Characterizing Strong Ignition Overpressure in Oxy-Methane Combustion Experiments

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1   Introduction

Continued interest in space flight has drawn particular attention to rocket engines employing liquid methane as fuel, as it is more cost-effective and has fewer manufacturing demands than other high specific impulse fuels such as liquid hydrogen. The density of methane results in a smaller volume necessary to store the fuel, which decreases the overall payload [1]. Additionally, methane has a higher boiling point (111.6 K) than hydrogen (20.3 K), requiring less energy to convert the gaseous fuel to a liquid. With methane being actively used as a primary propellant in rocket engines, it is imperative to understand the timescale on which the elementary reactions take place at rocket engine-relevant conditions to support informed design decisions regarding these vehicles.

In combustion science research, shock tubes and flame bombs are commonly used to study high-temperature chemical processes under precisely controlled conditions to measure fundamental parameters such as ignition delay time and laminar flame speed. The limits of experimental capability are determined by the material strength of the experimental facility and the overpressure produced by the combustion event. A potential explanation for the lack of published data for these mixtures lies in their extremely high energy release. The lack of a diluent causes high flame temperatures (>3000 K; Fig. 1a) and low global activation energy, leading to safety concerns regarding autoignition and blast overpressure in experimental facilities. For typical fuel-air mixtures, this overpressure is usually a factor of 6 to 9 above the initial pressure (Fig. 1b). However, experimental pressure data show that the overpressure regularly exceeds equilibrium predictions, especially for gas mixtures lacking a diluent or bath gas. The pressure rise in pure oxy-methane experiments exhibits detonation-like characteristics where a region of high pressure and density exists in a narrow timescale [2].

This work aims to characterize the overpressure produced from strong ignition (detonation) in oxy-methane mixtures by comparing overpressure data from two facilities at Texas A&M University: a shock tube and a constant-volume flame vessel, both of which are described in Section 2. Typical experimental pressure data for real fuel-air mixtures are contrasted in Section 3 with new pressure data for oxy-methane mixtures, showing the extreme conditions produced by undiluted combustion. The implications of these results are discussed in Section 4, highlighting the difficulties in measuring combustion properties of undiluted fuel-oxidizer mixtures, such as those used as rocket propellants. Ultimately, an understanding of what drives the overpressure strength will allow further measurements to be made in non-dilute mixtures where the kinetics models perform poorly.
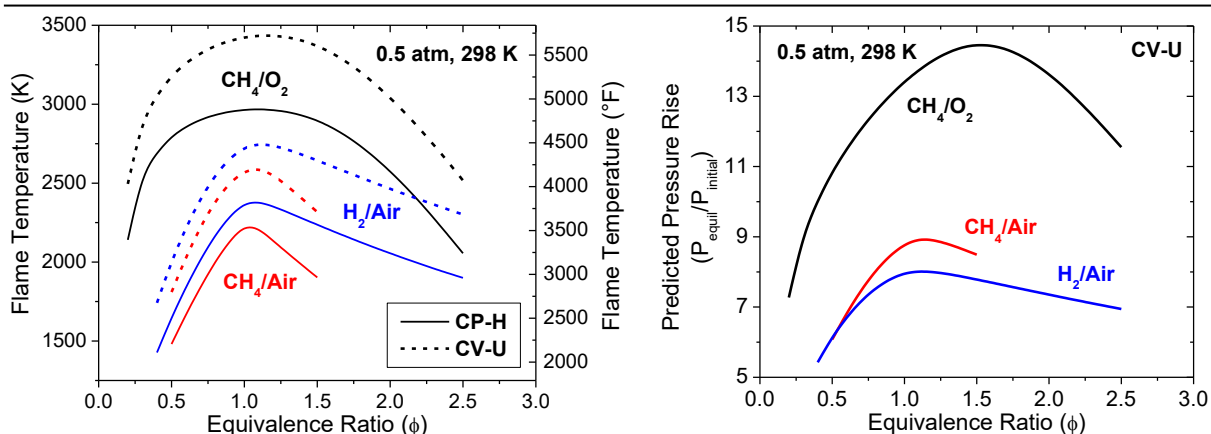
Figure 1: (left) Predicted adiabatic flame temperatures for various fuel/oxidizer mixtures at 0.5 atm and 298 K. (right) Predicted peak overpressure, normalized by the initial pressure, for the same mixtures and conditions.

