Challenges Associated with Shock-Tube Ignition Experiments in Undiluted Oxygen Environments

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1 Introduction

Depending on the shock-tube design and geometry, the window for performing precise chemical kinetics experiments in undiluted environments (i.e., only fuel and oxidizer are the reactants) may be particularly narrow. Because the fuel concentration is greater in undiluted mixtures, higher Mach numbers are required to produce a desired reflected-shock temperature compared to highly diluted mixtures, where at least 95% of the mixture is inert. This requirement is especially true for hydrocarbon fuels, as the polyatomic species contribute to a lower mixture specific heat ratio. Non-ideal gas-dynamic effects, such as a time-varying pressure rise (dp/dt) and reflected-shock bifurcation, are expected to be present, and perhaps be even more severe, in oxy-fuel experiments since existing empirical relationships include strong dependencies on both non-ideal Mach number and specific heat ratio [1-3].

The present work is concerned with additional challenges in undiluted experiments that when coupled with the aforementioned non-ideal effects may be responsible for the general lack of ignition data found in the open literature for pure oxy-fuels. Attention is placed first on the overpressures produced from highly exothermic reactions behind the reflected shock wave in the context of avoiding intermediate-, and especially high-, pressure experiments over concerns of laboratory safety and general facility limitations. Next, the reduced window where ignition occurs prior to a disturbance created from an interaction between the reflected shock wave and contact surface is presented for a stoichiometric CH_4/O_2 mixture. Finally, the limits of test-time extension using conventional tailoring methods with helium-based driver mixtures are illustrated using calculations from a new tailoring model developed for diverging shock tubes. Preliminary solutions and approaches to these challenges are discussed herein, and further details will be provided in forthcoming works with data obtained from ongoing experiments in the authors' laboratory.

2 Mixture Exothermicity and Resulting Overpressure

There is currently a sizable gap in the open literature regarding fundamental combustion measurements in oxy-fuel systems (i.e., those used in rockets) at the conditions of interest that could be used to validate kinetics models. This situation is primarily due to the absence of a diluent species leading to rapid and extreme chemical energy release upon ignition that may be coupled with additional gas dynamic processes, ultimately generating pressures existing beyond most facility limits. To illustrate the possible

