

THE INFLUENCE OF HALOGENATED FIRE SUPPRESSANTS ON THE
COMBUSTION OF C₁-C₂ HYDROCARBONS

V. Babushok', T. Noto**, D.R. Burgess, Jr., A. Hamins **W. Tsang**
National Institute of Standards and Technology
Gaithersburg, MD 20899
(301) 926-4513 FAX

A. Miziolek
U.S. Army Research Laboratory
Aberdeen Proving Ground, MD 21005-506
(410) 278-6157 Tel
(410) 278-6150 FAX

ABSTRACT

Numerical simulations of the combustion of a number of fuels; (CH₄, CH₃OH, C₂H₆, C₂H₄ and C₂H₂) in air, in the presence and absence of fire suppressants, (CF₃Br, CF₃I, CF₄, CHF₃, C₂F₆, and C₂F₅H) have been carried out. The simulations considered reactions in a plug flow reactor, in a well-stirred reactor and for a premixed laminar flame and were carried out with the Sandia CHEMKIN code. The input data consists of four blocks of rate constant information that describe the C-H-O, C-H-O-F, C-H-O-F-Br, and C-H-O-F-I systems. The specific properties in addition to species concentrations are (a) for the plug flow reactor; the induction delay time and time for destruction of oxidant and fuel, (b) for premixed laminar flame; flame velocity, (c) for the well stirred reactor, the self ignition temperature and extinction flow rates. The simulations showed that induction times are not an appropriate variable for ranking inhibition efficiency. All the other parameters track known behaviors of inhibition efficiency with good accuracy. The general ordering of inhibition strength is CF₃Br, CF₃I > C₂F₆ > C₂HF₅ > CHF₃ > CF₄, with the first two compounds clearly superior to the others.

* on leave from the Institute of Chemical Kinetics and Combustion,
Novosibirsk, Russia

** on leave from NKK Corporation, Kawasaki-Ku, Kawasaki, 210, Japan

INTRODUCTION

We summarize in this paper the results of recent numerical studies on the properties of combustion systems in the presence and absence of chemical inhibitors¹⁻⁴. The aim of the investigations is to use this methodology to (a) develop a better understanding of the inhibition process, (b) make experimental tests more meaningful and (c) examine the possibilities for the development of a rank order of inhibition efficiencies. The stimulus for this work is the need to replace brominated flame suppressants due to their serious impacts on the ozone layer. Indeed, this type of numerical work, applied to atmospheric chemistry, played an important role in the decision to phase out CF_3Br as a fire suppressant

An actual fire is an extremely complicated phenomena. Ultimately, the results of any laboratory and numerical study must be validated under actual field conditions.. However, full scale tests are very expensive and unless carefully thought out may not yield data that are extensible to other fire situations. Hence, the need for laboratory studies, and more recently, the use of computer simulations. Such "tests" can only hope to capture some portion of the phenomena represented by an actual fire. Nevertheless, they are better defined and much easier to carry out. It is expected that an iterative cycle involving laboratory and numerical studies with validation by fire tests may lead to the type of fundamental understanding that will make the selection of new fire suppressants easier than has hitherto been the case.

Numerical simulation represents a relatively new methodology in the arsenal of fire technologists for assessing inhibitor efficiency. It is a reflection of increasing computational capability for simulating complex physico-chemical phenomena on the basis of fundamental inputs. In addition many of the input elements, rate constants, thermodynamic and physical properties, can now be measured or estimated with considerable accuracy. However, a real fire is the result of the complex interplay of physical (fluid dynamics, mass and heat transfer and thermal effects) and chemical effects. At the present time the merger of these two fields in treating combustion is still a research frontier. Thus, even in principle, numerical methods, cannot be truly predictive. Furthermore, the inaccuracies in the input data can cause important uncertainties even in restricted work. Nevertheless, as will be seen below, numerical methods are capable of reproducing accurately some aspects of fire phenomena. The present work is carried out with the expectation that in these more clearly defined

areas, the chemical role of fire inhibition can be revealed. It should be emphasized again that this uncertainty, brought about by the necessity for simplification, applies equally to all laboratory tests as well. It is our view that the full benefits from numerical simulation are probably most likely to be found in deriving a better understanding of various test methods. For an arbitrary new inhibitor, the data base for simulation probably does not exist. However, if laboratory tests were better understood, in terms of their ranges of applicability, one would have much more confidence in the recommendations derived from them. This should be an important direction in future work.

