ESTIMATION OF FIRE EXTINGUISHING CONCENTRATION OF BINARY AGENTS

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Abstract

The search for a new fire extinguishing agent with all the desirable properties of halon 1301 has not been successful. During the last few years, several chemical groups with very low extinguishing concentrations have been identified. Most of these compounds have high boiling points and are not suitable replacements for halon 1301. However, mixtures of these chemicals in an inert gas could produce fire extinguishing agents with many of the desirable properties of halon 1301. To study binary fire suppressants, one has to determine the extinguishing concentrations for several compositions of a given chemical in an inert gas. This process is expensive and time consuming. A method to estimate the extinguishing concentrations would be helpful in reducing the number of experiments needed for any binary system.

In this study, a method based on adiabatic flame temperature calculations and the dependence of the rate of fire suppression of chemical agents on temperature, was used to estimate the extinguishing concentration of binary mixtures. The method was tested for five organic compound / nitrogen mixtures. Five compounds that have been shown to have very low extinguishing concentrations and very short atmospheric lifetime, were selected for this study. Cup burner experiments were conducted for several concentrations of each chemical in nitrogen. All the five binary systems showed synergism. As expected, the degree of synergism was highest at low concentrations of the chemical. For each binary system, extinguishing concentrations of the pure compounds and one binary data were used to predict the extinguishing concentrations for the entire range of binary composition. The predicted values are very close to experimental data.

Introduction

Halons are regulated by the international agreements because of concerns over their connection with the depletion of the stratospheric ozone layer. Scientists have therefore been forced to search for environmentally benign fire suppressants. A large number of chemical groups with low extinguishing concentrations have been identified during the last ten years[1-7]. None of the new compounds have all the desirable properties of halons. Bromotrifluoro methane (halon 1301) is a highly effective total flooding fire suppressant. It is a nonconductive and clean agent with a low toxicity. Most of the new chemical groups considered for halon replacement have high boiling points and are liquid at room temperature. They cannot therefore be used as total flooding agents. However, it has been shown that mixtures of these compounds in an inert gas can produce a gaseous agent suitable as halon 1301 substitute[8,9].

The effectiveness of binary fire suppressants has been studied by several investigators[10-13]. These studies indicate that when a mixture of an agent that reacts with free radicals in the fire (chemical effect) is diluted in an inert gas, synergistic interactions occur between the two compounds. The result is that the mixture is more effective than the sum of the individual inhibition effects of pure compounds. Similar experiments with mixtures of two agents that extinguish fires mainly by physical means have shown no synergism[11]. Another advantage of using binary fire suppressants is lower costs. Many of the new

chemical groups proposed as halon replacement are expensive. Mixtures of these compounds in inert gas provide affordable and effective fire extinguishing agents.

The effectiveness of any fire suppressant is usually assessed by determining the minimum concentration of the agent required to extinguish a flame or by measuring global parameters such as burning velocity, extinction strain rate and flame temperature. To assess the effectiveness of a binary mixture, a series of experiments must be conducted to measure one of these parameters (such as extinguishing concentration) for different compositions of the binary mixture. Obviously this process is expensive and time consuming. An accurate method to estimate extinguishing concentration of binary mixtures from a minimum number of experiments would be helpful. In this study, a method based on adiabatic flame temperature calculations and the dependence of the rate of fire suppression of chemical agents on temperature was used to estimate the extinguishing concentration of binary mixtures. The estimating method was tested for five new binary fire suppressants. Two bromofluoro alkenes, two fluoroethers, and one fluoro alkenane were selected for this investigation. All the compounds have been shown to have very low extinguishing concentrations and short atmospheric lifetimes. Different concentrations of each halogenated compound in nitrogen were prepared and their extinguishing concentrations were measured using a cup burner apparatus. The experimental data were compared with the predicted values.

