

Acceleration of Shock-Induced Ignition in CH₄/Air and CO/Air Mixtures Using Hydrogen Addition

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Introduction

When considering the shock-induced ignition of common fuels, it is well known that methane produces the longest ignition delay times of all the hydrocarbons (Lifshitz et al., 1971; Petersen et al., 1996). In contrast, hydrogen produces some of the shortest ignition delay times of all fuels, even when compared to higher-order hydrocarbons. For applications involving phenomena such as supersonic combustion or detonation waves, short ignition delay times are desirable. In situations where hydrocarbon fuels are preferred because of their higher energy densities, one way to accelerate the ignition process is to add hydrogen. In applications such as power generation gas turbines, the fuel blends may already contain levels of hydrogen, particularly coal-derived fuels containing mostly CO and H₂. Fundamental data on the effects of H₂ addition are useful for obtaining a better understanding of the chemical kinetics of ignition behind shock waves and the ignition of hydrogen-containing fuel mixtures in general.

To date, few shock-induced data exist from experiments wherein H₂ was added to a slower reacting fuel such as methane. Cheng and Oppenheim (1984) performed one major study involving combinations of H₂ and CH₄. They looked at a wide range of CH₄/H₂ mixtures and stoichiometry, with the % H₂ varying from 0 to 100%. For all cases, the argon dilution was 90%, and the pressure ranged from 1 to 3 atm. The focus of their work was on the transition from weak to strong ignition behind reflected shock waves. In an earlier study, Lifshitz et al. (1971) looked at the effect of small levels (< 10%) of hydrogen addition on methane ignition.

From all of these shock-tube experiments, the general conclusion was the same, i.e., the ignition of the methane-based mixtures was accelerated dramatically upon addition of hydrogen. The effect tended to increase with increasing levels of H₂. No shock-tube ignition studies were found that deal with the effects of hydrogen addition on CO/air mixtures, nor were there any hydrogen-enhanced ignition studies at pressures higher than a few atm prior to the present study. Presented in this paper are the results of a series of shock-tube experiments using CH₄/H₂ and CO/H₂ combinations in fuel-lean mixtures with air, at reflected-shock pressures as high as 25 atm.

Experimental Apparatus

A helium-driven shock tube with a 16.2-cm-Dia, 10.7-m-long driven section was used to measure the ignition delay times (Petersen et al., 2004, 2005). All experiments were performed behind reflected shock waves. The ignition times were defined as the time when ignition occurred in the gas mixture at the endwall; this was because the fuel/air mixtures were undiluted,

so that the large heat release at the time of ignition led to significant gas dynamic effects that make the sidewall ignition appear faster. The delay times were inferred from a PCB 134A pressure transducer and a photomultiplier tube (Hamamatsu 1P21) detector monitoring either CH ($A^2\Delta \rightarrow X^2\Pi$) (i.e., CH*) chemiluminescence through a 430 ± 5 nm bandpass filter or OH ($A^2\Sigma^+ \rightarrow X^2\Pi$) (i.e., OH*) chemiluminescence emission through a 310 ± 5 nm bandpass filter. For all experiments, ignition was marked by the rapid increase in the CH* or OH* signal. Since chemiluminescence from either species has been shown to be a good marker of ignition in shock-tube studies of hydrocarbon oxidation (Hall et al., 2005), τ_{ign} is defined herein as the sudden rise in either CH* or OH*.

Four different mixtures were studied, as shown in Table 1: two CH₄/H₂ and two CO/H₂ combinations. The results from these mixtures are presented as follows.

Table 1. Mixtures used in shock-tube ignition study.

Mixture	Blend	X _{CH4}	X _{H2}	X _{CO}	X _{O2}	X _{N2}
1	80/20% CH ₄ /H ₂	0.0466	0.0117	--	0.1978	0.7439
2	60/40% CH ₄ /H ₂	0.0420	0.0280	--	0.1950	0.7350
3	60/40% CO/H ₂	--	0.0694	0.1042	0.1736	0.6528
4	40/60% CO/H ₂	--	0.1042	0.0693	0.1736	0.6529

Methane/Hydrogen Ignition

Two fuel-lean CH₄/H₂/air mixtures were studied, with CH₄/H₂ ratios of 80/20 and 60/40 (Table 1). Both mixtures had fuel/air equivalence ratios (ϕ) of 0.5. The shock-tube data cover a small range of pressures near 21 atm (i.e., 18.2-25.3 atm) and temperatures from 1130 to 1460 K. These data are shown in Fig. 1 in a plot of τ_{ign} versus $1/T$. Also shown in Fig. 1 are the results from methane-only experiments for a similar pressure range, shown in the form of correlation lines from Petersen et al. (2005).