PAST WORK

The numerical study of flame inhibition processes involving bromine-containing organic compounds, with detailed chemical kinetics, was initiated by Dixon-Lewis et al.^{5,6} and Westbrook^{7,8}. The first studies described the effects of HBr, CF₃Br, CH₃Br, CH₃I, etc., on hydrocarbon flames. The importance of catalytic cycles for the reduction of H-atom concentration by bromine compounds was demonstrated. Westbrook showed that the fluorocarbon part of the retardant molecule can also make contributions in scavenging active species, thus enhancing the efficiency of CF₃Br as a flame suppressant'. Much of the older experimental work has been summarized by Ford⁹ and there are some significant discrepancies with the simulation results.

SCOPE OF WORK

The present study will be concerned with the following inhibitors; CF₃Br, CF₃I, CF, CHF₃, C₂F₆, and C₂HF₅. The fuels tested are CH₄, CH₃OH, C₂H₆, C₂H₄ and to a very limited extent C₂H₂. Air is the oxidizer. CF₃Br or Halon 1301 is the standard against which all other inhibitors must be judged. There has been much recent interest in CF₃I. The other fluorinated organics are among the candidates that have been considered as substituents

COMPUTER PROGRAMS

A very important driver for numerical simulation is the availability of standard programs for carrying out such work. The present simulations were carried out using three of the packages from the Sandia CHEMKIN¹⁰ code". The specific phenomena that will be simulated are (a) steady one-dimensional premixed laminar flames, (b) plug flow reactor and (c) well-stirred reactor. These programs are coupled with an internally written

graphical post processor, which has proved to be extremely useful for the visualization of the data

DATA BASE

In an earlier section we have mentioned the need for an accurate data base of kinetic and thermodynamic information as inputs for the simulation. The foundation of this data base is that developed for fluorine-containing $C_1/H/O$ and $C_2/H/O$ species at NIST¹² and used for the prediction of the influence of CF_2H_2 , CHF_3 and CF_4 additives on methane/air flames. With the addition of appropriate organic bromine and iodine species, the data base was used to deduce the influence of CF_3Br and CF_3I ². The subset of C_1-C_2 oxidation chemistry is from existing kinetic models¹³⁻¹⁶. Some rate constants were updated to match experimental dependencies of burning velocities of air mixtures of H_2 , CH_4 , CH_3OH , C_2H_6 , C_2H_4 and C_2H_2 on equivalence ratio⁴.

VALIDATION OF DATA BASE

The results of comparisons of our simulations with experimental measurements are contained in earlier publications¹. This includes not only ignition delay but also *species* concentration as a function of time for different systems (oxidation of H_2 , CH_4 , CH_2O , CH_3OH , C_2H_6 and additives CF_3H , CH_3Br and CF_3Br). The important point is that the main physico-chemical characteristics of the system are reproduced with reasonable accuracy. Unfortunately, there are not many high temperature experimental kinetic and ignition delay measurements involving iodine containing *species*. There does not appear to be any experimental data on CF_3I itself. Takahashi et al. have reported on the effect of CH_3I on the ignition of diluted CH_4 - and C_2H_6 - air mixtures behind shock waves (1.4-3 atm and 1200 - 2000K)¹⁷. Our numerical simulations demonstrate good agreement with these data. Westbrook^{7,8} has summarized the experimental data on the effect of bromine containing compounds on methane flames. With the present data base, the observed dependencies of flame velocity on suppressant concentrations can be reproduced with satisfactory accuracy.

