# THE INERTING OF METHANE - AIR MIXTURES by HALON 1301 ($CF_3Br$) and HALON SUBSTITUTES

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## ABSTRACT

The efforts to replace Halon fire extinguishing agents such as Halon 1301 ($CF_3Br$) are motivated by their contribution to ozone-layer depletion and the consequent calls for their elimination. Research is currently underway to find effective, non-toxic, and non contaminating replacements which are not harmful to stratospheric ozone. The premixed stoichiometric fuel-air mixture presents the greatest challenge for extinguishment, while lean and rich mixtures simulate the flame zone regions of large-scale fires. We have, therefore, chosen to study the effectiveness of $CF_3Br$, $SF_6$ (an ozone "safe" compound), and nitrogen (a strictly thermal inhibitor) in inerting **stoichiometric*(10%), "rich" (14%), and "lean" (6%) methane - air mixtures. The tests are conducted in a 20-L explosibility chamber of the type that is coming into wide use for dust explosion studies. This nearly spherical steel vessel is fitted with a vacuum outlet, gas inlet ports, and a mixing fan to prepare the gas mixtures. It contains a fixture for the 1000 J (calorimetric energy) pyrotechnic igniters used and a fast-acting pressure sensor. Both pressure and rates of pressure rise are monitored during the explosions. The results for stoichiometric methane-air containing various concentrations of the candidate inhibitor are particularly noteworthy, with inerting concentrations of 17, 18, and 38.5 % for added $CF_3Br$, $SF_6$, and $N_2$, respectively. The values for $N_2$ and $SF_6$ reported

here are comparable to the inerting levels measured using low energy igniters, but the value for $CF_3Br$ (17%) is considerably higher than the 4% value obtained using spark ignition. Moreover, the calculated adiabatic flame temperature at these inhibitor levels is in the range of 1500 - 1600 K. Such values are close to the calculated flame temperatures for **"lean"** (5%) and **"rich"** (17-18%) limit mixtures of methane in air, suggesting a common, thermal inerting process under these conditions. A similar picture emerges from the inhibited 6% and 14% $CH_4$ mixtures as well. The thermal decomposition of the $CF_3Br$ and $SF_6$ inhibitors at flame temperatures to give corrosive, irritating, and potentially toxic products such as $Br_2$, $HBr$, HF, $COF_2$, and $SO_2F_2$ is noted. The production of such products for Halons and Halon substitutes, as well as their relative effectiveness in fire and explosion suppression, must be carefully considered in deciding on suitable Halon replacements.

## INTRODUCTION

The exothermic combustion reactions responsible for fire and explosion phenomena generally proceed in a gas-phase mixture of fuel and oxidizer. Condensed phase fuels thus require evaporation, or pyrolysis of the liquid or solid to provide the necessary gaseous fuel species. For such fuels, the flame propagation process occurs in a mixing-limited diffusion flame mode [1,2,3] limited to the boundary between the emitted fuel vapor and the surrounding air. Thus the steady state propagation of the flame occurs in a limited volume of the fuel-air mixture whose composition is near the rich and lean limits of flammability for that fuel in air [4]. Explosions, on the other hand, can occur thoughout the vapor space and flammability range, without the mixing constraints that characterize fires.

Lean and rich flammability limit mixtures may be thought of as stoichio-metric fuel-air mixtures inerted with excess air and fuel respectively. The same stoichiometric mixture can be inerted by the addition of a third component that dilutes the mixture, absorbs some of the heat released by the exothermic fuel oxidation reactions, and may interfere with the combustion chain reactions. The latter effect characterizes a chemical inhibitor. In its absence, the effect of the inertant is strictly thermal and physical. Halon 1301 ($CF_3Br$) is an example of an important extinguishant that is considered to act via chemical, thermal, and physical processes [5-7]. Halon 1301 and several other halocarbons are currently used to protect a variety of sensitive areas such as computer centers, control rooms, archives, and aircraft spaces. A consensus has arisen, however, that release of Halons and chlorofluorocarbons (CFC's) to the atmosphere results in catalytic destruction of the protective ozone layer in the stratosphere. The production of these materials is therefore to be phased out by international agreement. Efforts are underway to find environmentally acceptable replacements for the Halons and CFC's. Totally fluorinated hydrocarbons are considered inert to stratospheric ozone, while hydrogen containing halocarbons tend to react and precipitate in the troposphere. Their extinguishing and inerting effectiveness, and toxicities must be established, however. Sulfur hexafluoride ($SF_6$) is an example of a non-toxic, totally fluorinated gas that could replace $CF_3Br$ if found to be effective as an extinguishant.

