Enhancing the Lean Detonability Limit of Hydrogen-Oxygen Detonations using Ozone

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1 Introduction

Hydrogen has emerged as a promising fuel in propulsion systems, fuel cells, automobiles, and various industrial processes. It has the potential for partial or complete substitution of traditional fossil fuels in combustion chambers of aviation and automotive engines. As a clean and highly energetic fuel, hydrogen holds the potential to revolutionize industries reliant on combustion technologies [1]. Recent advancements in propulsion systems have highlighted the advantages of detonation-based engines over conventional gas turbine and rocket engines. Detonation engines are characterized by their higher thermodynamic efficiency and simpler design. Hydrogen further enhances these advantages, owing to its excellent combustion properties [2]. This makes hydrogen a desirable fuel for detonation-based propulsion systems. However, challenges remain in handling and utilizing hydrogen effectively and addressing the operational limits of detonation-based engines. One of the primary challenges in detonation-based engines is the significant thermal load they experience during operation, particularly when burning a stoichiometric fuel-oxidizer mixture. Therefore, operating these engines at fuel-lean conditions could be a plausible solution to reduce the thermal load. However, initiation and stable propagation of detonations in fuel-lean mixtures are not entirely straightforward. Recent studies have reported that detonation-based engines can operate with fuel-lean mixtures in the presence of ozone. Such ozonated fuel-lean mixtures have the potential to reduce thermal load and can sustain prolonged operation of detonation-based devices [3-4]. Ozone has emerged as an excellent dopant in detonation studies due to its ability to accelerate chemical reactions in fuel–oxidizer mixtures [5-7]. The primary kinetic mechanism of ozone under detonating conditions is due to the decomposition in the post-shock state due to high temperatures [5]. Ozone decomposes into an oxygen molecule and a reactive oxygen radical ($O_3 + M \rightarrow O_2 + O + M$) behind the leading shock front. During ignition, the O-atom accelerates the chain branching process and significantly shortens the chemical length and time scales [6]. Ignition promoters, such as ozone, when used in trace amounts, can significantly reduce the ignition delay time of fuel-oxidizer mixtures without affecting their bulk thermodynamic and gas dynamics properties [6].

The study of detonability limits in gaseous mixtures is crucial for understanding the behavior of detonation waves, particularly in confined environments where the mixture approaches its failure threshold. Near the limits, the wave structure undergoes significant changes, transitioning from a complex multi-front cellular pattern to a simpler single-headed spinning structure. This transition marks the onset of detonability limits, where detonation can no longer sustain itself. These limits are determined by thermodynamic conditions and are influenced by factors such as boundary layer effects,

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stability of the mixture, and initiation [8-9]. Near the limit, unstable propagation modes, such as galloping and spinning detonations, become more prominent. Galloping detonation is characterized by periodic failure and re-initiation of the wave, leading to large velocity fluctuations during its cycle, and is typically observed in unstable mixtures [10]. Spinning detonation, on the other hand, involves a single dominant front rotating around the axis of the tube, further reflecting the instability of the system [11]. Therefore, evaluating the detonability limits and understanding the near-limit behavior is critical for the development of detonation-based propulsion devices. In the current work, experiments were carried out to evaluate the effect of ozone addition on the lean detonability limit (LDL) of the hydrogen-oxygen mixtures. The LDL is defined based on the mixture composition (equivalence ratio) and was evaluated for hydrogen-oxygen mixtures with and without ozone addition.

2 Methodology

Detonation tube experiments were carried out in a 3.6 m long stainless-steel tube having an inner diameter (d) of 73 mm (Fig. 1). The closed end of the tube featured multiple ports to accommodate a spark plug, gas feed line, vacuum pump, and a digital pressure gauge for monitoring and controlling initial test conditions. A Shchelkin spiral was installed immediately downstream of the spark plug to enhance flame acceleration and facilitate the transition to detonation. The Shchelkin spiral, having a blockage ratio of 0.3, induced turbulence and promoted detonation onset during each test. A dump tank was connected at the open end of the tube to purge out the combustion products. A mylar diaphragm separated the test section and the dump tank. The gas flow rates were precisely controlled using the sonic orifices. Ozone was generated using an in-line corona discharge ozone generator from the oxygen stream. The schematic of the experimental setup is shown in Fig. 1.

