FLAME EXTINGUISHMENT WITH HOMOGENEOUS SOLUTIONS OF A CHEMICAL AGENT DISSOLVED IN LIQUID CARBON DIOXIDE

Synergism between Physical and Chemical Extinguishing Agents

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ABSTRACT

A method is proposed for utilizing homogeneous solutions of a chemical agent dissolved in liquid carbon dioxide in fire-extinguishment. True solutions of a solute in CO_2 can be spontaneously discharged from the storage cylinder through a siphon tube and delivered to the fire as either a carbon dioxide 'snow' or a liquid mist. A nearly constant driving pressure, equal to the vapor pressure of the liquid solution, is maintained during use. Many types of agents may be employed, irrespective of their volatilities, and no separation of agent from CO_2 can occur in storage at temperatures below the critical temperature of the CO_2 solution (>31°C). Flame extinguishment tests have been performed with mixtures of CO_2 and a number of physical and chemical agents.

A simple model has been developed to predict the flame-extinguishment properties of gas mixtures containing one or more physical and chemical agents. Adiabatic flame temperatures are predicted from the known enthalpy of combustion of a fuel (for example, liquid heptane) and heat capacities of the physical and chemical agents, as well as gases present in the air and produced by combustion. A single adjustable parameter is introduced in the model to account for the activation energy of radical formation in the flame. Predicted and experimental results for mixtures of agents are compared; the observed cooperativity or synergism between physical and chemical agents in suppressing flames is related to the nonlinear temperature dependence of the steady state concentration of radicals in the flame.

INTRODUCTION

Carbon dioxide has long been used as an effective fire-extinguishment agent, either alone or in combination with other physical and chemical agents. It suppresses flames primarily through a dilution effect (reduction of oxygen partial pressure in the fuel-air mixture) and an enthalpic effect reflecting the increase in heat capacity caused by the presence of CO_2 in the gas mixture near the flame.

Many of the solution properties of fluid carbon dioxide are similar to those of the typical nonpolar liquid solvents. Thus, a wide variety of organic compounds (solids, liquids, and gases) are readily soluble either in liquid CO_2 or in the supercritical fluid. For example, the common liquid alkanes, numerous aromatic compounds, and many fluorinated organic compounds dissolve readily in CO_2, as do chemical flame-extinguishment agents such as Halon 1301 (CF_3Br) and Halon 1211 (CF_2ClBr).

It has recently been shown that partially fluorinated surfactants have a surprisingly large solubility in fluid CO_2.[1,2] Inverse micelle formation has been reported to occur in solutions of some of these surfactants in organic solvents. Inverse micelles are known to be quite effective in dissolving substantial concentrations of water and water-soluble salts. Therefore, water-soluble agents incorporated in the inverse micelles in liquid CO, might be useful in fighting fires.

The concept of delivering chemical fire-extinguishment agents dissolved in liquid CO, has many potential advantages. First, there is no volatility requirement for the delivered agent, which will exist in a homogeneous solution under its own vapor pressure, stored in a CO_2 cylinder. The concentration of the agent in CO_2 must of course be large enough for effective flame extinguishment, but this will ordinarily not require a solubility greater than 5 to 10 mole % in the homogeneous liquid phase. In suppressing fires, this CO_2-rich fluid will be dispensed through a siphon tube that is immersed well below the original liquid/vapor interface in the cylinder. As the homogenous liquid solution is rapidly discharged, it will escape through the nozzle as a CO_2 'snow' (finely divided dry ice particles) or a liquid mist, depending on the amount and nature of the dissolved agent. Ejection of the homogeneous fluid from the cylinder will continue until the level of the liquid has dropped below the lower end of the siphon tube. During discharge, the driving pressure will be the vapor pressure of the liquid solution, practically equal to that of pure liquid CO_2 at the ambient temperature. In fire-extinguishment use, the mixture would act by a combination of physical and chemical effects, thereby exploiting any cooperativity that may Occur when both types of agents are present.