Two observations are most notable. The first observation is that the addition of H₂ reduced the ignition delay time significantly when compared to the methane-only case. For example, the 20% H₂ addition decreased reaction times by a factor of 3, and the 40% addition by nearly a factor of 10. This is not unexpected, however, and the effect increases with increasing level of H₂ in the fuel mixture (Cheng and Oppenheim, 1984). The second observation is that the hydrogen addition did not seem to shift the dominant kinetic regime for the two CH₄/H₂ mixtures in this study; that is, the activation energies (or slopes) of the ignition delay time curves in Fig. 2 differ very little from the CH₄-only mixture over comparable temperature ranges (about 40 kcal/mol at higher T and 20 kcal/mol at lower T).

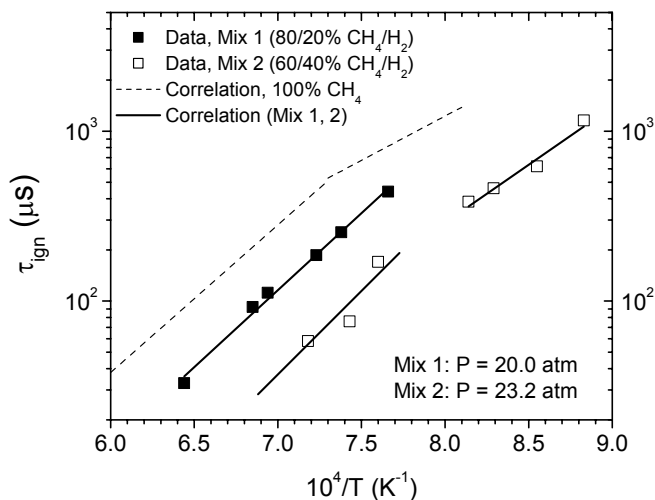


Figure 1. Ignition delay times for the methane/hydrogen fuel mixtures. The 100% CH₄ correlation is from Petersen et al. (2005).

Carbon Monoxide/Hydrogen Ignition

Table 1 shows the two CO/H₂ fuel blends studied, 60/40 and 40/60, both of which were mixed with air at $\phi = 0.5$. These fuel combinations were considerably more reactive than the CH₄/H₂ mixtures. Because of their high reactivity, shock-tube experiments leading to reflected-shock pressures on the order of 10-20 atm could not be performed because the mixtures reacted behind the incident shock wave at the higher pressures, causing an acceleration of the incident wave. Presented herein are the results of experiments covering reflected-shock pressures on the order of 1 atm and temperatures between 900 and 1260 K. Chemiluminescence from OH* was used as the ignition marker. The results of both mixtures at a pressure of 1 atm are provided in Fig. 2. Most notable is the small activation energy (~ 14 kcal/mol) exhibited by both mixtures at the higher temperatures and the marked change in slope at lower temperatures, reminiscent of the second explosion limit in pure H₂ oxidation (Petersen et al., 2004). Interestingly, both mixtures have similar ignition delay times over the same temperature range.

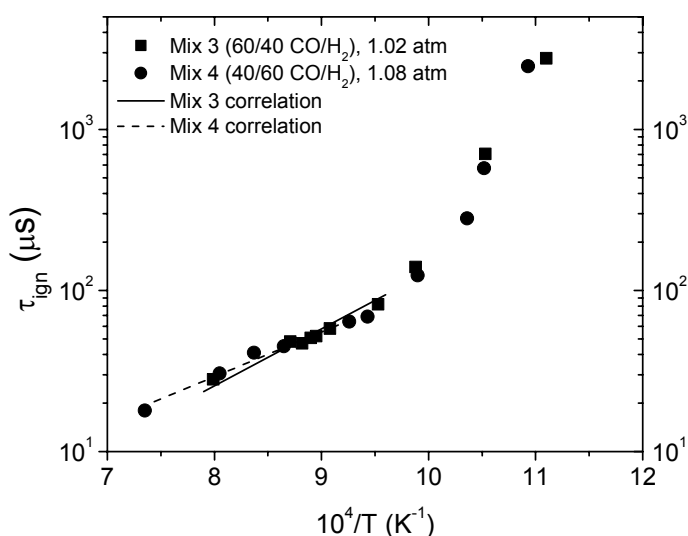


Figure 2. CO/hydrogen fuel mixture ignition delay times.