2 Experimental Facilities and Methodology

2.1 Aerospace Shock Tube Facility

The Aerospace Shock Tube Facility (AST) at Texas A&M University (TAMU) was used to conduct the oxy-methane experiments behind reflected shock waves. This facility is constructed of a 3.13-m driver section with an internal diameter of 7.62 cm and a 7.33-m driven section with an inner diameter of 16.20 cm. A breech assembly, which houses the polycarbonate diaphragms, separates the driver and driven sections. Diaphragm thickness ranged from 0.127-1.016 mm which produced pressure-driven shock waves of varying strengths. Industrial-grade helium was used as the driver gas. A custom cutter is located immediately downstream to influence uniform rupture and repeatability. The incident shock wave speed is recorded using five, ultrafast-response (<1-μs) PCB P113A piezoelectric pressure transducers located at fixed distances along the last 1.44 m of the driven section. The transducers are triggered by the compression of the shock wave, and the time between each response is recorded. The last transducer is located 1.6 cm from the endwall so the velocity can be reliably inferred to the endwall [3]. The one-dimensional normal shock relations were used to calculate the reflected-shock conditions with uncertainties in T_5 and P_5 of 0.8% and 1.0%, respectively [4].

To ensure purity during each test, a high-vacuum pumping system is incorporated in both the driver and driven sections to obtain pressures less than 10^{-6} Torr. Along with a pressure transducer at the sidewall, reaction progress was monitored with chemiluminescence from the electronically excited hydroxyl radical, OH*, during the $A^2\Sigma^+ \rightarrow X^2\Pi$ transition at 307 nm. The OH* beam path was allowed to escape through an optical port outfitted with sapphire windows where emitted light was focused onto a 307-nm filter and detected by a Hamamatsu photomultiplier tube (PMT). The signal was sent to an onboard data acquisition system. Four stoichiometric oxy-methane mixtures were prepared in a separate 30.3-L stainless-steel mixing tank with argon dilution percentages of 71%, 50%, 26%, and 0%, respectively. Test gases implemented in this work include ultrahigh purity (UHP) CH_4 (99.97%), UHP O_2 (99.99%), and UHP Ar (99.99%).

2.2 Turbulent Flame Speed Vessel

Spherically expanding flame experiments were conducted using the Turbulent Flame Speed Vessel (TFSV) at TAMU. The TSFV is a constant-volume, stainless steel chamber of approximately 34 L of internal volume and has four optical ports of 12.7 cm in diameter. The chamber is equipped with mixing fans to ensure homogeneous gas mixtures. Additional details of the TFSV are provided by Morones et al. [5]. High-speed schlieren imaging (Oriel Corporation mercury arc lamp, model 66003; Photron FastCam SA1.1) was employed to measure laminar flame speed and study the development of the flame

front. In-chamber pressure was recorded using an Endevco 8511A-5K unit, a piezoresistive static pressure sensor rated to measure linearly over the range 0-5000 psia. The 8511A-5K output was amplified by an Endevco 136 signal conditioner before being recorded by GageScope software. For each experiment, the pressure for the entire combustion event is recorded, allowing for verification of the constant-pressure assumption for measurement of laminar flame speed and verification of the peak post-combustion pressure. The pressure recordings are analyzed to check that peak pressure did not exceed the safety limit for the chamber.

3   Experimental Pressure Data in Non-Dilute Mixtures

During a typical shock-tube experiment, pressure time histories display instantaneous pressure increases from the passage of both the incident and reflected shock waves followed by a delay in which the reflected-shock conditions are relatively constant. This region of elevated temperature and pressure exists anywhere from hundreds of microseconds to milliseconds. Once the gas has been subjected to this extreme environment, ignition is observed either through spikes in the pressure signal or through the use of a secondary diagnostic, such as excited species emission. Highly dilute experiments (>95%) have been shown to exhibit both no rise in pressure during an ignition event or an increase in pressure, dependent on the dilution level. Conversely, in pure oxy-methane experiments, a strong ignition event is observed after some delay in the reflected-shock region, occasionally followed by a detonation-like event in which the overpressure produced from a shock-induced ignition front can exist on the order of 2 to 15 times that of the reflected-shock pressure.

