Effect of Ozone Addition on the Detonation Wave Structure of Ethylene-Oxygen Systems

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1 Introduction

Detonation-based propulsion systems have garnered significant attention in recent years due to their potential for high efficiency and energy release. The ethylene–oxygen mixture has been extensively studied as a model fuel–oxidizer system due to its relatively simple chemical structure and high reactivity, making it an ideal candidate for advanced propulsion systems. The performance of detonation engines is essentially linked to the stability of an underlying multidimensional detonation wave. Enhancing the strength and stability of these waves is essential for optimizing combustion processes, and various approaches have been explored to achieve this goal. Recently, ozone has emerged as an excellent kinetic enhancer in detonation studies due to its ability to accelerate chemical reactions in fuel–oxidizer mixtures [1]. Ozone's primary kinetic enhancement mechanism under detonating conditions is due to its decomposition in the post-shock state due to high temperatures [2]. 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 detonation length and time scales. Due to excellent ignition promotion capabilities, ozone has been used extensively in detonation studies. The addition of ozone to a detonable mixture only affects the kinetics of the mixture without affecting the bulk thermodynamic and gas dynamic properties of the mixture. The addition of ozone to saturated hydrocarbon fuels has been extensively studied. The ignition promotion effect of ozone addition to saturated hydrocarbon fuels is due to ozone decomposition. However, the addition of ozone to unsaturated hydrocarbon fuels is not entirely straightforward. The direct reaction of an unsaturated hydrocarbon fuel molecule with ozone is referred to as an ozonolysis reaction. Sun et al. evaluated the effect of ozone sensitization and ozonolysis on the detonation chemistry of $C_2H_4/O_2/Ar$ mixtures using one-dimensional computations [3]. The study primarily focused on ignition energy and the role of ozonolysis reactions, but did not thoroughly investigate the effect of ozonolysis on the structure of detonation waves. Thus, despite numerous studies on detonations in ozonated mixtures, the impact of ozonolysis on the cellular detonation structure remains largely unexplored. Notably, no prior investigations have assessed the influence of ozone addition on the cellular structure of detonations in ethylene–oxygen mixtures. The present study will help fill in a data gap by evaluating the effects of ozone addition and ozonolysis on detonation cell size and structure. Two-dimensional numerical simulations were performed using the compressible reactive Navier-Stokes equations coupled with a validated reduced chemical mechanism to capture the chemical kinetics. The

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findings offer new insights into the role of ozone in modifying detonation behavior and contribute to the design and optimization of advanced detonation-based propulsion systems utilizing unsaturated hydrocarbon fuels.

2 Methodology

The two-dimensional numerical simulations were carried out by solving the compressible reactive Navier-Stokes equations using DetonationFOAM [5], an OpenFOAM-based solver with dynamic meshing via structured adaptive mesh refinement (AMR) based on AMROC. The governing equations are given below,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho V) = 0 \tag{1}$$

$$\frac{\partial (\rho V)}{\partial t} + \nabla \cdot (\rho V V) = -\nabla P + \nabla \cdot \tau \tag{2}$$

$$\frac{\partial (\rho E)}{\partial t} + \nabla \cdot [(\rho E + P)V] = -\nabla \cdot q + \nabla \cdot (V \cdot \tau) \tag{3}$$

$$\frac{\partial (\rho Y_k)}{\partial t} + \nabla \cdot [\rho (V + V_k) Y_k] = \omega_k\,, \quad k = 1,2,\dots,N \tag{4}$$