Estimation of Extinguishing Concentration

The extinguishments of flames is achieved by: (1) reducing the concentration of oxygen to a point where combustion ceases (dilution effect) – (2) reducing the flame temperature to a point that no activated atoms or free radicals are formed (cooling effect) – (3) reducing the concentration of free radicals and thus interrupting the flame chemistry of the chain reaction of combustion (chemical effect). Inert gases extinguish fire mainly by physical means (dilution and cooling effects), and heat capacity plays an important role in reducing the flame temperature. Halogen containing compounds suppress fire mainly by chemical means and therefore the ability of the compound to remove free radicals is important. For a binary fire suppressant containing an inert gas and a halogenated compound, both physical and chemical effects become important. The inert gas reduces the flame temperature, which in turn decreases the number of free radicals produced in the fire. Fewer number of free radicals means that less halogen containing fire suppressant is needed to extinguish the fire. The amount of halogenated compound needed depends on temperature, and the temperature of the fire is a function of the amount of the inert gas present. It is therefore possible to develop relationships between the amount of inert gas and halogenated compound in a binary mixture needed to extinguish fires.

The effect of an inert gas on the flame temperature can be determined by adiabatic flame temperature calculations. The heat generated by burning a fuel (heat of combustion) is used to raise the temperature of combustion products and inert gas:

$$\Delta H_C = \left[\sum (n_i C_{Pi})_{products} + n_I C_{PI}\right](T - T_{in}) \qquad (1)$$

where ΔH_C = heat of combustion per mole of air,
n_i = moles of product "i" per mole of air,
C_{Pi} = heat capacity of product "i",
n_I = moles of inert gas per mole of air,
C_{PI} = heat capacity of inert gas,
T = flame temperature,
T_{in} = inlet temperature.

If there is no fire suppressant (inert gas), equation (1) reduces to:

$$\Delta H_C = \left[\sum \left(n_i C_{Pi}\right)_{products}\right]\left(T_F - T_{in}\right) \quad (2)$$

Where T_F is the flame temperature with no fire suppressant present. The value of T_F depends on the type of the fuel and the fuel /oxidizer ratio. For example, the flame temperature of stoichiometric mixture of n-heptane in air is about 2290 °K[14]. Substitution of equation (1) into (2) yields the following relation:

$$n_I = \frac{\sum \left(n_i C_{Pi}\right)_{products}}{C_{PI}} \cdot \frac{T_F - T}{T - T_{in}} \quad (3)$$

If enough inert gas is used, the flame temperature reduces to a point that no free radicals are formed and fire is extinguished. At extinction, equation (3) is written as:

$$n_I^0 = \frac{\sum \left(n_i C_{Pi}\right)_{products}}{C_{PI}} \cdot \frac{T_F - T_{Ex}}{T - T_{in}} \quad (4)$$

Where n_I^0 = moles of inert gas per mole of air required for extinction,
T_{Ex} = temperature at extinction.

The extinction temperature, T_{Ex}, is reported to be approximately 1600 °K for diffusion flames[15, 16]. Dividing equation (3) by (4) and rearrangement of the resulting relation yields:

$$T = \frac{\frac{T_F\left(T_{Ex} - T_{in}\right)}{\left(T_F - T_{Ex}\right)} + \frac{n_I}{n_I^0} \cdot T_{in}}{\frac{n_I}{n_I^0} + \frac{\left(T_{Ex} - T_{in}\right)}{\left(T_F - T_{Ex}\right)}} \quad (5)$$

Flame temperature T, can be calculated for a given value of n_I / n_I^0 (fraction of minimum amount of pure inert gas needed for extinction) from equation (5).