Representative experimental traces for two different argon dilution levels, 71% and 0% (pure oxy-methane), are shown in Fig. 2, where the peak pressure varies with dilution level. Each experiment was taken near atmospheric pressure, and in temperatures characteristic of the high-temperature reaction kinetics of methane. Although a sharp spike reminiscent of a shock-driven event is visible in each pressure trace, the peak pressure is much larger in the pure oxy-methane mixture, demonstrating the energy release in non-dilute experiments.
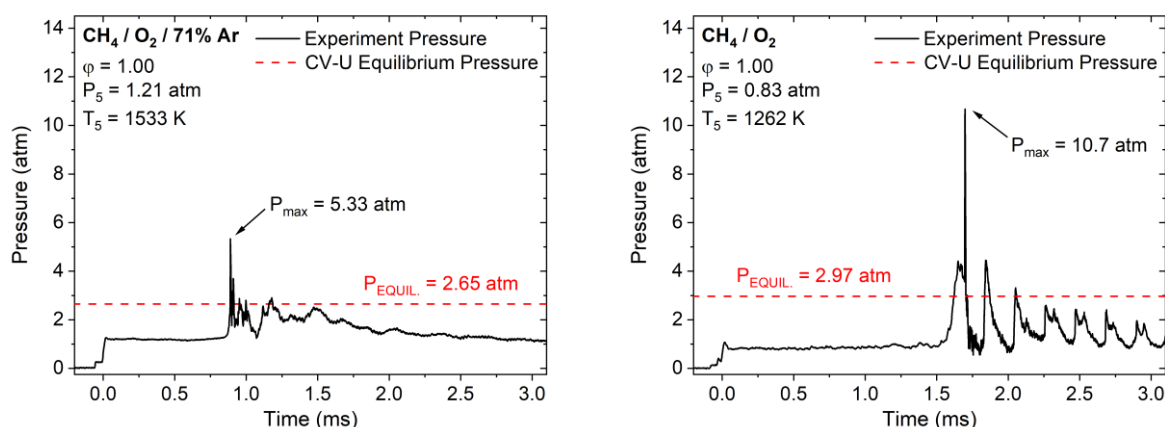

Figure 2: Experimental overpressure traces for oxy-methane ignition with two different dilution levels: (left) 71% argon and (right) 0% argon (pure O_2-CH_4). Peak pressure is larger in pure O_2-CH_4 although both dilution levels exhibit pressures greater than CV-U equilibrium predictions (red-dashed line).

In the spherically expanding flame experiments, the combustion overpressure typically develops as a smooth rise from the initial pressure to the peak pressure, as shown in Fig. 3. The pressure remains constant for the initial phase of flame propagation, allowing for the laminar flame speed (S_L) to be measured. Once the flame becomes large enough, the pressure in the chamber begins to rise isentropically until the flame nears the wall of the chamber and extinguishes, at which point the pressure reaches a maximum and begins to decrease as the gas cools. This peak pressure typically matches the predicted equilibrium pressure within 2%. However, in many experiments, there are secondary ignition