where ρ, V, P, Y_k, V_k, and ω_k are the density, velocity, pressure, species mass fractions, diffusion velocities, and production rates, respectively. The computational domain was a 100 mm × 4 mm rectangular channel filled with a stoichiometric ethylene-oxygen mixture at 300 K and 25 kPa. The boundary conditions were selected to ensure physical accuracy. The adiabatic slip-wall conditions were applied along the top, bottom, and inlet boundaries, while a zero-gradient condition was imposed at the outlet. Detonation simulations were carried out using ultrafine meshes, where adaptive mesh refinement based on density gradients was used. A grid independence test was carried out with grid sizes of 10 µm, 5 µm, and 2.5 µm. The detonation structure and the detonation cell size showed minimal variation when the grid size was changed from 5µm to 2.5 µm. Therefore, a grid size of 5 µm was used for the computations. To ensure accurate resolution of the induction zone, the detonation simulations employed at least 20 computational cells across the induction length. The second-order accurate Kurganov scheme was utilized for shock capturing, and a central differencing scheme was used for discretizing the diffusion terms. To resolve the chemical source terms in the compressible Navier-Stokes equations, the stiff ODE solver Implicit Seulex was employed. All simulations were performed in the laboratory (Eulerian) frame, with the detonation wave propagating through a quiescent, premixed ethylene–oxygen–ozone mixture. The numerical soot foils were generated by tracing the maximum pressure contour, and a minimum of 50 cells were measured using the soot foils.

The chemical kinetics of C_2H_4-O_2 mixtures were modelled using a reduced reaction model based on USC Mech II [6]. The Princeton ozone sub-model [7] was incorporated to model the ozone chemistry, and the ozonolysis reactions were adopted from the work of Rousso et al. [8]. The combined kinetic model includes 28 species and 70 reactions. The ozonolysis reactions of ethylene are given below,

$$\mathrm{C_2H_4 + O_3 \leftrightarrow CH_2O + CO + H_2O} \tag{R1}$$

$$\mathrm{C_2H_4 + O_3 \leftrightarrow CH_2O + CO_2 + H_2} \tag{R2}$$

$$\mathrm{C_2H_4 + O_3 \leftrightarrow CH_2O + CO_2 + H + H} \tag{R3}$$

$$\mathrm{C_2H_4 + O_3 \leftrightarrow CH_2O + HCO + OH} \tag{R4}$$

The detonation experiments were conducted in a 3.6 m long straight tube with a 73 mm inner diameter. To promote deflagration-to-detonation transition (DDT), a 300 mm long Shchelkin spiral with an 8 mm wire diameter and a blockage ratio of 0.3 was installed just downstream of the spark plug to generate turbulence. The open end was connected to a dump tank via a Mylar diaphragm, which isolated the test mixture until detonation and allowed the safe release of combustion products. The cellular detonation structure was experimentally captured using the soot foil technique. A minimum of 50 cells were measured by hand. Further details on the experimental procedure and diagnostics can be found in the literature elsewhere [9].

3 Results and Discussions

3.1 Ozonated ethylene-oxygen detonations

The experimental and the numerical soot foils are presented in Fig. 1. The experimental detonation cell size for a stoichiometric ethylene-oxygen mixture at 25 kPa was found to be 1.406 mm, whereas the numerical cell size was found to be 1.211 mm. The experimental and numerical cell sizes match closely with a deviation of ~ 14%. The excellent agreement between the experimental and numerical cell size exhibits the ability of the numerical simulations to replicate the cellular detonation structure. This also validates the numerical methodology adopted in the present work and allows us to evaluate the effect of ozone addition on ethylene-oxygen mixtures. Experiments with ozone sensitization were not performed due to the possibility of autoignition in ozonated ethylene-oxygen mixtures. Numerical simulations of ethylene-oxygen mixtures with and without ozone demonstrate the impact of ozone doping on the detonation structure. The CJ detonation velocity for a stoichiometric C_2H_4-O_2 mixture at 25 kPa is 2306 m/s, and in numerical simulation, the detonation wave propagated with an average velocity of 2205 m/s, which amounts to a velocity deficit of 4.37%. The observed velocity deficit improved with ozone sensitization (2.8 % velocity deficit). The average detonation cell width (from 2D simulations) was also found to decrease from 1.211 mm (0 ppm ozone) to 1.003 mm (5000 ppm ozone).

