

Numerical study of detonation suppression with chemical inhibitors

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1 Introduction

The objective of this work is to study numerically the suppression of gaseous detonations with chemical inhibitors. In particular, we perform direct numerical simulations of the evolution of an already established detonation wave in a zone that contains a flame extinguisher (inhibitor). Halogenated compounds such as CF_3Br and CF_2Br are agents that have been commonly used as flame extinguishers. However, halons such as CF_3Br have high ozone depleting potentials and their manufacturing has been banned by the Montreal Protocol on Substances that Deplete the Ozone Layer. Consequently, the identification and study of alternative flame suppressants has been the subject of intense research thus far.

In this context, several experimental studies of detonation suppression with alternative inhibitors have been conducted; see, for example Moen et al. [1], Evariste et al. [2], Van Tiggelen & Lefebvre [3] and references therein. These studies suggest that the efficiency of the inhibitors is quite sensitive to the composition of the mixture and that there is no inhibitor as efficient as CF_3Br . Further, it seems that the bromine or iodine atom is necessary to induce chemical inhibition, as opposed to thermal suppression by large amounts of additives. In view of these results, it is deemed useful to try to simulate numerically the propagation characteristics of detonations in mixtures containing chemical inhibitors. Such studies can be used to test the efficiency of simplified kinetics models and model reduction methodologies. They can also be used for code validation via comparisons with experimental results. Further, they are useful in advancing our understanding of the interplay between the complex chemical and hydrodynamic phenomena that take place in supersonic combustion.

2 Description of the mathematical and chemical kinetics model

The system under study is assumed to be a reactive mixture of ideal gases. Neglecting dissipation mechanisms, as is usually the case in detonation studies, the non-dimensionalized mass, momentum and energy balance laws of the mixture read,

$$\frac{\partial}{\partial t}\rho + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (1a)$$

$$\frac{\partial}{\partial t}(\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) + \nabla p = 0, \quad (1b)$$

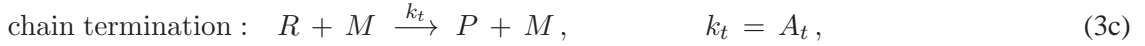
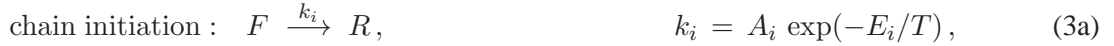
$$\frac{\partial}{\partial t}(\rho e_T) + \nabla \cdot (\mathbf{u}(\rho e_T + p)) = 0, \quad (1c)$$

where e_T is the total energy of the mixture, and the pressure p and density ρ are related with the temperature T via the ideal-gas state equation, ie,

$$e_T = \frac{1}{\gamma - 1} \frac{p}{\rho} + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} - q, \quad p = \rho T. \quad (2)$$

with γ being the specific heat ratio and q being the local heat release of the combustion.

The chemical-kinetics model employed herein is essentially the three-step chain-branching reaction model of Dold & Kapila [4], suitably modified to take into account of the presence of a chemical inhibitor. In particular, we consider a mixture of 4 species: reactant F , radical R , inhibitor I , and product P , plus a third body M . Our model consists of the following four reaction stages,



In other words, our scheme consists of the original model (3a)-(3c) of [4] plus the additional *endothermic* chain-inhibition stage (3d). The second column of equations above contains the expressions of the rate constants of each reaction stage. Further, for simplicity purposes we assume that the consumption rate of fuel F and inhibitor I is kept constant. In other words, the following relation holds between the concentrations of I and F , Y_I and Y_F respectively,

$$Y_I = r Y_F, \quad (4)$$

with r being a proportionality constant, determined by the initial composition of the mixture. Given that, in general $k_i \ll k_b$, this assumption is equivalent to assuming that the rate constants of the chain branching k_b and chain inhibition k_h are (almost) equal. Evidently, this is a rather strong assumption; however in view of the kinetic data reported in [2] and [3], this assumption is not deemed unreasonable, at least for small concentrations of the inhibitor I . Given the above assumption, the balance laws for the fuel and radical concentrations, Y_F and Y_R , respectively, read

$$\frac{\partial}{\partial t} Y_F + \mathbf{u} \cdot \nabla Y_F = -Y_F k_i - \rho Y_f Y_R k_b, \quad (5a)$$

$$\frac{\partial}{\partial t} Y_R + \mathbf{u} \cdot \nabla Y_R = Y_F k_i + \rho Y_f Y_R (k_b - r k_h) - Y_R k_t. \quad (5b)$$

Equations (1a)-(1c) and (5a)-(5b) form a system of balance laws that is closed by the constitutive relations (2) and an expression for the local heat release of the combustion process. By assuming that the reaction stages (3a)-(3c) are purely exothermic and that the reaction (3d) is purely endothermic, the expression for the local heat release reads

$$q = \frac{1}{r + 1} (q_F + r q_I) (1 - Y_F - Y_R), \quad (6)$$

where $q_F > 0$ is the heat of combustion of the fuel F and $q_I < 0$ is the heat of reaction of the inhibitor.