PLUG FLOW REACTOR

The scenario for the plug flow reactor simulation is that of a volume of gas raised to a temperature above that for self-ignition and then maintained under adiabatic conditions. Temporal history for a stoichiometric methane/air mixture can be found in Figure 1. Initially, there are no signs of reaction. However, radicals are in fact being

created. **These** radicals will interact with the oxygen in the system. Above a certain minimum there is a sudden acceleration of the rate brought about by the chain branching nature **of** the combustion process with the added driving **force** of a rapidly increasing temperature due to the reaction exothermicity. The consequence **is** virtually a step-like increase **in** the temperature and decrease in fuel and oxidant. The situation can be characterized by (1) the induction period (ignition delay) where active radicals are generated, (2) the reaction period, where a considerable amount **of** the reactant is consumed and is characterized by large temperature increases and (3) relaxation towards the equilibrium state **or** completion **of** reaction. We are concerned with the first **two** periods. It is highly improbable that the third time period should have much influence on the combustibility **of** a mixture.

Figure 2 contains typical results **on** the induction time **as** a function of initial temperature for a number **of** inhibitors. The important observation is that under certain conditions the inhibitor **can** act **as** a promotor in the sense of decreasing the induction time before actual combustion; clearly **not** **inhibiting** the reaction. The reason for this behavior is that many inhibitors, for example CF_3Br , are thermally less stable than the fuel. **Thus, as** the inhibitor decomposes, the free radicals that are formed can initiate chain reaction and this is sufficient to overcome any of the processes that the inhibitor **or** its products may undergo **to** reduce radical concentration by scavenging. At the higher temperatures, the fuel produces many more free radicals, thus the balance **swings** back for scavenging.

We next examine the region where most **of** the fuel and oxidant are destroyed. This is **also** the region of maximum energy release. Figure 3 contains typical computational results. Although, from Figure 1, the decrease in concentration appears to be infinitely steep, this **is** actually a function of the scale that is used. From the calculational results it is possible to determine the slope **of** this line. The conclusion **as** **can** be deduced from Figure 3 is that the inhibitor **in** all cases reduces the rate **of** energy release **or** equivalently the rate **of** destruction **of** the fuel and **oxidant**. Compared to CF_3H , CF_3Br and CF_3I are clearly **superior**. In line with this result, it is interesting to consider the consequences on **radical** concentrations. Figure 4 **shows** the concentration of H, OH and O in the absence and presence of various inhibitors. Hydrogen atom concentration is seriously reduced by their presence. This reduction is particularly marked for the case of CF_3I and CF_3Br . Most

interestingly, OH and O concentrations are much less sensitive. **This** result is in line with earlier conclusion^{2,4} that a major route for chemical inhibition is the recombination of hydrogen atoms to form H₂ through catalytic cycles involving the halides.

Probably the most important conclusion from these simulations is the demonstration that the induction time prior to combustion is not a valid measure of inhibition effectiveness. **Instead**, maximum rate of fuel or oxidant loss or energy release is a more valid inhibition parameter. From the radical profiles, it is concluded that this is brought about by a reduction in the H-atom concentration. This is not unreasonable and is in accord with earlier conclusions from flame simulations. **A** particularly attractive feature of plug flow simulations is that they are relatively *easy* to carry out in terms of time. Thus it is possible to carry out a large variety of "what if" experiments on the computer.

LAMINAR PREMIXED FLAME VELOCITIES

A large amount of the published data on the action of inhibitors on combustion systems have focused on the ability of inhibitors to reduce the flame velocity. Figure 5 presents typical results on the flame velocity as a function of quantity of inhibitors in stoichiometric methane-air flames. There is a monotonic decrease in the flame velocity with increasing inhibitor concentrations. Note the different slopes of the curves. These are reflections of the differences in inhibition efficiencies for the various inhibitors that used. The ordering is CF₃Br, CF₃I > C₂F₆ > C₂H₂F₂ > CHF₃ > CF₄. This general trend is followed by the other fuels that have been tested (ethane, methanol, ethylene and acetylene). Ethane and methanol appear to be less sensitive to retardant action than methane. The bromine and iodine compounds are clearly the most efficient flame suppressants. They are in general of equal effectiveness except in methanol where CF₃I is superior. The retardants are more effective for rich mixtures than for lean. With 1% inhibitor concentration, the decrease in burning velocity is most pronounced for unsaturated fuels. The general ordering of retardant efficiency is consistent with calculational results on flame thickness and radical concentrations. There is in fact a direct correlation between decreases in flame velocity and maximum hydrogen atom concentration.