This paper reports the results of a comparison of $CF_3Br$, $SF_6$, and nitrogen ($N_2$) in inerting premixed "lean" (6%), **"stoichiometric"** (10%), and **"rich"** (14%) mixtures of methane ($CH_4$) and air. $N_2$ is included as a prime example of a simple thermal and physical inertant. Methane is used as the fuel since it has been extensively studied. Previous work [8] has shown little sensitivity of inerting requirements to the carbon number of a saturated hydrocarbon fuel, but additional studies are needed to confirm that conclusion for any proposed Halon substitute.

## EXPERIMENTAL

The determinations of the explosion pressures, rates of pressure rise, and inerting levels for **"stoichiometric"** (10%), "rich" (14%), and "lean" (6%) $CH_4$/air mixtures by $N_2$, $CF_3Br$, and $SF_6$ inhibitor gases were conducted in a nearly spherical, steel explosibility chamber with a 300 psi pressure rating and a volume of about 20 L, of the type coming into wide use for dust explosibility studies [9]. It was modified for gas explosion studies by inserting a mixing fan and providing valved inlets for gas admission. The gas mixtures to be tested were prepared by first evacuating the chamber and adjusting the partial pressures of the various gases to give the desired $CH_4$, inhibitor, and air concentrations. The gases were mixed by fan for at least 3 minutes and then allowed to come to rest for 1 minute prior to the activation of a 1000 J pyrotechnic ignitor for each test. These ignitors are the most energetic ignition sources suitable for methane gas explosions in this size chamber. Stronger ignitors lower the minimum explosible concentration (lean limit) of $CH_4$/air below the accepted value of 4.9 - 5.1 % due to compression and preactivation of the unburned gas by the ignitor [10]. The much lower energy of a spark is, however, responsible for the somewhat narrower flammability range that it gives for $CH_4$/air relative to the 1000 J values. The "true" rich limit for $CH_4$/air is uncertain, but a range of 17-18% is given by different, but adequate ignition sources and explosion volumes. Spark ignition also results in appreciably lower inerting values (4%) for $CF_3Br$ mixtures with stoichiometric $CH_4$/air, due to ignition limitations.

## RESULTS

The results of the measurements are summarized in Table 1. which lists both the volume % and mass concentration ($g/m^3$) of the inhibitors required to inert 6, 10, and 14% $CH_4$/air. The halogenated gases are seen to inert $CH_4$/air at approximately half the volume or mole % of $N_2$, but at more than twice the mass concentration of the latter. The striking difference is due to the much higher molecular weights of the $CF_3Br$, and $SF_6$. The

$CF_3Br$ is seen to be most effective in "rich" methane-air mixtures, while $SF_6$ is most effective in "lean" mixtures and least effective in "rich" mixtures. The results of the adiabatic calculation of flame temperatures produced by the NASA-LEWIS thermodynamic equilibrium computer code (CEC-80) [11] for the above inerting concentrations are summarized in Table 2. The table also includes the calculated temperatures for uninhibited $CH_4$/air at the flammability limits of 5 and 17-18 % $CH_4$, and at 6, 10, and 14% $CH_4$, for comparison purposes. The limit flame temperatures are seen to be in the range of 1500 - 1600 K, except for the "rich" $CF_3Br$ mixture which shows a somewhat higher temperature.