In all above relations, thermodynamic variables have been non-dimensionalized with respect to the pre-shock state. Also, the components of the velocity vector \mathbf{u} have been non-dimensionalized with respect to the sound speed in the pre-shock state. Finally, lengths are scaled by the half-reaction length of the one-dimensional steady-wave solution of the above system, $L_{1/2}$.

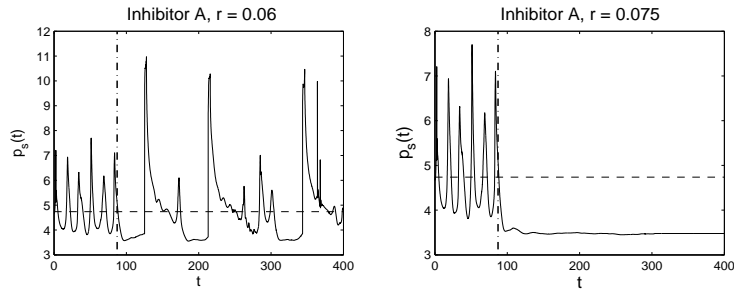


Figure 1: One-dimensional simulations of a mixture with inhibitor A: Shock pressure history. The dashed horizontal lines represent the shock pressure of the steady-wave solution. The dash-dot vertical lines show the time that the detonation reaches the inhibited zone.

3 Numerical Results and Discussion

In our study we have conducted both one and two-dimensional numerical simulations of detonations in planar geometry. As initial condition, we have employed the steady one-dimensional wave solution of the governing system (1a)-(1c) and (5a)-(5b) in an uninhibited mixture. Inflow (Dirichlet) condition is specified along the upstream boundary and outflow (Neumann) condition is specified along the downstream boundary. Also, in two-dimensional simulations, the width of the domain is $10 L_{1/2}$ and periodic conditions are specified along the longitudinal boundaries. The computational domain consists of two zones. Only the mixture in the second zone, downstream, contains a chemical inhibitor. Thus, the detonation wave propagates in the uninhibited zone first, so as the flow instabilities develop before it reaches the inhibited zone.

The numerical integration of the governing system is performed with the unsplit algorithm of Papalexandris et al. [5], [6]. It is a shock-capturing scheme for hyperbolic conservation laws with source terms that integrates all terms of the equations simultaneously, thus avoiding time or dimensional splitting. The resolution employed in our simulations is 20 pts./ $L_{1/2}$ and the CFL number is set equal to 0.5.

The following parameters are for the chain initiation, branching and termination reactions are

$$A_i = 2.5 \times 10^4, \quad A_b = 1 \times 10^5, \quad A_t = 3.0, \quad E_i = 20.0, \quad E_b = 15.0, \quad q_F = 3.0. \quad (7)$$

Also, the specific heat ratio is set equal to $\gamma = 1.2$. These values are chosen so as to roughly correspond to the properties of an $H_2/CO/O_2/Ar$ mixture. The initial profile is a slightly overdriven steady wave; its overdrive factor is $f = (D/D_{CJ})^2 = 1.1$, with D_{CJ} being the velocity of the Chapman-Jouguet steady-wave solution of the system (1a)-(1c) and (5a)-(5b).

Two types of inhibitors are considered, namely,

$$\text{inhibitor A : } \quad A_h = 2.5 \times 10^5, \quad E_h = 15.0, \quad q_I = -3.0, \quad (8a)$$

$$\text{inhibitor B : } \quad A_h = 1.8 \times 10^5, \quad E_h = 15.5, \quad q_I = -3.0. \quad (8b)$$

These values are chosen so that inhibitors A and B roughly correspond to CF_3Br and CF_2HCl , respectively.