The relative importance of physical and chemical effects can be made clearer by carrying out simulations with and without the set of reactions of a particular inhibitor. Results in methane are summarized in Figure 6. The fractional chemical contribution is

defined as $(S_{uc}-S_{ui}/ S_{uo}-S_{ui})$ and the subscripts ui, uc and uo refer to calculations with and without inhibition chemistry and without inhibitor, respectively. An advantage of simulation experiments is precisely the capability of examining this type of issue. In this case, the numerator represents the change in flame velocity brought about solely by chemistry, while the denominator is the total change. The large chemical component for inhibition by CF_3Br and smaller contributions for the other suppressants are clearly displayed. These results are in accord with the conclusions of Sheinson et al.¹⁸ regarding the contributions from physical and chemical effects in suppressant action of CF_3Br . An additional consequence of this treatment is that there appears to be a maximum value for the chemical contribution to inhibition. The results in Figure 5 can be used to determine the hypothetical heat capacity of a compound that will give the equivalent drop in flame velocity as the inhibitors studied here. For CF_3Br , we find that this will require a non-reactive C_8F_{18} molecule.

Reaction pathway analysis demonstrates the importance of the regeneration of reactive scavengers through radical combination processes. Inhibition is largely brought about through the scavenging of hydrogen atoms. A distinction is made between scavenging with and without regeneration of the scavengers. Fluorinated fragments belong in the latter category. In the presence of iodine and bromine, regeneration of the hydrogen halides is brought about by various cycles. These involve not only radical attack on the fuel, inhibitor and their breakdown products, but equally important (particularly for iodine), also processes initiated by radical reaction with the halogen atom. For methanol, with CF_3I as the inhibitor, a particularly important reaction is $I + HO, \Rightarrow HI + O$, which regenerates HI while removing HO, radicals in the flame zone.

STIRRED REACTOR SIMULATIONS

The ideal stirred reactor consists of a vessel with inflow and outflow ducts where complete mixing occurs and therefore reaction processes are controlled by chemical kinetics. In actual practice, these conditions are difficult to achieve and deviations must be considered. Fig. 7 contains the results of simulations of the oxidation of a stoichiometric methandair mixture in a CSTR for inlet temperatures of 850 and 863 K, respectively. It can be seen that the range of CSTR operations is covered by low and high temperature regimes. At low inlet temperatures, a high-temperature steady state isola type solution exists (Fig. 7a). Increasing the inlet temperature until the self-ignition temperature is

achieved leads to tangency of the low-temperature steady state solution with the unstable solution curves at approximately **863 K** (Figure **7b**). Further increases in the inlet temperature lead to a broadening of the intersection region and the appearance of left and right hysteresis loops (**mushroom**). We will be concerned with the behavior on the right side of curve. The top and lower turning points of the curve can be identified with extinction and ignition.

Addition of 1% CF_3H , CF_3Br and CF_3I (individually) to stoichiometric air/methane mixtures leads to an increase in the self-ignition temperature or equivalently the need for higher inlet temperatures to effect the transition from isola to hysteresis loop behavior. The general situation is illustrated in Fig. 8. Addition of inhibitors destroys the mushroom. The **mushroom** shape is not recaptured for the inhibited system until inlet temperatures of 870K, 1010K and 1060K are reached for CF_3H , CF_3Br and CF_3I , respectively. This is in contrast to a temperature of **863 K** for the uninhibited system. The results for the inert high heat capacity additive are also included and it can be seen that the changes are small.

Fig. 9 shows that the addition of inhibitors leads to longer residence times at the extinction point. However, near the extinction point the stationary states for the systems with the additives cross that of the stoichiometric methane/air mixture. Thus, the ordering is lost. For the large heat capacity chemically inert additive which produces the same reduction in burning velocity as CF_3Br , there is a general decrease in the temperature. Thus, the two effects which are known to increase flame inhibition capability may well cancel each other in a CSTR experiment.