events as the compressed but unburned "end-gas" at the edges of the chamber experiences autoignition. These autoignition events cause significant pressure spikes, as shown in Fig. 3, which can occur before, at, or after the "baseline" peak pressure is reached. Figure 3 contains pressure traces from experiments far from stoichiometry. Figure 3a shows an example of mild autoignition occurring well after the peak pressure for a $\phi = 0.25$, 0.5-atm oxy-methane flame, while Fig. 3b shows much stronger autoignition occurring at the peak for a $\phi = 2.2$ flame. These resonating oscillations cause the peak pressure to be much higher (15-65%) than predicted by constant-volume chemical equilibrium. All of these experiments produced laminar flame speed measurements which are described by Turner and Petersen [6].
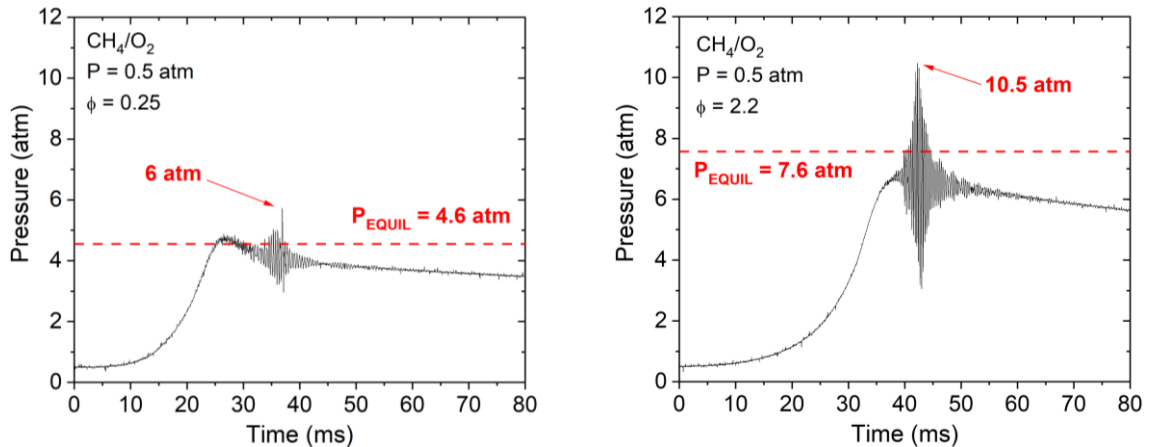

Figure 3: Experimental overpressure traces from 0.5-atm CH_4/O_2 flames at equivalence ratios far from stoichiometry (left) $\phi = 0.25$; (right) $\phi = 2.2$. Both cases exhibit knock events with characteristic frequencies and peak pressures above the equilibrium prediction.

More-energetic mixtures, e.g., those near $\phi = 1$ as shown in Fig. 4, produce oscillations in the early pressure rise which quickly escalate into a sharp, narrow spike that exceeds equilibrium predictions by over 90%. These pressure traces exhibit heavy noise levels and a large drop in pressure after the sharp spike that tends to recover to a quasi-equilibrium plateau, which then decays as the gas cools. These strong ignition events produce pressure responses in the CV flame vessel that resemble the pressure events in the shock-tube experiments (Fig. 2). This behavior was only seen for equivalence ratios at or near stoichiometry.
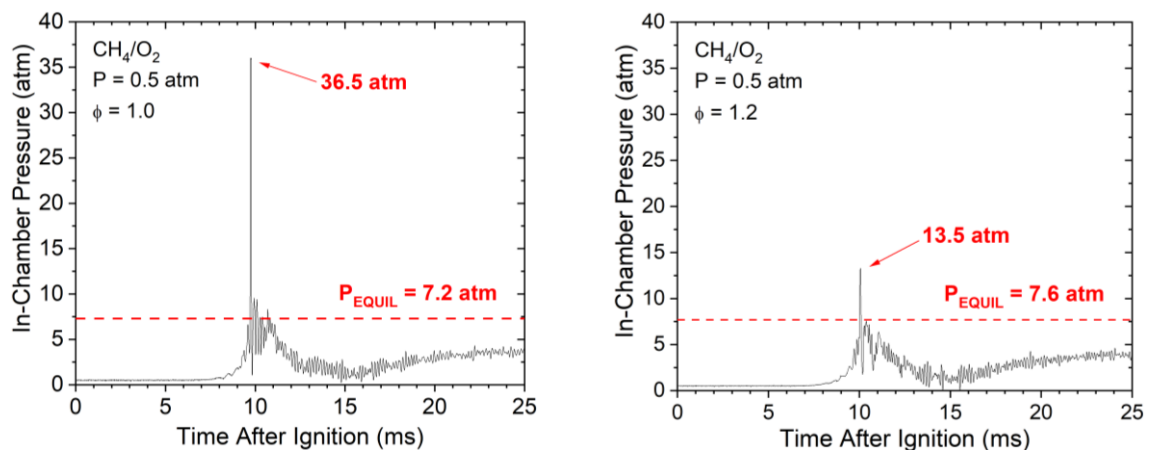

Figure 4: Overpressure traces for CH_4/O_2 flames at and near stoichiometry (left) $\phi = 1.0$; (right) $\phi = 1.2$. Both measurements exhibit extremely high but narrow peak readings well above the equilibrium prediction, followed by a large drop.

