SYNERGISM IN FLAME EXTINGUISHMENT: NEW RESULTS FOR MIXTURES OF PHYSICAL AND CHEMICAL AGENTS

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ABSTRACT

Flame extinguishment results for mixtures of physical and chemical agents have been obtained with a new total flooding apparatus. Mixtures of agents that operate primarily through enthalpic (heat capacity, phase change) effects and radical chain stoppers show pronounced synergism. The enhancement in flame suppression occurring in mixtures is predictable with a simple model employing an Arrhenius-type equation to account for the steady state concentration of free radicals in the flame and adiabatic flame temperature calculations using heat capacities of agents and other gases in the combustion chamber. The advantage of synergism in fire fighting is that chemical agents approved for fire suppression use can be employed in mixtures with the much safer physical agents, so that the required amounts of both agents are greatly reduced.

The new testing procedure makes it possible to study the flame suppression ability of agents having partial pressures under ambient conditions of only a few torr or less, yielding percentages of individual agents or agent mixtures required for flame suppression in total flooding and related applications. Results are quite consistent with those obtained in standard cup-burner tests. Predictions can be made of the compositions of mixtures of physical agents (including CO_2, inert gases, FM200, and water) and chemical agents (the halons, iodinated or brominated HFC's, metal carbonyls, and halogenated methanes) required to suppress flames.

A particularly attractive potential agent, for use alone or mixed with CO, or other physical agents, is CH_2I_2, which should contribute negligibly to ozone depletion or global warming. The agent poses little threat to personnel during use in confined spaces. CH_2I_2 by itself is capable of suppressing flames at only 1.58 volume (or mole) percent in the air, and the required amount is drastically reduced by mixing it with CO_2 and/or other physical agents.

INTRODUCTION

Recent work from our laboratories has shown the important effect of synergism between chemical and physical fire extinguishment agents[1-3]. Thus, mixtures of the two classes of agents are much more effective than if primarily additive effects occurred. For example, if a given type of flame can be suppressed by a minimum of 20 mole or volume percent of CO_2 present in air, and if 3% of a chemical agent (acting alone) will suppress the same flame, the presence of 1% of the chemical agent and 10% of CO, together will be more than sufficient for flame extinguishment. A simple mathematical model accounts for physical (thermal) effects and chemical (radical chain-stopping) effects of agents and their mixtures. In the case of physical agents, the assumption is made that the same minimum flame temperature is reached at extinction for all such agents and their mixtures. With chemical agents, the highly nonlinear dependence of radical formation on temperature leads to an important phenomenon in relation to the effectiveness of mixtures of physical agents and chemical agents used to suppress flames. Very small quantities of a chemical agent can lower the required concentration of a physical agent (for flame suppression) by large amounts. A ratio, the physical agent reduction factor (PAR), is defined to indicate the enhancement in flame suppression ability that can be attained by adding small quantities of an effective radical chain-stopping agent to a physical agent. PAR ratios in excess of 40 have been observed (and predicted by the model) for some mixtures.

We report here new results for a series of perfluoro- and partially fluorinated hydrocarbons, including compounds with and without I and Br substituents. Data are obtained by using a new laboratory-scale total flooding apparatus, which has been shown to yield results comparable to cup-burner data, hut applicable in studying fire-suppression agents and their mixtures at much lower vapor concentrations than in conventional cup burner tests. Thus, highly-effective chemical agents having vapor pressures of 1 torr or less at room temperature have been studied with the method. The dependence of burning times (in the combustion flask of the total-flooding apparatus) on agent composition(s) can be predicted quantitatively with the model used to calculate mixture compositions for flame extinguishment.

EXPERIMENTAL

A recent manuscript describes the development and testing of a new method for determining limiting agent concentrations that cause flame extinguishment in total-flooding tests'. Figure 1 is a schematic diagram of the apparatus, which in the examples given here utilizes propane from a tank, with valves and regulators to control the flow of the gas to the burner. In operation, the burner is lighted outside the flask, which initially contains dry air. With the stopcocks of the flask opened, the burner is elevated into the flask, secured by the rubber stopper (covered with a polymer film) inserted into the standard taper joint at the bottom of the flask. The time required for the flame to self-extinguish is determined, with the stopcocks left open *so* that the total system pressure will remain at one atmosphere during combustion. Next, the experiment is repeated, with the flask containing a known concentration of a particular flame-suppression agent or a mixture of agents (added as a liquid, gravimetrically, or as a vapor with a gas-tight syringe). If the added agent(s) are effective in contributing to flame suppression, the burning time will be significantly diminished. Knowledge of the flow rate of propane to the burner, burning time, and volume of the flask make it possible to calculate the concentration of gases (combustion products, agents, oxygen, and nitrogen) at the instant the flame extinguishes. It is assumed in each experiment that the stoichiometry of the combustion reaction is given by $C_3H_8 + 5O_2 = 3CO_2 + 4H_2O$. The measured final concentration of CO_2 in the flask (by infrared analysis) agrees well with that predicted from the stoichiometric combustion reaction. Analysis of exhaust gases in cup burner tests shows that only negligible quantities of CO are produced. In the total-flooding experiments, burning times varied from 60 s (with no added agent) to as low as 10 s. Extrapolations to zero burning time were readily made from a series of measurements at varying agent concentration(s), to provide extinguishment information in the limit where the production of combustion products and oxygen depletion do not occur.

Cup-burner experiments on heptane flames were performed as described previously[1,2], using volatile chemical agents delivered from pressure cylinders and combined with gaseous physical agents such as nitrogen and carbon dioxide. Results from both the total-flooding and cup-burner tests were expressed as composition of gases in the air just sufficient to extinguish the flame. Where both total-flooding (propane flame) and cup-burner (heptane flame) experiments could be performed with the same agents, the results were virtually identical. Because the total-flooding experiments can be performed both with volatile agents and with compounds having relatively low vapor pressures, we have preferred to use the flooding method rather than the more complicated cup-burner or pan-burner tests for the rapid screening of potential fire-suppression agents and agent mixtures. The total-flooding experiments are performed in a non-flow system, so that the limiting agent concentration required for extinction is not at all influenced by total mass flow through the apparatus or the ratio of cup diameter to chimney diameter, among other design parameters. Our recent results encourage us to believe that the concentrations of agents obtained from the new total flooding apparatus are fundamental physical data. The inferred values of the limiting concentrations of agents needed to extinguish the propane flame should be valuable in designing agent delivery systems for any total flooding application. Of course, in particular fire-fighting situations, it will be necessary to consider inhomogeneities of gases in large enclosures, loss of agents during delivery to the conflagration, and the need to deliver an excess of agents to ensure flame extinguishment. These are difficulties that arise independent of the method used to obtain flame extinguishment data.