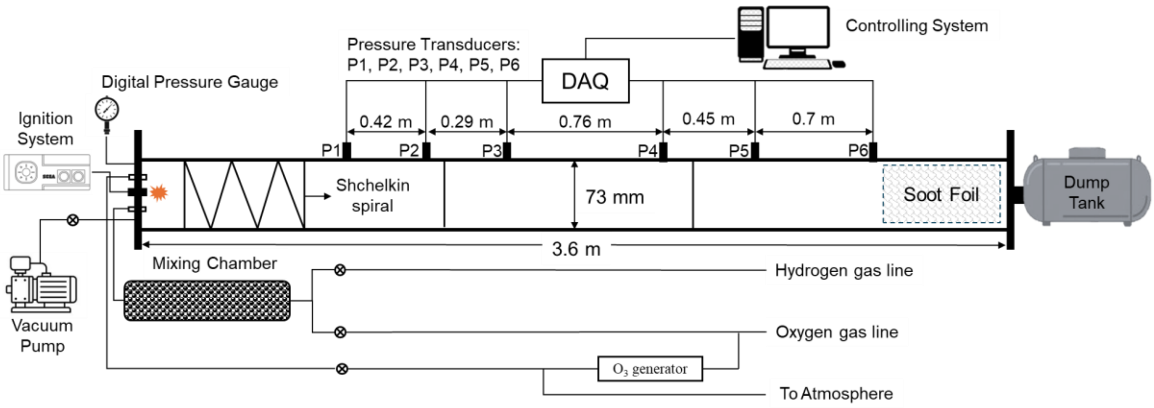

Figure 1: Schematic of the experimental setup.

Before each experiment, the tube was evacuated to achieve an absolute pressure below 50 Pa. The detonation velocity in the tube was measured using six piezoelectric pressure transducers. The detonation propagation velocity in the tube was evaluated based on the time of arrival data. A high sampling rate of 500 kHz was used to ensure high accuracy in the measurement of the time of arrival data. The detonation velocity (V) reported in the current work is the average of the five sets of measurements between the adjacent transducers. The uncertainty in the measurement of velocity was found to be less than 3%. The methodology for uncertainty quantification can be found in our previous work [1]. The cellular detonation structure was captured using the soot foil technique. A soot-coated foil was inserted into the open end of the tube before each experiment to capture the cellular structure. A minimum of 50 cells were measured by hand from the post-detonation soot foils, and the measurement of cell widths encompasses a statistically significant sample size. ZND computations were also carried out for experimental conditions using the Caltech Shock and Detonation Toolbox [12]. The computations were used to evaluate the CJ detonation velocity (V_{CJ}), the velocity of sound in the products (a_{CJ}), and the reduced activation energy, ($\theta = E_a/RT_{VN}$) [13].

3 Results and Discussions

The detonability limits refer to the conditions under which a steady detonation wave can propagate in the tube without degenerating into a deflagration wave. These limits are governed by the thermodynamic and kinetic properties of the reactive mixture, as well as geometric confinement [7]. In this study, detonability limits are defined based on the composition of the reactant mixture. The limits are approached by gradually reducing the equivalence ratio for a given initial pressure and tube diameter. A reduction in the equivalence ratio decreases the sensitivity of the mixture, which corresponds to an increase in the detonation cell size. The lean detonability limit (LDL) is defined as the lowest equivalence ratio at which a steady detonation wave can propagate with negligible velocity deficit. The criteria for identifying the limits are: (i) presence of a cellular structure on the soot foil and (ii) the average propagation velocity within $0.98V_{CJ}$ – $1.02V_{CJ}$. The cellular structure is a characteristic feature of multidimensional detonations, and its absence indicates that the propagating wave is not a detonation. The mixture compositions for which either criterion is not met are classified as no-detonation cases.

