

Experimental Study on the Laminar Flame Speed of Hydrogen Doped with Trimethyl Phosphate

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1 Introduction

Due to the removal of the fire suppressant CF_3Br (Halon 1301) under the Montreal protocol, the fire safety community has great interest in organophosphorus compounds (OPCs) such as trimethyl phosphate (TMP). OPCs have low toxicity, high environmental safety, low cost, and may be a green rival to halogenated compounds [1]. OPCs are also used as simulants for the destruction of chemical warfare agents such as sarin [2]. The lithium-ion battery (LiB) community is also interested in OPCs for flame inhibition, given the increase of LiBs in electric vehicles and their potential to fail and cause fire incidents [3]. Guo et al. details how LiB fires can be traced back to the combustion of electrolytes and that they can be attenuated with functional fire suppressant additives such as TMP.

TMP is a P-containing fire suppressant with the structure shown in Fig. 1. There are a few studies that detail TMP's impact at low concentrations on the laminar flame speed (LFS) of H_2 /air mixtures. Rybitskaya et al. tested the effects of 0.06% TMP on the LFS of H_2 /air mixtures [2]. Korobeinichev et al. investigated the addition of 0.04% TMP by volume to laminar $\text{H}_2/\text{O}_2/\text{N}_2$ flames [4]. There are limited studies that examine TMP addition in varying concentrations. Wang et al. examined the combustion inhibition by TMP on methane/air turbulent flames with a range of 0.0 to 0.9% volume fraction [5]. Bolshova et al. tested the promotion and inhibition mechanisms of TMP and H_2 /air/Ar flames ranging from 0.05% to 1% TMP addition [6]. The potential of TMP to be commonly used in LiBs is a serious consideration, and thus TMP warrants further study to clearly shape its role as a fire suppressant.

The objective of this study was to explore how the equivalence ratio (Φ) of a H_2 /air mixture doped with 0.5% TMP impacts the LFS. Understanding this question is important as different LiB types are created and upon failure may create fires with different Φ . This information could be used to enhance safety and attenuation of LiB fires. In this work, the LFS of a H_2 /air mixture at an elevated temperature with and without a TMP additive was experimentally collected. The experimental methods are presented in the next section and then followed by the LFS results. The results are then compared to the estimations of a mechanism and the results from the literature.

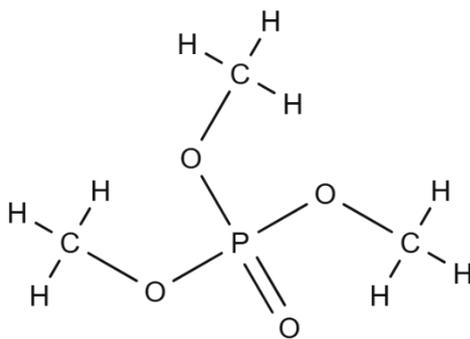


Fig. 1. Structural formula of TMP $(\text{CH}_3\text{O})_3\text{PO}$.

2 Methods / Experimental

This study used spherically expanding flame experiments performed in Texas A&M University's Turbulent Flame Speed Vessel (TFSV). More details on this vessel are provided in Morones et al. [7]. The rig contains 33.8 L of internal volume in a cylindrical shape that is filled with gas mixtures (see Fig. 2). The flame images are viewed through two, 12.7-cm diameter ports placed across from each other. The TFSV has a safety rating that allows experiments up to 10 atm. Ignition of mixtures was accomplished using a spark generated by an ignition coil and an ignitor electrode.

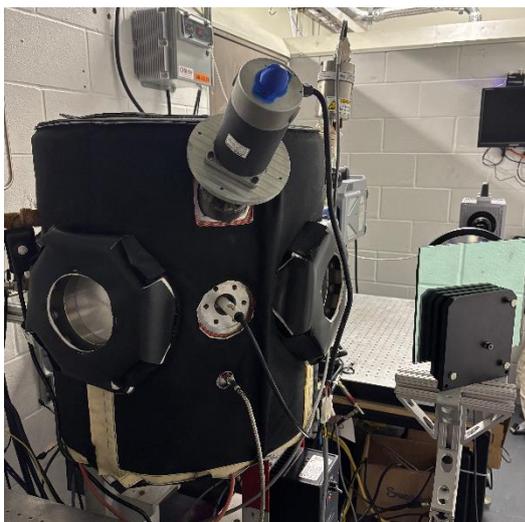


Fig. 2. Turbulent Flame Speed Vessel (TFSV) at the TAMU facility.