One-dimensional Simulations

Our one-dimensional simulations predicted that the minimum concentration of inhibitor A that is required to suppress the detonation is $r(A) = 0.075$. Figure 1 shows the shock-pressure histories for two mixtures with different inhibitor concentrations, namely, $r(A) = 0.06$ and $r(A) = 0.075$. It can be seen that when the detonation enters the inhibited zone, the strength of the precursor shock starts to drop. In

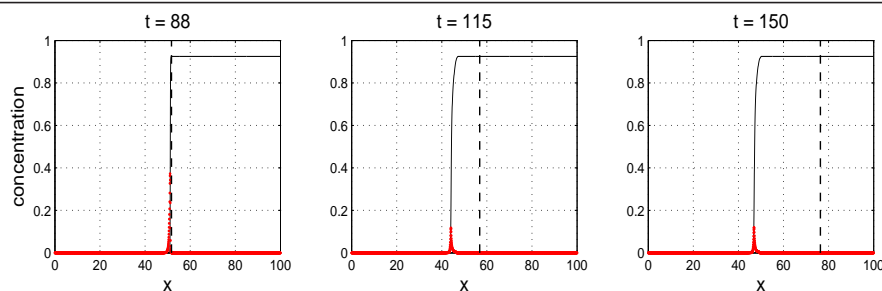


Figure 2: One-dimensional simulation of detonation suppression with inhibitor A: concentration profiles of fuel F (continuous line) and radical R (red dotted line), at various times for $r(A) = 0.075$. The dashed vertical line shows the location of the precursor shock.

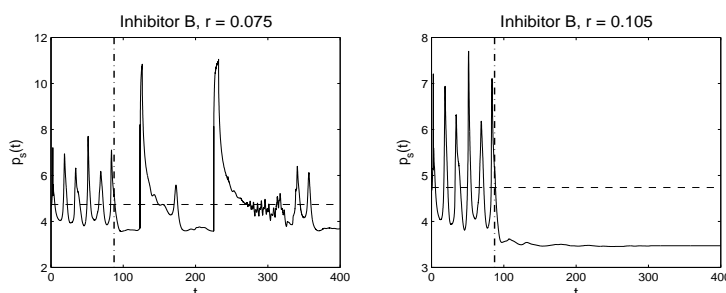


Figure 3: One-dimensional simulations for mixtures with inhibitor B: Shock pressure history. The dashed horizontal lines represent the shock pressure of the steady-wave solution. The dash-dot vertical lines show the time that the detonation reaches the inhibited zone.

the case of low inhibitor concentration, $r(A) = 0.06$, this drop is not permanent. Pockets of unreacted material are formed which eventually burn due to thermal runaway. As they burn, they emit pressure waves that propagate up to the precursor shock. Consequently, the precursor shock increases its strength and re-ignites the mixture, thus helping sustain the detonation. On the other hand, in the case of high inhibitor concentration, $r(A) = 0.075$, the drop in the strength of the precursor shock once it enters the inhibited zone is permanent resulting to detonation suppression; see Figure 2.

The numerical simulations further predicted that when inhibitor B is used, then higher inhibitor concentrations are needed to suppress the detonation. In particular, the minimum concentration of inhibitor B that is required suppress the detonation is $r(B) = 0.105$; see Figure 3. This is to be expected, since the pre-exponential factor of the chain-inhibition reaction with inhibitor B is substantially larger than with inhibitor A. As a matter of fact, the ratio of the minimum concentrations for detonation suppression, $r(A)/r(B) = 0.075/0.105 = 0.714$ is almost equal to the inverse of the ratio of the corresponding pre-exponential factors, cf (8a)-(8b). In other words, the simulations predict that once the pre-exponential factor is lowered by a certain percentage, the inhibitor concentration must be increased by the same percentage. Finally, it should be mentioned that the characteristics of the detonation evolution did not change when we increased the spatial resolution, up to 100 pts. $L_{1/2}$.

Two-dimensional simulations

Our two-dimensional simulations predicted that, for both A and B inhibitors, the minimum inhibitor concentration for detonation suppression is higher than in the one-dimensional cases. More precisely, when inhibitor A is used, the minimum concentration is $r(A) = 0.115$, as opposed to $r(A) = 0.075$ for the one-dimensional case. Also, the minimum concentration of B for detonation suppression is raised to $r(B) = 0.16$, as opposed to $r(B) = 0.105$ for the one-dimensional case.

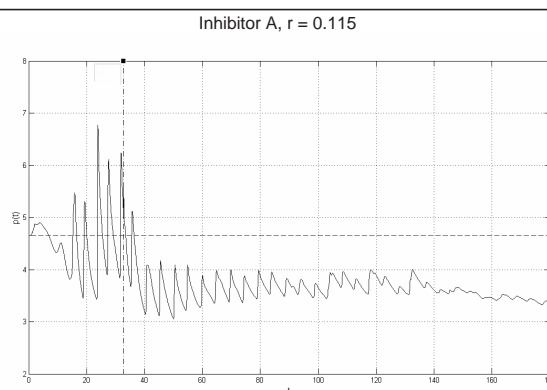


Figure 4: Two-dimensional simulation of detonation suppression with inhibitor A: shock pressure history. The dashed horizontal line represents the shock pressure of the steady-wave solution. The dash-dot vertical line shows the time that the detonation reaches the inhibited zone.