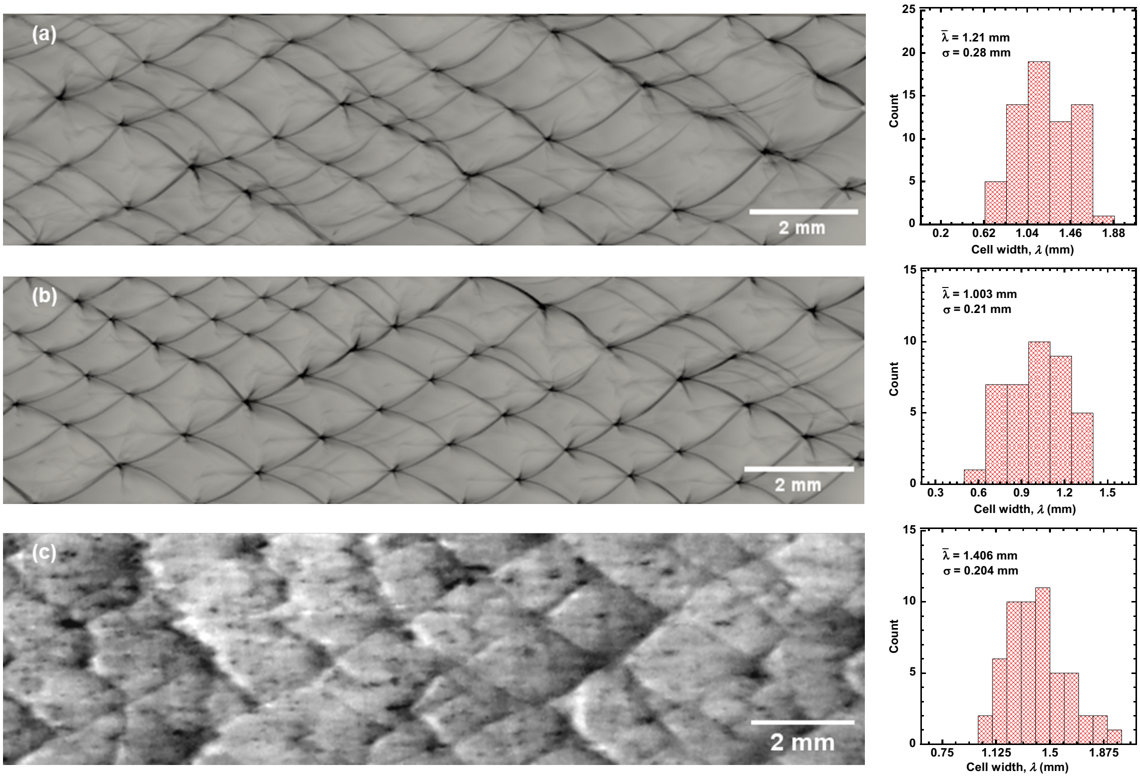

Figure 1**:** (left) Soot foils and (right) detonation cell width distribution for stoichiometric ethylene-oxygen detonations at 25 kPa and 300 K. (a) numerical simulation with 0 ppm ozone, (b) numerical simulation with 5000 ppm of ozone, and (c) experimental soot foil without ozone. $\bar{\lambda}$, represents the average detonation cell width.

This represents a 17% reduction in cell size due to ozone sensitization. The reduction in the cell width under these conditions is primarily due to the decomposition of ozone in the post-shock region. The cell size distributions are also shown in Fig. 1.

The propagation of transverse waves in confined geometries plays a crucial role in sustaining stable detonation waves. The interaction of transverse waves with the incident shock and Mach stem forms triple points, which act as localized ignition sites, promoting energy release. The presence of multiple transverse waves significantly enhances the robustness of the detonation by reducing the detonation cell size. Figure 2 illustrates the density gradient contours for both undoped and ozone-doped ethylene-oxygen detonation. The undoped mixture exhibits an irregular wave front dominated by two transverse waves. However, with 5000 ppm ozone, the number of triple points increases to three, promoting the formation of additional transverse waves and reducing the detonation cell size as shown in Fig. 2.