MATHEMATICAL MODELLING

The model employed to correlate total-flooding data is the same as that used in treating cup-burner test results[1-3], although we have developed a nonlinear least squares method to simplify determination of the optimum value of the extinguishment percent required for a new chemical agent. Some details of the calculations are given here.

1. Physical agents and their mixtures. Adiabatic flame temperature calculations are performed with the assumption that the fuel (propane gas) burns stoichiometrically to produce CO_2 and H_2O, and that the final flame temperature is determined by equating the magnitude of the heat of combustion to the heat required to bring the product gases (including combustion products, nitrogen in the air, and agent) from ambient temperature to the final temperature. Rather than introducing constants to account for the dissociation of any of the product gases at elevated temperatures, we have used a value of the heat of combustion of propane that is 5%

less than experimental. In this way, we calculate the maximum flame temperature for propane burning in air (without added physical **or** chemical agents) to be T_{max} **= 2272 K,** and the minimum flame temperature for propane burning at the extinguishment limit for **CO, (19.5%)** to be T_{min} = **1840** K. These values are in good agreement with the values for the maximum and minimum flame temperatures calculated by Ewing, et al.: T_{max} **= 2265 K** and T_{min} = **1860** to 1900 **K for** various physical flame-extinguishment agents and hydrocarbon fuels[4]. We have assumed that when any physical agent or any mixture of physical agents is present at the extinguishing percent in air, the flame will reach the same minimum temperature **(1840 K)** calculated for CO,. Nonlinear search methods are used to calculate the percent of any physical agent **or** agent mixture needed to reduce the flame temperature to exactly **1840 K,** at which temperature the flame will be extinguished.

Detailed equations for calculating flame temperatures will not be given here, but the calculations require knowing the heat capacities **as** a function of temperature for all of the gases that are heated adiabatically by the flame; this includes nitrogen (which is always present), carbon dioxide and water vapor produced by combustion, and any physical agents (such as carbon dioxide and the **HFC's)** which are added to the combustion flask initially. The total enthalpy change is calculated for heating all of these gases, present initially **or** produced in stoichiometric amounts by the combustion of propane, from **298** K to the variable flame temperature, T. When only physical agents are present, the magnitude **of** the enthalpy change attributable to combustion of the propane must exactly balance the enthalpy change for heating the gases (at their extinguishing concentrations) to the minimum flame temperature, T_{min} **= 1840 K.**

In predicting results obtained by the new total flooding method, it is necessary to account for the dilution of nitrogen and oxygen caused by adding physical agents to the flask and by the combustion reaction itself, which (slightly) changes the total number of moles in the flask. The stoichiometric reaction accounts for the depletion of oxygen and production of carbon dioxide and water by the combustion of propane: 5 moles of oxygen are used up and **3** moles **of** carbon dioxide and **4** moles of water are produced for each mole of propane burned. The number of moles of propane that have been burned at the extinguishment point is calculated from the measured burning time and the known volume flow rate of propane into the flask. By forcing the magnitude of the enthalpy of combustion of propane to equal the enthalpy change for heating all of the gases from **298 K** to **1840 K,** it is possible to predict the concentration of the physical agent(s) corresponding to any arbitrary burning time. The energy balance can be applied at any extinguishment point, corresponding **to** known final concentrations of all chemical species present in the flask at a known burning time. The final concentrations are calculated from the known initial concentrations of gases in the flask, corrected for changes in concentration of gases caused by the combustion reaction and dilution.

The results of calculations for the addition of varying percentages of CO, to the combustion flask initially are represented by the straight line drawn in Figure **2. A** maximum burning time of 60 seconds is predicted from the known rate **of** introduction of propane through the inlet tube **(22** mL/minute) and the known volume of the flask. Values of the burning time are plotted against the initial volume **(or** mole) percent of carbon dioxide in the combustion chamber. The excellent agreement between the experimental data (represented by the points in

Figure 1) and the calculated straight line is encouraging, because no adjustable parameters are required to fit the particular data set, beyond the use of the minimum and maximum flame temperatures computed from the model, as described above. These temperatures are used without modification in all of the studies of propane with physical flame-extinguishment agents.

Analogous calculations can be performed for any of the physical flame-suppression agents and their mixtures, so that in every case the enthalpy change required for heating the product mixture from 298 K to $T_{min} = 1840$ K is balanced by the heat of combustion of propane. Extinguishing concentrations in each case can be calculated, corresponding to any burning time between 0 and 60 s. The heat capacity of any added physical agent must of course be expressed as a function of temperature in order to calculate the enthalpy change of the agent for a temperature increase from 298 K to the flame temperature. When heat capacity data are not known for an agent, approximation methods can be used to estimate them from data for similar compounds[3].

The data in Figure 3 for perfluoromethylcyclohexane (PFMC), representing burning time as a function of the known initial percentages of PFMC in the combustion flask, are quite accurately reproduced by the model just described. Because the heat capacity of the perfluoromethylcyclohexane is not known, a scale factor has been used in the equation representing heat capacity as a function of temperature to obtain the best fit of data[3]. A limiting value of the percentage of perfluoromethylcyclohexane required for extinguishment ($H^\circ = 3.7\%$) was obtained in this way. The apparent linearity of the plot is a good indication that perfluoromethylcyclohexane acts primarily as a physical flameextinguishment agent. Note that in the limit as the burning time approaches zero, neither CO, nor water vapor are present in the flask because no combustion has occurred. It should be mentioned that although an adjustable scale factor was used to fit the line (by least squares) to the data, this would not be necessary if the heat capacity of the agent were known as a function of temperature.