An alternative way of viewing the data at the extinction point is given in Fig. 10. This contains a plot of the $\text{CO}_2/[\text{CO} + \text{CO}_2]$ ratio near the extinction region. This function is related to the efficiency of combustion. The stationary states for the stoichiometric methane/air mixture near the extinction point completely overlap those for the system with additives and it is thus possible to make a rank ordering of the effectiveness of the additives.

These results suggest that CSTR experiments may be a useful test method for ranking inhibition efficiency. Particularly interesting is the distinction between self-ignition and extinction behavior. One notes the large differences in temperature, so that clearly different type of chemical mechanisms are involved. Finally, we note that the sensitivity of the ignition temperature to the presence of inhibitors is in marked contrast to the situation

with respect to ignition delay,

ACKNOWLEDGEMENT

This work was carried out with the partial support of the Strategic Environmental Research and Development Program (SERDP).

REFERENCES

1. Babushok, **V.**, Burgess, D. R., Tsang, W. and Miziolek, **A.** "Simulation Studies on the Effects of Flame Retardants on Combustion Processes in a Plug Reactor" in "Halon Replacements Technology and Science." (Miziolek, **A.** and Tsang, W. ed.) ACS Symp. Ser., 1995, 611,275.
2. Babushok, V., Noto, T., Burgess, D. R., Hamins, **A.** and Tsang, W. "Influence of CF_3I , CF_3Br and CF_3H on the High Temperature Combustion of Methane", Combustion and Flame, (in press)
3. Babushok, V., Noto, T., Burgess, D. R., Hamins, **A.** and Tsang, W., "Inhibitor Influence on the Bistability of **A** CSTR" Combustion and Flame (in press)
4. Noto, T., Babushok, **V.**, Burgess, D. R. Jr., Hamins, **A.**, Tsang, W., and Miziolek, A. "Effect of Halogenated Flame Inhibitors on C_1 - C_2 Organic Flames", 26th Symposium (Int'l) on Combustion (in press) 1996
5. **Dixon-Lewis**, G., and Simpson, R.J., Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1977, pp.1111-1119.
6. Day, M.J., Stamp, D.V., Thompson, K, and Dixon-Lewis, G., Thirteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1971, pp.705-712.
7. **Westbrook**, C.K., Nineteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1982, pp.127-141.
8. Westbrook, C.K., Combust.Sci.Technology 34:201-225 (1983).
9. Ford, C. L., "An Overview of Halon 1301 Systems", in "Halogenated Flame Suppressants" (Gann, R., ed.) American Chemical Society, 16, pp. 1, 1975
10. Certain commercial materials and equipment are identified in this paper in order to specify adequately the procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the material or equipment is necessarily the best for the purpose.
11. Kee, **R.J.**, Miller, J.A., Jefferson, T.H. CHEMKIN: A General-Purpose, Problem Independent, Transportable, Fortran Chemical Kinetics Code Package. SANDSO-8003, Sandia National Laboratories, 1989.

12. Burgess, D.R.F., Jr., Zachariah, M.R., Tsang, W., and Westmoreland, P.R., Thermochemical and Chemical Kinetic Data for Fluorinated Hydrocarbons, NIST Technical Note 1412, 1995.

13. Miller, J.A., and Bowman, C.T., Prog. Energy Comb. Sci. 15:287 (1989).

14. Egolfopoulos, F.N., Du, D.X., and Law, C.K., Combust. Sci. and Tech. 83: 33-75 (1992).

15. Egolfopoulos, F.N., Zhu, D.L., and Law, C.K., Twenty-Third Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1990, pp.471-478.

16. Bowman, C.T., Frenklach, M., Gardiner, W., Golden, D., Lissianski, V., Smith, G., and Wang, H., GRIMECH, upcoming Gas Research Institute Report, 1995.