One observation directly related to the high reactivity of the CO/H₂ mixtures was the tendency for the ignition process to exhibit detonation-like characteristics at lower temperatures, corresponding roughly to the temperature regime of the slope change seen in Fig. 2. This phenomenon is exhibited in Fig. 3. In this figure, endwall pressure traces are plotted for experiments with reflected-shock test temperatures of 1002 K and 941 K. The higher-temperature experiment exhibits an increase in pressure at ignition similar to that of a constant-volume explosion. However, the lower-temperature pressure trace exhibits a rather steep increase in pressure at the time of ignition. The pressure spike produces a pressure increase that is a factor of ten over the initial reflected-shock pressure, resembling the pressure increase from a C-J detonation wave.

While strong ignition is often seen in shock-tube studies with highly exothermic mixtures, previous work in this area usually indicates that the tendency for strong ignition increases with temperature so that experiments at the higher temperatures would be more likely to accelerate to a detonation wave (Cheng and Oppenheim, 1984). The opposite was seen in the present study with the CO/H₂ mixtures in that the detonation-like phenomena were observed at the lower temperatures. This result may be due to the chemical kinetics and radical buildup at the lower temperatures or to the increased residence times, but further study is required in this area. Although strong ignition pressure spikes were also observed in both CH₄/H₂/air mixtures, the pressure increases were only on the order of 2-3 times the initial reflected-shock pressure.

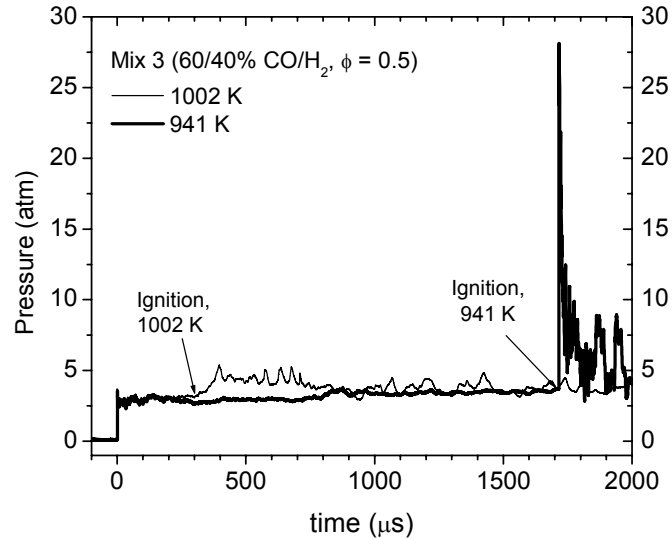


Figure 3. Endwall pressure traces showing ignition phenomena at two different temperatures. The lower-temperature test exhibits detonation-like behavior.

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References

- RK Cheng, AK Oppenheim 1984 "Autoignition in Methane-Hydrogen Mixtures," *Combustion and Flame* 58: 125-139.
- JM Hall, EL Petersen, MJA Rickard 2005 "Comparison of Characteristic Time Diagnostics for Ignition and Oxidation of Fuel/Oxidizer Mixtures Behind Reflected Shock Waves," *Combustion Science and Technology*, in press.
- A Lifshitz, K Scheller, A Burcat, GB Skinner 1971 "Shock-Tube Investigation of Ignition in Methane-Oxygen-Argon Mixtures," *Combustion and Flame* 16: 311-321.
- EL Petersen, JM Hall, SD Smith, AR Amadio, MW Crofton 2005 "Ignition of Lean Methane-Based Fuel Blends at Gas Turbine Pressures," ASME Paper GT2005-68517.
- EL Petersen, DM Kalitan, MJA Rickard 2004 "Reflected Shock Ignition of SiH₄/H₂/O₂/Ar and SiH₄/CH₄/O₂/Ar Mixtures," *Journal of Propulsion and Power* 20 (4): 665-674.
- EL Petersen, M Röhrig, DF Davidson, RK Hanson, CT Bowman 1996 "High-Pressure Methane Oxidation Behind Reflected Shock Waves," *Proceedings of the Combustion Institute* 26: 799-806.