2. Extension of the model to include chemical agents. Previously, we have argued that adiabatic flame temperature calculations for systems in which chemical agents are present require introducing an equation to account for the interaction of chemical (free-radical producing) agents with radicals in the propagating flame[1-3]. To account for the nonlinear effects of a chemical agent, we proposed that a single Arrhenius-type equation can be used to represent the temperature dependence of the steady state concentration of free radicals in the flame[2,3]. Then, assuming that the required percent of chemical agent added to the air to cause extinguishment (H) is proportional to the steady state concentration of free radicals, we derive the equation

$$H/H^\circ = [\exp(-E/RT) - \exp(-E/RT_{min})]/[\exp(-E/RT_o) - \exp(-E/RT_{min})] \quad (1)$$

where H° is the percent of chemical agent required when only that agent is added to air. This one equation, combined with the equations needed in the adiabatic flame calculations, has proven to be remarkably reliable in modelling results for a wide range of radical-producing agents mixed with physical agents. The constant E in equation 1 is an activation energy for production of radicals in the flame and R is the ideal gas constant. In principle, E can be used as a variable parameter in fitting data for different types of flames and agents, but we have found it quite adequate to use the constant value $E/R = 35,000$ K in all modelling of data for propane and heptane flames with equation 1. Three temperatures are involved in the equation: T, the variable flame temperature at extinguishment; T_{min}, the minimum flame temperature (1840 K) reached with only physical agents present; and T_o, the temperature of the flame for a hypothetical situation in which the chemical agent is present at its limiting extinguishment concentration (H^o) and contributes only its heat capacity (physical) effect, but not its radical chain-stopping ability. A more detailed explanation of equation 1 and its use in modelling flameextinguishment results has been given in a recent report?.

As in modelling results for physical agents, dilution factors are introduced to allow for the slight decrease in chemical agent concentration in the flask caused by the combustion reaction. Heat capacities are required in calculating enthalpy changes for the chemical agent, but at the very small agent concentrations required at extinguishment, approximate forms (C, as a function of T) are usually quite adequate. In predicting results for mixtures of the chemical agent with one or more physical agents, the limiting extinguishment concentration (H") is treated as the single adjustable parameter. This constant is, in our opinion, the most important parameter relating to the extinguishing ability of a chemical agent, because it represents the minimum volume percent of the agent in air (acting alone) that will be just sufficient to extinguish the flame.

Finally, it should be mentioned that the model described above is capable of predicting the high degree of synergism in flame extinguishment that occurs when a small amount of an effective chemical agent is added to a large amount of a physical agent. No parameters are introduced in modelling except the value of H^o, which, once determined for each individual agent, is used in predicting results for this agent mixed with arbitrary physical agents or their mixtures. Thus, it is an important advantage in studying the effectiveness of mixed systems to be able to use a very limited amount of information about the flame-suppression ability of individual agents to predict the characteristics of arbitrary mixtures of chemical and physical agents, throughout wide ranges of agent compositions.

RESULTS FOR MIXTURES INCLUDING CHEMICAL AGENTS

Results have been obtained in our laboratory for a large number of chemical and physical agents, both as single components and mixed with various other agents. Table 1 includes values of the limiting extinguishment percentages, H^o, inferred for individual agents from the new total-flooding technique.

Table I. Limiting agent concentrations (%)

agent	H^o(%)	agent	H^o(%)	agent	H^o(%)
c-$CF_3C_6F_{11}$	3.7	CHBr,	1.6	CF_3Br	3.0
CH_2Br_2	2.7	$C_6F_{13}I$	2.4	CO_2	19.5
CH_2I_2	1.6	$C_8F_{17}Br$	1.7	HBr	3'

* Value uncertain by -.5% owing to reactivity of HBr.

The usual procedure in studying a new agent is to introduce it to the combustion flask at known concentrations and to measure the burning time in each case. Plots of burning time vs. agent percent (analogous to Figures 2 and 3) are prepared and the data fitted to the mixture model described above. Note that as the burning proceeds in each experiment, CO, is produced and oxygen is removed, so that the overall composition of the gas mixture is continuously changing. The mathematical model applies at each self-extinguishment point, where the enthalpy changes contributed by all of the species present are accounted for by integration of heat capacity data as functions of temperature. Figure 4 shows a burning time plot for Halon 1301 (CF_3Br), an agent that is sufficiently volatile so that its volume percent in air can exceed the extinguishment percentage, H°. By nonlinear least squares analysis, we determine that H° = 3.0 ± 0.2%. within the range of previous estimates of this quantity from cup-burner tests'. The curvature observed in Figure 4 is characteristic of the burning curves for systems containing an agent that has substantial radical chain-stopping ability.

When chemical agents are not sufficiently volatile to study at concentrations as large as H", it is possible to obtain data throughout wider ranges of composition by introducing a known percent of chemical agent into the flask and also adding an arbitrary percent of CO,. In this way, one obtains a series of burning curves - - at fixed initial concentrations of agent - - as shown in Figure 5 for the slightly volatile compound perfluorooctylbromide (PFOB). The burning time is plotted as the ordinate and the percentage of CO_2 added to the flask is plotted as the abscissa: the initial percentages of PFOB are indicated in the legend. In this series of results, fitted by nonlinear least squares, the value of H° is 1.7 ± .1%. Note that the value of H° is the only adjustable parameter needed in fitting all of these data, for an agent that is a good flame-suppression agent, contributing both thermal and free radical-stopping effects. Although plots of data in the form shown in Figure 5 do not highlight the expected synergistic effects for mixtures of a chemical and a physical agent, synergism clearly occurs, as is indicated by the fact that the total concentration of mixtures of PFOB and CO, required to extinguish the flame is much less than if the agents contributed additively to flame extinguishment.

Preliminary data for a promising new chemical agent (methylene iodide, CH_2I_2) are shown in Figure 6. CH_2I_2 has a vapor pressure of only 1.0 torr at 25 °C, so it has been a challenge to investigate it with the total flooding method. Results are plotted as burning time vs. the percent of added CO_2, for two fixed percentages of CH_2I_2 initially present in the air. The lines are calculated by utilizing the least squares value of the extinguishing percentage, H° = 1.58%.

Data are shown in Figure 7 for bromoform ($CHBr_3$), which is volatile enough to be studied at concentrations approaching the limiting H° value for the compound. Bromoform appears to have nearly the same fire-suppression ability as CH_2I_2, so it is a useful analog for the less volatile CH_2I_2. (Bromoform is, however, more toxic and less environmentally friendly than CH_2I_2, so we are not suggesting that it be used as an agent in fire fighting.) Superimposed on the plot for bromoform are data sets for CH_2I_2; all of these results, and data obtained with 5% of CO_2 added initially to the flask (not shown), can be represented quite satisfactorily by using the same limiting extinguishment percentage (H" = 1.58 ± 0.04%). The pronounced curvature of the plot in Figure 7 for CH_2I_2 and CHBr,, analogous to that shown in Figure 4 for Halon

1301, is characteristic of agents that function primarily by radical chain-stopping mechanisms, with relatively minor contributions from physical (thermal) effects.

The results obtained for CH_2I_2 indicate that this compound ranks among the best of the halogenated alkanes that have been studied in cup-burner and pan-burner tests, particularly if comparisons among agents are made on a weight basis. Moreover, the low volatility of the compound and its low toxicity should make it attractive as a flame-suppression agent, both environmentally and as regards human safety.

