

Constrained Reaction Volume: A Strategy for Reflected Shock Wave Kinetics Experiments

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1 Introduction

Ignition experiments behind reflected shock waves in unconstrained reaction volumes can exhibit several types of undesired phenomena, including non-localized (remote) ignition and heat-release-induced pressure changes that negate the common assumptions of a constant volume reaction environment. We report here a strategy for conducting high-temperature kinetics experiments behind reflected shock waves in a constrained reaction volume. We demonstrate that this strategy successfully eliminates the occurrence of non-localized ignition; furthermore, we show that the same strategy can also effectively minimize or eliminate any pressure changes due to ignition heat release, thereby enabling kinetics modeling that extends through the complete ignition event using a simple and straightforward specified pressure and enthalpy constraint.

We present the results of ignition experiments conducted behind reflected shock waves in a high-purity kinetics shock tube and we show the utility of using a staged-filling strategy to constrain the combustible test gas to a small volume adjacent to the endwall of the shock tube. Pressure and OH emission measurements from hydrogen-oxygen experiments are shown to demonstrate that experiments with a constrained reaction volume do not exhibit remote ignition, and also that reduction in the size of the constrained reaction volume leads to removal of heat-release-induced pressure change during ignition. Ethylene-oxygen ignition experiments were also conducted, and we show that temperature and OH mole fraction time-history measurements compare well with kinetic simulations under an assumption of specified pressure and enthalpy.

2 Experimental method

The experimental apparatus and diagnostics have been described in detail elsewhere [1]; thus, only a brief description will be provided of the details relevant to the current work. The Stanford University ultra-high-purity kinetics shock tube has an 8.54-m-long driven section, where five axially-spaced pressure transducers are located at 2 cm, 38.8 cm, 69.3 cm, 99.7 cm and 130.2 cm away from the endwall. Optical access ports were located at the axial location 2 cm from the endwall where optical diagnostics were set up to measure OH emission, ethylene mole fraction [3], OH mole fraction [4], and temperature [5]. Tailored driver gas mixtures of nitrogen in helium were used to achieve reflected-shock test times of greater than 6 ms. Non-reactive experiments in this shock tube show that

a nearly steady pressure rise of $dP_5/dt \approx 1.7\%/ms$ is present in all experiments due to non-ideal facility-dependent effects.

The conventional operation procedure for ignition experiments behind reflected shock waves in this facility involves filling the driven section of the shock tube with a premixed combustible test gas mixture until a desired pressure P_I is achieved. An incident shock wave, created through rupture of a diaphragm, is sent through the test gas to heat and compress the combustible mixture before a reflected shock wave further heats and compresses the test gas to the desired temperature T_5 and pressure P_5 . In this conventional shock tube operation, the reaction volume (i.e., the compressed volume of the combustible test gas) can extend a length of a few, typically one to three, meters from the driven section endwall, if completely compressed by the reflected shock wave.

To minimize the volume of reactive gases to a small volume that extends just past the measurement location in the shock tube, we used the staged-filling strategy presented here. First, the driven section is filled with the desired combustible test gas mixture to a pressure P_I^a . Immediately after the test gas filling, argon is introduced slowly into the driven section at an axial location 40 cm from the diaphragm until a total pressure of P_I is reached, effectively compressing the test gas to a small reaction volume near the measurement location with a nominal length $L_I = (8.54 \text{ m} - 0.40 \text{ m})(P_I^a)/(P_I)$ that extends from the driven section endwall, assuming no mixing at the interface of the argon and the test gas. The incident shock wave is then generated as quickly as possible, and after compression by the reflected shock wave, the heated reaction volume will extend a length of $L_5 = (L_I)(T_5 P_I)/(P_5 T_I)$ from the driven section endwall, again assuming no mixing at the interface of the nonreactive and reactive gases. Figure 1 illustrates the different length scales in this staged-filling technique.