3.1 Lean detonability limit (Φ_L) of H_2-O_2 detonations with and without ozone

The lean detonability limits (Φ_L) of hydrogen-oxygen mixtures were experimentally determined at various initial pressures (25 kPa, 50 kPa, 75 kPa, and 100 kPa), with and without ozone (3000 PPM). The LDL measurements were performed with a resolution of an equivalence ratio of 0.05. However, in specific cases, experiments were conducted with a finer resolution of 0.01. Figure 2 (a) presents the LDL for hydrogen-oxygen mixtures across a range of initial pressures in the presence and absence of ozone. For the non-ozonated hydrogen-oxygen mixtures, the LDLs were found to be 0.30, 0.25, 0.20, and 0.20 at initial pressures of 25 kPa, 50 kPa, 75 kPa, and 100 kPa, respectively. However, with the addition of 3000 PPM ozone, these limits were reduced to 0.25, 0.20, 0.17, and 0.17, respectively, demonstrating a consistent enhancement in the detonability of given mixtures. The soot foils obtained under these conditions are shown in Fig. 3. The results indicate that the lean detonability limit shifts towards lower equivalence ratios with increasing initial pressure and with ozone addition. It reflects the enhanced reactivity of the mixture under these conditions. The role of ozone as a potent ignition promoter is well established. The high temperature ozone decomposition behind the leading shock front leads to enhanced reactivity due to radical proliferation [3-7,14]. This radical proliferation accelerates chain-branching reactions, thereby reducing the ignition delay time and increasing the overall sensitivity and reactivity of the detonable mixture.

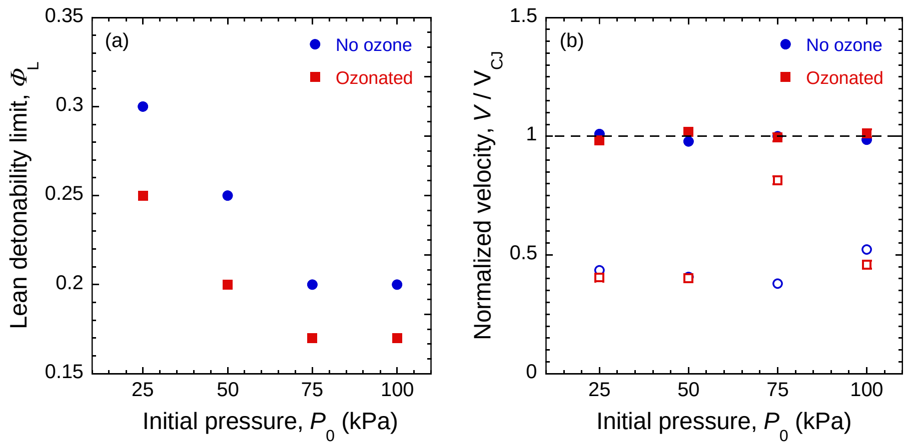

Figure 2: (a) The lean detonability limit and (b) normalized detonation velocity corresponding to the lean detonability limit (filled symbols) and at equivalence ratios below the LDL (hollow symbols), for H_2-O_2 mixtures at different initial pressures (P_0), with and without 3000 PPM of ozone.

Figure 2(b) shows the normalized detonation velocity (V/V_{CJ}) at the LDL (filled symbols) and at equivalence ratios below the LDL (hollow symbols) for both ozonated and non-ozonated mixtures. While ozone addition extends the detonability limit, its influence on the detonation velocity near the limit is minimal. This observation aligns with previous studies, where ozone was shown to kinetically enhance detonation by promoting the chain-branching reactions, without significantly altering the bulk thermodynamic or gas-dynamic properties of the mixture.

Zhang et al. identified three propagation modes at near-limit conditions, a steady mode ($0.8V_{CJ} < V < V_{CJ}$), unsteady mode ($a_{CJ} < V < 0.8V_{CJ}$) and fast flames ($V < a_{CJ}$). Here V_{CJ} is the CJ detonation velocity and a_{CJ} is the speed of sound in detonation products [15]. The velocities measured at the LDL indicate a steady propagating detonation wave ($0.98V_{CJ} < V < 1.02V_{CJ}$). However, the ratio, V/V_{CJ}, for the no-detonation cases (below LDL) were found to be significantly lower (~ $0.5V_{CJ}$), thereby indicating that a self-sustained detonation was not observed under these conditions. The comparison between the measured velocity and a_{CJ} indicate the propagation of fast flames for most of the non-detonation cases. However, the wave propagation velocity was found to be higher than a_{CJ} for ozonated hydrogen-oxygen mixtures at 75 kPa and 100 kPa.