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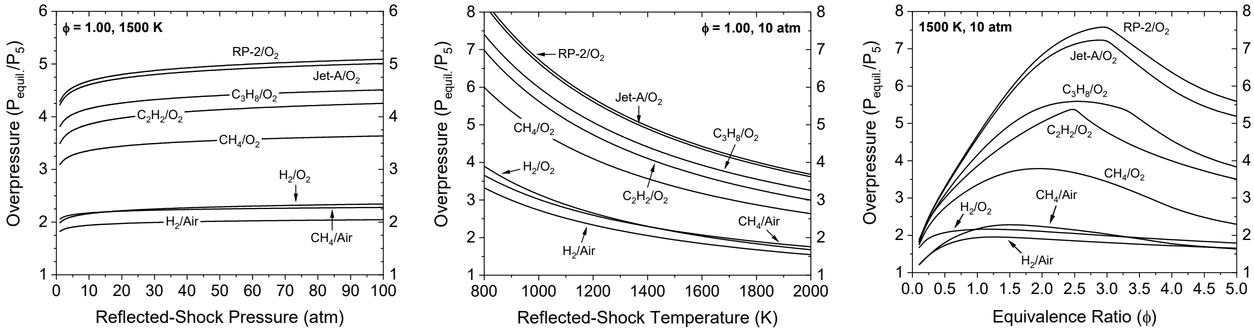
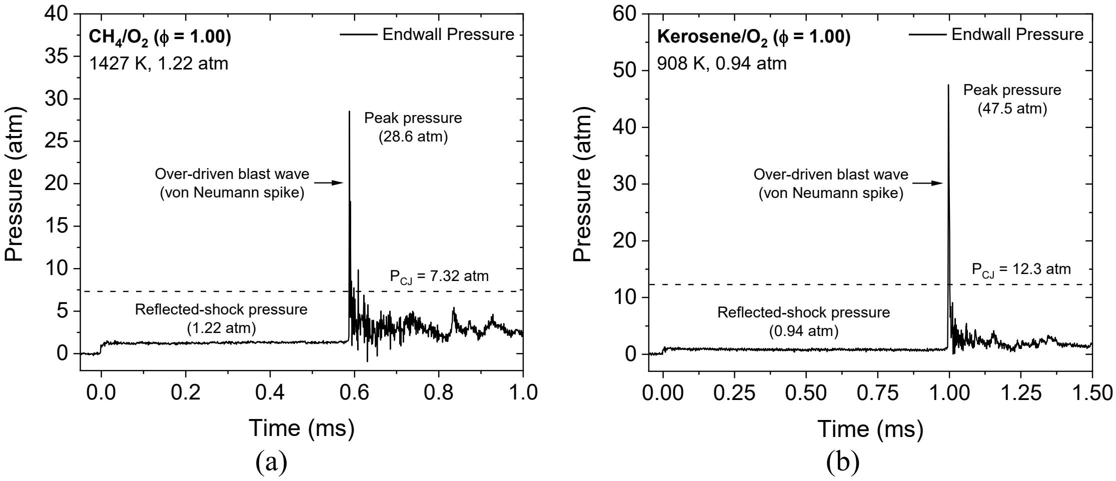
post-ignition pressures in oxy-fuels at laboratory-scale conditions, a chemical equilibrium analysis (CEA) via a Gibb's free-energy minimization was performed using the chemical and phase equilibrium model in Chemkin-Pro 2019 R2 package from ANSYS with constant volume-internal energy (C*V*-*U*) assumptions [4]. Chemical reactions and thermochemical data from FFCM-2 [5] were used for all oxy-fuel systems with the exception of Jet-A/O_2 and RP-2/O_2, for which chemical reactions and thermochemistry were obtained from the Hybrid Chemistry (HyChem) model [6]. The CEA results for stoichiometric hydrogen-oxygen, hydrocarbon-oxygen, and two fuel-air systems are presented in Fig. 1 for a wide range of conditions germane to shock-tube kinetics experiments, where two distinct overpressure regimes separate the behavior of oxy-fuel and fuel-air systems. Overpressure was defined herein as the equilibrium pressure associated with the exothermicity of the chemical reaction ($P_{\text{equil.}}$) relative to the reflected-shock pressure (P_5). Shock-induced ignition at 1500 K across test pressures up to 100 atm in the hydrocarbon-oxygen fuel systems is anticipated to produce post-combustion pressures approximately 3–5 times greater than the test pressure where fuel-air systems are equilibrated at approximately 1.75–2.25 times that of the test pressure (Fig. 1a). A noteworthy result is that H_2/O_2 behaves similarly to the fuel-air systems, suggesting a wider range of conditions may be safely explored in current facilities compared to the other oxy-fuels (Figs. 1a, b, and c).



(a) (b) (c)

Figure 1: Overpressure estimation via chemical equilibrium analysis (C*V*-*U*) for various fuel/O_2 mixtures and two fuel/air mixtures: (a) trends with reflected-shock pressure; (b) trends with reflected-shock temperature; (c) trends with equivalence ratio

While equilibrium analysis is useful in describing aspects of the post-combustion environment for a range of experimental conditions, the final thermodynamic state can often be underpredicted by constraining the energy available to influence changes in temperature and pressure to chemistry alone and neglecting the presence of gas-dynamic processes that may result from high mixture exothermicity. If the chemical reaction behind the reflected shock wave is sufficiently exothermic, the resulting high-temperature gases will rapidly expand away from the endwall region and form a strong shock front, ultimately creating the conditions necessary to sustain a detonation [7]. Recent experiments performed in the authors' laboratory have captured extreme pressure spikes, reminiscent of a detonation-like event, in both CH_4/O_2 and a kerosene-based fuel in pure O_2, demonstrating the energy release in non-dilute experiments (see Fig. 2). Endwall pressure data sampled at 1 MHz revealed the presence of a steep front forming near instantaneously from the reflected-shock conditions where the peak pressure exceeds the Chapman-Jouguet pressure by a factor of approximately 4 in both oxy-methane and oxy-kerosene. Note that greater peak pressures during the experiments in Fig. 2 may exist beyond what is presented, but capturing further details would require faster sampling rates. Nonetheless, the authors recommend caution when performing shock-tube experiments in oxy-hydrocarbon mixtures at any condition, as experimental pressures regularly exceed both C-J and CEA predictions.



