

Effect of Initial Conditions on the Inhibition Process of H₂-O₂/air Detonations Using CF₃I, CO₂, and H₂O

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1. Introduction

Accidental explosions often occur during the storage and transportation of fuels, primarily due to gas leaks and fuel spillage. In the case of highly reactive fuels such as hydrogen, the chemical reactions and species molecular diffusion rates are higher. Therefore, the flame accelerates rapidly, leading to fast deflagrations or even a detonation through the DDT phenomenon. A fully developed detonation wave propagates at supersonic velocities (> 1800 m/s) with a tightly coupled shock-flame complex, thereby reaching overpressures of more than 20 bars. The mechanical load associated with a blast wave of such high overpressures is a major destructive factor accompanying a gas explosion. Therefore, Wang et al. suggested that the flame acceleration and the DDT phenomenon must be taken into consideration for safety and hazard evaluation [1].

Due to the low ignition energy and a wide explosion limit of hydrogen fuel, several accidents of hydrogen explosions have been reported in the production, storage, and refueling stations [2]. Hydrogen is a small molecule, and due to its low viscosity, it is more prone to leakages from pipeline connections as compared to other hydrocarbons. The leakage of hydrogen from storage tanks or transport pipelines results in the formation of large vapor clouds; the hydrogen vapor mixes with air and forms a flammable mixture before ignition occurs. Oran et al. showed that such vapor clouds under favorable conditions could undergo a DDT phenomenon even in the absence of any confinement and could lead to huge losses of life and resources [3,4]. Vapor cloud explosions have been widely studied in the literature due to their resemblance to practical explosion scenarios [3-6].

The use of chemical inhibitors and diluents for detonation and fire suppression has been widely studied by researchers worldwide [7-10]. The chemical inhibitors, when added to a fuel-oxidizer mixture, interfere with the oxidation chemistry of the detonating mixture. The primary objective of the addition of a chemical inhibitor to a fuel-oxidizer mixture is to alter the mixture's detonability and thus reduce detonation hazard. Halogenated hydrocarbons, especially those containing more than one halogen compound, are very effective in detonation inhibition [7]. Mostly, the studies reported in the literature are specifically carried out at stoichiometric conditions and standard initial pressure and temperature. The hydrogen explosions occurring, especially in confined spaces and nuclear reactors, can have a range of initial mixture composition and pressure-temperature gradients. The boiling water reactors and pressurized water reactors operate at very high initial pressures; also, partially combusted fuel-oxidizer mixtures can heat the unburned mixture and change the initial thermodynamic state of the flammable

mixture [11]. Thus, it becomes evident to study the use of these chemical and thermal inhibitors at varying mixture initial conditions.

In the present study, the effect of the initial thermodynamic state of the fuel-oxidizer mixture on the inhibition efficiency of trifluoroiodomethane (CF_3I), carbon dioxide (CO_2), and steam (H_2O) is evaluated. The primary objective of the present work is to study the influence of initial mixture conditions on the efficiency of detonation inhibitors using a detailed chemical kinetics model for hydrogen oxidation. The computations carried out include varying the initial mixture composition, initial pressure, and temperature of $\text{H}_2\text{-O}_2/\text{air-CF}_3\text{I}/\text{CO}_2/\text{H}_2\text{O}$ mixtures. In the current work, the inhibition efficiency of the detonation inhibitors is evaluated based on the factor of increase in the induction length/time of $\text{H}_2\text{-O}_2/\text{air}$ detonations with the addition of inhibitors.

2. Numerical Computations

In the present work, the one-dimensional ZND detonation model was used to study the efficacy of detonation inhibitors on $\text{H}_2\text{-O}_2/\text{air}$ mixtures at different initial conditions. The CalTech Shock and Detonation Toolbox was used for the ZND computations [12]. The chemical kinetic computations were carried out using CANTERA integrated with MATLAB and python. The Foundational Fuel Chemistry Model – 1 (FFCM-1) was used to model hydrogen oxidation. The FFCM-1 model consists of 39 species and 301 reactions [13]. The reaction mechanism adopted by Leclerc et al. for CF_3I was incorporated into the FFCM-1 reaction mechanism to model CF_3I chemistry [14]. The details regarding the model selection and validation can be found elsewhere [10].