DISCUSSION

Previously, small nonlinear effects were observed in the flame-suppressing ability of mixtures of a physical and a chemical agent[5], although these results were not interpreted as evidence for synergism. It was also suggested that synergism in mixtures might occur because of the different modes of action of chemical and physical agents[6], but only now are the remarkably large synergistic effects between chemical and physical agents being documented[1-3]. The extent of synergism is particularly large when a small amount of a very effective radical chain-stopping agent is added to a physical agent. By using only a small amount of such an agent, compared to the amount of a physical agent, it is possible to obtain a very impressive reduction in the quantity of both agents required for flame extinguishment. There are many ways this effect might be exploited in fire fighting: several schemes for doing this are discussed here.

Synergism and the use of mixtures of physical and chemical agents. Both experimental data and the simple model for predicting fire-suppression properties of mixtures of chemical and physical agents indicate the large degree of synergism these mixtures exhibit. The highly-nonlinear temperature dependence of steady state free radical concentrations in a hydrocarbon flame ensures that any agent that effectively interferes with the radical chain reactions will also drastically reduce the concentrations of physical agents required in flame suppression. Thus, if a chemical agent has an extinguishing percent (H^o) equal to 1.58%.the presence of only a fraction of a percent of this agent in air can reduce the percentage of a physical agent needed for flame extinguishment by 50% or more. In the case of many of the mixtures studied *so* far, the reduction in the required concentration of a physical agent, caused by the presence of a chemical agent, can be more than an order of magnitude greater than the concentration of chemical agent added. An example showing the importance of synergism in mixtures of chemical agents and CO, is given below.

To indicate the efficiency of a chemical agent in reducing the amount of a physical flame-suppression agent needed in fire fighting, we have introduced a ratio, the physical agent reduction (PAR) factor. The PAR factor is defined by

$$PAR = (H^o_{physical} - H_{physical})/H_{chemical} \tag{2}$$

where $H^o_{physical}$ is the concentration of a physical agent (acting alone) required to extinguish a flame; $H_{chemical}$ and $H_{physical}$ are the required concentrations of chemical and physical agents in an extinguishing mixture. Because $H_{physical}$ is always less than $H^o_{physical}$, the numerator of equation (2) and hence the PAR factor will always be positive. Table 2 lists PAR values for

Table 2. Physical agent reduction (PAR) factors for mixtures of CO_2 and either CH_2I_2 or CHBr,

% CH_2I_2 or CHBr,	% CO,	decrease in % CO_2	PAR factor
1.6	0		- -
0	19.5		- -
.047	17	2.5	54
.10	15	4.5	45
.22	12	7.5	34
.36	9.8	9.7	27
.58	7.0	12.5	22
.80	4.9	14.6	18

mixtures of CO, and either CH_2I_2 or CHBr,, calculated with the mathematical model, using $H^o_{physical} = 19.5\%$ The percentages of chemical and physical agent needed to suppress the flame are given in columns 1 and 2, for each pure agent and for several extinguishing mixtures relatively rich in CO_2. The third column indicates the decrease in the required % of CO, caused by the presence of the small percentages of chemical agent. The PAR factor values for mixtures of the physical and chemical agents (column 4) are quite large, particularly at the very lowest concentrations of chemical agent. According to the calculations, the presence of 0.22% of either CH_2I_2 or CHBr, in air decreases the amount of CO, required to suppress a propane flame by 7.5%, nearly 40% of its original extinguishing percentage. Similar reductions can be obtained with other physical agents.

Use of chemical agent - physical agent synergism in the total flooding of manned spaces. Dr. Homer Carhart of the Naval Research Laboratory has proposed that nitrogen (or other nearly inert gaseous agents) might be used to suppress fires in enclosed, manned spaces, as for example on a submarine.' By increasing the concentration of added N, to approximately 33% in air, flame extinguishment could be achieved, without killing personnel, although they would probably suffer moderately severe symptoms of the bends (aeroembolism). It has occurred to both Dr. Carhart and our group that mixtures of small amounts of a suitably benign chemical agent and gaseous nitrogen might be ideal flame-suppression agents for use in manned (or unmanned) spaces. Thus, if the required incremental volume percent of nitrogen added to the air could be reduced to 15 or 20%, by using less than a percent of a chemical agent, both agents could be used advantageously without endangering human life and with minimal impact on the environment.

It has been suggested that a major fraction of our remaining supplies of the halons (Halon 1211 and 1301) might be reserved for use as fire suppressants in the cargo compartments and elsewhere on large military and civilian aircraft. If in fact mixtures of these agents with nonreactive gaseous physical agents were to be used in aircraft, and perhaps also on submarines, the needed amounts of the halons would be so small that existing stores of these agents could very well last many decades. Less than 1% of either Halon 1301 or 1211 in the air can reduce the amount of nitrogen needed to less than half of what is required if the physical agent is used alone. Of course this proposal does nothing to prevent the ultimate transfer of the halons into the ozone layer, but it does argue that we can make very effective use of the remaining amounts of the halons, helping to buy time until the real 'magic bullet' chemical agent can be found.

Use of chemical agent - physical agent mixtures as replacements for physical agents. We suggested previously that dissolving chemical agents in liquid CO_2 or other liquid physical agents might produce effective agent mixtures that could serve as 'drop-in' replacements wherever these physical agents are normally used[1-3]. Several experiments indicate that large concentrations of agents like the perfluorinated hydrocarbons and partially fluorinated alkanes can be delivered to fires in this way. However a number of possible chemical agents, including the metal carbonyls, are not particularly soluble in liquid CO_2; some of these agents may also be only slightly soluble in liquid FM200. On the other hand, many of the highly volatile physical agent fluids will be quite soluble in liquid organic compounds under ambient conditions[8]. Thus, for example, toluene (not suggested here as a flame-suppression agent!) is not soluble to the extent of even one mole percent in liquid CO_2 at 25°C, but CO_2 dissolves in liquid toluene to produce a solution at saturation that contains approximately 50 mol % of each component[1]. Such a mixture has, of course, the same vapor pressure as the CO_2-rich solution, containing > 99 mole % CO_2 and $< 1\%$ toluene. Therefore, by using solutions of CO_2 dissolved in a chemical agent like CH_2I_2 at somewhat less than the saturation concentration, one might circumvent difficulties caused by the fact that the chemical agents have limited solubility in carbon dioxide. Given the large driving force provided by the vapor pressure of the physical agent, it should be possible to deliver a stream of the chemical agent/physical agent mixture at a nearly constant flow rate in flame extinguishment, including large-scale systems and hand-held fire extinguishers. In fire-fighting applications where an over-pressure of nitrogen or inert gas is used in cylinders containing a physical agent, the chemical agent/physical agent mixture (rich in chemical agent) might be an ideal drop-in replacement for the pure physical agent. A considerable weight advantage could be achieved, because a much smaller volume percent of the chemical agent/physical agent mixture would be required, compared to the physical agent used as a single component.