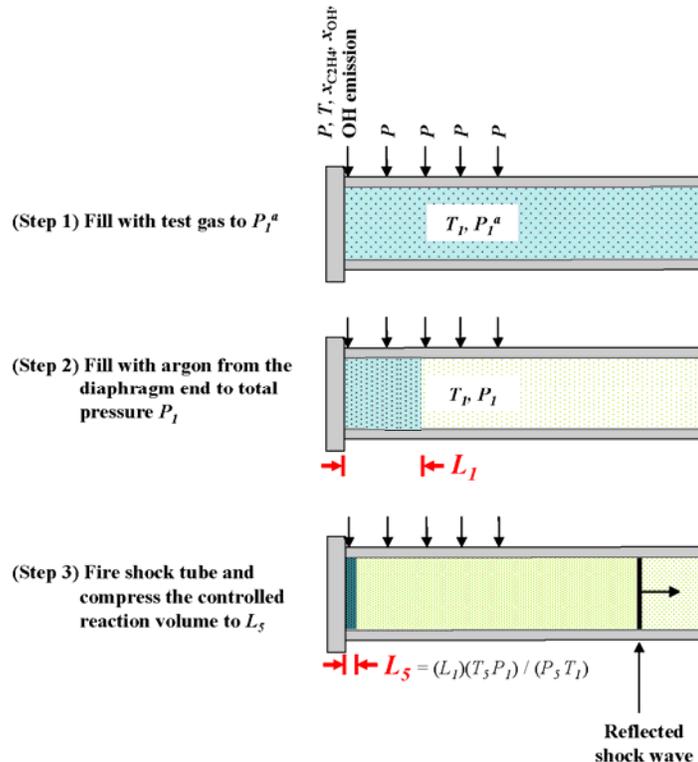


Figure 1. Schematic of the test gas volumes during each step in the staged-filling strategy. Shown is the ideal test gas volume with L_5 such that the constrained reaction volume extends just past the measurement location.

To characterize the mixing and possible dilution of the test mixture in the constrained reaction volume by argon, we conducted extensive tests with variable filling rates. We used laser absorption at 10.532 μm at multiple axial locations to measure ethylene mole fraction in a non-reactive test gas mixture of 0.5% C_2H_4 . The results indicated that a constrained reaction volume of length greater than or equal to $L_5 \approx 15$ cm was sufficient for our particular staged-filling strategy, in order to achieve negligible dilution of the test mixture at the measurement location of 2 cm from the endwall. For a constrained reaction volume of length $L_5 = 6$ cm, we found that a dilution resulting in a 20% ethylene loss occurred due to mixing with the argon introduced in the second filling stage.

4 Hydrogen-oxygen ignition results

Figure 2 presents the measured pressure time-histories at five different shock tube axial locations for an experiment of a 4% H_2 , 2% O_2 , argon reactive mixture in an unconstrained reaction volume at $T_5 = 965$ K and $P_5 = 3.4$ atm. These results clearly illustrate the occurrence of non-localized ignition where heat-release-related pressure change clearly occurs 38.8 cm from the endwall before being observed at 2 cm from the endwall. We have found that in our shock tube facility, this non-localized ignition phenomenon occurs for a mixture of 4% H_2 , 2% O_2 , balance argon at temperatures below approximately 1000 K, and that the location of the first ignition varies with temperature.

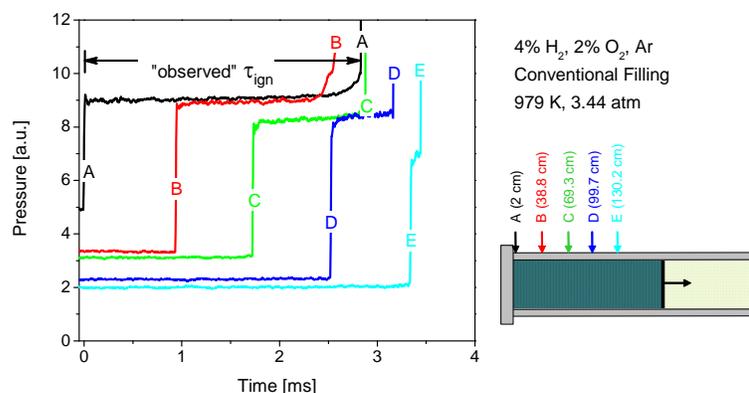


Figure 2. Pressure traces at five measurement locations for a stoichiometric hydrogen-oxygen mixture with conventional shock tube operation; non-localized ignition originates at measurement location B. The pressure traces are staggered vertically for differentiability; the first rise indicates the passing of the reflected shock wave and the second rise is the ignition. The “observed” experimental ignition delay time at the measurement location A is also indicated.