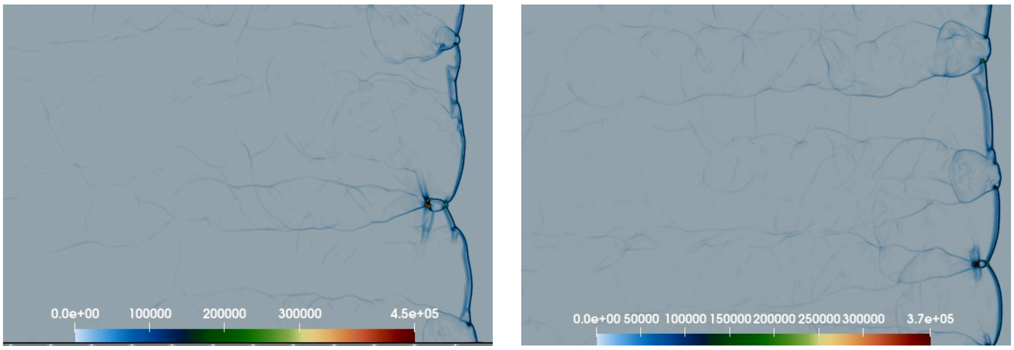

Figure 2: Density gradient contours (kg/m^4) for stoichiometric ethylene-oxygen detonation at 25 kPa and 300 K with, left: 0 ppm of ozone and right: 5000 ppm of ozone.

3.2 Effect of ozonolysis on the detonation cell width

Ozonolysis reactions play a crucial role in altering the properties of the mixture, significantly affecting the thermodynamic state and composition of the reactant mixture. To evaluate the effect of ozonolysis on the cellular detonation structure, constant volume simulations were performed before detonation initiation. CV simulations allowed the ethylene-oxygen-ozone mixture to undergo ozonolysis, leading to a change in the thermodynamic state and the chemical composition of the reactant mixture. The entire domain is initially filled with ethylene-oxygen-ozone (5000 ppm) mixture, and the premixed mixture was allowed to react for a fixed period (residence time) in an adiabatic 2D constant volume reactor.

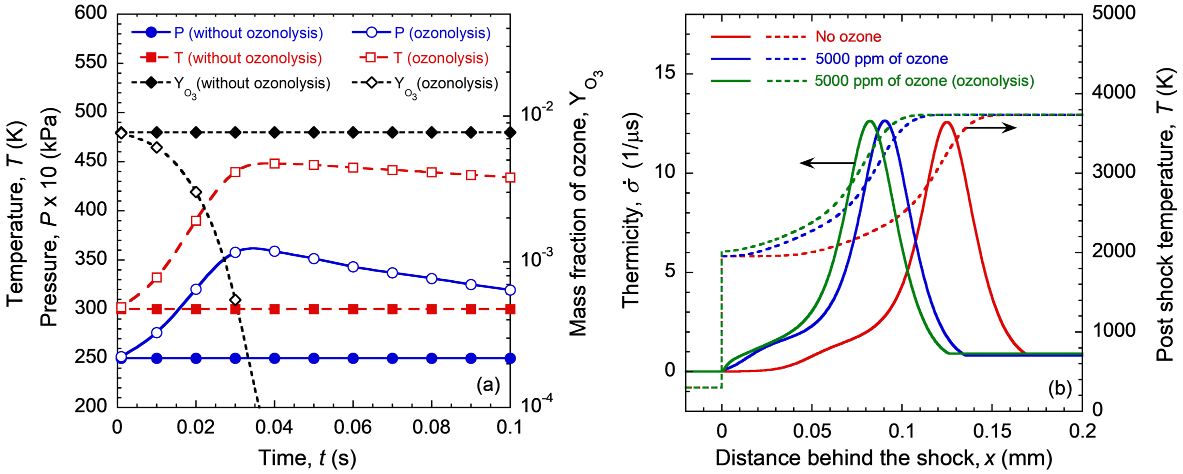

Figure 3: a) Temporal evolution of temperature, pressure, and ozone mass fraction with and without ozonolysis obtained from 2D constant volume simulations. b) Thermicity and temperature profiles of a ZND detonation structure for a stoichiometric ethylene-oxygen mixture with and without ozone.