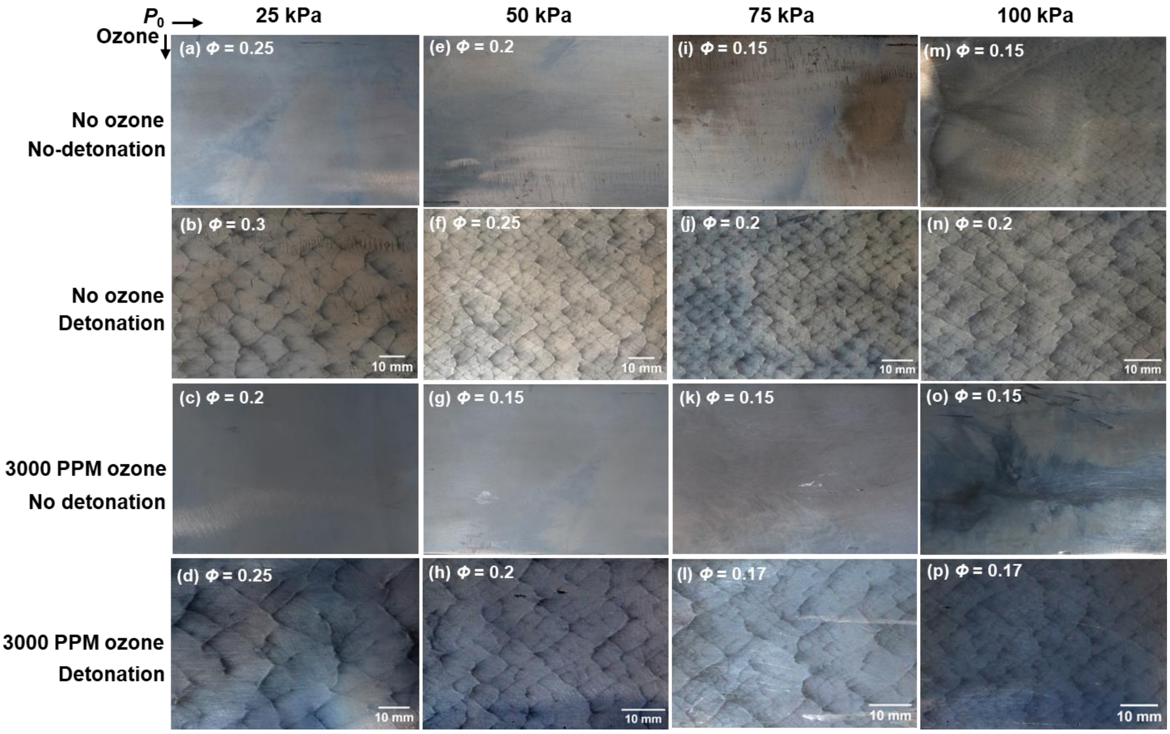

Figure 3: Section of soot foil records of hydrogen-oxygen detonations at and below the lean detonability limit with and without ozone (3000 PPM) at various initial pressures.

3.2 Cellular detonation structure near the lean detonability limits

Figure 3 presents soot foil imprints obtained from the detonation tube experiments at and below the lean detonability limit, at different initial pressures with and without ozone. Each column from left to right corresponds to increasing initial pressure (25, 50, 75, and 100 kPa), while each row from top to bottom represents: (1) no ozone, no detonation, (2) no ozone, successful detonation, (3) 3000 PPM ozone, no detonation, and (4) 3000 PPM ozone, successful detonation. The presence of characteristic cellular structures (formed by propagation of the triple points) serves as a clear indicator of successful detonation propagation, while the absence of cellular patterns confirms detonation failure.