## DISCUSSION

Combustion reactions are normally driven by several coupled processes; the autoaccelerating, strongly exothermic reactions leading to stable products; the fast chain-branching reactions featuring mobile, "hot", radical species such as H atoms; and the back diffusion of heat and free radicals across the flame zone to the unburned reactants. Chemical inhibitors have the ability to tie up the H atoms and similar reactive chain carriers. Such action is reflected in a reduction in burning velocity and rate of pressure rise untill extinction occurs at a sufficiently high inhibitor concentration. In the case of fires, the combination of fuel/air mixing limitations and the slowing of the combustion chain reactions will also lead to extinguishment. Purely thermal inerting, on the other hand, requires that an inhibitor reduce the flame temperature to a critical minimum value. For hydrocarbon fuels, that limiting flame temperature appears to be roughly 1500 K [12]. It is noteworthy, therefore, to find this approximate temperature for nearly all the limiting mixtures reported here. The one exception is the "rich" $CH_4$/air mixture inerted with $CF_3Br$, which has an adiabatic temperature of 1760 K. But it is precisely this inertant that has been shown [6,7] to exhibit chemical interference with combustion chain reactions.

Such chemical interference may also be inferred from the 50% reduction in the rate of pressure rise of 10% $CH_4$/air noted at low concentrations **(1%)** of $CF_3Br$. $CF_3Br$ thus appears to be acting in both thermal and chemical inhibition modes. Inerting levels for explosions, however, appear to be determined primarily by equilibrium flame temperatures, even for $CF_3Br$. $SF_6$, in comparison, shows little or no sign of chemical interference. It does undergo decomposion reactions at flame temperature which are generally endothermic and which enhance its effectiveness in lean mixtures. For rich mixtures, the ample supply of $CH_4$ leads to much HF formation, and a partial reduction of sulfur from the +6 oxidation state in $SF_6$ to the +4 state in $SF_4$ and $SOF_2$ both lead to a net exotherm at low $SF_6$ concentrations. Such an exotherm is reflected in a rise in calculated flame temperature and observed explosion pressures, and in a reduced inerting effectiveness for rich mixtures. The latter result is more consistent with extinguishment measurements of diffusion flames reported for $CF_3Br$ and $SF_6$ using a cup-burner apparatus **[13]**. On a mass basis, neither $CF_3Br$ nor $SF_6$, can compete, however, in a premixed gas test with a simple thermal inertant such as $N_2$. This observation alone offers hope that more effective, less corrosive, and ozone "safe" Halon substitutes can be found. The search for Halon replacements should also not exclude solids. The suppression of stoichiometric $CH_4$/air explosions by mass concentrations as low as 250 $g/m^3$ has been reported for very finely divided and fluidized **"ABC"** ($NH_4H_2PO_4$) powder **[14]**.

Both the equilibrium calculations and qualitative observations of explosion residues show that thermal decomposition of the halogen compounds can produce corrosive, irritating, and toxic compounds. The calculations predict the presence of HF, $COF_2$, HBr, and $Br_2$ in $CF_3Br$ mixtures, and HF, $COF_2$, $SF_2$, $SF_4$, $SO_2$, $SOF_2$, $SO_2F_2$, and even $F_2$ in $SF_6$ mixtures. The presence of $Br_2$, water-reactive residues, and corrosion and sulfiding of the steel chamber was noted. The presence of HF in the products produced in extinguishing flames by $CF_3Br$ and $SF_6$ has also been reported [13]. The relative production of such objectionable products by Halons and their candidate replacements must be monitored and considered in deciding on Halon replacements.

## CONCLUSION

The data presented here on the inerting of premixed methane-air-inhibitor mixtures in the absence of ignition limitations suggests a common thermal mechanism for the action of Halon 1301 ($CF_3Br$), $SF_6$, and nitrogen. The utility of equilbrium calculations of flame temperatures for fuel-air-inhibitor mixtures in predicting inerting levels is also demonstrated. Evidence for the smaller contribution of a chemical mechanism to inerting by $CF_3Br$ is also presented. The inerting effectiveness of the halogenated agents studied is shown to be half that of nitrogen when expressed on a mass basis. The latter observation lends optimism to the quest for more effective and ozone "safe" agents to replace the Halon extinguishants currently used. The presence of harmful degradation products from both halogenated agents suggests that the relative production of such species from Halons and their candidate replacements must be carefully monitored and considered in the decision on replacement agents.