Mixed agent fire-extinguishment data (obtained primarily from cup-burner tests) are presented for mixtures of CO_2 and individual chemical agents, and for CO_2/N_2 mixtures. Additional data for CO_2/agent mixtures and for N_2/agent mixtures have been obtained.[3] A simple but reliable model has been developed to correlate fire-extinguishment results for such mixtures. The model clearly differentiates between the physical effects of all agents in diluting the oxygen concentration in the air and increasing heat capacity and the chemical effects of agents that contribute free radicals which scavenge the radicals responsible for flame propagation.

According to the experimental results and the model, a strong cooperative effect occurs between physical and chemical agents when only about 5 to 10 mol% of the chemical agent is present in the CO_2/agent mixture delivered to the flame. The model attributes this type of synergism to the marked nonlinearity in the temperature-dependence of the steady-state concentration of radicals in the propagating flame. Hence, delivery of moderate amounts of a physical agent to the flame greatly decreases the concentration of a chemical agent needed for flame extinguishment.

EXPERIMENTAL METHODS

Solubility and pressure measurements

A vapor pressure apparatus has been constructed to measure pressures of known quantities of CO_2 and CO_2 plus dissolved agent, contained in a cylinder at controlled temperatures in the range 0° to 25°C. Figure 1 is a schematic diagram **of** the apparatus; a main cylinder contains the CO_2 and the high-pressure stainless steel lines connect to a vapor pressure transducer, to a **tank of** CO_2 and to valves, traps, and safety vent. Liquid CO_2 or solutions of agents dissolved in liquid CO_2 are delivered through a siphon tube, the bottom end of which is well below the liquid level in the cylinder.

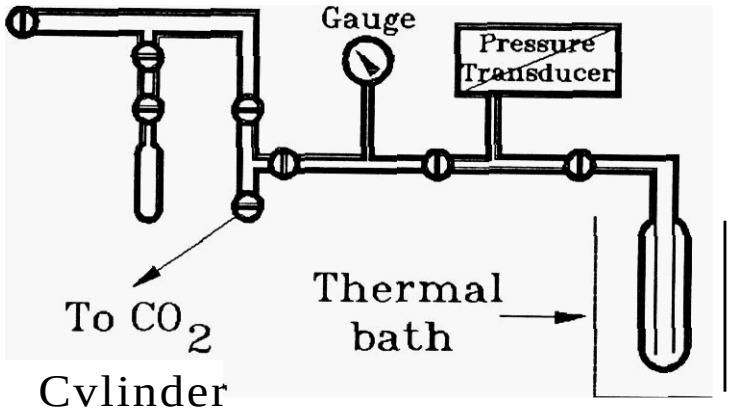

Figure 1. CO_2 Apparatus

In studies with mixtures, the cylinder is first weighed empty, and then after filling with agent, after addition of CO_2 from the tank, and after some **of** the fluid has been vented from the cylinder. Material balance relations make it possible to determine whether or not an agent is soluble in liquid CO_2 at the observed temperatures and pressures. Vapor pressure-temperature data are obtained for pure liquid CO_2 and for the homogeneous liquid solutions of CO_2 plus agent.

When a mixture having a known mole percent of added agent is discharged from the cylinder through a nozzle, the substance **is** dispersed either as the familiar dry ice 'snow' or as a clear liquid mist. For example, a 1.8 mol% solution of perfluorooctyl bromide in CO_2 discharges as 'snow', whereas 3.6 mol% of perfluoromethylcyclohexane in CO_2 discharges **as** a clear liquid. Although we have not explored the potential advantages of liquid vs. solid aerosols for **use** in fighting fires, it may be mentioned that the availability **of** a clear liquid CO_2 discharge may reduce visibility problems significantly.

