Using Ozone and Hydrogen Peroxide for Manipulating the Velocity Deficits, Detonabilility, and Flammability Limits of Gaseous Detonations

D. Santosh Kumar and Ajay V. Singh

Abstract Self-sustained propagation of detonation waves near limits is essential for the successful operation of detonation-based combustors since they suffer from high-velocity deficits near limits due to geometric constraints. This can potentially lead to its failure or attenuation near limits. The failure or attenuation of a detonation wave under such circumstances could lead to the failure of a detonation-based engine altogether. Existing models like Fay's model reasonably predict detonation velocity deficits for only stable mixtures. The present work focuses on estimating velocity deficits for both stable and unstable mixtures. The proposed model is similar to Fay's model with the modified reaction zone thickness calculated using $x = c(\Delta_i + \Delta_r)$. The value of c is found to be 33.2, 8.6, and 19.5 for H_2–air, CH_4–O_2 (unstable mixtures), and H_2-O_2-Ar mixtures (stable mixture) using existing experimental data. The proposed model predicts velocity deficits better than other existing models for both stable and unstable mixtures over a range of pressure ratios and tube diameters and also near the limits. The addition of O_3 and H_2O_2 at modest concentrations was shown to reduce the velocity deficits near propagation limits. The present work shows that the use of ignition promoters in trace amounts could help in the widening of detonation limits for detonation-based combustors.

Keywords Detonation cycle engines · Detonation limits · Ignition promoters · Induction length (Δ_i) · Induction time (τ_i) · Reaction length (Δ_r) · Stability parameter ((χ) · Velocity deficit (ΔV)

1 Introduction

The widening of detonation propagation limits in gaseous detonations is one of the fundamental problems that needs to be addressed for the successful operation of detonation-based engines, such as the rotating detonation engine (RDE). These detonation-based engines are expected to operate in a variety of conditions using

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fuels that currently range from energy-dense liquid hydrocarbon fuels to gaseous fuels [1, 2]. One of the significant problems associated with RDEs is the stabilization and sustainment of detonation waves in the narrow channel of the combustor, where they can destabilize around tight curves. This, in particular, is important for the development of a small-scale detonation device for propulsion applications. Generally, detonations within limits will propagate with a stable velocity close to the Chapman-Jouguet velocity (V_{CJ}) with relatively small fluctuations. However, if the conditions approach the limits or are far from the limits, detonations propagate with significant velocity variations and deficits. The self-propagation of a detonation wave will depend on boundary conditions, particularly near the limits. The effect of the boundary condition is to reduce the propagation velocity below V_{CJ}, resulting in a velocity deficit and causing the detonation to attenuate and fail. This velocity deficit can be due to the heat and momentum losses and can be attributed to the boundary layer effects as proposed by Lee [3]. The finite thickness of the reaction zone is responsible for detonation vulnerability to boundary layer effects. The detonation wave velocity suffers from high-velocity deficits in smaller passages, and in general, $\Delta V / V_{CJ}$ is inversely proportional to the tube diameter as proposed by several researchers [4–10]. The higher the tube diameter ($1/d \rightarrow 0$), the closer the detonation wave would be to V_{CJ}. The detonation velocity is greatly influenced by the boundary layer when the diameter of the tube or channel is comparable with the boundary layer thickness.

Zeldovich [11] first investigated the effects of heat and momentum losses. Zeldovich [11] proposed that since the total momentum associated with a detonation wave is a function of volume, and because heat transfer and viscous drag are proportional to the wetted area of the tube, the velocity deficit in gaseous detonations should depend on the ratio of surface area to volume and thus on $1/d$. However, such a simplified treatment could not account for the two-dimensional effect of losses adequately. Manson and Guenoche [12] proposed an alternate mechanism for the velocity deficit. They considered a layer of reactive mixture adjacent to the wall quenches as a result of heat losses. In such scenarios, the reaction rate decreases significantly, leading to a decrease in the total chemical energy that goes to support the detonation. Again, this mechanism produced a dependence on the surface area-to-volume ratio. More definitive treatment of losses in 2-D was presented by Fay [13], in which the boundary layer was assumed to cause a divergence in the reaction zone, thereby resulting in a velocity deficit. In Fay's theory, the boundary layer causes the streamlines in the reaction zone to diverge and thus is responsible for a reduction in the detonation velocity. The flow divergence is due to the negative boundary layer thickness with respect to a reference coordinate system fixed to the shock wavefront. The boundary layer in the reaction zone responsible for the divergence of the streamlines will further result in a curved detonation front. Also, the detonation wave curvature is observed to be proportional to the rate of increase of the flow area away from the shock wavefront. For small curvatures, the detonation can be modeled as a quasi-1-D ZND model.

