

# AN INVESTIGATION OF EXTINGUISHMENT BY THERMAL AGENTS USING DETAILED CHEMICAL KINETIC MODELING OF OPPOSED FLOW DIFFUSION FLAMES

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## 1. INTRODUCTION

The manufacture of halons, which are widely used in fire extinguishing systems, was banned in 1984. The search for effective alternatives continues with a large effort known as the Next Generation Fire Suppression Technology Program (NGP). As part of the NGP, NIST is investigating whether highly effective thermal agents, which obtain their effectiveness solely by heat extraction and dilution, are feasible. The paper by Sheinson et al. provides a good introduction [1]. Simple heating (i.e., heat capacity), phase changes, endothermic molecular decomposition (which is classified as a physical process as long as the initial agent and its products do not participate in the combustion chemistry), and simple dilution can modify flame temperatures and therefore contribute to flame extinction.

This paper summarizes the results of a detailed chemical kinetic modeling investigation of laminar opposed-flow methane/air diffusion flames designed to provide an improved understanding of the extinguishment of fires by thermal agents. A particular focus was to test the hypothesis that the effectiveness of a thermal agent depends on the location of heat absorption relative to the flame zone. An internal report has been prepared summarizing the kinetic modeling and also includes the results of an extensive data base search of potential thermal agents and modeling results for the effectiveness of thermal agents in cooling solid surfaces [2].

## 2. DETAILED CHEMICAL KINETIC MODELING

An opposed flow laminar diffusion flame model was selected because for the majority of fires the fuel and air are initially separated and therefore burn as diffusion flames. Two excellent reviews have been provided by Tsuji [3] and Dixon-Lewis [4]. These flames are usually modeled as pseudo one-dimensional flow systems using a similarity transform to reduce the two-dimensional equations. Fuel and oxidizer velocity profiles at the burner exits are assumed to be plug flows having exit strain rates equal to  $0 \text{ s}^{-1}$ . Absolute strain rates increase as the flow moves toward the stagnation plane. With increasing exit flow velocities the flame is subjected to higher strain rates, and it gradually becomes weaker until it abruptly undergoes extinction. A number of parameters are used to quantify the effect of strain rate on a laminar flame including a global strain rate,  $a_g$ , the maximum strain rate outside of the thermal boundary layer on the oxidizer side,  $a_o$ , and the stoichiometric scalar dissipation,  $\chi_s$ .

For this investigation, a series of laminar opposed flow diffusion flames of methane and oxidizer have been calculated as a function of exit flow velocities (assumed to have equal magnitudes) and the concentration of various thermal agents added to the air. For each concentration of added agent, an extinction condition is identified which corresponds to a given velocity magnitude and corresponding measures of strain rate and  $\chi_s$ . A focus of this work is the identification of the minimum concentration of an agent required to extinguish buoyancy dominated fires. The extinguishing concentration is therefore expected to correspond to a particular extinction condition.

## 3. CALCULATIONAL APPROACH

The code Oppdif [5] developed by Sandia National Laboratories, now available from Reaction Design\* of San Diego, CA, was used. Oppdif solves the pseudo-one-dimensional equations for plug flows. The detailed chemical mechanism used was GRI-Mech 1.2 [6] which consists of 32 chemical species undergoing 177 reactions.

Figure 1 includes a plot of maximum temperature,  $T_{max}$ , versus exit flow velocities calculated for a methane/air diffusion flame (0% added  $N_2$ ). The fuel is 100% methane and air is assumed to be composed of 0.781  $N_2$ , 0.210  $O_2$ , and 0.009 Ar mole fractions. As expected,  $T_{max}$  decreases with increasing velocity. Extinction is calculated to occur for a velocity of 320 cm/s with a maximum flame temperature of 1785 K. The value of  $|a_o|$  at extinction is  $509 \text{ s}^{-1}$  which is roughly 25% higher than measured experimentally [7,8,9]. Tanoff et al. have shown

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\*Certain commercial equipment, instruments, or material are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

that calculated values of  $a_o$  are highly dependent on the detailed mechanism [10] and also found that GRI-Mech over predicts the extinction strain rate.