The experiments operated at a pressure of 1 atm and 62°C. The temperature was elevated using a custom heating jacket to ensure that the targeted partial pressure of TMP, 0.5% of total pressure ~3.8 torr, was well below that of its vapor pressure (7.6 torr at 62°C). The vapor pressure was calculated with the Clausius-Clapeyron equation using existing vapor pressure data available from Cameo Chemicals and the NIST Chemistry WebBook. This value for vapor pressure was verified as to prevent condensation of the compound in the TFSV during the experiment. Prior to each experiment, the vessel was brought to a near vacuum, and the temperature was verified using a type K thermocouple. Dalton's Law of partial pressures was used for each gaseous mixture. The TMP was provided by Sigma Aldrich with a 99.0% purity, and the gases H_2 and synthetic air (21.0% O_2 , 99.990%; 79.0% N_2 , 99.998%) were provided by Praxair. For the hydrogen-air mixtures doped with 0.5% TMP, TMP was the first component to be added to the vessel as its partial pressure was the lowest of the three components. The liquid TMP was degassed

prior to injection to avoid introducing air. The equivalent mass of TMP to generate 3.8 torr of pressure was injected and was given 30 minutes to settle or until a consistent pressure reading was recorded. After injection, the vessel was filled with H₂ and then air according to the partial pressure calculations that would generate the desired equivalence ratio for the experiment. Fans installed in the rig homogenized the mixture before ignition. The same procedure was followed for the baseline H₂/air experiments without the TMP injection.

A modified z-type schlieren setup like that shown in Fig. 3 captured images of the flame's density gradient after ignition of the mixture. The setup involved the use of a mercury lamp whose light was focused through the TFSV's viewing ports using lenses and mirrors. A Photron FastCam SA-1.1 high-speed camera recorded images of the flame's density gradient as the flame propagated. Due to the characteristics of hydrogen flames, the camera recorded at a frame rate of 25,000 frames per second and a shutter speed of 1 microsecond.

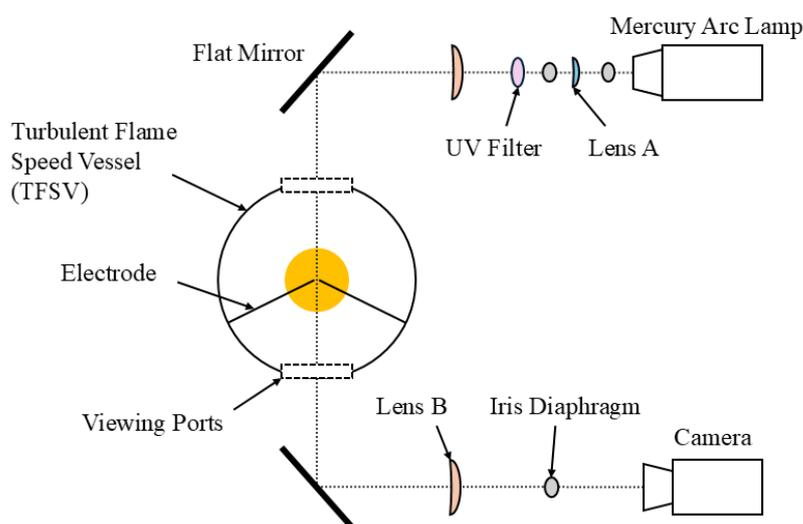


Fig. 3. Diagram of the TFSV schlieren setup.