Kumar and Singh, in their work, pointed out the dual nature of CF_3I addition to $\text{H}_2\text{-O}_2/\text{air}$ mixtures [10]. They observed detonation promotion at a small molar concentration of CF_3I addition (< 1200 PPM for $\text{H}_2\text{-air}$ mixtures and < 6000 PPM for $\text{H}_2\text{-O}_2$ mixtures) [10]. Therefore, to overcome the ambiguity of any promotion effect, the addition concentration of the inhibitor was fixed as 50000 PPM or 5% molar concentration. The ZND computations were carried out at these concentration levels, and no promotion effect was observed. Therefore, the inhibitor concentration of 50000 PPM or 5% molar concentration was used for carrying out further computations.

3. Results and Discussions

Effect of varying equivalence ratio on the inhibition efficiency

$\text{H}_2\text{-O}_2/\text{air-CF}_3\text{I}$ mixtures

The induction length and time were evaluated for $\text{H}_2\text{-O}_2/\text{air-CF}_3\text{I}$ mixtures with 5% CF_3I addition at an initial pressure, $P_0 = 1$ bar, and initial temperature, $T_0 = 295$ K. It is known that CF_3I shows a chemical inhibition effect at higher concentrations, where it drastically increases the induction length and time [10]. The chemical inhibition effect of CF_3I is primarily due to the radical scavenging of active radicals (specifically H radical) in the combustion environment. The recombination of active radicals with the halogenated atom is the major inhibition step for all halogenated inhibitors. The reaction cycle responsible for the inhibition effect is given below,



The above reaction cycle is responsible for the depletion of active radicals H and O in the reaction pool and its corresponding substitution with a less reactive CF_3 . The reactions R1-R3 compete with the conventional chain branching reactions R4-R6 and thus produce an inhibition effect on $\text{H}_2\text{-O}_2/\text{air}$ detonations.





The addition of 5% CF_3I to $\text{H}_2\text{-O}_2/\text{air}$ mixtures increases the induction zone length and time for all the equivalence ratios (0.4 – 2.0), as shown in Figure 1. This is because the post-shock temperature, T_{VN} which governs the chemical kinetics in the induction zone, decreases drastically with the addition of CF_3I . Thus, the addition of CF_3I decreases T_{VN} substantially, leading to a larger induction length and time. Also, it can be observed that the induction length for $\text{H}_2\text{-O}_2/\text{air-}\text{CF}_3\text{I}$ mixtures is more than an order of magnitude larger than for $\text{H}_2\text{-O}_2/\text{air-}\text{CO}_2/\text{H}_2\text{O}$ mixtures at the same addition levels (5% molar concentration). Thus, CF_3I is a far better inhibitor than CO_2 and H_2O at all the equivalence ratios studied.

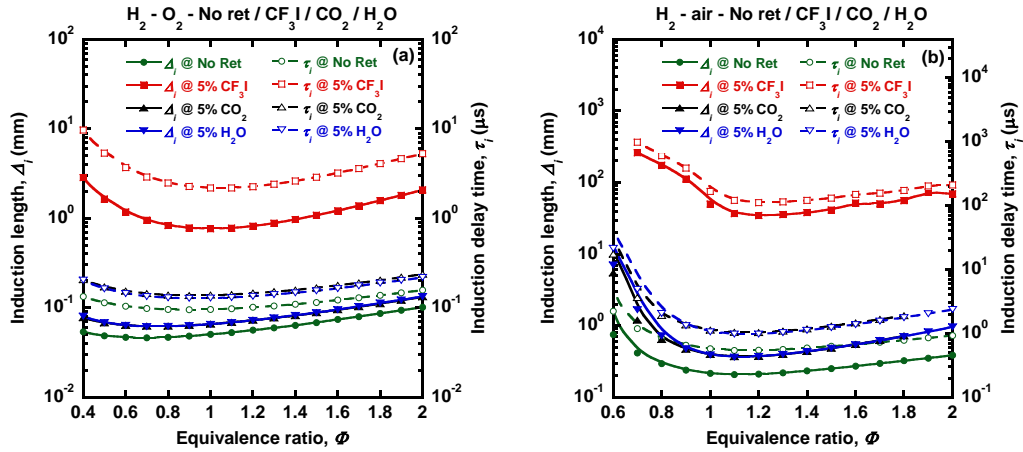
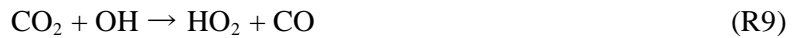


Figure 1: Effect of varying initial mixture composition on the induction length and induction time with and without retardants (5% CF_3I , CO_2 , and H_2O molar concentration). (a) $\text{H}_2\text{-O}_2$ detonations, and (b) $\text{H}_2\text{-air}$ detonations at $P_0 = 1$ bar and $T_0 = 295$ K.