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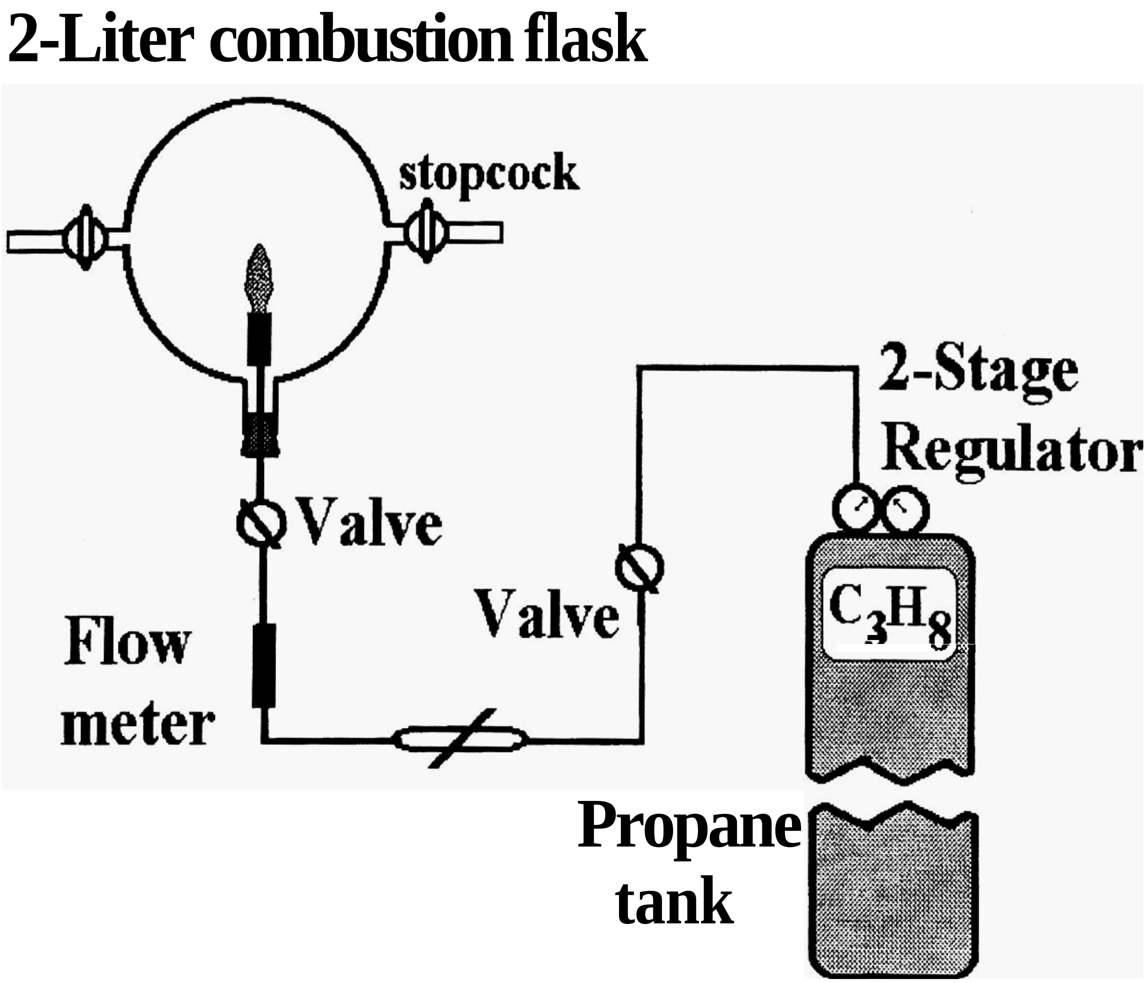

Figure 1. Total flooding apparatus.