#### 4. METHANE FLAMES BURNING IN AIR DILUTED WITH THERMAL AGENTS

Only two experimental measurements of extinguishing concentration for methane flames burning in air diluted with a thermal agent were identified. Simmons and Wolfhard [11] and Ishizuka and Tsuji [12] reported values of 33.8% and 31.9%, respectively, for nitrogen added to air. Calculations were performed for methane reacting with air containing various percentages of added nitrogen. Figure 1 includes the results. As the percentage of added nitrogen increases, the fuel and oxidizer exit velocity magnitudes sufficient to cause flame extinction decrease. The  $T_{max}$  at extinction also decreases with increasing nitrogen concentration. Plots of  $T_{max}$  versus velocity magnitude become steeper as the nitrogen concentration increases. The value of  $T_{max}$  for the experimental extinguishing concentration is 1545 K. This is close to the experimental value of 1483 K [12]. The velocities of the fuel and air at extinguishment are calculated to be 21.42 cm/s, corresponding to an absolute value of global strain rate of  $a_g = 37.5 \text{ s}^{-1}$ .

An important question is what strain rate is appropriate to use when determining the minimum value of an added thermal agent required to extinguish diffusion flames at normal gravity? The only discussion of this point of which we are aware was presented by Hamins et al. [13]. These authors compared cup burner measurements (heptane fuel) of extinguishing concentrations for a variety of agents with corresponding measurements made in a counterflow flame. When the concentrations of added agents for the opposed flame were comparable to those observed to cause extinguishment in the cup burner test, the global strain rate was on the order of  $50 \text{ s}^{-1}$ . Due to the use of different boundary conditions and fuels between the current investigation and those for Hamins et al., as well as slightly different definitions for the global strain rates, absolute quantitative comparisons are not appropriate. However, it is clear that the strain rates have comparable magnitudes in each case.

It is interesting to speculate about why lower and lower strain rates can not be sustained for flames at normal gravity. The most likely reason is that buoyancy effects result in a lower limit for the minimum strain rate perpendicular to a flame surface. Buoyancy always accelerates hot combustion gases relative to the cold oxidizer with the result that the flame surface is subject to a nonzero strain rate. The results of Hamins et al. [13] and the current findings suggest this minimum strain rate is on the order of a few tens of inverse seconds.

As already pointed out, we have identified no additional measurements of extinguishing concentrations for thermal agents added to methane/air diffusion flames. However, Ishizuka and Tsuji did make measurements for methane burning in an artificial "air" consisting of 21% oxygen and 79% argon diluted with argon [12]. The extinguishing argon concentration was 54.3%. Extinction for a calculated flame burning in Ar "air" with the extinguishing concentration of added Ar occurred for a  $T_{max}$  of 1473 K and exit velocities of 15.9 cm/s. These values are both slightly lower than found for the methane/air flame diluted with nitrogen. However, they are remarkably close when one recalls that the use of argon instead of nitrogen results in a significantly different flame structure. In fact, if one simply assumes that extinguishment occurs for the same maximum flame temperature, i.e., roughly 1550 K, as for the nitrogen-diluted air flame, it is possible to estimate the required argon concentration as 52%. This is only 4% less than the experimental value. Thus, assuming that flame extinguishment occurs for the concentration necessary to reduce the maximum calculated flame temperature at extinction to 1550 K should provide an excellent estimate for the percentage of an arbitrary thermal agent required to extinguish a fire.

Opposed flow diffusion flame calculations have been used to estimate the extinguishing concentrations, i.e., the concentration necessary to lower the maximum flame temperature at extinction to 1550 K, for methane burning in air diluted with Ar, He,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . Each of these gases is expected to act primarily as a thermal agent. The

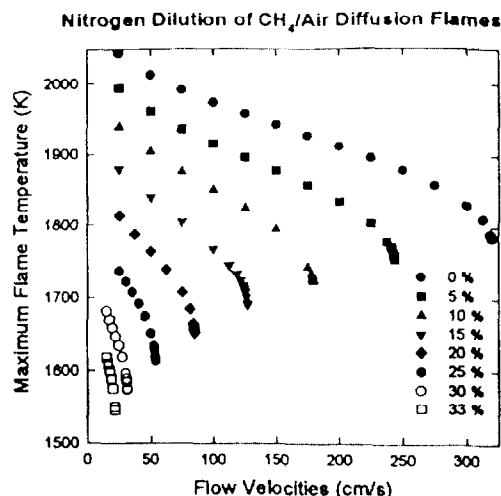


Figure 1. Maximum flame temperature versus flow velocity magnitudes for methane burning in nitrogen-diluted air.

