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# Measurements and interpretation of shock tube ignition delay times in highly $CO_2$ diluted mixtures using multiple diagnostics

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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 $CO_2$ 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 $CO_2$ mole fraction was varied between a value of $X_{CO_2} = 0.00$ to 0.895. The ignition delay time was determined from three different measurements at the sidewall: broadband chemiluminescent emission captured via a photodetector, $CH_4$ 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 $CO_2$ 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 pressures. 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].

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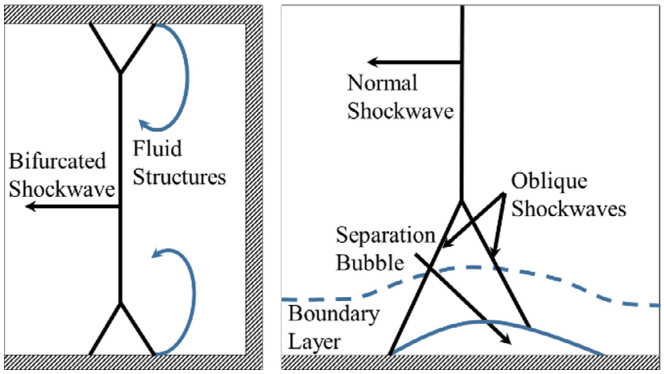


**Fig. 1.** Schematic for the bifurcation of reflected shock wave. As a result of the bifurcation, the fluid behind the reflected shock wave is no longer quiescent.

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.

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 $CO_2$) 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 ($< 100\,\mu$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 a 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 $CO_2$ diluted mixtures that are applicable to the supercritical carbon dioxide cycle ($sCO_2$) [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, $CO_2$ 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 $sCO_2$ cycles (pressures up to 300 atm). This difference can be seen at pressures far below the $CO_2$ 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 300 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 $CO_2$ diluted mixtures and how to interpret the data that is created behind reflected shock waves.

Specifically, this paper looks at how $CO_2$ 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