Flame-extinguishment tests

Cup-burner results have been obtained using a method described in the literature[4]. Pure heptane is used **as** the fuel, and various mixtures of CO_2 or N_2 and CF_3Br or CF_2ClBr **of** known composition are produced by metering the pure compounds into the air stream using rotameters. Additional studies have been made of systems containing mixtures **of** CO_2 and perfluoromethylcyclohexane or perfluoroethyl iodide. The minimum vapor phase concentration of pure or mixed

agents required to extinguish the flame is determined by gradually increasing the agent concentration until the flame abruptly vanishes. A pan burner test facility has been constructed and preliminary tests are underway with CO_2 and CO_2/agent mixtures.

RESULTS

Vapor pressures have been measured for liquid solutions of several relatively nonvolatile solutes in CO_2. For example, at 10 "C, the vapor pressure of a 0.07 mole fraction solution of **perfluoromethylcyclohexane** in liquid CO_2 is 600 psig, compared to a vapor pressure for pure CO_2 of 650 psig. At **20** "C, the vapor pressure of a 0.07 mole fraction solution of this agent in CO_2 is 750 psig, and the vapor pressure of pure CO_2 is **833** psig. The indicated reduction in vapor pressure is relatively small. Therefore, solutions of agents like perfluoromethyl-cyclohexane in CO_2 will have nearly the same driving force **as** pure CO, in forcing the liquid mixture to exit through the siphon tube.

Cup-burner test results are shown in Figure **2** for mixtures of CO_2 and N_2 added to the inlet air *stream,* using heptane as the fuel. Ordinate values are the volume or mole percentages of the individual gases in the **air** (required for extinguishment) and the total of these percentages; the abscissa denotes the relative percentage of the two gases in the mixture. (The relative percentage variable is the percentage of CO, present in mixtures of N_2 and CO_2 added to the air flowing into the cup-burner chimney.) **Thus, 32%** of nitrogen or 21% of CO_2 acting alone will extinguish the flame; when the relative percentage of CO_2 is 50% , the mole percentage of each gas in the air **stream** is **12%** and the total mole percentage required for extinguishment is 24%. The experimental results indicate that the curves are slightly nonlinear, but there is no evidence for cooperativity or anti-cooperativity in the mixture data for these two supposed physical agents. Points in the figure represent experimental results, whereas the curves are drawn **as** predicted by the model described in the following section.