Using Fay's model, the velocity deficit for a given mixture and tube diameter can be calculated if the reaction zone thickness is known for estimating the boundary

layer thickness. The reaction zone thickness can be determined from the ideal ZND detonation model. However, researchers in the past found it to be unsatisfactory while predicting the velocity deficits as the theoretical reaction zone thickness was found to differ from the experimental value by at least two orders of magnitude. Some researchers used the detonation cell size, λ, rather than the ZND reaction zone length, for predicting the velocity deficits in real detonations. In real detonations, λ provides a more appropriate length scale to characterize the thickness of a cellular detonation. In a separate study [3], it was proposed to use cell length $L_c \approx 1.5\lambda$ in place of reaction zone thickness for unstable detonations. Moen et al. [14] later showed that critical tube diameter d_c could also be chosen as a length scale to characterize a real detonation front. The critical tube diameter can be related to the cell size using the following correlation of $d_c \approx 13\lambda$, which is valid for most explosive mixtures. One of the primary reasons for using critical tube diameter as the length scale for calculations of velocity deficit is because it can be determined less unambiguously. The critical tube diameter may be defined as the minimum diameter through which a planar detonation wave could emerge into an open space and continue to propagate as a spherical detonation. Using the correlation of $d_c \approx 13\lambda$ implies that $\lambda \approx d_c/13 \approx 0.077 d_c$. Therefore, the cell length $L_c \approx 1.5\lambda \approx 0.11 d_c$. Using the experimental values of detonation cell size or the critical tube diameter, since they are readily known for a variety of explosive mixtures, the cell length can be determined for a given fuel-oxidizer mixture. The calculated cell length can be used as the reaction zone thickness for a real detonation, where it can be used to calculate the area of divergence ξ from the displacement thickness δ^*. Therefore, the velocity deficit in various-diameter tubes can be obtained.

Laberge et al. [15] measured velocity deficits for stoichiometric acetylene-oxygen mixtures with high concentrations of argon dilution (stable mixtures), and the experimental results were found to agree with the Fay's model. Since the transverse waves in stable mixtures are relatively weak when compared to unstable mixtures, stable mixtures exhibit a regular cell pattern. Fay's model was found to predict the velocity deficits with reasonable accuracy in such mixtures. However, experimental results of unstable mixtures like C_2H_2 and C_2H_4 by Moen et al. [14] with low percentages of argon showed a considerable discrepancy in velocity deficit when compared with Fay's model. This indicates that boundary layer effects do not influence unstable detonations, since their propagation mechanism is dominated by instability in the detonation structure. In unstable detonations, transverse waves are strong, and cell patterns are irregular as opposed to stable detonations. For unstable detonations, as in the case of fuel–air mixtures, the velocity deficits were found to deviate from Fay's theory. Thus, it becomes essential to know whether the mixtures are stable or unstable for the application of Fay's model. Fay's model, in its present form, could only be applied for stable mixtures.

The initial studies on stability were made by Fickett et al. [16] using a one-step reaction model. The importance of transverse waves on the stability of mixtures for self-sustained detonation was carried out by Dupre et al. [17], Teodorczyk and Lee [18], and Radulescu and Lee [19]. Later, Ng et al. [20] defined the stability parameter based on the ratio of the induction to the reaction zone length. They also

included the temperature sensitivity of the induction reaction into the definition of the stability parameter. It is known that a long reaction time would tend to spread out the energy release and would reduce the effect of fluctuations in the induction time, which in turn could increase the stability of the mixtures. The numerical simulations by Radulescu et al. [21] with varying concentrations of argon in acetylene-air mixtures indicate that the shock pressure oscillations change from low-amplitude, high-frequency to low-frequency, and high-amplitude mode with a decrease in argon dilution from 90 to 70%. The effect of the addition of argon was found to increase the stability of mixtures. The same phenomenon was observed by Ng et al. [20], where they characterized the mixtures using the stability parameter, χ. The results by Ng et al. [20] indicate that the deviation of the stability parameter to higher values from the neutral stability boundary will increase the instability in mixtures. In contrast, the values below the neutral stability boundary would indicate stable mixtures. Various researchers mostly use the stability parameter, χ used by Ng et al. [20] for a quantitative description of the stability of detonation waves.