As it was stated previously, the amount of halogenated compound (chemical agent) needed to extinguish the fire depends on flame temperature. Lott et al.[10] assumed an exponential relationship between the concentration of chemical agent and flame temperature:

$$n_C = AEXP\left(\frac{-B}{T}\right) \quad (6)$$

Where n_C is the moles of chemical agent per mole of air and A and B are constants. As temperature approaches extinction temperature (T_{EX}), n_C should approach zero (no chemical agent is needed at extinction temperature). Equation (6) however, does not satisfy this condition. The following relationship was therefore used to represent the effect of temperature on the amount of halogenated suppressant needed to extinguish fire:

$$n_C = AEXP\left(\frac{-B}{T - T_{EX}}\right) \quad (7)$$

For pure chemical suppressant (no inert gas), the mass of agent needed for extinction is:

$$n_C^0 = AEXP\left(\frac{-B}{T_F - T_{EX}}\right), \quad (8)$$

where n_C^0 is the number of moles of pure halogenated compound per mole of air needed for extinction. Dividing equation (7) by (8) one gets the following relation:

$$n_C = n_C^0 EXP\left[-B\left(\frac{1}{T - T_{EX}} - \frac{1}{T_F - T_{EX}}\right)\right] \quad (9)$$

n_I^0 and n_C^0 are related to extinguishing concentrations of pure inert gas and pure halogenated compound, respectively:

$$n_I^0 = \frac{C_I^0}{100 - C_I^0}, \quad (10)$$

$$n_C^0 = \frac{C_C^0}{100 - C_C^0}, \quad (11)$$

where C_I^0 = extinguishing concentration of inert gas, volume%.

C_C^0 = extinguishing concentration of halogenated compound, volume%.

n_I and n_C are related to the extinguishing concentration of binary mixtures:

$$n_I = \frac{C(1 - X)}{100 - C} \quad (12)$$

$$n_C = \frac{C\,X}{100 - C} \quad (13)$$

Where C is the extinguishing concentration of the binary mixture, and X is mole fraction of chemical agent in the binary mixture.

Equations (5) and (9) along with equations (10) through (13) are used to estimate extinguishing concentrations of binary agents as a function of mole fraction of halogenated compound. For each system, the constant B is found from one experimental data point. Then the equations are used to generate the extinguishing concentration of the binary mixture for the entire range of composition.

Experimental

The chemicals, manufactures, and purities are given in Table 1. Chemicals were used without additional purification. Binary mixtures of halogenated compounds (one fluoro alkene, two bromo fluoro alkenes, and two fluoroethers) in nitrogen were tested in this investigation. Properties of all the pure suppressants are given in Table 2.

The apparatus used for determining fire extinguishing concentration of gaseous mixtures was the same one described in the previous papers[8, 9]. It consisted of a cup burner, a liquid fuel delivery unit, a unit for preparing gaseous mixtures (extinguishing agents), and an agent / air delivery unit. The burner (made of quartz) was constructed based on the specifications given in ISO 14520 (determination of the flame extinguishing concentration of gaseous extinguishants by the cup burner method). For each experiment, a known concentration of organic compound in nitrogen was prepared in a tedlar bag and kept under pressure (11 psig). The fuel (n-heptane) and air (with a flow rate of 10 L/min.) were introduced into the burner. The fuel was then ignited and allowed to burn for a period of at least two minutes. The extinguishments process was then initiated by starting the flow of the binary agent (mixture of halogenated compound and nitrogen). The flow was increased in increments until flame was extinguished. The concentration of the agent (in air) at the time of extinction was recorded. Each experiment was repeated at least twice.

Results and Discussion

The results of cup burner experiments for the five halogenated compound / nitrogen mixtures are given in Figures 1 – 5. The extinguishing concentration of binary suppressants (concentration at extinction) was calculated from the following equation:

$$C = \frac{V_{agent} / V_{air}}{1 + V_{agent} / V_{air}}, \qquad (14)$$

where V_{agent} / V_{air} is the volume of binary suppressant per unit volume of air (or mole ratio) at extinction. For all the five binary suppressants, experimental data were collected at compositions of halogenated compounds less than 20 mole%. This is due to the limit on how much organic compound could be added to nitrogen (saturation concentration).The results clearly show that addition of small amounts of halogenated compound to inert gas reduces the extinguishing concentration drastically. As the concentration of chemical in inert gas increases, extinguishing concentration of binary agent decreases. However, the rate of reduction in the extinguishing concentration drops as the mole fraction of chemical in the binary mixture increases. This is in agreement with the previous studies[10, 17].