The residence times (1 ms, 10 ms, and 100 ms) govern the extent of ozonolysis in the reactant mixture. The evolution of mixture temperature, pressure, and mass fraction of ozone due to ozonolysis is shown in Fig. 3a. It can be seen that pressure and temperature increase with increasing residence time due to ozonolysis reactions (R1-R4). Ozone gets completely consumed by ~ 40 µs, where the peak pressure and temperature also occur. However, in the case of no ozonolysis (ozonolysis reactions omitted from the kinetic mechanism), the pressure, temperature, and ozone mass fraction remain constant during the CV simulations. Thus, it can be concluded that ozonolysis significantly pretreats the reactant mixture and changes its thermodynamic state and chemical composition.

The thermodynamic state and the composition of the ethylene-oxygen-ozone mixture at different residence times (1 ms, 10 ms, and 100 ms) were used as initial conditions for unsteady compressible detonation simulations to evaluate the effect of ozonolysis on the cellular detonation structure. Initially, the detonations were significantly overdriven, but they rapidly transitioned to a steady propagation wave. The detonation wave propagated with an average velocity of 2258 m/s, 2250 m/s, and 2266 m/s at 1 ms, 10 ms, and 100 ms, respectively. The corresponding velocity deficits were 2.09%, 2.38%, and 1.69%. The numerical soot foils for ethylene-oxygen-ozone mixtures are shown in Fig. 4. At 1 ms (Fig. 4a), ethylene ozonolysis begins, and the temperature rises slightly. The detonation cell structures appear irregular, qualitatively matching the no ozonolysis case (Fig. 1 b). The cell size without ozonolysis was found to be 1.003 mm, whereas at 1 ms it is 0.949 mm, suggesting little effect of ozonolysis reactions. The detonation cell width decreases further at 10 ms, and the structure becomes more regular, as confirmed by the decreased standard deviation of cell width (refer to Fig. 4b). However, at 100 ms (Fig. 4c), contrary to the expected trend of further detonation cell width reduction due to increased mixture temperature and pressure, the detonation cell width increases slightly.