Because this non-localized ignition phenomenon can complicate the interpretation of measured ignition delay times, we applied our staged-filling strategy to achieve a constrained reaction volume such that there is no reactive mixture to ignite away from the measurement location. Figure 3 shows a set of measured pressure traces for constrained reaction volumes with length $L_5 = 22$ cm and $L_5 = 11$ cm for experiments at a nominal temperature of $T_5 = 965$ K. We can see that in a constrained reaction volume with length $L_5 = 22$ cm, heat release due to reaction (leading to minor pressure rise near 2 ms) originates away from the endwall near the 38.8 cm axial location, but an abrupt rise in pressure occurs first at the measurement location 2 cm from the endwall. By reducing the size of the constrained reaction volume to $L_5 = 11$ cm, we can completely eliminate the appearance of any initial remote pressure rise due to reaction occurring.

We can reduce the effect of reaction heat release on the post-ignition pressure change by further reducing the size of the constrained reaction volume; Figure 4 shows a set of measured pressure traces for constrained reaction volumes with length $L_5 = 6$ cm and $L_5 = 4$ cm for experiments at a nominal temperature of $T_5 = 965$ K, where the pressure trace measured for the $L_5 = 4$ cm is nearly linear, with negligible ignition-induced change and rising only to follow the facility-induced dP_5/dt measured in the non-reactive experiments. As shown in Figure 4, the OH emission can be used to mark the time of ignition when no pressure change occurs. Although some dilution of the initial reactive mixture occurs with $L_5 = 4$ cm, the actual reactive mixture composition can be quantified by laser absorption measurements (typically of the fuel component) at the 2 cm measurement location just before or immediately after the reflected shock passage.

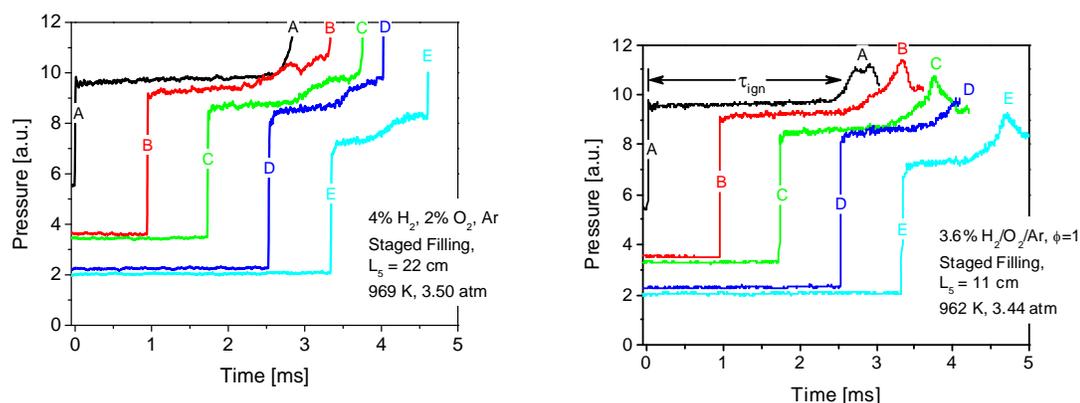


Figure 3. Pressure traces for hydrogen-oxygen mixture with the staged-filling strategy to achieve a constrained reaction volume of different lengths with negligible dilution of the test mixture. Measurement locations are the same as in Figure 2. (LEFT) $L_5 = 22$ cm and (RIGHT) $L_5 = 11$ cm.