17. Takahashi, K., Inomata, T., Moriwaki, T., Okazaki, S., Bull. Chem. Soc. Japan, 62:636-638 (1989).

18. Sheinson, R. S., Penner-Hahn, J. E and Indritz, D., Fire Safety J. 15:437 (1989).

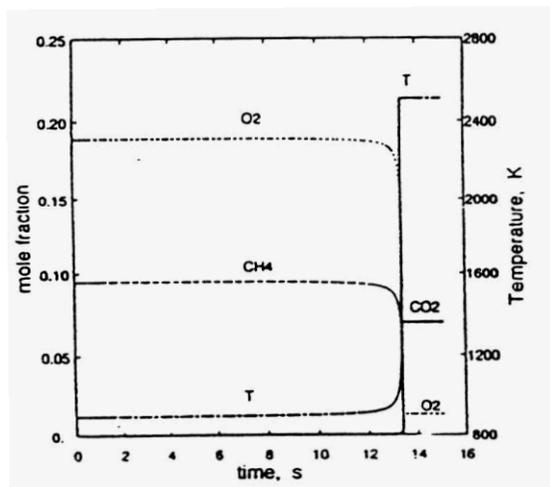


Figure 1. Temporal Behavior of Fuel and Oxidant for stoichiometric methane/air system (900K, initial temperature)

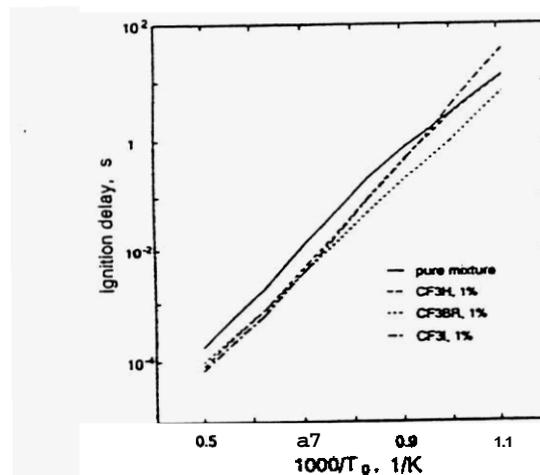


Figure 2 Ignition delay versus initial temperature in stoichiometric methane/air system with 1% inhibitor

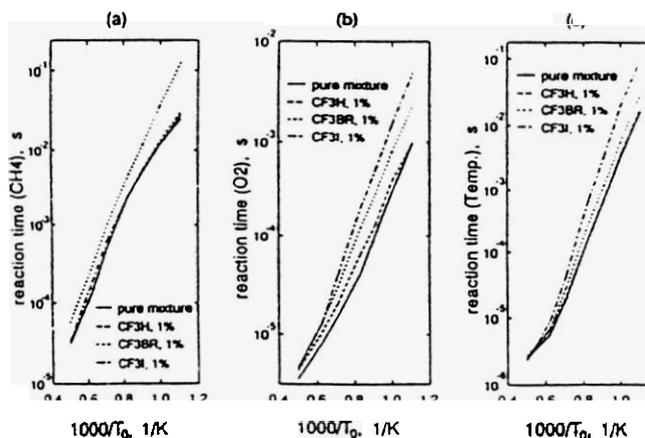


Figure 3. τ_i for substantially complete reaction as a function of initial temperature