The explanation for this difference between one and two-dimensional simulation predictions is the following. As is well known, in multi-dimensional flows the transversal instabilities result in the formation of triple points on the precursor shock. The transverse waves emanating from these triple points increase the temperature of the unreacted material in the wake of precursor shock. As a result, this material burns fast generating pressure waves that propagate up to the precursor shock, thus helping sustain the detonation. Therefore, in two-dimensional flows, higher inhibitor concentrations are indeed required to compensate for the effects of the transverse waves.

The shock pressure histories of two-dimensional simulations of detonation suppression with $r(A) = 0.115$ and $r(B) = 0.16$ are shown in Figures 4 and 5, respectively. In these figures it can be observed that the drop in the shock strength is not monotone, as in one-dimensional simulations. Instead, the shock pressure oscillates around a value, which is nonetheless lower than the steady-wave shock pressure. These oscillations are due to the transverse-wave effects, described above. In particular, the pressure waves that are generated by the burning of the unreacted material are not strong enough so as to substantially increase the precursor shock strength. Thus, the detonation eventually quenches, albeit at considerably longer times than in one-dimensional flows. Nonetheless, the ratio of the predicted concentration thresholds for detonation suppression for the two inhibitors, $r(A)/r(B) = 0.115/0.16 = 0.718$ is again almost equal to the inverse ratio of the corresponding pre-exponential factors of the inhibiting reactions, as in the case of one-dimensional simulations.

We further note that the experimental studies with $H_2/CO/O_2/Ar$ mixtures reported in [2] and [3] show that the required inhibitor concentrations for detonation suppression are 2 ~ 5% for mixtures containing CF_3Br , and 9 ~ 12% for mixtures containing CF_2HCl , depending on the H_2/CO concentration ratio. These studies also show a strong dependence of the required inhibitor concentration on the pressure of the mixture. Thus, our numerical predictions are not far from the experimental data.

4 Conclusions

A study on detonation suppression with chemical inhibitors has been performed, via one and two-dimensional direct numerical simulations. A simplified four-reaction chain-branching kinetics model has been employed. Our study shows that the minimum inhibitor concentration required for detonation suppression is inversely proportional to the pre-exponential factor of the inhibition reaction. One-dimensional simulations underestimate considerably, by approximately 35%, the amounts of inhibitor

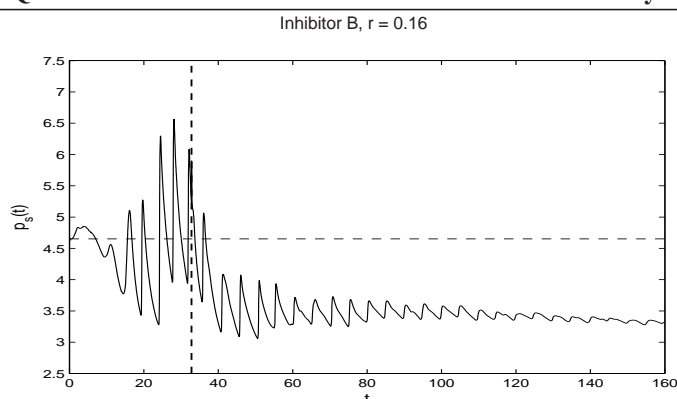


Figure 5: Two-dimensional simulation of detonation suppression with inhibitor B: shock pressure history. The dashed horizontal line represents the shock pressure of the steady-wave solution. The dash-dot vertical line shows the time that the detonation reaches the inhibited zone.

that are required for detonation suppression because they do not account for the stabilizing effect of the transverse waves that emanate from the leading front. Thus, multi-dimensional simulations are necessary for accurate numerical predictions. The simplified kinetics model can be sufficiently accurate for employment in detonation simulations, provided that values for the pre-exponential factors and activation temperatures are judiciously chosen. Nonetheless, since experimental data show that the required inhibitor concentration for detonation suppression vary with pressure, the simplified model should eventually be generalized to take into account pressure dependent kinetics; see, for example, Liang & Bauwens [7] for a pressure-dependent simplified chain-branching model. Numerical convergence studies of two-dimensional simulations should also be performed to confirm these observations.

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