The velocity deficits are also greatly influenced by the type of boundary surfaces like smooth walls, rough walls, and porous walls. The maximum velocity deficits in smooth-walled tubes will be ~15% at detonation limits before it fails. However, a self-sustained detonation with rough walls can be observed with a velocity deficit of over 50%. The temperature behind the shock wave at very high-velocity deficits is very low for auto-ignition to occur, thus requiring new ignition and combustion mechanism for auto-ignition. Lee et al. [3] proposed that surface finish effects have to be taken into account for studying detonation phenomena, e.g., for smooth and rough-walled tubes. In smooth-walled tubes, it was observed that with an increase in the concentration of nitrogen for C_3H_8–O_2 mixtures, the detonation would transform from a multi-headed spin structure to a single-headed spin, as the limit is approached. The detonation in a smooth tube fails with the decoupling of the leading shock front from the reaction zone. However, the rough-walled tube can maintain the detonation wave with higher velocity deficits. Hence, rough-walled tubes have a positive effect on maintaining a self-sustained detonation wave with large velocity deficits of ~50%. These detonations with velocity deficits as high as 50% are known as low-velocity detonations.

Teodorczyk et al. [22] carried out experiments to study the detonation phenomenon on the effect of obstacles for rough-walled tubes to explain the ignition mechanism where temperatures behind the shock are well below auto-ignition temperature. It is observed that the diffraction of detonation waves around an obstacle is responsible for the failure of detonation by decoupling of reaction zone from the shock front. However, the reflected shocks from obstacles merge with the leading shock front to form detonation again. Therefore, obstacles or barriers in the flow path play an active role in the generation of strong transverse waves in rough walls. Thus, it can be understood that detonation in rough tubes can be more robust and can maintain steady propagation even with higher velocity deficits, where detonation fails in smooth walls. The roughness of tubes can also be increased by inserting a spiral coiled wire, in which the quasi-steady detonation wave speeds can be achieved with velocities as low as half of the CJ velocity. The role of boundary conditions, the nature of the

surface, the stability of mixtures, and obstacles or barriers in the path of detonation wave play a significant role in the determination of velocity deficits, which is essential in the design of detonation-based engines like RDE, as proposed by Randall et al. [23], Bykovskii and Vedernikov [24], Lu and Braun [25], and Kailasanath [26].

In real detonations, it is understood that detonation velocity will succumb to very high-velocity deficits of ~15% for stable mixtures and ~40% for unstable mixtures near their propagation limits before it fails. Since the velocity deficit is a function of reaction zone thickness, lower reaction zone thickness will lead to lower velocity deficits. Hence, reducing the length and time scales of a detonation wave without changing the gas dynamics and the thermodynamic properties of the resulting mixture can be a promising solution for the reduction of velocity deficits near the limits. Ignition promoters such as ozone and hydrogen peroxide offer the opportunity to resolve the problem of velocity deficit. We propose to use ozone and hydrogen peroxide as fuel-sensitizers for reducing the velocity deficits near the propagation limits. This methodology of sensitizing detonations with ignition promoters at low quantities can reduce the velocity deficits near the propagation limits. The effect of such doping is to reduce the velocity deficits by changing the ignition kinetics tremendously without changing the gas dynamics and relevant thermodynamic properties of both unburned and burned mixtures. Recent results by Magzumov [27], Crane et al. [28], and Kumar et al. [29] for gaseous detonations support this notion of fuel-sensitization, and results by Liang et al. [30], Kumar et al. [29], and Ivin et al. [31] show that ozone can be used in enhancing the detonability limits of detonating mixtures.

2 Objective

The objectives of the present work are:

- To formulate a modified theoretical model similar to Zhang and Liu [32], which can predict the velocity deficits in hydrogen and methane-oxygen detonations.
- To investigate the effects of ignition promoters on velocity deficits near the detonation limits.
- To examine the impact of ignition promoters on the stability parameter.

3 Methodology

3.1 Fays Model

In Fay's theory [13], the boundary layer causes the streamlines in the reaction zone to diverge and is responsible for the reduction in detonation velocity. If the divergence area is small, the flow in the reaction zone can be approximated as quasi-1D flow, and the conservation equation can be written as:

$$d(\rho u A) = 0 \tag{1}$$

$$\rho u A du + A dp = 0 \tag{2}$$

$$d\left(h' + \frac{u^2}{2}\right) = 0 \tag{3}$$

where h′ includes the chemical energy Q. Integrating the above equations between the shock and the CJ plane gives Eqs. (4)–(6),

$$\rho_1 u_1 = \rho_2 u_2 (1 + \xi) \tag{4}$$

$$p_1 + \rho_1 u_1^2 = \left(p_2 + \rho_2 u_2^2\right)(1 + \xi) - \int_0^{\xi} p d\xi \tag{5}$$

$$h_1 + Q + \frac{u_1^2}{2} = h_2 + \frac{u_2^2}{2} \tag{6}$$

where ξ is the area divergence defined by, $\xi = \frac{A_2 - A_1}{A_1} = \frac{A_2}{A_1} - 1$.