$\text{H}_2\text{-O}_2/\text{air-}\text{CO}_2/\text{H}_2\text{O}$ mixtures

The induction length and time increase with the addition of CO_2 and H_2O at 5% molar concentration to $\text{H}_2\text{-O}_2/\text{air}$ mixtures at all the equivalence ratios. The inhibition effect of CO_2 is due to the rapid recombination of the H, O, and OH active radicals with CO and CO_2 (R7-R11). The consumption of these reactive radicals inhibits the chain branching process and thus increases the induction length/time.



Similarly, H_2O also inhibits detonation by removing the active H radical from the reaction pool. However, for H_2O , only one reaction is critical (R12), in which the O and OH radicals get recombined to form steam (H_2O) [10]. Thus, the reactions R7-R11 for CO_2 and R12 for H_2O compete with the chain branching and chain propagating reactions (R4-R6) and inhibits detonation.



Carbon dioxide and water vapor act like a suppressant or inhibitors over a wide range of fuel-air equivalence ratios (see Figure 1). The post-shock temperature, T_{VN} , also decreases with the addition of CO_2 and H_2O . The decrease in the post-shock temperature is slightly greater for CO_2 than H_2O , but it is substantially less than that of CF_3I . The reduction in the post-shock temperature affects the kinetics in the induction zone and governs the induction zone length and time. Thus, CO_2 and H_2O are comparable

inhibitors at all the equivalence ratios but are inferior to CF_3I as the increase in Δ_i is higher for CF_3I than CO_2 and H_2O under the conditions tested.

The inhibition efficiency of the inhibitors CF_3I , CO_2 , and H_2O vary considerably with the fuel-oxidizer equivalence ratio, specifically for fuel-air-inhibitor mixtures. It can be concluded that the variation in the inhibition efficiency is the result of two separate governing parameters, the post-shock temperature, T_{VN} , which changes with the addition of inhibitor, and the radical abstraction mechanism of the inhibitors, which can be quantified by evaluating the maximum H-concentration.

Effect of varying initial pressure on the inhibition efficiency

$\text{H}_2\text{-O}_2/\text{air-}\text{CF}_3\text{I}$ mixtures

The induction length decreases with an increase in initial mixture pressure from 0.2 bar to 5 bar at the stoichiometric condition with and without any additives, as shown in Figures 2 (a) and (b). The addition of CF_3I to $\text{H}_2\text{-O}_2$ and $\text{H}_2\text{-air}$ mixtures will increase the induction length due to the suppression or inhibition effect at any pressure. Hydrogen-oxygen and hydrogen-air mixtures diluted with CF_3I have larger induction zone lengths and times than the mixtures without dilution (refer to Figure 2). Although the addition of inhibitor offers an inhibiting effect for most $\text{H}_2\text{-O}_2$ and $\text{H}_2\text{-air}$ mixtures at any pressure, the inhibition efficiency decreases with increasing pressure. For example, the addition of 5% CF_3I at an initial pressure of 0.6 bar increases the induction length for a stoichiometric hydrogen-oxygen mixture by a factor of ~ 15.4 compared to the case with no CF_3I . However, for the same dilution at a higher initial pressure of 5 bar, the induction length increases by a factor of ~ 11.8 compared to the case with no CF_3I . Thus, the inhibition efficiency of CF_3I seems to decrease with increasing pressure, but still, CF_3I is a far better inhibitor than CO_2 and H_2O . At higher initial pressures, the recombination reaction $\text{O}_2 + \text{H} (+\text{M}) \rightarrow \text{HO}_2 (+\text{M})$ competes with the branching reaction (R4) and causes an increase in the induction length and time scales due to a decrease in the radical pool concentration. Since detonations are already inhibited by the effects of this competition for H atoms, the addition of CF_3I does not have a more significant impact on the Δ_i and τ_i as the pressure is increased.

