.5
	1726	400.0	364.5	325.5	424.5		374.0	99.0
	1839	236.0	195.5	150.5	259.5	n/a	209.5	109.0
	1874	205.5	170.0	137.0	182.0		167.5	68.5
	1951	156.0	116.5	81.0	114.5		128.0	75.0

Table 3: Ratio of the flame area to the cross-sectional area of the shock tube. Flame area was assumed to be circular and be the maximum extent of the flame as determined by the high-speed imaging. The ratio of the visible flame to the cross-sectional area was calculated (Flame Area Ratio).

Mixture	P ₅ [atm]	T ₅ [K]	Flame Area Ratio
1	0.780	1672	0.984
	0.756	1687	0.953
	0.625	1749	1.000
	0.737	1770	0.984
2	0.944	1750	0.712
	0.866	1797	0.710
	0.833	1920	0.806
3	0.608	2038	0.431
4	1.093	1724	0.288
	1.043	1726	0.389
	0.993	1839	0.484
	0.946	1874	0.410
	0.919	1951	0.452