Subscript 1 indicates the unburnt gaseous mixture upstream of the shock wave, and subscript 2 indicates the burned mixture downstream of the CJ plane, as shown in Fig. 1.

The velocity deficit can be expressed as

$$\frac{\Delta V}{V} = \left(\frac{V_{CJ} - V}{V_{CJ}}\right) \tag{7}$$

where V_{CJ} is the theoretical CJ detonation velocity, V is the actual detonation velocity, and ΔV is the detonation velocity deficit.

Solving the above Eqs. (4–6) and applying boundary conditions will result in a velocity deficit described as,

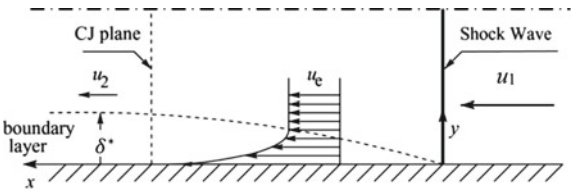

Fig. 1 Steady flow in the detonation wave near the tube wall (velocities are measured with respect to the coordinate system fixed to the shock front). The dotted lines indicate the outer edge of the boundary layer, which develops at the tube wall behind the shock front

$$\frac{\Delta V_1}{V_1} = 1 - \left[\frac{(1-\nu)^2}{(1-\nu)^2 + \gamma_2^2(2\nu - \nu^2)} \right]^{\frac{1}{2}} \tag{8}$$

where γ is the specific heat ratio, and ν is defined as

$$\nu = \frac{\varepsilon\xi}{(\gamma_2 + 1)(1 + \xi)}. \tag{9}$$

The area divergence ξ can be reduced in terms of boundary layer thickness δ^* for a round tube of radius R and diameter d, as

$$\xi = \frac{A_2}{A_1} - 1 = \frac{\pi(R + \delta^*)^2}{\pi R^2} - 1 \approx \frac{2\delta^*}{R} = \frac{4\delta^*}{d} \tag{10}$$

For smooth tubes, the boundary layer displacement thickness has been determined in shock tube experiments by Gooderum [33] as,

$$\delta^* = 0.22x^{0.8}\left(\frac{\mu_e}{\rho_1 u_1}\right)^{0.2} \tag{11}$$

where x is the distance from the shock front, μ_e is the viscosity of the gas in the reaction zone, and ρ_1 and u_1 are the density and the velocity in front of the shock (in the shock-fixed coordinate system).

Eqs. (7–11) can be solved for a given mixture with initial conditions by computing the value of reaction zone thickness x. According to Fay's model, the x is calculated by an empirical formula. Lee et al. used cell length, L_c, in place of reaction zone thickness, x, for the calculation of velocity deficit.

3.2 Modified Theoretical Model

In the present study, a new modified version of Fay's model was used for calculating the velocity deficits in gaseous detonations. The recent work by Crane et al. [28] suggested that detonation cell length can be modeled in terms of induction length, Δ_i and exothermic length, Δ_r. Zhang and Liu [32] carried out velocity deficit calculations using the Fay's model with modified reaction zone thickness as suggested by the work of Crane et al. [28] as, $x = c(\Delta_i + \alpha\Delta_r)$, where c is a constant and α is the proportionality factor between Δ_i and Δ_r, i.e., $\Delta_i / \Delta_r = \alpha$. The value of c is calculated by carrying out velocity deficit experiments and solving equations from (7) to (11). The equation used by Zhang and Liu [32], for calculating reaction zone thickness, x ultimately simplifies to a function of Δ_i, i.e., $x = c(2\Delta_i)$, after substituting 'α' in $x = c(\Delta_i + \alpha\Delta_r)$. In the modified theoretical model proposed in this work, the reaction zone thickness (x) is modeled as $x = c(\Delta_i + \Delta_r)$, where Δ_i and

Δ_r represent the induction, and exothermic zone lengths, respectively, and can be calculated using a 1-D ZND model. The value of c in the above expression depends on the mixture composition. The value of 'c' was evaluated from the velocity deficit experimental data reported in the literature elsewhere [32, 34, 35].