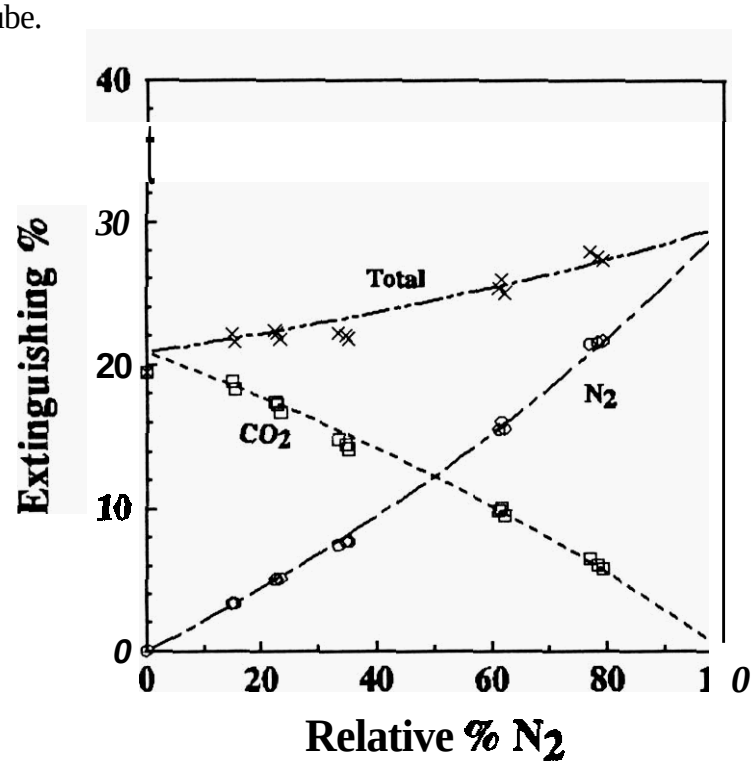

Figure 2. Cup-burner N_2/CO_2 Mixtures

Similar cup burner data for mixtures of CO_2 and **perfluoromethylcyclohexane** have been obtained. Owing to the fact that the vapor pressure of **perfluoromethylcyclohexane** is relatively small, it **is** somewhat difficult to obtain cup-burner measurements for mixtures of **this** compound and CO_2 outside the CO_2-rich region. It has been reported that **3.5%** of the fluorocarbon is required for cup-burner extinguishment[5], and reduced percentages of this substance are needed

in the presence of added CO_2. Presumably this compound acts primarily as a physical agent, and, in fact, the data for these mixtures show no evidence of cooperative or anti-cooperative flame-extinguishment effects.

Data for mixtures of CF_3Br and C_2F_5I with CO_2 are presented in Figures 3 and 4. Clear evidence for cooperativity or synergism is shown for the mixtures; for example, when the CO, extinguishment percentage is reduced to half the mole percentage required for extinguishment by CO_2 acting alone (i.e., to ~10.5%), the required percentage of the Halon in each case is reduced to approximately 25 to 30% of the value required for the agent acting alone. Quite similar cooperative effects have been observed in cup-burner test results for mixtures of Halons with nitrogen?

The magnitude of the synergistic effect is made clearer by calculating values of the extinguishment factor, F, defined by the equation

$$F = \%H/\%H^o + \%CO_2/\%CO_2^o$$

where $\%H^o$ is the minimum percentage of Halon required to extinguish the fire in *the absence of* CO_2 and $\%H$ is the percentage of halon required to extinguish the flame in the mixture; similarly, $\%CO_2^o$ is the percentage of CO_2 required to extinguish the flame *when only CO, is added* and $\%CO_2$ is the percent of CO_2 required for extinguishment in the