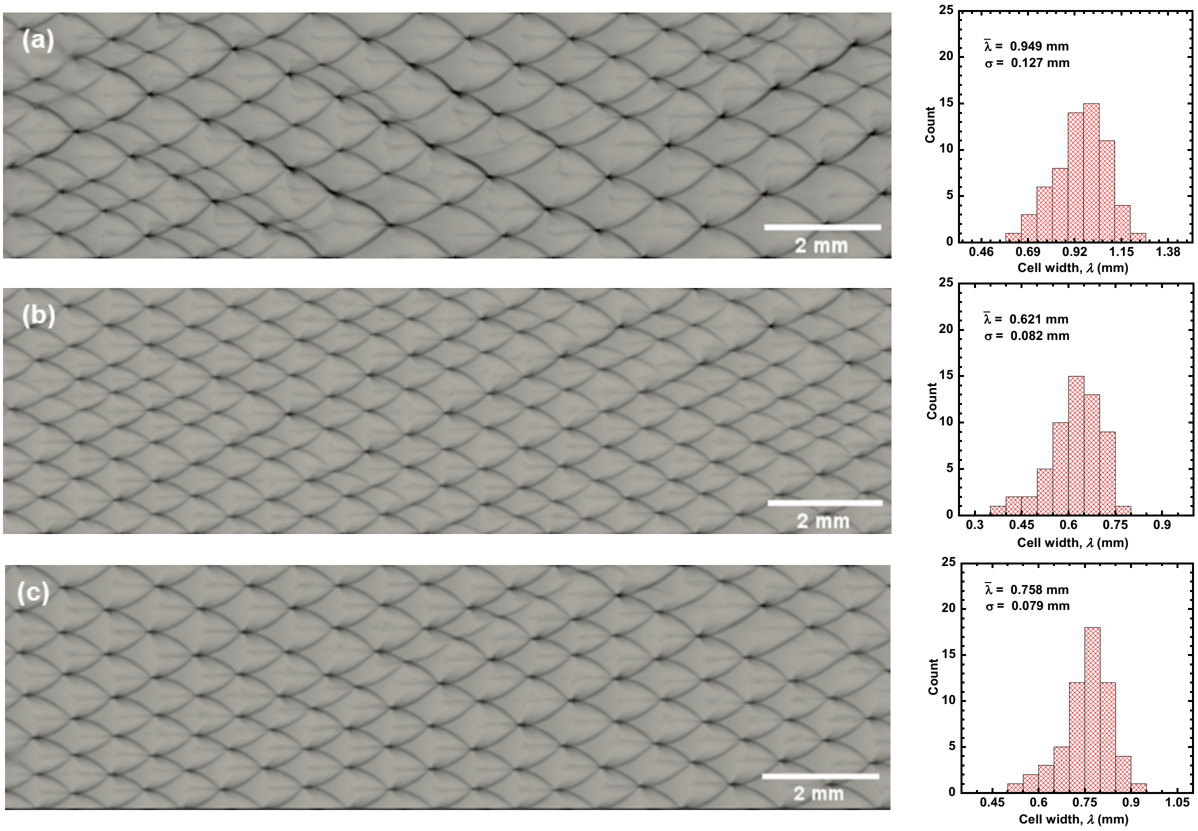

Figure 4: Evolution of detonation cell size for ozonated ethylene-oxygen mixtures. (left) Numerical soot foils and (right) detonation cell width distribution for a stoichiometric ethylene-oxygen mixture with 5000 ppm ozone, evaluated at (a) 1 ms, (b) 10 ms, and (c) 100 ms, $\bar{\lambda}$ represents the average detonation cell width.

This deviation is linked to ozone depletion. As seen in Fig. 3a, the ozone concentration decreases due to ozonolysis. The mass fraction of ozone dropped from 0.006 at 10 ms to 1.8×10^9 at 100 ms. Thus, in the 100 ms case, no ozone is available for post-shock decomposition (unlike the 10 ms case). Therefore, the cell width increases at 100 ms. The results indicate that ozone pretreats the reactive mixture, influencing the detonation structure, with ozonolysis reactions providing alternate chemical pathways. The effect of ozonolysis reactions on the ZND detonation structure was also evaluated using the same methodology, where one-dimensional CV computations were carried out before the ZND computations. The thermicity and the temperature profiles are shown in Fig. 3b. The thermicity peak shifts towards the leading shock front with the addition of 5000 ppm ozone and in the absence of ozonolysis reactions. It shifts further towards the leading shock front due to ozonolysis reactions. Thus, ozonolysis also affects the ZND detonation structure and leads to an increased coupling between the leading shock and the reaction zone.

4 Conclusions

The effect of ozone doping on detonation propagation in stoichiometric ethylene-oxygen mixtures was investigated in the current work. The experimental detonation cell size for a stoichiometric ethylene-oxygen mixture at 25 kPa was found to be 1.406 mm, whereas the numerical cell size was found to be 1.211 mm, yielding a numerical-experimental discrepancy of approximately 14%, thereby validating the numerical methodology. Numerical simulations reveal that ozone reduces the detonation cell width from 1.211 mm (0 ppm) to 1.003 mm (5000 ppm), representing a 17% reduction due to ozone sensitization. The introduction of ozonolysis pathways through CV simulations further reduces the cell width (at 10 ms). The detonation cell width reduces to 0.949 mm and 0.621 mm at 1 ms and 10 ms, respectively, due to ozonolysis reactions. These trends highlight the sensitivity of detonation wave structures to initial thermochemical conditions. In numerical simulations, the detonation wave initially propagated with an average velocity deficit of 4.37%, which was improved with ozone sensitization, which demonstrates the effectiveness of ozone in stabilizing detonation propagation. The detonation wave velocities at 1 ms, 10 ms, and 100 ms were recorded as 2258 m/s, 2250 m/s, and 2266 m/s, respectively, with corresponding velocity deficits of 2.09%, 2.38%, and 1.69%. Overall, these findings highlight the effect of ozonolysis and ozone doping as an effective strategy to enhance detonation and minimize velocity deficits.

Acknowledgments

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