3.3 ZND Numerical Calculations

ZND computations were carried out using a modified version of the CalTech Shock and Detonation Toolbox (2018) [36]. Cantera (2018) [37], integrated with MATLAB and Python, was used for chemical kinetics simulation and to calculate the ZND length scales for H_2–O_2 and CH_4–O_2 detonations. The Foundation Fuel Chemistry Model Ver 1.0 (FFCM-1) by Smith et al. [38] is used in the present study. The Princeton ozone sub-model by Zhao et al. [39] was used to carry out calculations with ozone as a dopant. The uncertainties associated with the FFCM-1 model and the ozone sub-models can be found in the literature elsewhere [28]. The complete FFCM-1 model, including the ozone chemistry sub-model, comprises 39 species and 301 reactions. The governing equations for ZND model have been discussed in the literature elsewhere [40].

4 Results and Discussions

The present work focuses on studying velocity deficit experiments in three mixtures, $2H_2$–O_2 (unstable mixtures), CH_4–O_2 (unstable mixtures), and $2H_2$–O_2–3Ar (stable mixtures). The reaction zone thickness (x) in the present study is modeled as $x = c(\Delta_i + \Delta_r)$, where Δ_i and Δ_r represent the induction and exothermic zone lengths, respectively. The velocity deficit experimental data of [32, 34, 35] for different tube diameters for the above three mixtures were used for the evaluation of c. The value of c is calculated by using velocity deficit values from experimental results and solving equations from (7) to (11) using a 1-D ZND model. If the velocity deficit is calculated from the experiment for a particular tube diameter, initial pressure, temperature, and equivalence ratio, the only unknown in Eqs. (7)–(11) is 'c' value and the rest parameters can be calculated from 1-D ZND model. The nonlinear Eqs. (7)–(11) were solved simultaneously using MATLAB with velocity deficit experimental data of [32, 34, 35], where 'c' values for different initial conditions were calculated for stable and unstable mixtures.

4.1 Unstable Mixtures

For unstable mixtures, the experimental data of [32, 34] for $2H_2 + O_2$ and $CH_4 + 2O_2$ mixtures at stoichiometric equivalence ratio are used to evaluate the value of c in $x = c(\Delta_i + \Delta_r)$, see Fig. 2a and b. It can be seen that the value of c varies over a wide range of pressure, and the average value was calculated based on statistical averaging. The value of c is found to be 33.2 and 8.6 for hydrogen and methane-oxygen mixtures, respectively, as shown in Fig. 2a and b. The reaction zone thickness was modeled as $x = 33.2(\Delta_i + \Delta_r)$ and $x = 8.6(\Delta_i + \Delta_r)$ for $2H_2 + O_2$ and $CH_4 + 2O_2$ mixtures, respectively. The modeled reaction zone thickness was then used in the Fay's model to calculate the velocity deficits in the respective mixtures. It can be seen from Fig. 3a and b that the proposed modified theoretical model predicts better when compared to Fay's model and the theoretical model proposed by Zhang and Liu [32]. Similar is the case for methane-oxygen detonations, where the modified reaction zone thickness given as $x = 8.6(\Delta_i + \Delta_r)$ reasonably predict the velocity deficits (see Fig. 3c). Fay's model does not predict velocity deficits for unstable mixtures when reaction zone thickness is modeled with cell length L_c. However, the same is not the case with the proposed theoretical model, which reasonably predicts the velocity deficit data for both $2H_2 + O_2$ and $CH_4 + 2O_2$ mixtures. Thus, the proposed modified model (designated as FFCM1 here) is more robust in predicting the velocity deficits in unstable mixtures when compared to earlier models. The same can be seen in Fig. 3, where the modified theoretical model (FFCM1) is observed to predict the experimental velocity deficit data trends quite accurately when compared to other models (Fays and Bo Zhang model).

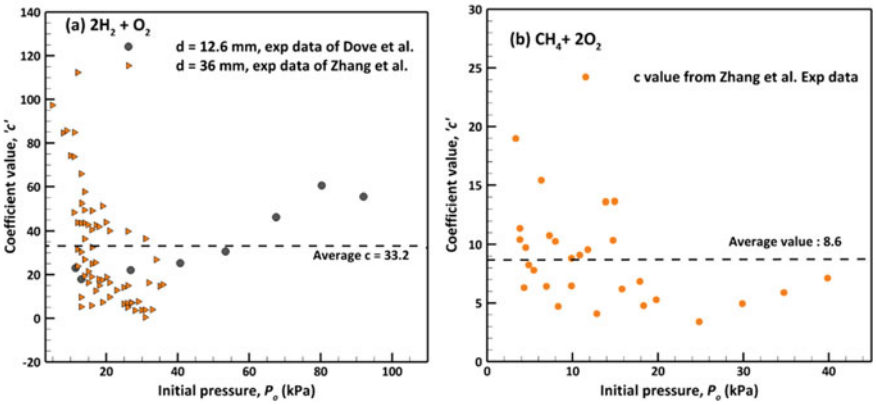

Fig. 2 Calculation of value of c in reaction zone thickness formula $x = c(\Delta_i + \Delta_r)$ for **a** $2H_2 + O_2$ mixtures and **b** $CH_4 + 2O_2$ mixtures. ZND calculations were carried out at a stoichiometric equivalence ratio and an initial temperature of 295 K