4   Peak Overpressure Prediction in Shock-Tube Experiments

The TAMU AST was used to conduct the oxy-methane experiments where overpressure, defined as the peak pressure (P_{max}) normalized by the reflected-shock pressure (P_5), was recorded for each test. Reflected-shock pressures ranged from 0.23 to 1.40 atm, while reflected-shock temperatures ranged from 1237 to 1743 K. Overpressure strength varied between each mixture and subsequently between each test. The effect of the reflected-shock conditions on overpressure strength were examined first, as they represent the initial conditions relative to the detonation-like ignition event. There appears to be no observable relationship between reflected-shock pressure and overpressure strength (Fig. 5a); however, overpressure appears to decrease with increasing reflected-shock temperature for each argon dilution amount (Fig. 5b). Since argon is a monatomic gas, it absorbs the energy transfer from the shock process exclusively in the translational energy mode resulting in large achievable temperatures in the reflected-shock region. Therefore, one can conclude the mixtures containing the largest amounts of argon would exhibit the highest reflected-shock temperatures and lowest overpressures. This trend is indeed observed in Fig. 5b. However, when isolating each mixture, the overpressure clearly decreases with reflected-shock temperature increase for mixtures containing 71%, 50%, and 0% argon. Further examination into hotter test temperatures would be necessary to conclude the same effect takes place in the mixture with 26% argon.

Although analyzing the effect of reflected-shock conditions on overpressure is worthwhile, it is not conclusive enough with the data herein to draw an overall predictive metric to estimate overpressure strength. Consequently, the overpressure for each test was recorded as a function of the argon dilution in each mixture (Fig. 6a). Here, peak overpressure appears to increase with decreasing argon mole fraction until near 30% argon dilution where the peak overpressure remains constant at just under 15 times the reflected-shock pressure. A polynomial fit was applied to the maximum overpressure observed in each respective mixture where overpressure was shown to vary with argon dilution as

$$(P_{\max}/P_5) = -37.083(x_{Ar})^2 + 16.125(x_{Ar}) + 13.117 \qquad (1)$$

where (P_{max}/P_5) is the overpressure, and X_{Ar} is the mole fraction of argon in the mixture. Equation 1 has a coefficient of determination (R^2) of 0.98, and the strength of this correlation is displayed in Fig. 6b. The correlated overpressures agree well with the measured overpressures, especially in mixtures containing less than 30% argon where peak overpressure is the largest.
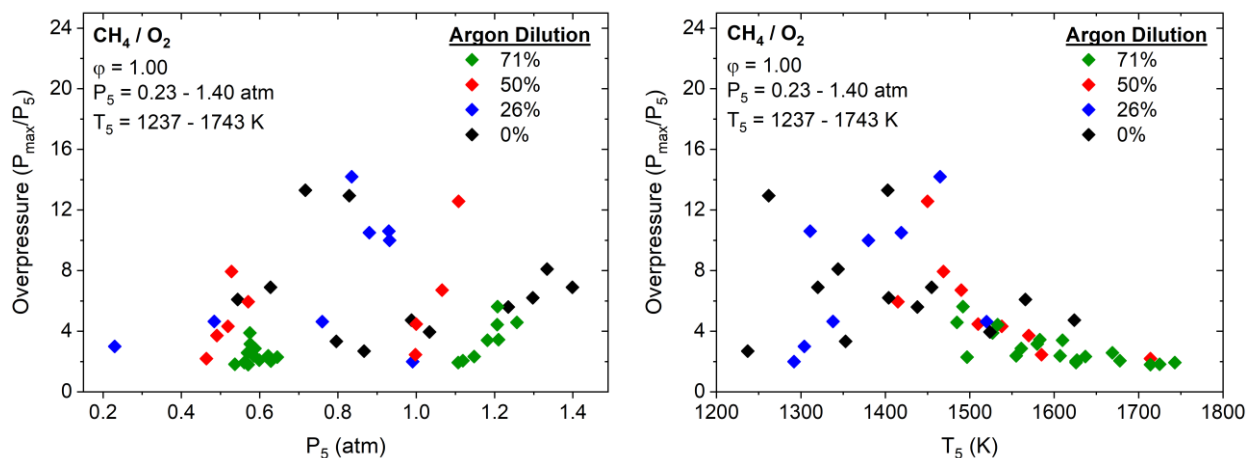