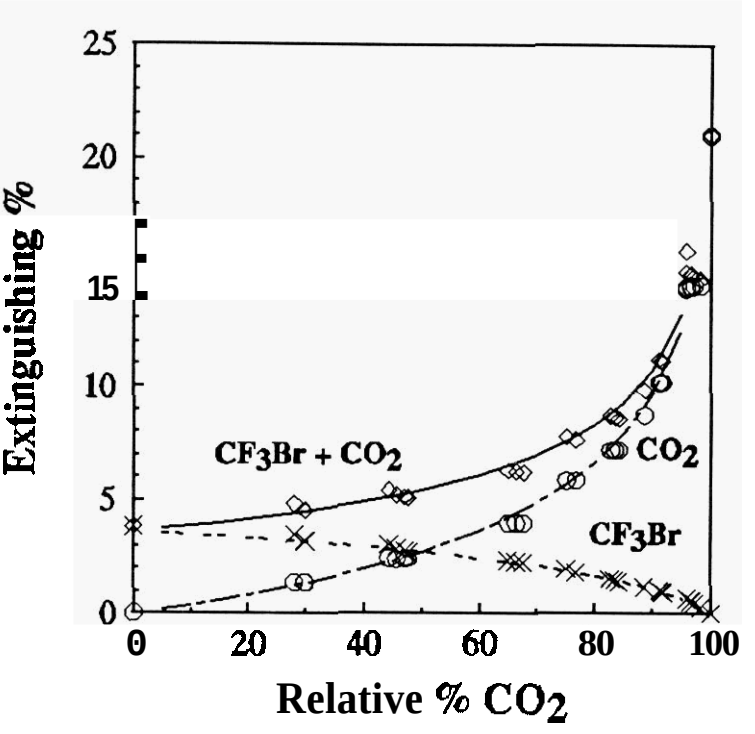

Figure 3. Cupburner CF_3Br/CO_2 Mixtures

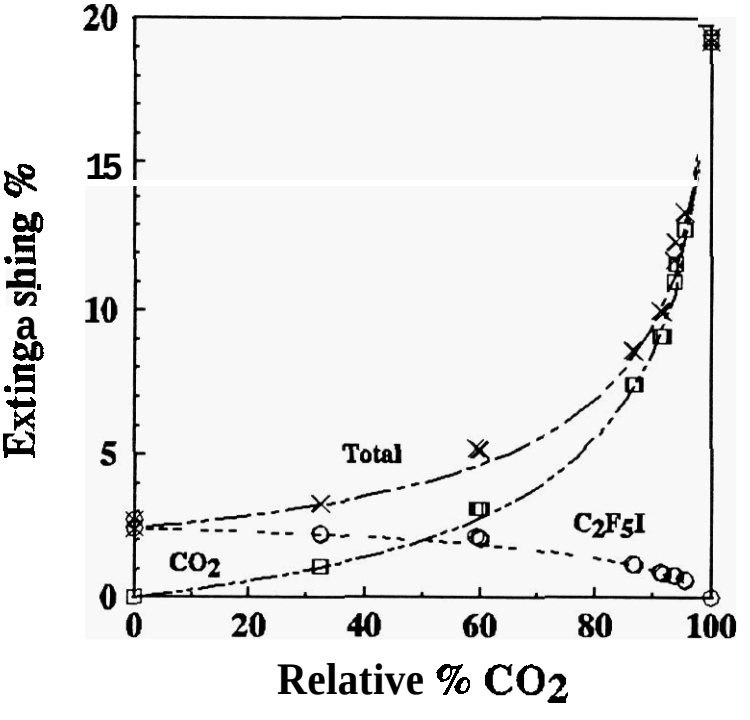

Figure 4. Cupburner C_2F_5I/CO_2 Mixtures

mixture. Note that the extinguishment factor would be equal to unity if there were no improvement in flame extinguishment capacity in the mixture, as compared to an assumed additivity of physical and chemical effects. Values of F are plotted in Figure 5 for the Halon 1211-CO_2 system as a function of the relative percentage variable defined above. A sharp minimum occurs in the plot of actual data and in the model-fitted curve, at approximately 90 to 95% relative concentration of CO_2. We interpret the curve as implying that a 90:10 molar mixture of CO, and agent may be quite effective in extinguishing flames; if the cup-burner results apply in larger-scale fire-fighting situations, total flooding should be quite effective when the air contains approximately 12% CO, and 1.3% of either of the Halons tested. This prediction will be tested by obtaining pan-burner and larger-scale fire-extinguishment test reaults for the Halons and other more environmentally-acceptable chemical agents.

One disadvantage of using CO_2 by itself in total flooding situations has been the health hazard this gas presents at the mole percentages required to suppress the flame. Obviously reducing the requirement for CO_2 by a factor of 2 in mixtures containing an added chemical agent can greatly decrease the risk to personnel. Moreover, if only one-third to one-fourth as much chemical agent is required as if that agent were used alone, health and environmental risks will be much reduced for the mixtures as compared to the individual agents. There is also an obvious economic advantage in reducing the required concentrations of expensive chemical agents by 70% or more. Although the results given here are for the Halons, for which numerous fire-extinguishment test results are available, the information obtained about the combined effect of chemical and physical agents in flame suppression will be readily transferrable to other systems that include a wide variety of Halon-replacement agents.

