# COMPUTATIONS OF INHIBITION EFFECTIVENESS OF HALOGENATED COMPOUNDS IN PREMIXED FLAMES

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The burning velocity, $S_u$, is an important parameter which characterizes the inhibition efficiency of halogen-containing additives employed as flame retardants. The burning velocity decreases with increasing inhibitor concentration. Rosser et al. [1] studied experimentally the inhibition effect of different additives on methane flames and found that the burning velocity decreased linearly with increasing additive concentration for concentrations less than 0.5 % by volume. In addition, Rosser et al. [1] used the parameter $\Phi$ ($=dS_u/dC_{in}$) as a measure of inhibition efficiency. Based on the linear dependence of $S_u$ on additive concentration, Fristrom and Sawyer [2] suggested using a dimensionless inhibition parameter $\Phi_{FS}$ for evaluation of the inhibitive efficiency of additives:

$$\Phi_{FS} = [(S_0-S_u) \cdot C_{O2}] / [S_0 \cdot C_{in}] \qquad (1)$$

where, $S_0$ and $S_u$ are the burning velocities for $CH_4$-air flames without and with additives, respectively, $C_{in}$ is the additive mole fraction, $C_{O2}$ is the initial concentration of oxygen in the mixture. Fristrom and Van Tiggelen [3] suggested that the parameter $\Phi_{FS}$ could be written as the sum of the inhibition indices $\phi_i$ for each atom constituting the additive molecule:

$$\Phi_{FS} = n_H\phi_H + n_C\phi_C + \sum n_x\phi_x \qquad (2)$$

Here, the subscript x indicates a halogen atom. The assumption of a linear dependence of the burning velocity on inhibitor concentration is, however, not consistent with other studies. Parks et al. [4] showed that for $CF_3Br$ addition over a wide range of additive concentrations and mixture compositions, the flame speed of premixed methane-air and propane-air flames decreased exponentially.

In this study, flame structures were computed for stoichiometric laminar flames burning mixtures of air with methane, ethylene, ethane, and methanol at atmospheric pressure and an initial temperature of 298 K. From these computations the burning velocity was determined. The following halogenated retardants were considered: $CF_3H$, $C_2HF_5$, $C_2F_6$, $CF_4$, $CF_3Br$ and $CF_3I$. The PREMIX code was employed [5] with the data base for the C/H/O system based on existing kinetic models. A comprehensive set of elementary reactions for fluorine-containing $C_1$-$C_2$ species and the kinetic sub-models for bromine and iodine containing species were the same as that in our earlier work.

Calculations showed that for the halogenated additives $CF_3Br$, $CF_3I$, $CF_3H$, $C_2HF_5$, $C_2F_6$ and $CF_4$, the burning velocity of $C_1$ - $C_2$ hydrocarbons decreased exponentially with increasing additive concentration over a wide range of additive concentrations consistent with experimental results. The inhibition parameter $\Phi$ proposed by Fristrom and Sawyer [2] indicating inhibition efficiency was modified to the expression:

$$\Phi=(C_{O2}/C_{in}) \cdot \ln(S_0/S_u) \qquad (3)$$

which accounts for the nonlinear dependence of burning velocity over a wide range of additive concentrations. The inhibition indices for halogen atoms and groups were obtained for stoichiometric premixed $C_1$ - $C_2$ hydrocarbon-air flames. Calculations showed that increasing agent concentration leads to saturation of chemical effects. Subsequent additive action is due to physical influences including heat capacity and dilution effects.

Scavenging of chain carriers by a flame inhibitor is controlled by the reactions which regenerate the scavenging agent and due to the concentration of a chemically active inhibitor [6]. The superior efficiency of $CF_3Br$ and $CF_3I$ as flame inhibitors, as compared to $CF_4$ and other fluorinated hydrocarbons, is due to the regeneration cycle associated with HBr and HI, respectively. It is possible to define a regeneration coefficient which indicates the effective number of catalytic cycles involving the inhibitor during the combustion process. The regeneration coefficient (RC) is determined by the ratio of the total concentration of scavenging agent (HBr, HI) consumed (or produced) to the initial concentration of this species which formed the agent:

$$RC = [HBr]_{total} / [CF_3Br]_{initial} \quad (4)$$

The total HBr consumed is determined by integration of the rate of reactions in which HBr is consumed in extent to maximum of H atom concentration. Calculations showed that the regeneration coefficient varied from seven to five as the $CF_3Br$ concentration in stoichiometric $CH_4$/air flames varied from 0.5 to 4 percent by volume. The regeneration coefficient for HI was approximately four.

**References**


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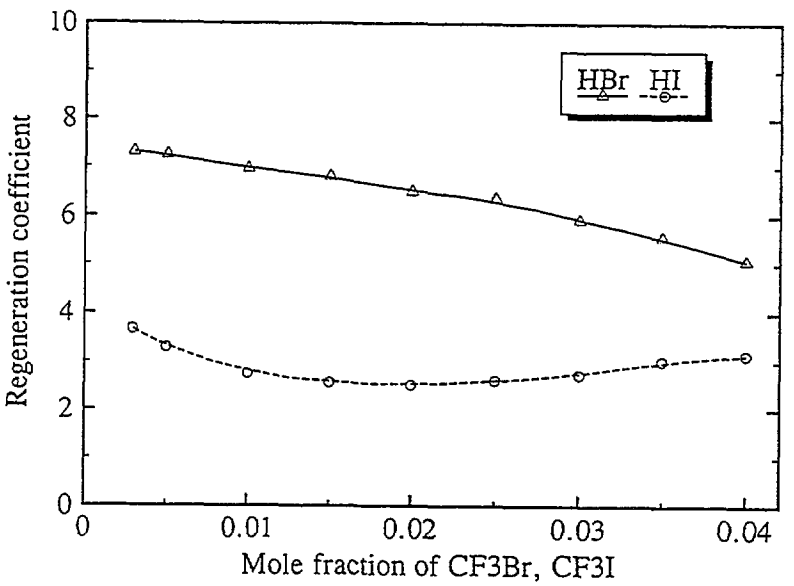


Figure 1. Regeneration coefficients of HBr and HI as a function of $CF_3Br$ and $CF_3I$ mole fraction in stoichiometric $CH_4$/air flames.