The cellular pattern was recorded at an equivalence ratio of 0.3 (Fig. 3b) and an initial pressure of 25 kPa for the non-ozonated hydrogen-oxygen mixture, but at the same initial pressure, no cellular structure was observed at an equivalence ratio of 0.25 (Fig. 3a). Accordingly, Fig. 3a corresponds to the no detonation case, while Fig. 3b corresponds to the successful detonation case. A similar observation applies to the ozonated cases at 25 kPa, where Figs. 3c and 3d represent the no-detonation and the successful detonation case, respectively, for hydrogen-oxygen mixtures at 25 kPa and with 3000 PPM ozone. This pattern is consistently followed throughout the remainder of Fig. 3 for mixtures at initial pressures of 50 kPa, 75 kPa, and 100 kPa. Interestingly, Fig. 3m, corresponding to the non-ozonated mixture at 100 kPa and Φ = 0.15 displays faint cellular traces in the latter part of the soot foil, suggesting a transition to detonation over the soot foil. However, the average propagation velocity under these conditions was measured to be approximately 52% of V_{CJ}, indicating significant deviation. Therefore, in alignment with the detonation limit criteria adopted in this study, requiring the presence of a cellular structure and propagation velocity within $\pm$2% of V_{CJ}, the aforementioned condition (Φ = 0.15 at 100 kPa) is not considered as the lean detonability limit of the mixture. This also highlights the robustness of the detonability criteria adopted in the present work. It helps to ensure a clear distinction between self-sustained steady detonation and marginally reactive or non-detonative cases.

The experimental results at higher pressures (75 kPa and 100 kPa) for both ozonated and non-ozonated mixtures show distinct cellular structures at an equivalence ratio of 0.2 and no cellular structure at Φ = 0.15. Therefore, to investigate the effect of ozone addition on detonability at 75 kPa and 100 kPa, additional experiments were conducted at Φ = 0.16 and Φ = 0.17 for both ozonated and non-ozonated mixtures. At Φ = 0.16, no soot foil traces or measured velocities indicated the presence of detonation for either the ozonated or non-ozonated mixtures (at both 75 kPa and 100 kPa). However, at Φ = 0.17, a propagating detonation wave was observed for the ozonated mixtures (refer to Fig. 3l (75 kPa), and Fig. 3p (100 kPa)), suggesting that ozone plays a crucial role in extending the lean detonability limit.

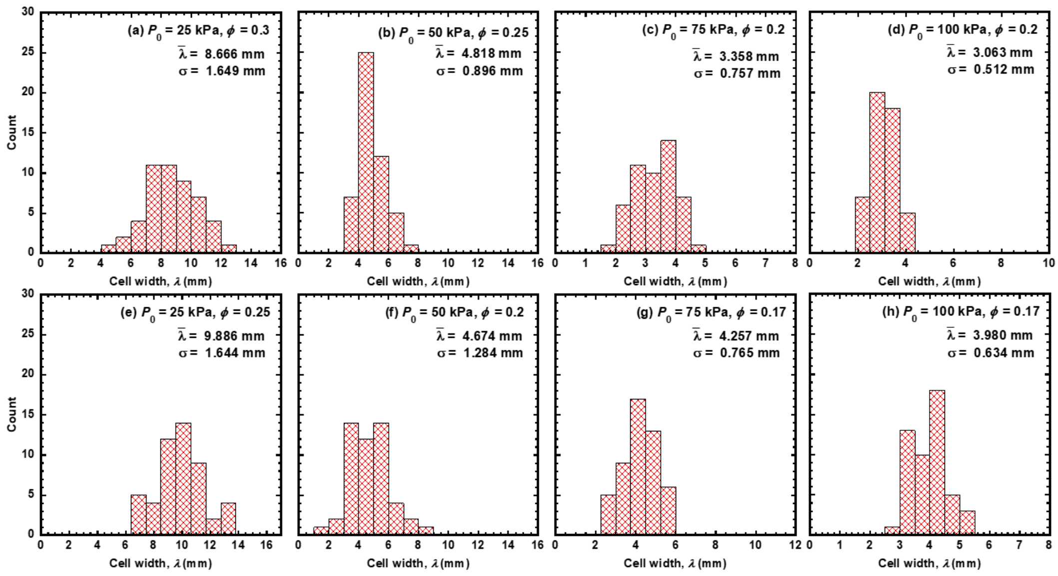

Figure 4: Cell size distributions for H_2-O_2 mixtures at LDL (successful detonation cases in Fig. 3).