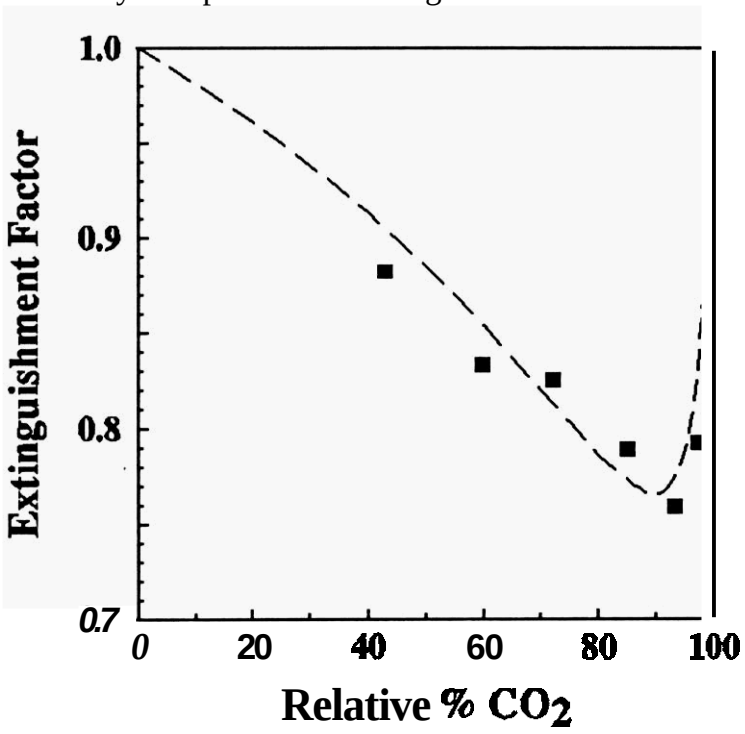

Figure 5. F for Halon 1211/CO_2 Mixtures

MODEL FOR EXTINGUISHMENT BY MIXTURES OF PHYSICAL AND CHEMICAL AGENTS

In modelling fire-extinguishment results for systems containing one or more physical agents, adiabatic flame temperatures are calculated from the known enthalpy of combustion of liquid heptane and heat capacities of the gases in the product mixture (including total CO_2, N_2, other added agents, and water vapor). Although adiabatic flame temperatures calculated in this way

are somewhat higher than actual flame temperatures, the discrepancy is not great enough to cause the model to fail for mixtures of agents like nitrogen and carbon dioxide gases. A minimum flame temperature of approximately 1800 °C is calculated for the combustion of heptane, using the observed percentages of pure CO, and pure N_2 required for extinguishment. The minimum flame temperature is not exactly the same for the two agents, but CO_2 data lead to a slightly higher calculated temperature than that inferred from N_2 data. In predicting the extinguishment concentrations for arbitrary mixtures of N_2 and CO_2 (or other physical agents) it is assumed that the same (mean) minimum flame temperature is always reached at the condition of extinguishment. Therefore, heat capacity calculations alone can be used to predict the partial percentage of each agent that will be required for extinguishment for any relative mole percentage in the mixture. The total and partial percentage curves in Figure 2 have been calculated in this way. The nonlinear behavior predicted by the model (which requires no adjustable parameters for mixtures of physical agents) is in good agreement with the experimentally determined extinguishment results.

An extension of the model is required when chemical as well as physical agents are present. Chemical agents, of course, will also act physically by contributing enthalpic effects which reduce the flame temperature; these effects can be calculated for any arbitrary percentage of the chemical agent, provided that the requisite heat capacity data are available. However, the characteristic mode of action of chemical agents is their ability to produce free radicals capable of interacting with (and scavenging) free radicals present in the flame at any given temperature. Both the physical and the chemical effects of radical chain-stopping agents need to be included in any model for correlating or predicting mixture data. In the case of flame-extinguishing agents that are effective at low concentrations, the predominant effect will be chemical, but methods have been proposed for determining the relative importance of chemical and physical effects for various agents.[6,7]