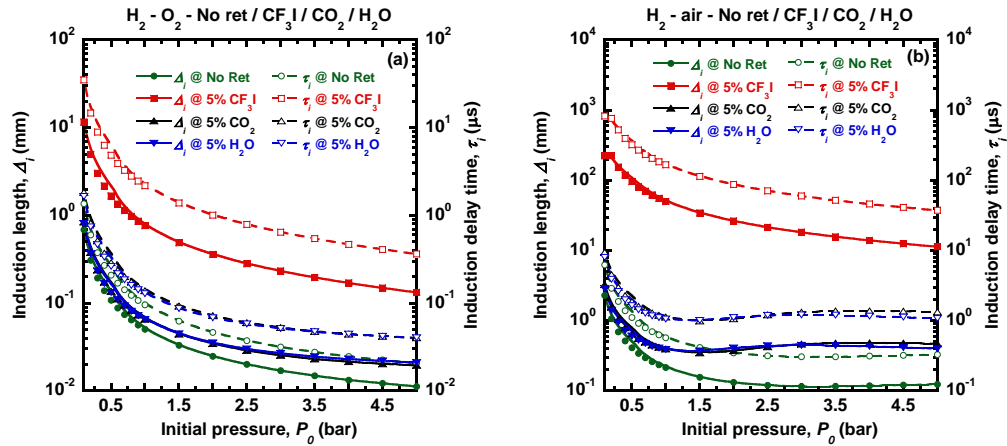


Figure 2: Effect of varying initial mixture pressure on the induction length and induction time with and without retardants (5% CF_3I , CO_2 , and H_2O molar concentration). (a) $\text{H}_2\text{-O}_2$ detonations, and (b) $\text{H}_2\text{-air}$ detonations at $\Phi = 1$ and $T_0 = 295$ K.

3.2.2 $\text{H}_2\text{-O}_2/\text{air-}\text{CO}_2/\text{H}_2\text{O}$ Mixtures

The addition of CO_2 and H_2O provides an inhibiting effect for hydrogen-oxygen and hydrogen-air mixtures at any pressure, and also, the inhibiting efficiency of these inhibitors increases rapidly with increasing pressure (refer to Figure 2). For example, the addition of 5% CO_2 at an initial pressure of 0.2 bar increases the induction zone length for a stoichiometric hydrogen-oxygen mixture by a factor of ~ 1.23 compared to the case with no CO_2 . However, for the same dilution levels of CO_2 at a higher initial

pressure of 5 bar, the induction length increases by a factor of ~ 1.75 compared to the case with no CO_2 . For mixtures diluted with H_2O , the addition of 5% H_2O at an initial pressure of 0.2 bar increases the induction zone length for a stoichiometric hydrogen-oxygen mixture by a factor of ~ 1.2 compared to the case with no steam. However, for the same dilution levels of steam at a higher initial pressure of 5 bar, the induction length increases significantly by a factor of ~ 1.9 compared to the case with no steam. Thus, the inhibitors CO_2 and H_2O seem to have increased inhibition efficiency with increasing pressure.

Effect of varying initial temperature on the inhibition efficiency

$\text{H}_2\text{-O}_2/\text{air-CF}_3\text{I}$ mixtures

Hydrogen-oxygen and hydrogen-air mixtures diluted with CF_3I have larger induction zone lengths than the same mixture without dilution. However, it can be observed that the induction length and time for CF_3I diluted $\text{H}_2\text{-O}_2/\text{air}$ mixtures decrease with an increase in the initial temperature, whereas it increases for CO_2 and H_2O diluted $\text{H}_2\text{-O}_2/\text{air}$ mixtures. Although the addition of CF_3I increases the induction length and time and offers an inhibiting effect for most hydrogen-oxygen and hydrogen-air mixtures at all mixture temperatures, the inhibiting effect is observed to decrease rapidly with increasing temperature (refer to Figure 3). For example, the addition of 5% CF_3I increases the induction zone length for a stoichiometric hydrogen-oxygen mixture by a factor of ~ 14.8 at 300 K compared to the case with no CF_3I . However, for the same dilution level at a higher initial temperature of 1000 K, the induction length increases by a factor of ~ 0.88 only compared to the case with no CF_3I . Thus, the inhibiting efficiency of CF_3I decreases rapidly with increasing temperature.