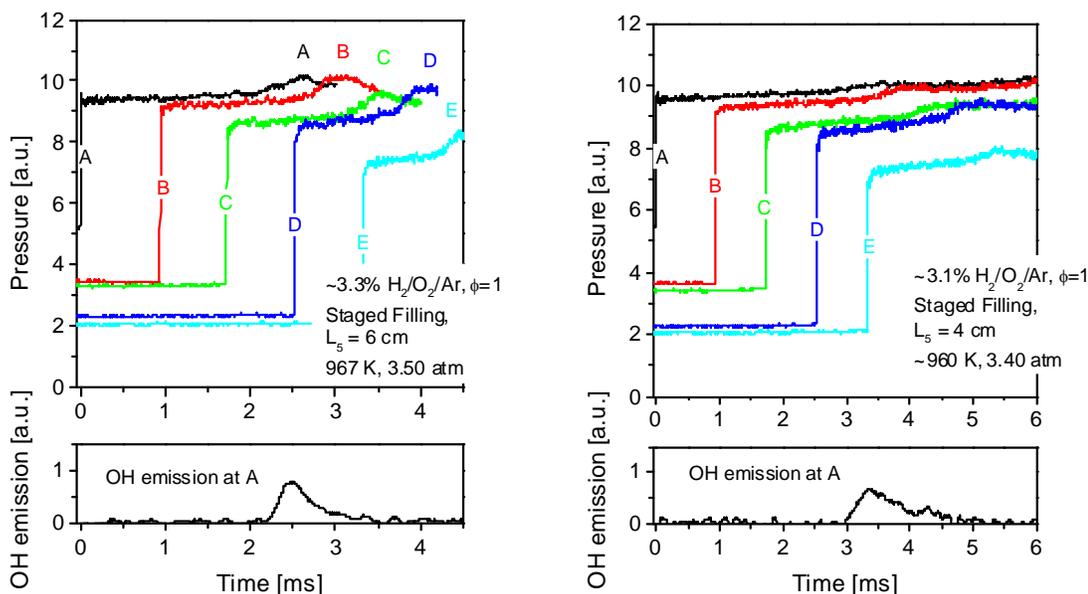


Figure 4. Pressure traces for hydrogen-oxygen mixture with the staged-filling strategy and a constrained reaction volume of different lengths; some dilution of the nominal test mixture is present, but this can be quantified by laser absorption measurements of the mixture composition at measurement location A. Measurement locations are the same as in Figure 2. (LEFT) $L_5 = 6$ cm and (RIGHT) $L_5 = 4$ cm. The measured OH emission is also shown for both cases.

5 Ethylene-oxygen ignition results and constant P and H modeling

Experiments were carried out in a constrained-reaction-volume mixture of 0.38% C_2H_4 , 3.8% O_2 , 1.5% CO_2 , argon. Example measured pressure and temperature traces for a constrained reaction volume of length $L_5 = 6$ cm at reflected-shock conditions of $T_5 = 1135$ K and $P_5 = 2.3$ atm is shown in Figure 5, illustrating that using the staged-filling strategy to achieve a constrained reaction volume can also effectively eliminate the post-ignition pressure rise during ethylene-oxygen ignition; in comparison, in a similar experiment with an unconstrained reaction volume, a heat-release-induced pressure rise of approximately 30% occurs at the onset of ignition.

Due to the absence of pressure change at ignition in the constrained reaction volume experiments, we expect that we can successfully model the kinetics of the combustion reaction through the ignition event using a specified P and H constraint in the CHEMKIN-Pro suite of programs by Reaction Design (where the time-varying P is specified to have a gradual pressure rise of 1.7%/ms, the measured dP_5/dt). The simulated temperature time-histories using the GRI-Mech 3.0 [6] and JetSurF 2.0 [7] mechanisms are shown in Figure 5 in comparison to measurements based on two-line CO_2 laser absorption. The temperature simulation from the GRI-Mech 3.0 [6] mechanism fails to predict the temperature time-history during ignition; however, the JetSurF 2.0 mechanism under our specified P and H constraints is in excellent agreement with the data, supporting our hypothesis that the specified P and H assumption is an accurate assumption for constrained-reaction-volume experiments where there is negligible pressure change due to ignition.