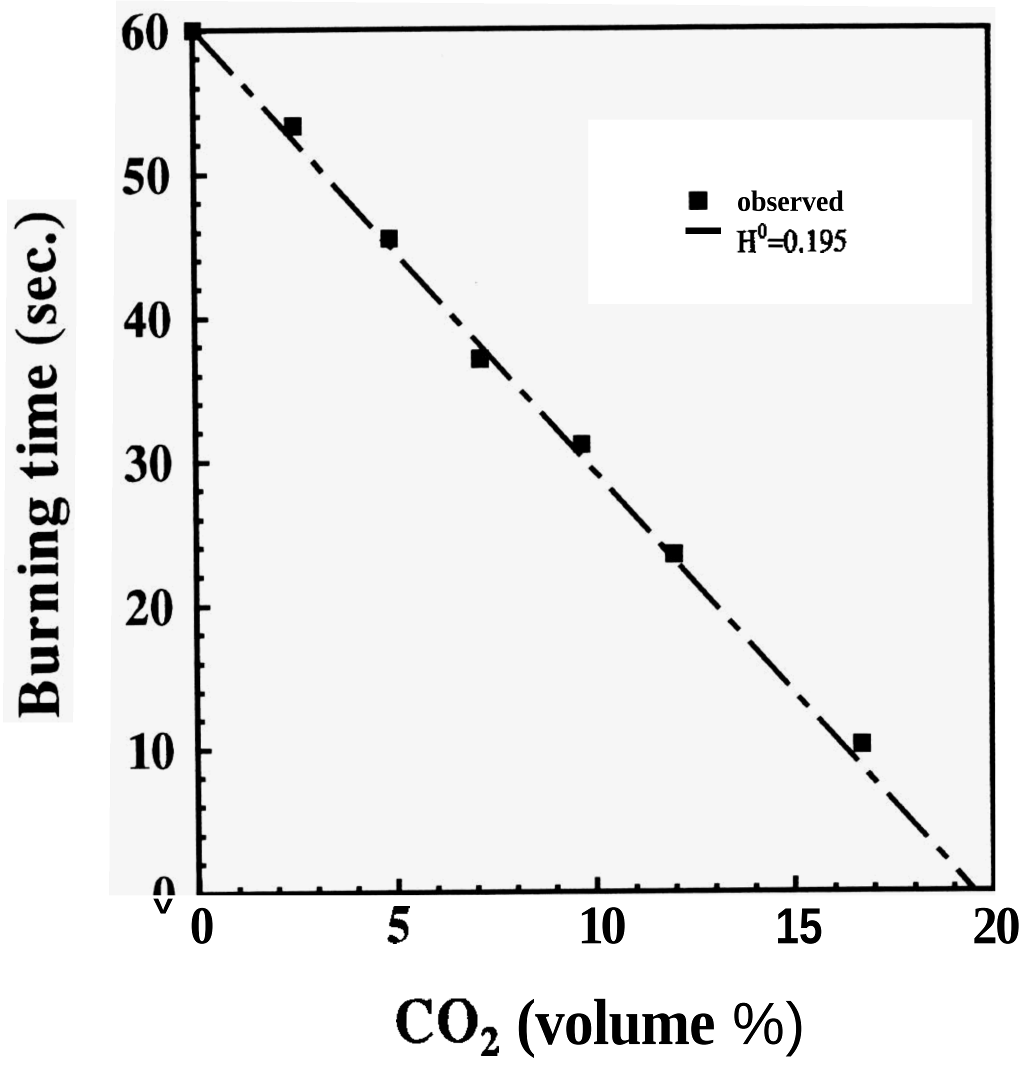

Figure 2. Burning time to self-extinguishment as a function of percent of CO_2 added initially to the combustion flask. Line is calculated with the model described in the text, utilizing a value of T_{min} = 1840 K for physical agents and their mixtures.

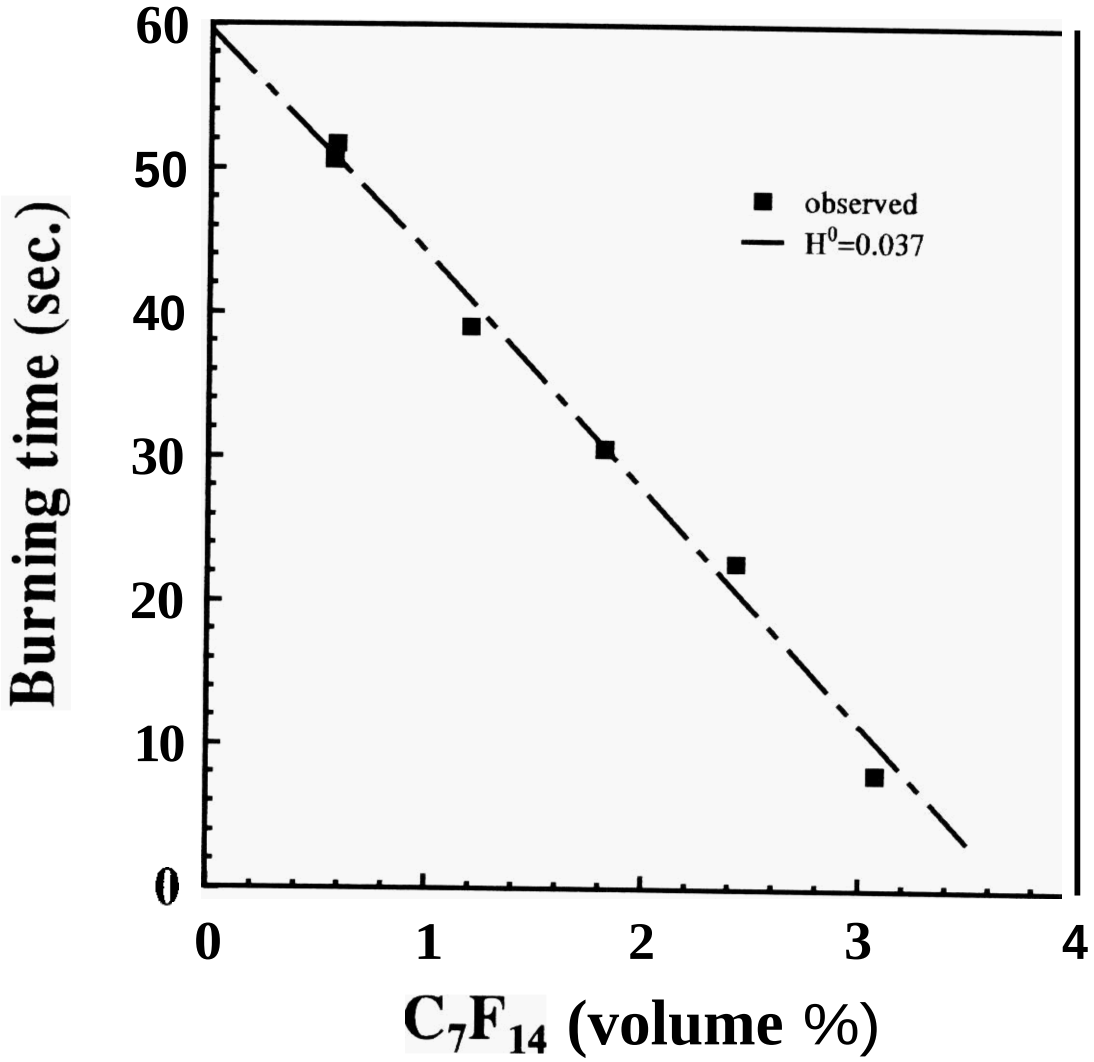

Figure 3. Burning time as a function of percent of perfluoromethylcyclohexane (PFMC) added initially to the combustion flask. Line is calculated with the model described in the text.