Extinguishing concentrations of mixtures of 1-bromo 2-(trifluoromethyl) 3,3,3 trifluoropropene, 4-bromo 3,3,4,4 tetrafluoro 1-butene and heptafluoropropyl 1,2,2,2 tetrafluoroethyl ether in nitrogen are very similar. A 5% mixture of these compounds in nitrogen has an extinguishing concentration of about 17 to 18 volume%. This corresponds to a 46 – 49% reduction in the extinguishing concentration of pure nitrogen. These three compounds have comparable extinguishing concentrations (2.6 to 3.7 volume %). Figure 4 shows that a binary mixture containing 5 mole% 1-brom 1-propane in nitrogen has an extinguishing concentration of about 20 volume %. This is a 40% reduction in the extinguishing concentration of nitrogen. Pure 1-methoxynonafluorobutane has the highest extinguishing concentration of all the compounds studied (6.1%). Figure 3 shows that a 5% mixture of this compound in nitrogen has an extinguishing concentration of about 28 volume %. This corresponds to a 17% reduction in the extinguishing concentration of nitrogen.

The theoretical method described in the previous section was used to predict the extinguishing concentration of each binary suppressant for the entire rage of mole fraction of halogentated compound. The input data required for calculations are temperature of uninhibited flame (T_F), extinction temperature (T_{EX}), extinguishing concentration of pure compounds, and one binary data. The flame and extinction temperatures used in all calculations were 2290 °K and 1600 °K respectively. The values of the extinguishing concentrations of pure suppressants are given in Table 2. The results of calculations are shown as solid lines in Figures 1 – 5. The agreement between the experimental data and the predicted values of extinguishing concentrations is good. A limited number of experimental data can therefore be used to predict the entire extinguishing concentration curve for a binary suppressant.

Synergism

It has been shown that when a fire suppressant that reacts with free radicals in the fire is mixed with an inert gas, synergistic interactions occur between the two compounds. The result is that the mixture is more effective than the sum of the individual inhibition effects. In order to determine whether a binary mixture shows synergistic effects, its inhibition effectiveness should be compared with that of the binary system if no interaction between the pure compounds occurs. Let n_1^0 and n_2^0 represent moles of pure agents 1 and 2 per mole of air needed for fire extinction respectively. If no synergistic effect occurs between the two compounds, then

$$\frac{n_1}{n_1^0} + \frac{n_2}{n_2^0} = 1, \qquad (15)$$

where n_1 and n_2 are moles of compounds 1 and 2 in the mixture (per mole of air) required to extinguish the fire. The mole fraction of compound 1 in the binary mixture, X, is given by:

$$X = \frac{n_1}{n}, \qquad (16)$$

where

$$n = n_1 + n_2. \qquad (17)$$

Combining equations (15) – (17), the following relation is obtained.

$$n = \frac{1}{\frac{X}{n_1^0} + \frac{1-X}{n_2^0}}. \qquad (18)$$

n_1^0, n_2^0, and n are related to extinguishing concentration of pure agents 1, 2 and the binary mixture respectively

$$n_1^0 = \frac{C_1^0}{100 - C_1^0} \tag{19}$$

$$n_2^0 = \frac{C_2^0}{100 - C_2^0} \tag{20}$$

$$n = \frac{C}{100 - C} \tag{21}$$

Substitution of equations (19) – (21) into equation (18) yields:

$$\frac{C}{(100 - C)} = \frac{1}{\frac{X(100 - C_1^0)}{C_1^0} + \frac{(1 - X)(100 - C_2^0)}{C_2^0}} . \tag{22}$$

Equation (22) provides a relationship for the extinguishing concentration of a binary mixture with no synergism, in terms of the extinguishing concentrations of pure agents and the composition of the mixture. The results of calculations for the five halogenated compound / nitrogen mixtures are given as broken lines in Figures 1 through 5. For every binary suppressant system, the actual extinguishing concentration curve is below the "no synergism" curve. This is an indication of synergistic effects between the two compounds in each binary system. The results clearly show that the degree of synergism is much higher at low concentrations of the halogenated compounds.