## REFERENCES

1. Burke, S.P. and Schumann, T.E.H., "Diffusion Flames", First Combustion Symposium, The Combustion Institute (1928) p. 2

2. Hertzberg, M., "The Theory of Free Ambient Fires.", Combustion and Flame <u>21</u> (1973) p. 195

3. Burgess, D., and Hertzberg, M., "Radiation from Pool Flames", chap. 27 Scripta Book Co., Washington D.C. (1974) p. 413

4. Hertzberg, M., Cashdollar, K., Litton, C., and Burgess, D., " The Diffusion Flame in Free convection", Bureau of Mines, RI 8263, (1978)

5. Hertzberg, M., Johnson, A.L., Kuchta, J.M., and Furno, A.L.,

"The Spectral Growth, Flame Temperature, and Flammability Behavior of Large Scale, Spherical Combustion Waves", 16th Symposium (International) on Combustion, The Combustion Institute (1976) p. 767

6. Biordi, J.C., Lazzara, C.P., and Papp, J.F., "Chemical Flame Inhibition using Molecular Beam Mass Spectrometry. Reaction Rates and Mechanisms - 0.3% $CF_3Br$ Inhibited Methane Flame", Bureau of Mines, RI 8029 (1975)

7. Biordi, J.C., Lazzara, C.P., and Papp, J.F., "Chemical Flame Inhibition using Molecular Beam Mass Spectrometry. Reaction Rates and Mechanisms - 1.1% $CF_3Br$ Inhibited Methane Flame", Bureau of Mines, RI 8307 (1978)

8. Zabetakis, M.G., "Flammability Characteristics of Combustible Gases and Vapors", Bureau of Mines, Bulletin 627 (1965)

9. Cashdollar, K.L., Hertzberg, M., "20-L Explosibility Chamber for Dusts and Gases", Rev. Sci. Instrum. <u>56</u> (1985) p. 596

10. Hertzberg, M., Cashdollar, K.L., and Zlochower, I.A., "Flammability Limit Measurements for Dusts and Gases: Ignition Energy Requirements and Pressure Dependences.", 21st Symposium (International) on Combustion, The Combustion Institute, (1986) p. 303

11. Gordon, S. and McBride, B.J.,"Computer Program for Calculation of Complex Equilibrium Compositions", NASA, SP-273 (1976)

12. White, A.G., "Limits for the Propagation Flame in Inflammable Gas-Air Mixtures. III. The Effect of Temperature on the Limits", J. Chem. Soc. <u>127</u> (1925) p. 672

13. Sheinson, R.S., Penner-Hahn, J.E., and Indritz, D., "The Physical and Chemical Action of Fire Suppressants", Fire Safety Journal, <u>15</u> (1989) p. 437

14. Hertzberg, M., Cashdollar, K.L., Zlochower, I.A., and NG, D.L., "Inhibition and Extinction of Explosions in Heterogeneous Mixtures.", 20th Symposium (International) on Combustion, The Combustion Institute, (1984) p. 1691

TABLE 1. AMOUNT of GASEOUS INHIBITORS in VOLUME % and (g/m3) to INERT METHANE/AIR MIXTURES.

| | VOLUME % METHANE in METHANE/AIR MIXTURE | | | | | |
|---|---|---|---|---|---|---|
| | 6 % | | 10 % | | 14 % | |
| INHIBITOR | vol % | ($g/m^3$) | vol % | ($g/m^3$) | vol % | ($g/m^3$) |
| NITROGEN | 19.5 | (223) | 38.5 | (441) | 22 | (252) |
| HALON 1301 | 14 | (852) | 17 | (1035) | 8.5 | (517) |
| $SF_6$ | 7.5 | (448) | 18 | (1075) | 20 | (1194) |

TABLE 2. ADIABATIC FLAME TEMPERATURES (K) at 1 ATMOSPHERE.

| | VOLUME % METHANE in METHANE/AIR MIXTURE | | | | |
|---|---|---|---|---|---|
| INHIBITOR | 5 % | 6 % | 10 % | 14 % | 17-18 % |
| NONE | 1481 | 1678 | 2233 | 1872 | 1500-1600 |
| NITROGEN | | 1449 | 1628 | 1598 | |
| HALON 1301 | | 1559 | 1543 | 1760 | |
| $SF_6$ | | 1528 | 1591 | 1639 | |