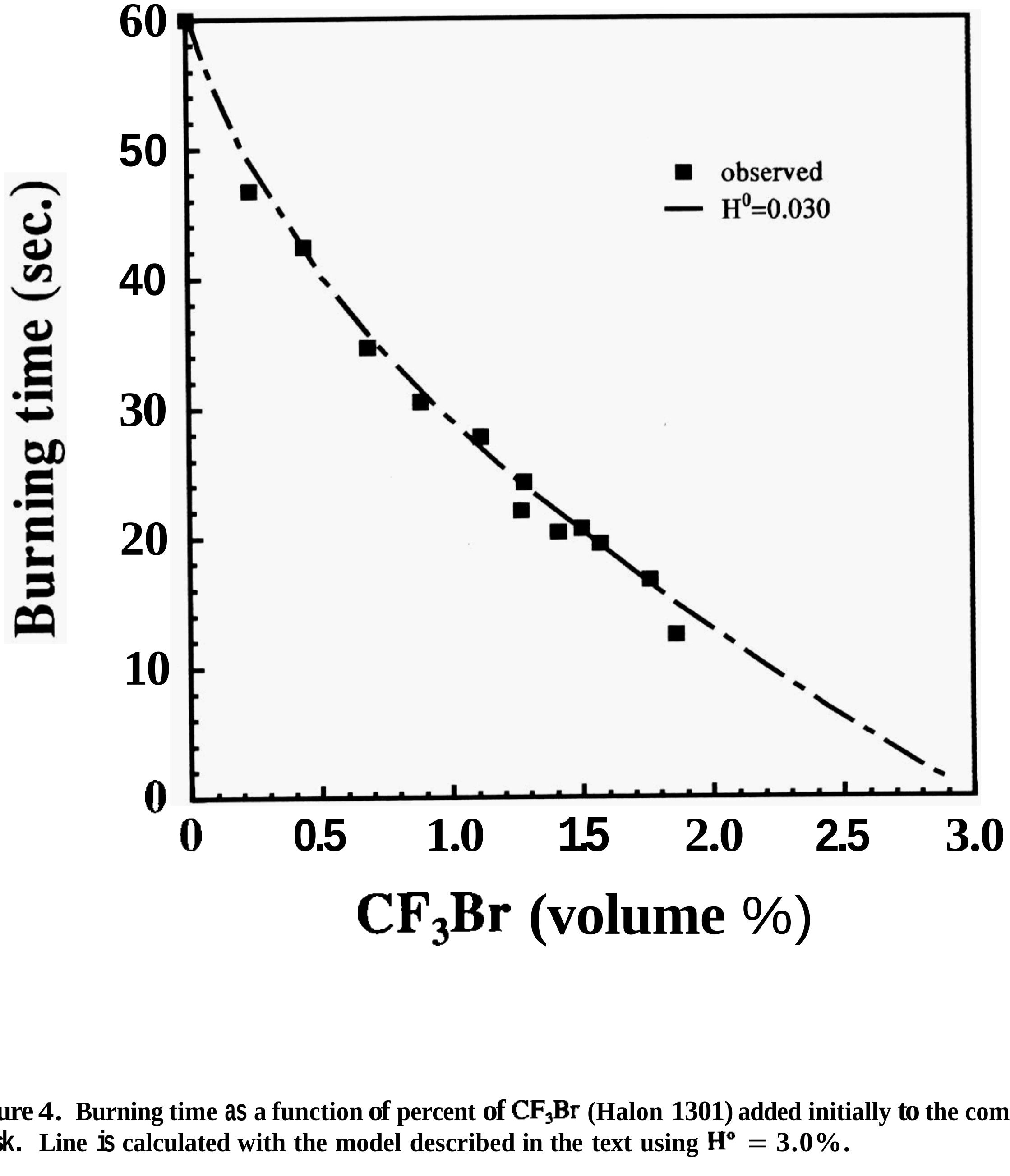

Figure 4. Burning time as a function of percent of CF_3Br (Halon 1301) added initially to the combustion flask. Line is calculated with the model described in the text using $H^{o} = 3.0\%$.

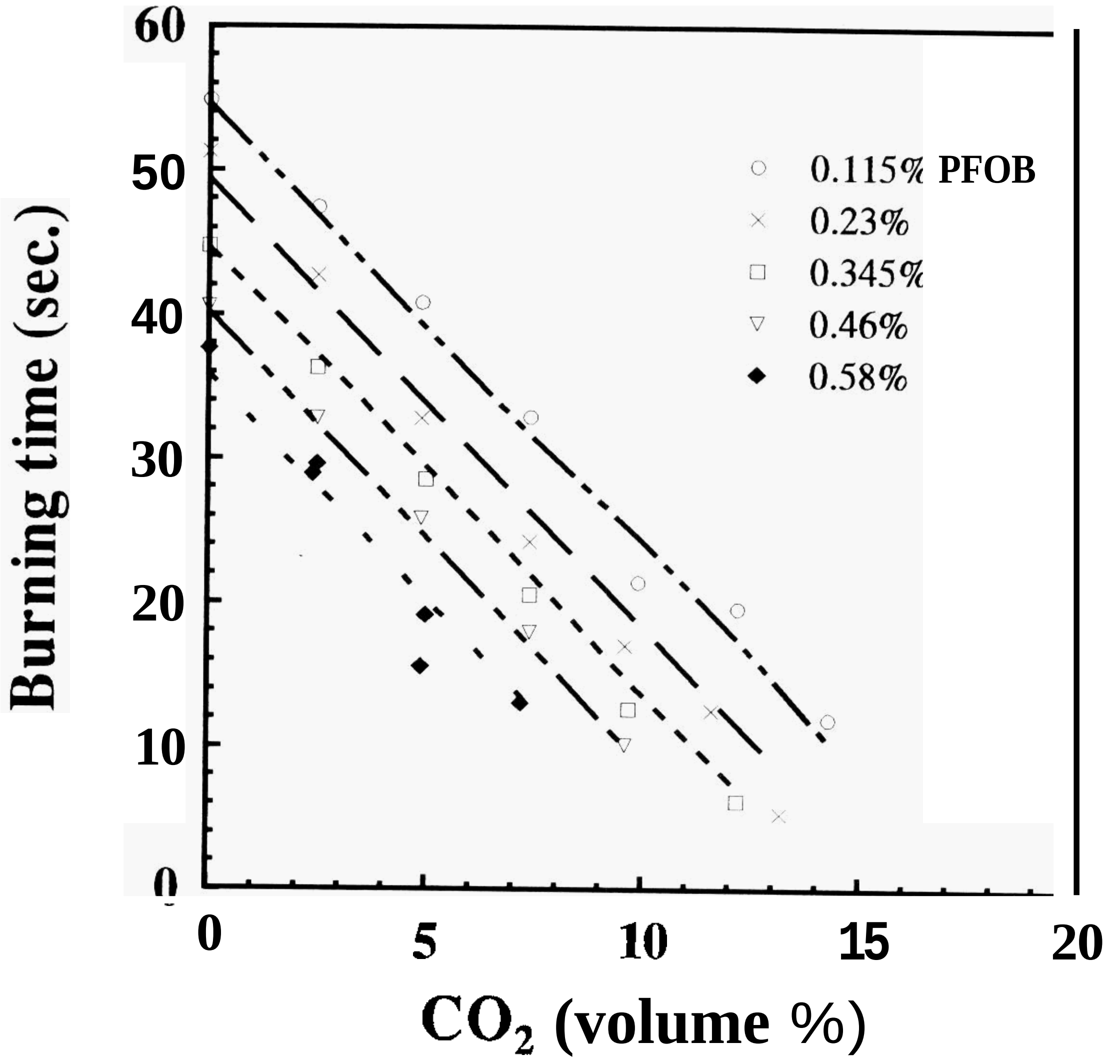

Figure 5. Burning time as a function of percent of perfluorooctylbromide and CO_2 added initially *to* the flask. Percentages of perfluorooctylbromide are indicated for each curve. Lines are calculated with the model described in the text, using the limiting extinguishment percentatge $H^o = 1.7\%$.