Figure 5: The influence of reflected-shock pressure (left) and reflected-shock temperature (right) on the overpressure strength in oxy-methane shock-tube experiments at relatively low pressures.
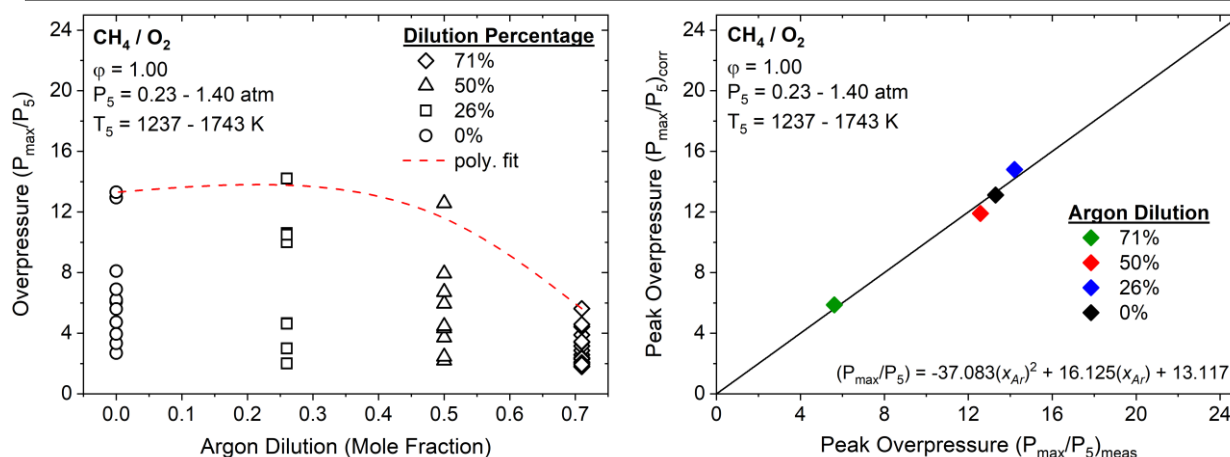
Figure 6: (left) The effect of argon mole fraction on overpressure and (right) comparison of the correlated overpressure values (Eq. 1) to the measured overpressure values for varying argon dilution percentages.

5   Conclusion

Two types of reaction vessels, namely the TAMU AST and TFSV, were used to measure the overpressure from oxy-methane experiments. Mixtures included in the shock-tube experiments were stoichiometric and argon dilution varied from 0-71%. Spherically expanding flame experiments examined pure oxy-methane mixtures with no diluent and varied the equivalence ratio from 0.2-2.2. Shock-tube initial conditions were represented by the reflected-shock conditions as these tests rely on the shock process compared to the flame experiments which are initiated by a spark. Significant overpressure, greater than predicted by CV-U chemical equilibrium calculations, was observed in both facilities as a consequence of the energy released during the ignition event. Peak overpressure was shown to vary primarily with equivalence ratio and fill pressure (P_1) in the TFSV, similar to the trend for laminar flame speed. Results in the shock-tube tests revealed peak overpressure decreases with increasing reflected-shock temperature and does not respond as strongly to changes in reflected-shock pressure in the range studied. An investigation into higher reflected-shock pressures may result in an increase in measured overpressure. Furthermore, argon dilution was shown to have the largest influence on peak overpressure. A correlation dependent on argon mole fraction was developed to predict peak overpressure and was performance tested against measured values in this study. As data in pure oxy-methane mixture are limited, results from this study serve as a guideline for future tests conducted in non-dilute mixtures, which can be used to better validate model predictions.

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