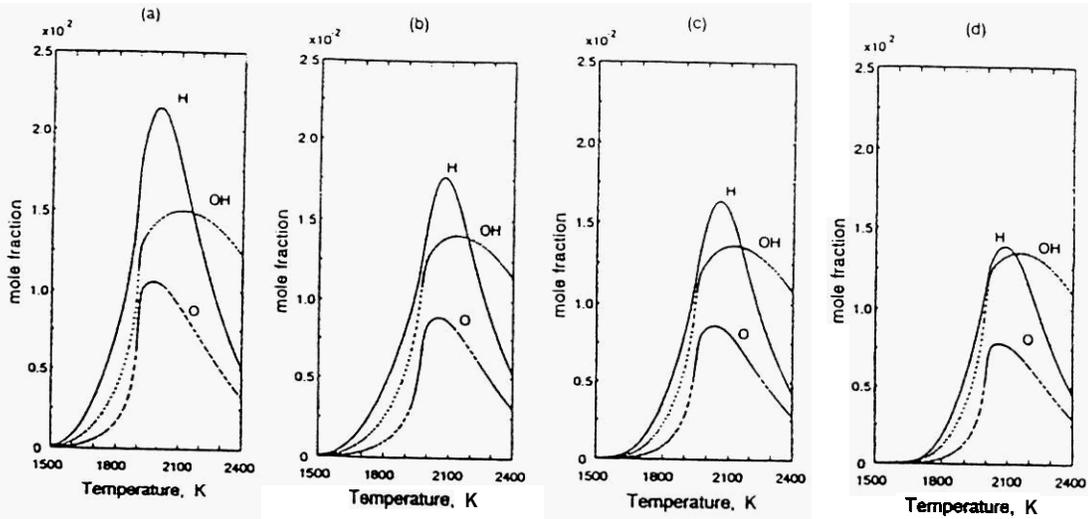


Figure 4. Concentration of reactive intermediates for various inhibitors under plug flow conditions (a) no inhibitor (b) CHF_3 , (c) CF_3Br , (d) CF_3I

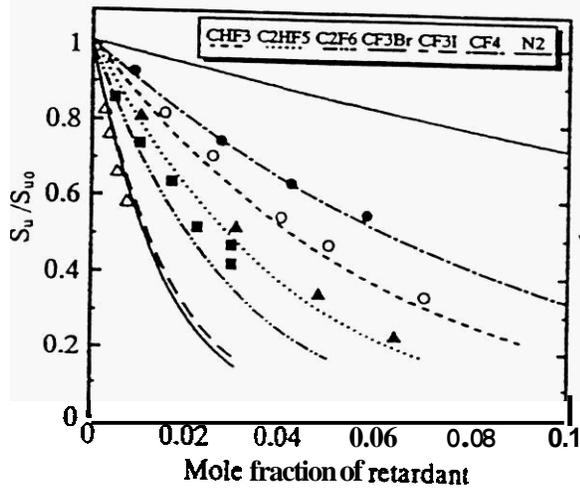


Figure 5. Flame velocities as a function of inhibitor concentrations. Points are experimental data

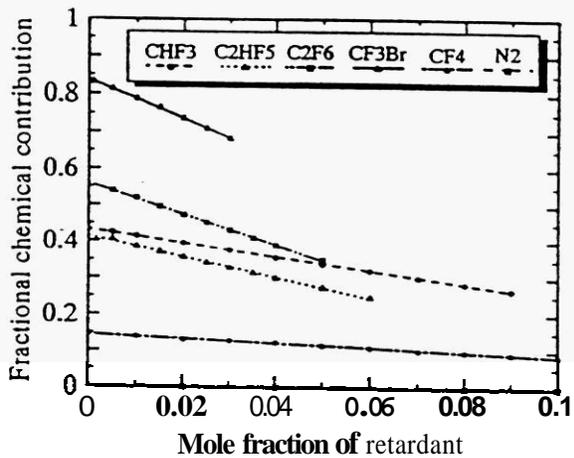


Figure 6. Chemical contributions as a function of inhibitor concentration

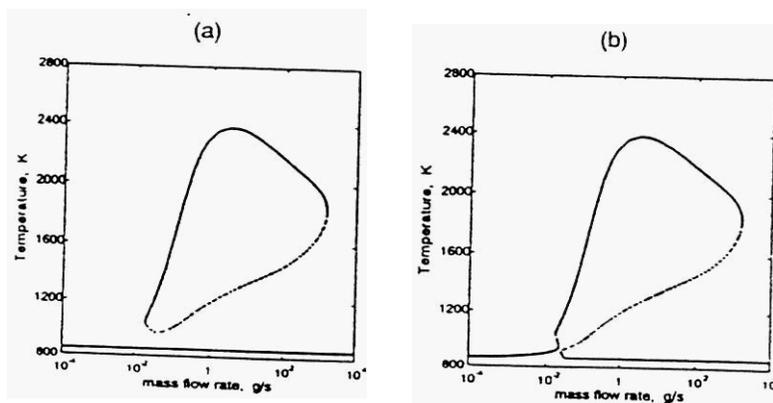


Figure 7. Stationary State Curves for Stoichiometric Methane/air mixture in CSTR at 850(a) and 863(b) K