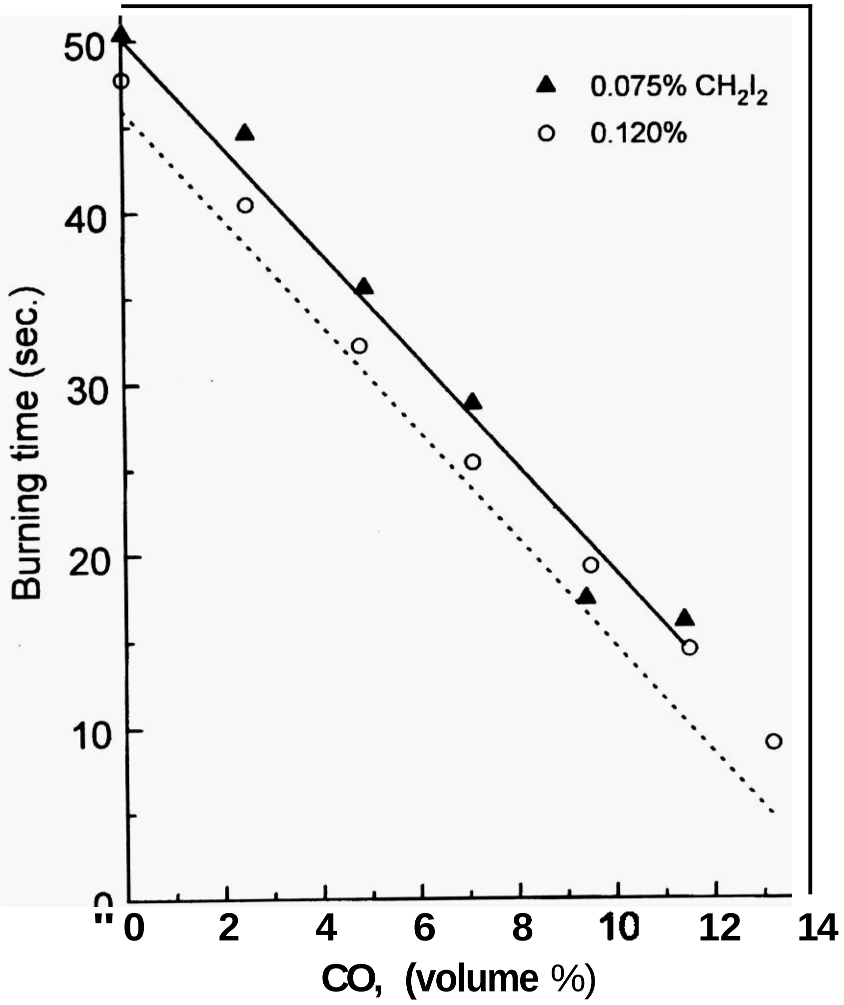

Fig. 6

Figure 6. Burning time as a function of percent of CH_2I_2 and CO_2 added initially to the combustion flask. The upper curve corresponds to 0.075 % of CH_2I_2 and the lower curve to 0.120 % CH_2I_2. The lines are calculated using H° = 1.58%.

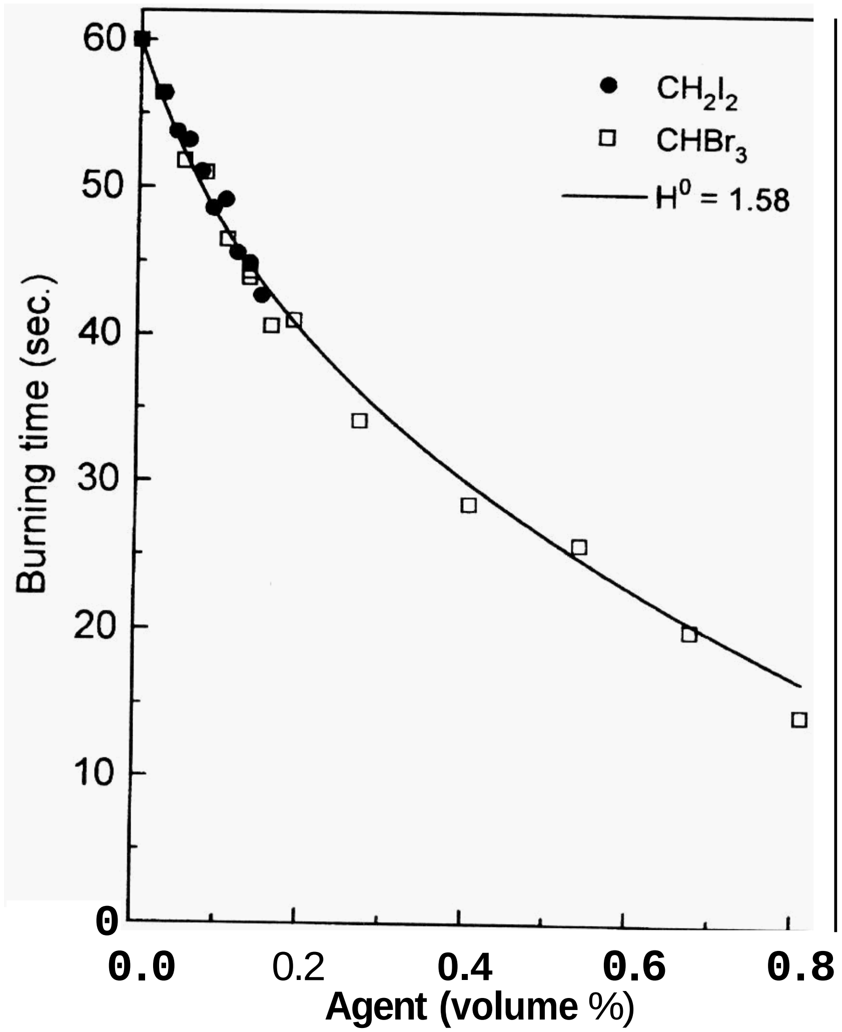

Fig. 7

Figure 7. Burning time as a function of percent CHBr, and percent CH_2I_2 added initially to the combustion flask. The line is calculated using $H^o = 1.58\%$.