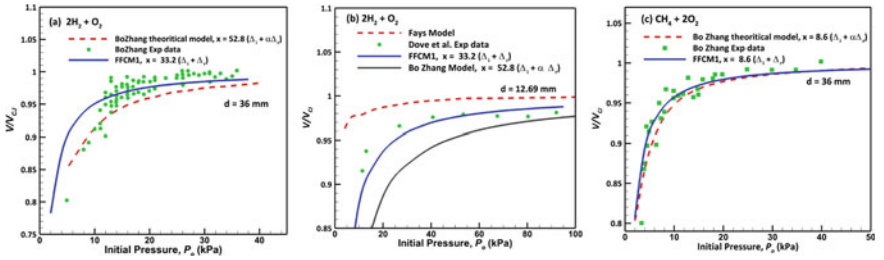

Fig. 3 Comparison of the proposed modified model (FFCM1) with other theoretical models for the prediction of velocity deficits in **a** and **b** hydrogen–oxygen detonations and **c** methane-oxygen detonations. Filled symbols represent the experimental data whereas dotted and solid lines represent the prediction by various theoretical models. ZND calculations were carried out for stoichiometric mixtures at an initial temperature of 295 K

4.2 Stable Mixtures

In the case of stable mixtures, the experimental data of $2H_2 + O_2 + 3Ar$ by Gao and Ng [38], as shown in Fig. 4a, are used to evaluate the value of c in $x = c(\Delta_i + \Delta_r)$. It can be seen that the value of "c" is reasonably constant over the range of initial pressures. The average c value for hydrogen–oxygen mixtures diluted with 50% Ar is found to be 19.5 (see Fig. 4a). In the case of stable mixtures, Fay's model reasonably predicts the velocity deficits. The experimental velocity deficit results of Gao and Ng [38] for $2H_2 + O_2 + 3Ar$ mixtures agree well with Fay's model, where

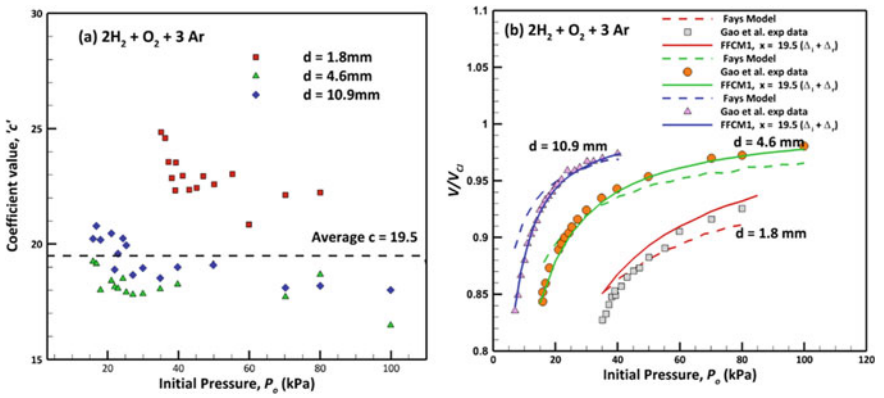

Fig. 4 **a** Calculation of c in the reaction zone thickness formula $x = c(\Delta_i + \Delta_r)$ for $2H_2 + O_2 + 3Ar$ mixtures diluted with 50% argon **b** comparison of velocity deficit results of the proposed modified model (FFCM1) with the experimental data of Gao et al. and Fay's model for $2H_2 + O_2 + 3Ar$ mixtures diluted with 50% Argon. Filled symbols represent the experimental data. Dotted and solid lines represent the prediction by Fay's and FFCM1 theoretical model, respectively. ZND calculations were carried out at a stoichiometric equivalence ratio and an initial temperature of 295 K

the reaction zone thickness is modeled as a cell length (see Fig. 4b). In the present study, the reaction zone thickness is also modeled as $x = 19.5(\Delta_i + \Delta_r)$, which is then used in Fay's model to predict the velocity deficit. It is observed that the proposed modified model (FFCM1) predicts the velocity deficit trends of Gao et al. more accurately when compared to Fay's model. It can be seen from Fig. 4b that near detonation limits, Fay's model, in its current form, performs poorly in predicting the velocity deficits for different tube diameters. However, using a modified theoretical model (FFCM1) proposed in the present work predicts the velocity deficits more accurately when compared to Fay's model for stable mixtures near the propagation limits. This is a remarkable result since, to date, no theoretical model can predict the velocity deficit trends in both stable and unstable mixtures. The proposed model of the present work is capable of predicting the velocity deficit trends in both the stable and unstable mixtures and holds a lot of promise for the detonation scientific community.