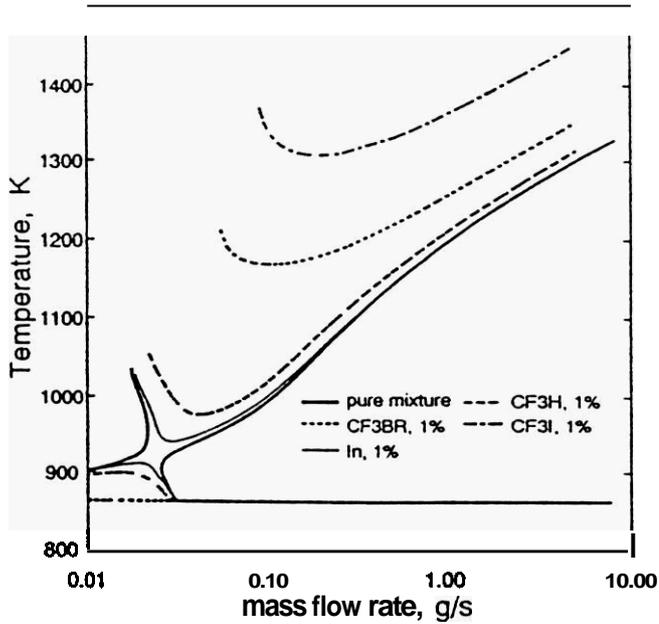


Figure 8: Detailed picture of ignition point from Figure 7b. Also included are results on the unstable steady state curves with 1% CF_3H , CF_3Br , CF_3I and 1% chemically inert additive(In) so as to produce same decrease in flame speed as 1% CF_3Br

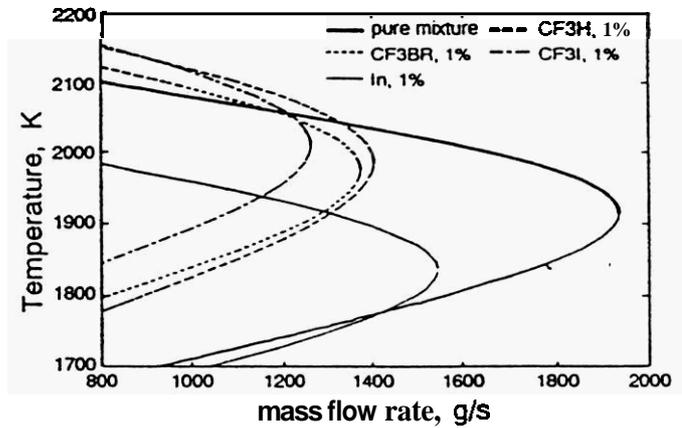


Figure 9: Additive influence on reaction behavior near ignition point at 1200K and 1 atm pressure for stoichiometric methane/air mixture with various additives at 1%

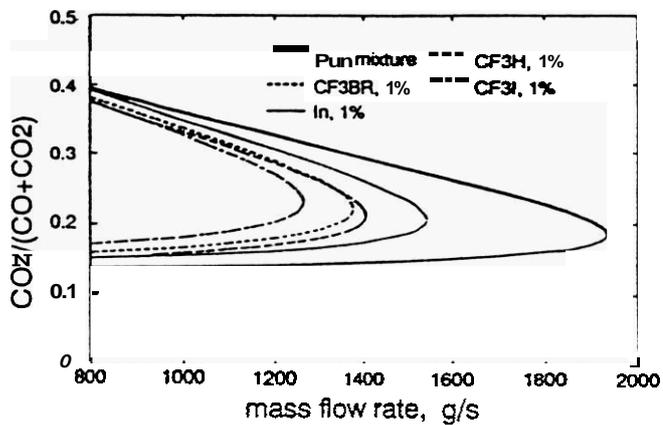


Figure 10: Stationary state ratios of $CO_2/(CO+CO_2)$ as a function of flow rate in CSTR with stoichiometric methane and various additives at 1%