Table 1. Extinguishing Concentrations (Mole Fraction) of Thermal Agents

Thermal Agent	Current Work	Cup Burner [1]	Cup Burner [14]	Cup Burner [15]	Cup Burner [16]
Nitrogen	0.33	0.30	0.33	0.32	0.30
Argon	0.43	0.41	-	0.41	0.38
Helium	0.34	0.32	-	0.31	-
Carbon Dioxide	0.22	0.21	0.20	0.23	0.20
Water	0.28	-	-	-	-

results are tabulated in Table 1. As already discussed, the only experimental values for opposed flow methane diffusion flames we have identified are for nitrogen. Cup burner values of extinguishing concentrations using heptane fuel have been reported for some of these agents by Sheinson et al. [1], Babb et al. [14], Hamins et al. [15] and Moore et al. [16] and are included in Table 1. The maximum difference between values calculated for methane and the experimental values for heptane is 12%, with the vast majority being less than 10%. With the exception of carbon dioxide, the cup burner measurements are somewhat lower than for the counterflow flame. These differences could be due to the use of different fuels or to the effects of burner configuration. The close tracking of the calculated results and the experimental findings suggests that detailed chemical kinetic modeling can accurately predict the amount of a thermal agent required to extinguish opposed flow diffusion and cup burner flames.

The differences in the extinguishing concentrations of helium and argon are interesting since these agents are both monatomic gases and have the same heat capacities. The fact that helium is a more efficient extinguishing agent means that at least one other parameter, in addition to heat capacity, is important in determining extinguishing efficiency. A related observation was reported by Coward and Hartwell for the inerting of premixed flames and was attributed to the much higher thermal conductivity of helium which distributes the heat of combustion over a larger region of space and therefore weakens the flame [17]. The same explanation is most likely valid for diffusion flames. Sheinson et al. reached the same conclusion [1].

## 5. SURROGATE AGENT STUDIES OF EXTINCTION AND EXTINGUISHMENT

A goal of the current work was to test the hypothesis that the effectiveness of a thermal agent depends on the location, relative to the high temperature flame zone, where heat extraction occurs. A surrogate thermal agent, X, was used as a test. The molecular weight, thermodynamic properties, and transport properties of X are identical to those of argon, but it can undergo a simple reaction with ambient gases to generate a new species, Y, i.e.,



Y is also very similar to argon, the only difference being that its heat of formation is assigned an arbitrary positive value instead of being zero. When Reaction (1) takes place it extracts heat and cools the local surroundings by an amount equal to the heat of reaction,  $\Delta H_{X-Y}$ . Since X and Y do not react with any other species, the reaction is simply a heat sink and therefore meets the definition of a thermal agent. The rate constant for Reaction (1) is expressed as

$$k_{X \rightarrow Y} = A T^{\beta} e^{-E_a/RT}, \quad (2)$$

where  $A$  is the pre-exponential factor,  $\beta$  is the temperature exponent,  $E_a$  is the energy of activation,  $R$  is the gas constant, and  $T$  is temperature. For the calculations which follow, initial values were chosen for  $A$  and  $\beta$ , and only the value of  $E_a$  was changed in order to vary  $k_{X-Y}$ .

Figure 2 compares calculated flame temperature versus distance from the fuel exit for two flames having fuel and oxidizer exit velocity magnitudes of 25 cm/s and with 5% X added to the air. For each  $A = 1 \times 10^{10}$  cm<sup>3</sup>/(mole s),  $\beta = 0$ , and  $\Delta H_{X-Y} = 96.1$  kJ/mole. The only difference between the two calculations is the value of  $E_a$  which equals 25.1 kJ/mole for one and 50.2 kJ/mole for the other. For the lower  $E_a$ , X begins to react immediately upon leaving the oxidizer exit which results in the temperature drop evident on the oxidizer side for positions well removed from the flame zone. When the  $E_a$  is increased to 50.2 kJ/mole the conversion of X to Y is very slow at room temperature, and there is no significant drop in temperature in the ambient region of the flow. However, as the temperature increases X begins to convert to Y, and heat is absorbed in higher temperature flame regions. Interestingly, maximum flame temperatures are identical within the uncertainty of the calculations. Since flame

extinguishment depends primarily on the maximum flame temperature at extinction, this suggests the effectiveness of a thermal agent is independent of the spatial location where the heat extraction occurs, indicating that the original hypothesis concerning the effect of heat extraction position was incorrect.

## 6. SUMMARY

It has been shown that detailed chemical kinetic modeling can be used to make quantitative predictions of the amount of a thermal agent required to extinguish a fire. Results for four well known thermal agents are in good agreement with experimental values. The calculations suggest that strain rates in fires are on the order of a few tens of inverse seconds and that the maximum flame temperature at extinction for the extinguishing condition is approximately 1550 K. The location of the heat absorption relative to the flame front does not affect the ability of a thermal agent to extinguish a flame as long as the agent is convected to the flame zone.