The recorded images were analyzed using an in-house python script equipped with contrast adjustment and Canny Edge detection [8] to extract the stretched flame's radius at each time step. The radii were then uploaded to a MATLAB script for further examination. This analysis is elaborated by Sikes et al. [9]. The analysis pulls the radii and their respective time steps from the edge detection's output. Then it finds the burned, unstretched laminar flame speed, S_b^0 , with a chosen nonlinear method. There are two nonlinear methods. Eq. (1), which is called NM I, is described by Chen et al. [10]. Eq. (2), referred to as NM II, was originally derived by Kelley and Law [11]. NM I is accurate when the Lewis number (Le) of a mixture is greater than unity, and NM II is accurate for Le less than unity. For this study, NM I was utilized since H₂/air mixtures at fuel rich conditions are known to have a Le greater than unity for $\Phi > 1$, and this study only examined the LFS for $\Phi > 1$ [12]. Figure 4 shows a sample chart of the burned-gas flame speed versus the stretch. It also demonstrates how images that were confinement-affected or nonlinear were excluded from the calculations to produce a more accurate laminar flame speed measurement. Once S_b^0 is acquired, Eq. (3) is used in conjunction with Eq. (4) to determine the unburned, unstretched laminar flame speed S_L^0 . The unburned (ρ_u) and burned (ρ_b) gas densities are provided by an equilibrium chemistry solver in Chemkin. The modeled laminar flame speeds were computed using the Lawrence Livermore National Laboratory (LLNL) OPC mechanism developed by Korobeinichev et al. [13].

$$S_b = S_b^0 - S_b^0 L_{M,b} \frac{2}{r} \quad (1)$$

$$\ln S_b = \ln S_b^0 - S_b^0 L_{M,b} \frac{2}{r S_b} \quad (2)$$

$$S_L^0 = \frac{S_b^0}{\sigma} \quad (3)$$

$$\sigma = \frac{\rho_u}{\rho_b} \quad (4)$$

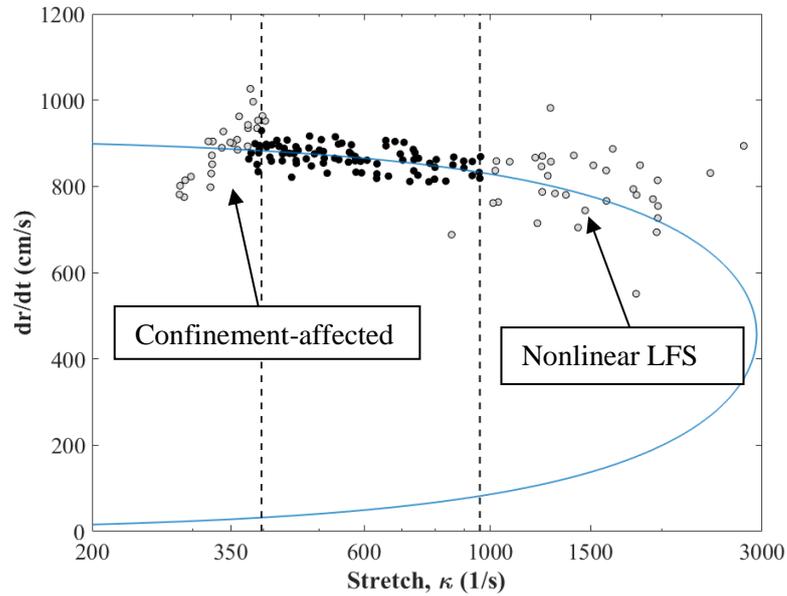


Fig. 4. Sample stretch plot from a TMP-doped mixture at $\Phi = 1.4$ to show confinement effects and nonlinearity in LFS and where the cutoffs are located.

3 Results and Discussion

The LFS of H_2 /air mixtures doped with 0.5% TMP are compared to the baseline H_2 /air mixtures from this study (see Fig. 5). The neat LLNL model slightly underpredicted the neat experimental data up until the mixture became very rich ($\Phi > 2.5$). The slight difference could be attributed to deficiencies in the mechanism at these conditions, or experimentally to the repeatability of the experiment, the temperature, the radius tracking, the MATLAB analysis, or the composition of the mixture [9]. The curve peaks around $\Phi = 1.7$, which matches the literature [12]. The model was expected to perform well due to the quality and volume of mechanism data on H_2 /air mixtures.