(a) (b)

Figure 2: Experimental endwall pressure data for stoichiometric (a) CH_4/O_2 at 1427 K and 1.22 atm; and (b) Kerosene/O_2 at 908 K and 0.94 atm.

3 Test-Time Limitation

Perhaps the most significant limiting factor in oxy-fuel ignition experiments is the test time available for chemical reactions to occur, especially in shock tubes with short section lengths. In a typical experiment, the conditions behind the reflected shock wave are uniform until a gas-dynamic event, such as an interaction between the reflected shock wave and the contact surface or the arrival of the reflected rarefaction fan, disturbs the test conditions. Due to the absence of a carrier gas coupled with high fuel loading, the strength of the shock required to produce a desired test temperature in non-dilute oxy-fuels often exceeds that of highly diluted or fuel-air mixtures. Consequently, the contact surface will travel faster as the gases behind the incident shock wave will have greater velocity (u_2), and therefore the collision with the reflected shock wave may occur sooner. In many cases, this collision results in a strong compression wave traveling into the test section, producing equilibrium pressures of up to 3 times that of the test pressure, and often occurring before kinetic (i.e., 0-D) ignition takes place at the reflected-shock conditions.

To illustrate the challenges that may arise when performing oxy-fuel experiments behind the reflected shock wave, unpublished data for undiluted CH_4/O_2 obtained in the authors' laboratory are presented. An experiment at a temperature of 1137 K is shown, where a compression of the unburned test gases takes place, leading to an undesired ignition event (see Fig. 3). Endwall pressure data was used as the primary diagnostic when analyzing the details of the experiment, and both sidewall pressure and endwall OH* data were used supplementarily to observe any non-idealities. A collision between the contact surface and the reflected shock wave generates a compression wave that arrives at the endwall at 910 μs. The test-gas pressure rises for approximately 400 μs before stabilizing near 1.46 atm where ignition then takes place at 1.84 ms, as evidenced by a steep rise in both the end- and sidewall pressure signal coupled with simultaneous OH* production observed at the endwall. Assuming an isentropic compression process, the corresponding temperature can be estimated at 1211 K. Consequently, ignition takes place sooner at this higher temperature than if it were to occur free from an additional compression.

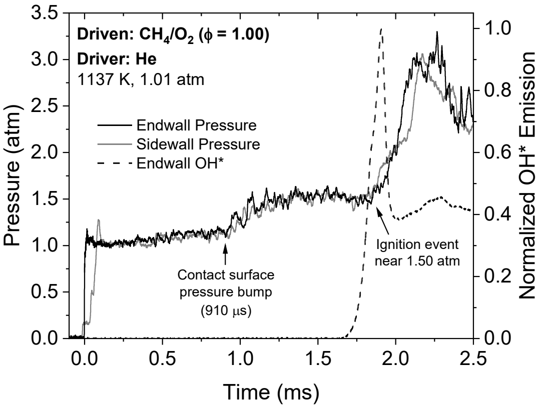


Figure 3: Representative experimental case of a test-gas compression prior to ignition from an interaction between the reflected shock wave and contact surface.