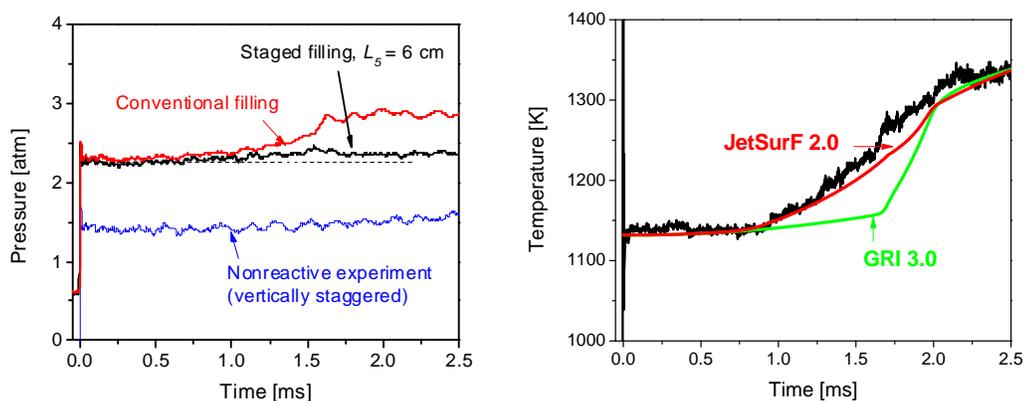


Figure 5. Measured (LEFT) pressure and (RIGHT) temperature time-histories for ethylene-oxygen ignition in a constrained reaction volume of $L_5 = 6$ cm, and also traces for a non-reactive experiment at similar conditions. Also shown are simulated temperature time-history from the GRI-Mech 3.0 [6] and JetSurF 2.0 [7] mechanisms. Reflected shock conditions: $T_5 = 1135$ K, $P_5 = 2.30$ atm. Test gas mixtures: 0.38% C_2H_4 , 3.8% O_2 , 1.5% CO_2 balance Ar.

OH mole fraction time-histories were also measured in the ethylene-oxygen ignition experiments; an example data trace is shown in Figure 6, compared with the simulated OH mole fraction from the GRI-Mech 3.0 [6] and JetSurF 2.0 [7] mechanisms. The GRI-Mech 3.0 mechanism accurately predicts the ignition delay time (marked by the long steep rise of OH mole fraction); however, the GRI-Mech 3.0 mechanism does not accurately predict the OH mole fraction profile shape. In comparison, the JetSurF 2.0 mechanism over-predicts the ignition delay time by approximately 5%; however, the simulated OH mole fraction from the JetSurF 2.0 mechanism captures the subtle features of the measured trace better than the GRI-Mech 3.0 mechanism, such as the initial formation of OH (near 600 μ s), and the steady rate of decay after the peak OH mole fraction (after 2 ms).

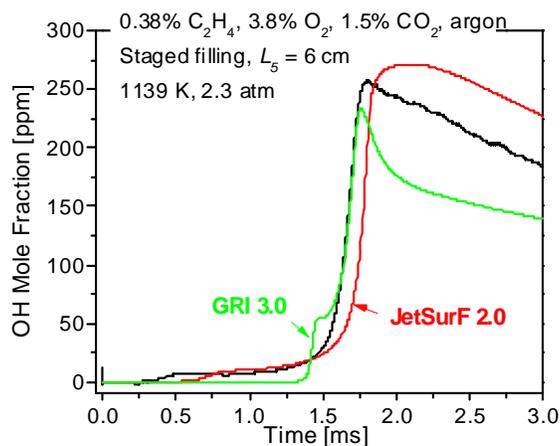


Figure 6. Measured OH mole fraction for ethylene-oxygen ignition in a constrained reaction volume of $L_5 = 6$ cm. Also shown are simulated time-histories from the GRI-Mech 3.0 [6] and JetSurF 2.0 [7] mechanisms.

6 Concluding remarks

The staged-filling strategy reported achieves a constrained reaction volume in reflected shock wave experiments, thereby eliminating non-localized (remote) ignition and also effectively eliminating pressure changes due to ignition heat release. This strategy has the potential for enabling more quantitative study of combustion kinetics in new shock tube experiments.

Acknowledgement

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