## 7. ACKNOWLEDGMENT

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## 8. REFERENCES

1. R. S. Sheinson, J. E. Penner-Hahn, and D. Indritz, *Fire Safety J.* **15**, 437, 1989.
2. W. M. Pitts, J. Yang, M. Huber, and L. G. Blevins, *Characteristics and Identification of Super-Effective Thermal Fire-Extinguishing Agents—First Annual Report*, NIST Internal Report, Gaithersburg, MD, 1999, to appear.
3. H. Tsuji, *Prog. Energy Comb. Sci.* **8**, 93, 1982.
4. G. Dixon-Lewis, *23rd Symp. (Intl.) Comb.*, The Combustion Institute, Pittsburgh, PA, 305, 1990.
5. A. E. Lutz, R. J. Kee, J. F. Grcar, and F. M. Rupley, *OPPDIF: A Fortran Program for Computing Opposed-Flow Diffusion Flames*, SAND96-8243, Sandia National Laboratories, Livermore, CA, 1996.
6. *GRI-MECH 1.2*, M. Frenklach, H. Wang, C.-L. Yu, M. Goldenberg, C. T. Bowman, R. K. Hanson, D. F. Davidson, E. J. Chang, G. P. Smith, D. M. Golden, W. C. Gardiner, and V. Lissianski, [http://www.me.berkeley.edu/gri\\_mech/](http://www.me.berkeley.edu/gri_mech/)
7. H. K. Chelliah, C. K. Law, T. Ueda, M. D. Smooke, and F. A. Williams, *23rd Symp. (Intl.) Comb.*, The Combustion Institute, Pittsburgh, PA, 503, 1990.
8. P. Papas, J. W. Fleming, and R. S. Sheinson, *26th Symp. (Intl.) Comb.*, The Combustion Institute, Pittsburgh, PA, 1405, 1996.
9. J. Du and R. L. Axelbaum, *26th Symp. (Intl.) Comb.*, The Combustion Institute, Pittsburgh, PA, 1137, 1996.
10. M. A. Tanoff, R. R. Dobbins, M. D. Smooke, D. R. Burgess, Jr., M. R. Zachariah, and W. Tsang, *Halon Options Technical Working Conference*, Albuquerque, NM, 116, May 6-8, 1997.
11. R. F. Simmons and H. G. Wolfhard, *Comb. Flame* **1**, 155, 1957.
12. S. Ishizuka and H. Tsuji, *18th Symp. (Intl.) Comb.*, The Combustion Institute, Pittsburgh, PA, 695, 1981.
13. A. Hamins, D. Trees, K. Seshadri, and H. K. Chelliah, *Comb. Flame* **99**, 221, 1994.
14. M. Babb, S. R. Gollahalli, and C. M. Sliepcevich, *J. Propul. Power* **15**, 260, 1999.
15. A. Hamins, G. Gmurczyk, W. Grosshandler, R. G. Rehwoldt, I. Vazquez, T. Cleary, C. Presser, and K. Seshadri, "4. Flame Suppression Effectiveness," in *Evaluation of Alternative In-Flight Fire Suppressants for Full-Scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays* (W. L. Grosshandler, R. G. Gann, and W. M. Pitts, Eds.), NIST SP 861, Gaithersburg, MD, April, 1994.
16. T. A. Moore, C. A. Weitz, and R. E. Tapscott, *Halon Options Technical Working Conference*, Albuquerque, NM, 551, May 7-9, 1996.
17. H. F. Coward and F. J. Hartwell, *J. Chem. Soc.*, 1522, 1926.

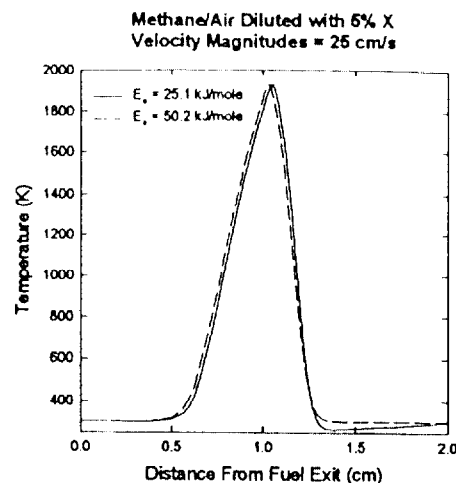


Figure 2. Temperature versus distance from fuel exit for methane/air diluted with 5% X flame.