Conclusion

The fire extinguishing concentration of binary mixtures of halogenated compounds (two bromfluoro alkenes, two fluoro ethers, and one fluoro alkane) in nitrogen were determined using a cup burner. All the five binary suppressants show strong synergistic interactions at low concentrations of the halogenated compound. Addition of small amounts of these compounds in nitrogen reduces the extinguishing concentration of nitrogen considerably. These binary suppressants can therefore be used as effective total flooding agents.

The main problem with the inert gases is the need for storing a large volume of gases in cylinders. Addition of halogenated compounds reduces the storage volume dramatically. Another advantage of using the binary mixtures is the fact that because only a small amount of chemicals are used, the production of acidic by-products such as HBr and HF during suppression is small (compared to the use of a pure chemical agent). Cost could also be an important factor in selecting these binary suppressants. Many of the halogenated compounds are very expensive. Mixtures of these compounds in an inert gas provide affordable and effective suppressants.

Acknowledgment

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Nomenclature

ΔH_c = Heat of combustion

A = Constant in equation (16)
B = Constant in equation (16)
C = Extinguishing concentration of binary mixture, vol.%
C_C^0 = Extinguishing concentration of pure halogenated compound, vol.%
C_I^0 = Extinguishing concentration of pure inert gas, vol.%
C_{Pi} = Heat capacity of component i
F = Synergism factor, defined in equation (23)
n_C = Moles of halogenated compound per mole of air
n_I = Moles of inert gas per mole of air
n_C^0 = Moles of pure halogenated compound per mole of air at extinction
n_I^0 = Moles of pure inert gas per mole of air at extinction
n = Moles of binary agent per mole of air at extinction
T = Temperature
T_{EX} = Temperature at extinction
T_F = Temperature of uninhibited flame
T_{in} = Inlet temperature
V_{agent} = Volumetric flow rate of binary suppressant
V_{air} = Volumetric flow rate of air.

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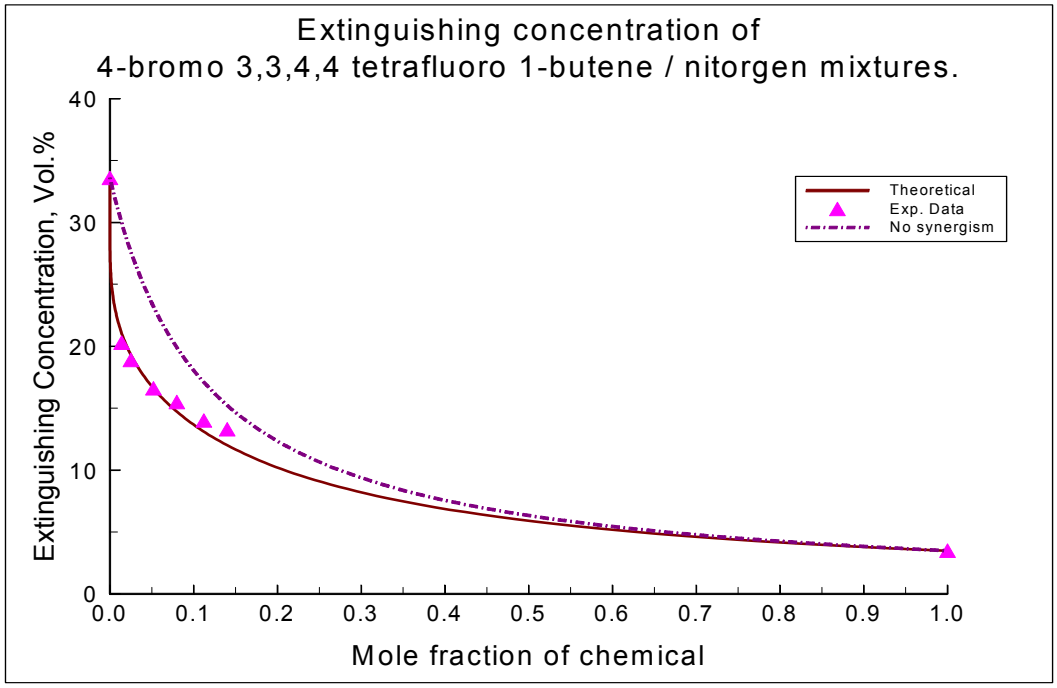
Table 1. Chemicals used