Using the methods of Gaydon and Hurle [7], the arrival of the contact surface in region 5 was estimated for a stoichiometric CH_4/O_2 mixture over 1300–1600 K in a high-pressure shock-tube facility at Texas A&M University (see Fig. 4). This arrival time depends on the thermodynamics of the mixture that govern wave propagation, the speed of the shock wave, and the length of the driven section. In this relatively narrow temperature range, the contact surface time of arrival is nearly linear when plotted on a logarithmic scale. Ignition delay times were simulated in Chemkin-Pro using the FFCM-2 and GRI-Mech 3.0 models [5,8]. For illustration, ignition delay time results are plotted against temperature, as opposed to the usual inverse of temperature, which give a decreasing trend. The intersection of the simulated ignition delay times with the contact surface time of arrival represents the effective test-time limit within the boundaries of this analysis. If an experiment were to occur to the left of this proposed limit, a disturbance from the contact surface would take place before ignition (slow chemistry) and therefore experiments become limited to a region of fast chemistry where ignition occurs before the arrival of the contact surface. For the driven section lengths of the high-pressure shock tube used in this study (L_{driven} = 4.92m), the estimated test time limit is posed to exist near 480 μs, which corresponds to reflected-shock temperatures in the range of 1439–1469 K. Since ignition delay times are not typically reported below 100 μs due to the relative uncertainty in a measurement on that timescale, this constrains a set of potential experiments to a narrow temperature range of less than 200 K. According to this procedure, the limit is clearly dependent on the kinetics model used, as results for simulated ignition delay may differ depending on the construction of the models, which have not been experimentally validated due to the lack of published data in pure-O_2-based mixtures.

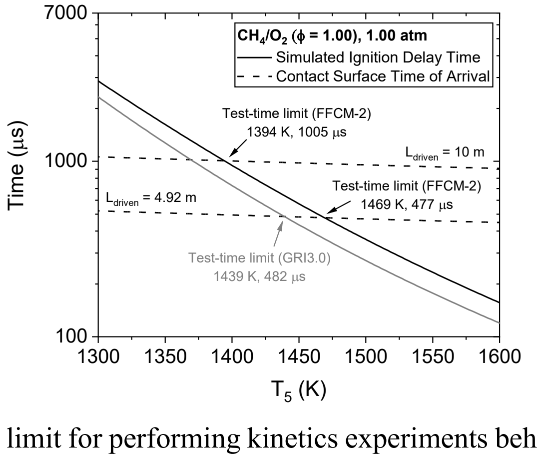


Figure 4: Estimated test-time limit for performing kinetics experiments behind the reflected shock wave for a stoichiometric CH_4/O_2 mixture across reflected-shock temperatures of 1300–1600 K.

4 Limitations of Conventional Tailoring Methods

Contact-surface tailoring is an established technique for extending experimental test times behind the reflected shock wave by mitigating resultant wave propagation in the test section after a reflected-shock/contact-surface collision. This phenomenon may not always be achievable in pure oxy-fuels when using helium as the primary driver gas. For demonstration, tailoring curves were generated for a non-reactive, "stoichiometric" CH_4/N_2 test mixture, as per the methods of Amadio et al. [9], to map the required heavy gas concentration in He to achieve the tailored condition at a specified reflected-shock temperature. The characteristics of each gas mixture, such as molecular weight and specific heat ratio, are plotted against one another, and the point where the tailored composition lies in each gas mixture is connected to form the tailoring curve. These curves can theoretically be generated for any gas mixture; however, Ar, N_2, CO_2, and C_3H_8 were chosen as the heavy gas species for their general availability and range of applicability in shock-tube experimentation. For highly diluted test mixtures (>95% Ar by vol.), He-based driver mixtures provide adequate tailoring over a wide temperature range, since monatomic species are more easily shock-heated (i.e., a lower M_s is required to produce T_5 in Ar than N_2). In contrast, pure oxy-fuels and their non-reactive substitutes (fuel/N_2) require larger Mach numbers due to the high fuel loading and lack of a diluent species. Therefore, the tailoring curves are shifted closer to pure helium and the overall temperature range where tailoring may be achieved becomes severely limited. In other words, the concentration of the heavy gas is dramatically reduced to ensure the required shock strength is achieved.