The detonation cell width at the LDL for ozonated and non-ozonated cases is nearly the same, specifically for mixtures at higher initial pressures. Thus, statistically, there is a minimal difference in cell size at the limits. The cell size distributions were evaluated at the limits. Figure 4 presents the cell-size distributions measured at the lean detonability limits for both non-ozonated and ozonated hydrogen–oxygen mixtures. Although these distributions correspond to different equivalence ratios and thus cannot be directly compared, it is clear that the maximum observed cell size remains below ~10 mm, substantially smaller than the πd (~ 229.4 for d = 73 mm) criterion traditionally associated with the single-headed spin mode at the detonation limit [9]. The single-headed spinning detonation represents the lowest-order self-sustained detonation, with a characteristic cell size of πd. However, it should be noted that single-headed spinning detonations were not observed in the current set of experiments. The absence of single-headed spinning detonations in the present study may be attributed to how the sensitivity of the mixture was varied, specifically, through discrete changes in the equivalence ratio. In the experiments, the mixture equivalence ratio was typically decreased in steps of 0.05, which may have bypassed the narrow range where single-headed spinning detonations typically occur. It is well established in the literature that spin modes often occur near the detonability limit, serving as a transitional regime between fully developed multi-headed detonations and complete failure. Therefore, it is plausible that the spin mode existed at some intermediate equivalence ratio but was not captured due to the limited resolution in mixture composition. Also, as the equivalence ratio decreases, the detonation cell size is expected to increase due to reduced mixture reactivity. For example, the cell size at $\Phi = 0.30$ (Fig. 4a) is ~ 8.7 mm; a gradual increase in cell size with decreasing Φ could potentially reach values of the order of πd, leading to the onset of single-headed spinning detonations. However, the relatively coarse step size in equivalence ratio may have skipped over the exact conditions under which this transition occurs. Hence, the absence of single-headed spinning detonation in the current study does not necessarily indicate its non-existence, but rather points to the need for finer resolution in mixture composition near the limit to accurately capture this transitional regime.

4 Conclusions

The present study investigated the lean detonability limits (LDL) of hydrogen–oxygen mixtures with and without ozone addition at various initial pressures. The experiments demonstrated that the addition of 3000 PPM ozone consistently extended the detonability limits across all pressures, due to enhanced radical generation via post-shock ozone decomposition. Cellular patterns recorded on soot foils revealed multi-headed detonation structures at the limit conditions, with maximum cell size ~ 9.9 mm. These values are significantly smaller than the πd threshold commonly associated with the onset of single-headed spin detonations, indicating that the observed limits did not correspond to the lowest-mode detonation. The absence of a single-headed spinning detonation was likely due to the resolution of equivalence ratio increments used in the present study.

Acknowledgments

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References

[1] Singh et al. (2024), *Int J Hydrogen Energy*, 80: 322–331.
[2] Gao et al. (2016), *Int J Hydrogen Energy*, 41(14): 6076–6083.
[3] Kumar et al. (2021), *Proc. Combust. Inst.*, 38(3): 3825–3834.
[4] Dahake et al. (2022), *Trans. Indian Natl. Acad. Eng., 7(*3): 1033–1042.
[5] Magzumov et al. (1998), *Combust. Explos. Shock Waves, 34(3):* 338–341.
[6] Crane et al. (2019), *Combust Flame*, 200: 44–52.
[7] Shi et al. (2021), Proc. Combust. Inst., 38(3): 3547–3554.
[8] Dupré et al. (1991), *Symposium (International) on Combustion, 23(1): 1813-1820.*
[9] Lee et al. (1984), Annual Review of Fluid Mechanics, 16: 311-336.
[10] Lee et al. (1995), *Shock Waves,* 5: 175-181.
[11] Zhang et al. (2017), *Aerosp Sci Technol*, 69: 193-200.
[12] Browne et al. (2023), California Institute of Technology, GALCIT Report.
[13] Manzhalei, (1977), *Combust. Explos. Shock Waves*, *13*(3): 402-404.
[14] Han et al. (2021), *Phys. Fluids*, 33(7).
[15] Zhang et al. (2019), *Fuel*, 253: 305–310.