As the flame temperature increases, the steady-state concentration of free radicals in the propagating flame will increase rapidly - - in fact, much more rapidly than linearly - - with increasing temperature. Therefore, the concentration of chemical agent required to extinguish the flame will also increase dramatically. We can account for this behavior by introducing a single exponential equation to calculate the relative amount of a chemical agent that will be required to extinguish the flame at any temperature. The mole percent of the chemical agent required for extinguishment at a temperature T is assumed to be proportional to the increase in concentration of radicals in the propagating flame, [rad], that occurs as the flame temperature increases from T_{min} to T. An Arrhenius-type equation is used to relate [rad] to temperature:

$$[\text{rad}], = [\text{rad}]_{T\text{min}} + const.[\exp(-\alpha/T) - \exp(-\alpha/T_{min})] \qquad (1)$$

where αR is a molar activation energy, introduced as a single adjustable parameter for correlating the mixture data. The concentration of the chemical agent required for flame extinguishment is assumed to be proportional to [rad], - $[\text{rad}]_{T\text{min}}$, but the proportionality constant in this relation is not required in modelling. Moreover, both *const.* and the constant $[\text{rad}]_{\text{min}}$ appearing in equation 1 cancel out of the simultaneous equations that are solved to calculate the partial extinguishment percentages for the individual agents in mixtures as functions of the relative percentage variable. T_{min} is known from adiabatic flame temperature calculations for systems containing only an added physical agent.

The curves drawn in Figures 2 to 5 represent predictions of the model, each set of curves being calculated for the individual systems. For mixtures of CO_2 or N_2 with CF_3Br, a is 35,000 K and for the corresponding mixtures with CF_2ClBr, α is 40,000 K. One might anticipate that the value of a should be the same for all chemical agents used to extinguish a given type of flame, because a is introduced to account for the temperature-dependence of the free radical concentration in the flame. In fact, by using a mean value of $a \sim 35000$ K for the several Halon systems, a good fit of all of the data is obtained. However, we have used individual values of this parameter to fit experimental data for each system as well as possible.

SUMMARY

We have explored the advantages of using homogeneous solutions of chemical agents dissolved in liquid CO_2 in flame-extinguishment. Synergistic effects between chemical and physical agents should make it possible to utilize considerably reduced quantities of both types of agents in total flooding and other fire-fighting procedures. The fact that many classes of organic compounds - - - nonvolatile as well as volatile, and including fluorinated substances - - are quite soluble in liquid CO_2 should facilitate the development of a new class of fire-extinguishment methods. The methods will utilize the ability of both the CO_2 and the chemical agents to suppress flames, while employing the high vapor pressure of CO_2 to propel the agents toward fires.

A successful model has been developed to predict the efficiency of mixtures containing multiple physical and chemical agents in extinguishing flames. The model is based on adiabatic flame temperature calculations, augmented by an exponential (Arrhenius-type) equation to predict the temperature dependence of the steady state concentration of free radicals in the propagating flame. A strong cooperative or synergistic effect is observed for mixtures of chemical and physical agents, owing to the highly-nonlinear dependence of the production of radicals in the flame on temperature. Results for given mixtures are well-correlated with a system of equations involving a single adjustable parameter which relates to the activation energy of formation of radicals in the flame.

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REFERENCES

1. Hoefling, T., D. Stofesky, M. Reid, E. Beckman, and R. M. Enick, *J. Supercrir. Fluids*, *5*, 237 (1992).

2. Johnston, K. P., K. L. Harrison, M. J. Clarke, S. M. Howdle, M. P. Heitz, F. V. Bright, C. Cartier, and T. W. Randolph, *Science*, 271, 624 (1996).

3. Lott, J. L., S D. Christian, C. M. Sliepcevich, and E. E. Tucker, submitted to *Fire Technology*, 1995.

4. Hirst, R. & Booth, K., *Fire Technology*, 13, 296 (1977). See also NFPA 2001, *Standard on Clean Agent Fire Extinguishing Systems," (National Fire Protection Association, Quincy, MA, ed. 1, 1994).*

5. "Cup-Burner Test Results," *Technical Update Series*, CGET 1, Center for Global Environmental Technologies, University of New Mexico, Albuquerque, NM, 1993, 8 pp.

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

7. Sheinson, R. S., *Proceedings of the Halon Alternatives Technical Working Conference*, Albuquerque, NM, page 71, April-1991.