Once such example of this limit is demonstrated in Fig. 5 for tailoring at lower temperatures of 800 and 1000 K. Note that the axes were scaled to highlight the details of the tailoring curve and therefore the profile of the gas composition curves are reduced significantly. When calculating the tailored condition with an area ratio of unity, no solution exists for temperatures beyond 1100 K, which necessarily implies that an interaction with the contact surface will influence disturbances behind the reflected-shock wave prior to ignition at greater temperatures. For example, simulations of stoichiometric CH_4/O_2 ignition at 1100 K and 1.00 atm from FFCM-2 result in an IDT of approximately 34 ms. A monotonic divergence at the diaphragm exaggerates this limitation, as greater pressure ratios are required to achieve a desired shock strength, which ultimately affects the tailored composition [10]. This behavior is evidenced in Fig. 5 by the tailoring curve for 800 K in a shock tube with $A_4/A_1 = 0.25$, where the tailored composition is almost entirely helium. Tailoring the contact surface for greater temperatures in a shock tube with these dimensions is not possible with He-based mixtures and therefore avoiding disturbances during experiments becomes especially challenging. To combat this constraint, alternative test-time extension methods must be explored. Experiments using H_2-based driver mixtures for tailoring the contact surface are ongoing in the authors' laboratory, and favorable results have been observed in CH_4/N_2, H_2/N_2, $(H_2{:}CO)/N_2$, and C_3H_8/N_2 mixtures over a wide reflected-shock temperature range.

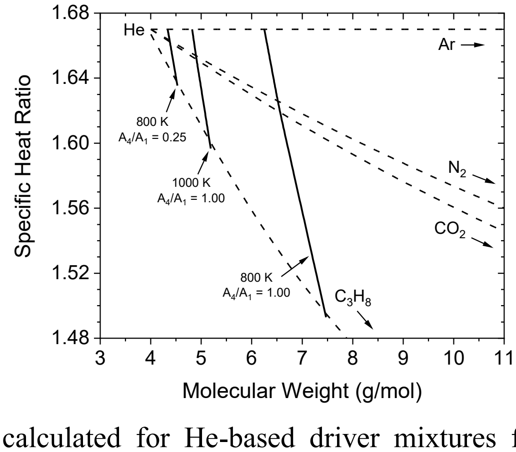


Figure 5: Tailoring curves calculated for He-based driver mixtures for 800 K and 1000 K in a conventional shock tube ($A_4/A_1 = 1.00$) and 800 K in a diverging shock tube ($A_4/A_1 = 0.25$).

5 Conclusion

Shock-tube ignition experiments in undiluted environments contain a unique set of challenges that exist in addition to known non-ideal effects, such as d*p*/d*t* and reflected-shock bifurcation. Significant reaction exothermicity, disturbances from strong interactions with the contact surface, and limitations of standard tailoring techniques can influence the range of conditions targeted for investigation and are likely responsible for the general lack of experimental data found in the open literature. Data obtained in our laboratory has revealed that measured overpressures in pure fuel/O_2 experiments can reach up to 50 times that of the reflected-shock pressure, which is well beyond both C-J and CEA predictions. A test-time estimation was performed for a stoichiometric CH_4/O_2 mixture where calculations show that precise kinetics measurements may be restricted to within a 200-K temperature range. Experiments have confirmed the collision with the contact surface prior to ignition occurs near this estimated temperature range, and extreme cases have resulted in up to a 300% increase in pressure for non-reactive fuel/N_2 mixtures. Test times may be extended by increasing driven section lengths; however, this endeavor may not be realistic within the dimensions of existing laboratory spaces.

Standard methods for tailoring the contact surface are generally unsuccessful when implementing common driver-gas mixtures with helium as the primary driver gas, especially in diverging shock tubes that require greater pressure ratios to achieve desired shock-tube flows. Adequate tailoring has been accomplished using H_2-based driver mixtures, and test times in four different non-reactive fuel/N_2 mixtures have been increased by up to 500%. Further details on d*p*/d*t* and bifurcation effects in undiluted mixtures are presented in an ongoing work. To the best of our knowledge, the experimental challenges presented herein have not been previously documented in the literature for the oxidation of fuels in undiluted environments.

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