4.3 Effect of O_3 and H_2O_2 on Velocity Deficit

The effects of ignition promoters like ozone and hydrogen peroxide are studied for both stable and unstable mixtures. It can be seen from Fig. 5a–c that the addition of O_3 and H_2O_2 will reduce the velocity deficits significantly near the limits for H_2–O_2, CH_4–O_2, and H_2–O_2 mixtures diluted with 50% argon for various tube diameters. The results by Crane et al. and other researchers [28, 41] show that ignition promoters like ozone and hydrogen peroxide can effectively reduce the activation energy and the associated chemical length and time scales. They also increase the chain branching reactions, leading to an increase in the generation of free radicals like H, O, and OH, which result in faster ignition kinetics. Thus, the reaction zone thickness reduces with the addition of ignition promoters, thereby decreasing the velocity deficits. From Fig. 5 and Table 1, it can be seen that the velocity deficits are significantly reduced near the limits with the addition of ignition promoters from 0 to 20,000 PPM. It can be seen from Table 1 that velocity deficits can be improved by up to 20%

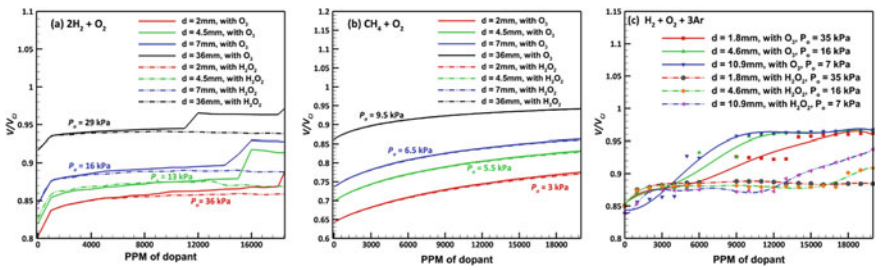

Fig. 5 Effect of O_3 and H_2O_2 on velocity deficits for **a** H_2–O_2 mixtures **b** CH_4–O_2 mixtures and **c** H_2–O_2 mixtures diluted with 50% argon. ZND calculations were carried out for stoichiometric mixtures at an initial temperature of 295 K

Table 1 Effect of O_3 and H_2O_2 on velocity deficits for stable and unstable mixtures

Composition	Dia (mm)	Critical pressure (kPa)	V/V_{CJ}	V/V_{CJ} @ O_3 at 20,000 PPM	V/V_{CJ} @ H_2O_2 at 20,000 PPM	% change @ O_3	% change @ H_2O_2
$2H_2$–O_2	2.0	29	0.80	0.90	0.86	12.50	7.50
	4.5	16	0.82	0.91	0.87	10.98	6.10
	7.0	13	0.85	0.93	0.88	9.41	3.53
	36.0	6	0.91	0.98	0.94	7.69	3.30
CH_4–O_2	2.0	9.5	0.64	0.78	0.77	21.88	20.31
	4.5	6.5	0.70	0.83	0.83	18.57	18.57
	7.0	5.5	0.74	0.86	0.86	16.22	16.22
	36.0	3	0.86	0.94	0.94	9.30	9.30
$2H_2$–O_2–3Ar	1.8	35	0.85	0.96	0.88	12.94	3.53
	4.6	16	0.85	0.97	0.90	14.12	5.88
	10.9	7	0.84	0.97	0.94	15.48	11.90

by using O_3 and H_2O_2 in trace amounts for methane-oxygen detonations, especially in narrow tubes. A similar improvement in the decrease of velocity deficit by ~13% can be seen for hydrogen-oxygen mixtures, with and without argon.