The TMP-doped data points also aligned very closely with the model's peak. Opposite to the neat model, the richer fuel points were overpredicted by the mechanism. This difference could again be a result of the model's deficiencies, or the experimental methods such as the injection of the TMP and any resulting uncertainties in the amount of TMP present in the gas-phase mixture. Similar to Sikes' experience with other OPCs, like triethyl phosphate (TEP), in Texas A&M's High Temperature High Pressure vessel [14], There were some issues arising from the use of TMP in the vessel. Each experiment would leave a thin layer of a brown residue with very low vapor pressure on the inside.

This residue would impede the camera's ability to capture clear images of the flame edge. Even at near vacuum (0.30 torr), the residue would take several hours to clear up before another experiment could be performed. It was found that this process could be sped up by cycling around 10 torr of outside air through the vessel for one hour after an initial vacuum of the combustion byproducts within the vessel. While a full experimental curve is pending ongoing experiments, both the model and the experimental results peak around $\Phi = 1.5$. This agreement supports the quality of the LLNL TMP mechanism at predicting the peak LFS.

Comparing the neat H_2 data with the TMP-doped data, the LFS of the TMP-doped mixtures are reduced by 53-65% for the range of Φ ($1.4 < \Phi < 2.0$). This change is a significant reduction in laminar flame speed. Korobeinichev found that 0.04% TMP reduced the LFS of a $H_2/N_2/O_2$ mixture with a dilution ratio of 0.1 by about 30% [4]. The present study used nearly 12 times more TMP than Korobeinichev for a near 60% reduction of LFS of H_2 /air mixtures. It may be inferred then that increasing the amount of TMP concentration has diminishing returns if fire suppression is desired.

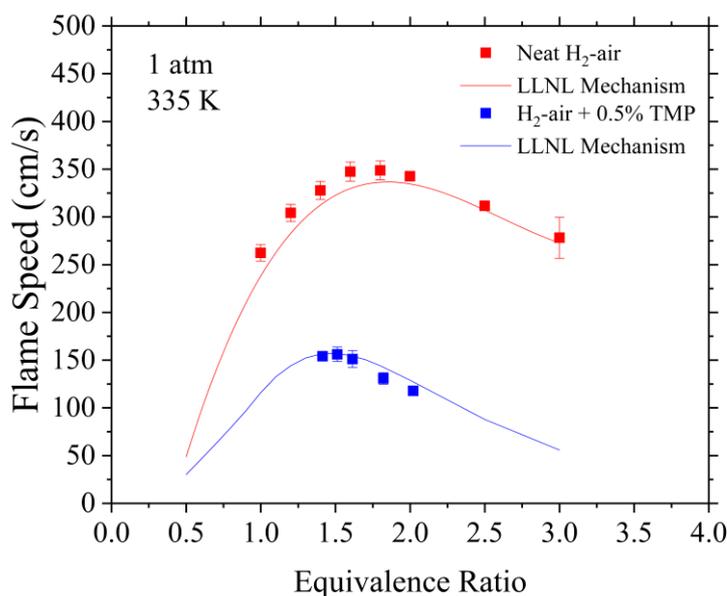


Fig. 5. LFS results comparing the baseline H_2 -Air results with the TMP-doped results, along with predictions from the LLNL chemical kinetics mechanism.

4 Conclusions

This work presented 1-atm data on LFS for neat H_2 /air mixtures and TMP-doped H_2 /air mixtures at an elevated temperature of 335 K. In general, the study showed that the LLNL chemical kinetics model used herein aligns well with experimental data. It also showed that doping H_2 /air mixtures with TMP causes a significant reduction in LFS and therefore should still be considered as a potential fire suppressant for the lithium-ion battery and fire safety communities.

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