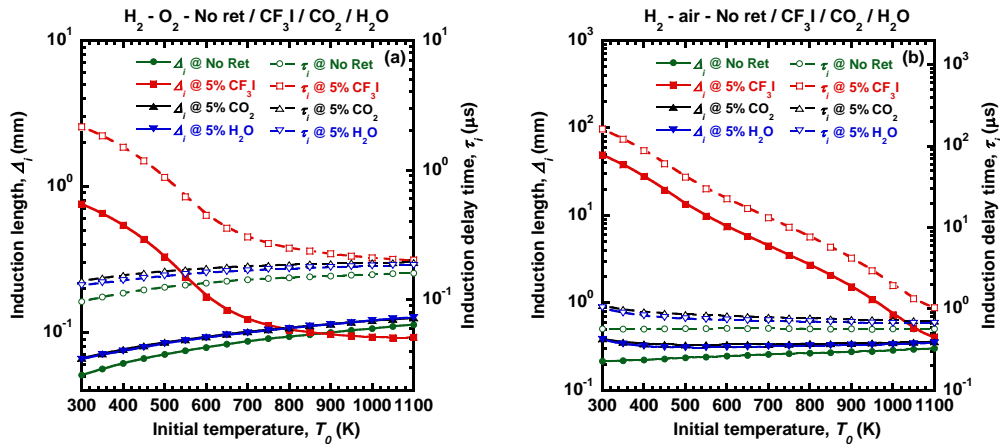


Figure 3: Effect of varying initial mixture temperature on the induction length and induction time with and without retardants (5% CF_3I , CO_2 , and H_2O molar concentration). (a) $\text{H}_2\text{-O}_2$ detonations, and (b) $\text{H}_2\text{-air}$ detonations at $\Phi = 1$ and $P_0 = 1$ bar.

$\text{H}_2\text{-O}_2/\text{air-CO}_2/\text{H}_2\text{O}$ mixtures

The addition of CO_2 and H_2O provides an inhibiting effect on $\text{H}_2\text{-O}_2/\text{air}$ mixtures; however, it can be seen from Figure 3 that the inhibition efficiency of these inhibitors is minimally affected by the increase in the initial temperature of the reacting mixture, unlike CF_3I diluted stoichiometric $\text{H}_2\text{-O}_2$ and $\text{H}_2\text{-air}$ mixtures. For example, the addition of 5% CO_2 at an initial temperature of 300 K increases the induction zone length for a stoichiometric hydrogen-oxygen mixture by a factor of ~ 1.3 compared to the case with no CO_2 . However, for the same dilution at a higher initial temperature of 1000 K, the induction length increases by only a factor of ~ 1.1 . This represents that the inhibition efficiency of CO_2 decreases slightly with the rise in initial temperature. For mixtures diluted with steam, the addition of 5% H_2O at an initial temperature of 300 K increases the induction zone length for a stoichiometric hydrogen-oxygen mixture by a factor of ~ 1.3 compared to the case with no steam. The same dilution of steam at a higher initial temperature of 1000 K increases the induction length by only a factor of ~ 1.1 . Thus, the inhibition efficiency of H_2O decreases with an increase in the initial temperature.

4. Conclusions

The efficiency of detonation inhibitors on H₂-O₂/air detonations was evaluated under varying mixture initial conditions using numerical computations. The inhibitors CF₃I, CO₂, and H₂O at 5% molar concentration were added to H₂-O₂/air mixtures, and the factor of increase in the induction zone length and time was used as an indicative parameter of the inhibition efficiency of the detonation inhibitors. It was found that CF₃I is a far better inhibitor than CO₂ and H₂O at all the mixture equivalence ratios studied in the current work. The addition of CF₃I drastically reduces the detonability of a given fuel-air mixture. It was also found that CO₂ and H₂O have a comparable inhibition efficiency at all the equivalence ratios but are inferior to CF₃I in inhibiting a detonation wave under similar initial mixture conditions. The inhibition efficiency was found to be the result of two separate governing parameters, the post-shock temperature, T_{VN} , which changes with the addition of inhibitor, and the chemical radical abstraction mechanism of the inhibitors. The inhibiting efficiency of CF₃I was found to decrease with increasing initial mixture pressure; however, it was still a better inhibitor when compared with CO₂ and H₂O. On the other hand, the inhibition efficiency of CO₂ and H₂O increased rapidly with increasing mixture pressure. The inhibition efficiency of CO₂ and H₂O is minimally affected by an increase in the initial temperature. A key takeaway from the current study is the effect of initial temperature on the inhibition efficiency of CF₃I. It was found that the efficiency decreased drastically at a higher mixture initial temperature. This result is of particular importance for flame and detonation suppression in nuclear reactors where the initial flammable mixture temperature is higher, and the results from the current findings can be used to make a proper choice of inhibitor under such conditions. The inhibiting effect of detonation inhibitors varied drastically with the initial conditions, and the same should be taken into consideration while designing fire and detonation safety systems for applications in petrochemical industries and nuclear reactors.

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