4.4 Effect of O_3 and H_2O_2 on Stability Parameter

The stability of mixtures can be better explained with the stability parameter. It is evident that stability of the detonation is a consequence of the temperature-sensitivity of the chemical reactions. Small fluctuations in the shock temperature result in large fluctuations in the induction delay time as well as the energy release rate of the recombination reactions. It should be noted that the induction time (or induction zone length) should be measured relative to the recombination time. A long reaction time will tend to spread out the energy release and thus reduce the effect of fluctuations in the induction time. Thus, a long reaction time has a stabilizing effect and this is taken into consideration explicitly in the stability parameter of Ng [20]. Large values of the stability parameter leads to gasdynamic instabilities in the reaction zone. The lower value of the stability parameter, χ, below the neutral stability boundary, represents more stable mixtures with regular cell pattern, and higher values of χ represent unstable mixtures with irregular cell pattern. It is desired to have stable mixtures with regular and uniform cell structures for lower velocity and pressure fluctuations. The addition of ignition promoters like ozone and hydrogen peroxide can have a significant impact on the stability parameter, where they reduce the activation energy and the ratio of the induction—to the reaction-zone length. The effects of the addition

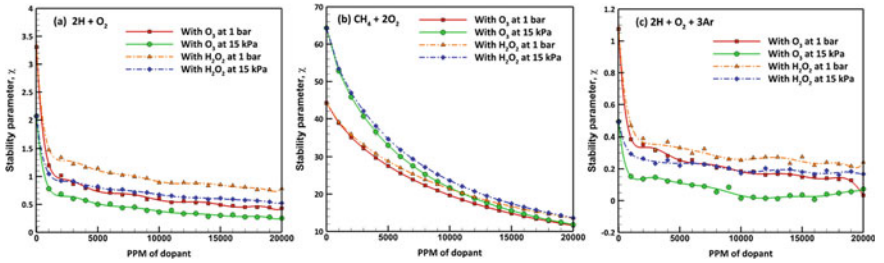

Fig. 6 Effect of O_3 and H_2O_2 ignition promoters on the stability parameter for **a** H_2–O_2 mixtures **b** CH_4–O_2 mixtures **c** H_2–O_2 mixtures diluted with 50% argon. ZND calculations were carried out for stoichiometric mixtures at an initial temperature of 295 K and initial pressure of 15 kPa and 1 bar

of ignition promoters like O_3 and H_2O_2 on the stability of H_2–O_2, CH_4–O_2, and H_2–O_2 mixtures diluted with 50% argon were estimated at initial pressures of 15 kPa and 1 bar. The results are presented in Figs. 6a–c. It can now be understood that the stability parameter reduces significantly with the addition of ignition promoters for both the stable and unstable mixtures.

Hence, it can be inferred that the addition of ignition promoters can steer the mixtures from unstable regimes toward stable regimes. Thus, the presence of ignition promoters not only reduces the velocity deficits but also seems to have a stabilizing effect on a detonating wave structure. The critical role of ignition promoters in detonating mixtures cannot be neglected, where they not only prevent the attenuation of a detonation wave but also stabilizes them, thus making it more robust near its propagation limits. This methodology can be successfully implemented in detonation-based engines to reduce the velocity deficits for varied flow conditions and engine geometries. Similarly, detonability and flammability limits can be extended for various fuel-oxidizer mixtures in the presence of ignition promoters at modest concentrations.

5 Conclusions

The proposed theoretical model for the prediction of velocity deficits in gaseous detonations in tubes was developed by modeling the reaction zone thickness as $x = c(\Delta_i + \Delta_r)$ and using it as a length scale in Fay's model. The reaction zone thickness x was calculated using ZND chemical length scales like induction length, Δ_i, and exothermic length, Δ_r. The value of c was estimated to be 33.2, 8.6, and 19.5 for the H_2–O_2 (unstable mixtures), CH_4–O_2 (unstable mixtures), and H_2–O_2 mixtures diluted with 50% argon (stable mixtures), respectively, by using experimental velocity deficit data from earlier works. The proposed theoretical model reasonably predicts velocity deficits for both unstable and unstable mixtures over a wide range of pressures, tube diameters, and also near the detonation limits. The

addition of ignition promoters like O_3 and H_2O_2 in modest concentrations to fuel-oxidizer-diluent mixtures significantly impacts the detonation structure, where it reduces the chemical length and time scales significantly. The overall effect of such a doping would be to reduce the velocity deficits in gaseous detonations. This methodology of sensitizing a given fuel-oxidizer-diluent mixture with the help of ignition promoters like ozone and hydrogen peroxide can be used as a promising solution for reducing the velocity deficits in gaseous detonations, especially near the propagation limits. With this methodology, the detonation limits can be widened, and lower velocity deficits can be attained, which is essential for the sustenance of detonation waves for propulsion applications for a variety of engine geometries and varied flow conditions. This methodology could also prevent the failure of detonation waves near their propagation limits. The results from the present study show that the addition of O_3 and H_2O_2 at modest can significantly lower the stability parameter (χ), even for unstable mixtures. Ozone and H_2O_2 could have a stabilizing effect on irregular gaseous detonations and can be used to steer the unstable detonations toward a stable regime.

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