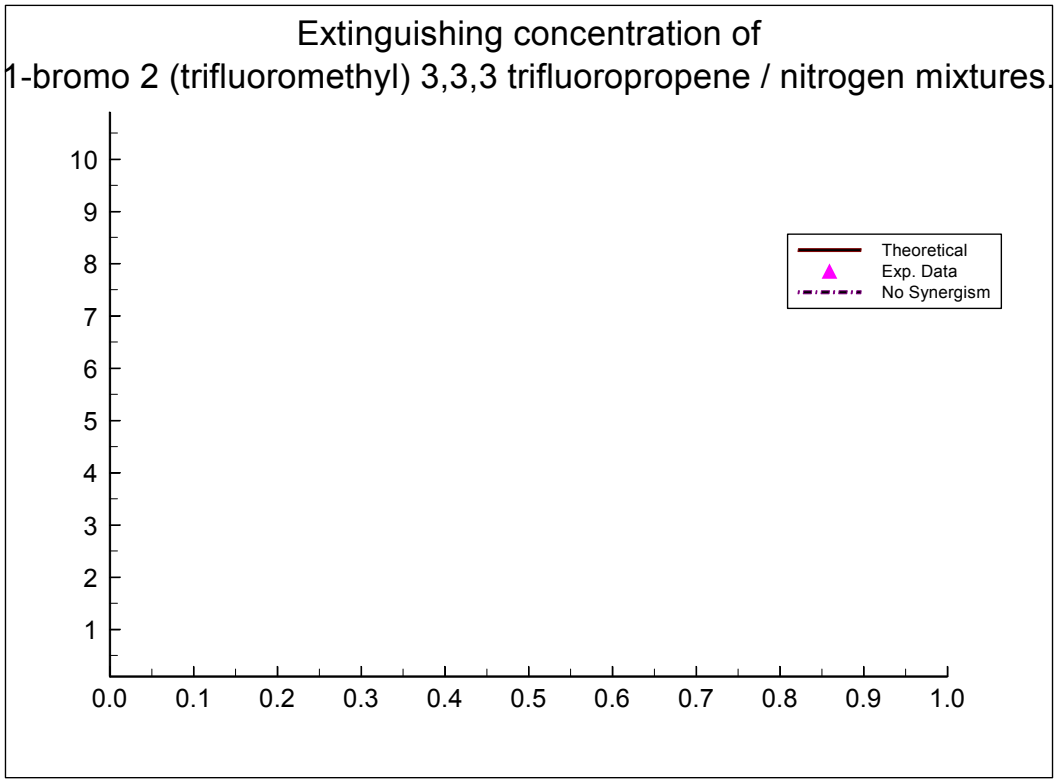
Compound	Purity	Source
1-bromo 2 (trifluoro methyl) 3,3,3 trifluoropropene $CHBr=C(CF_3)_2$	97%	Syn Quest Laboratories, (Alachua, FL)
4-bromo 3,3,4,4 tetrafluoro 1-butene $CH_2=CHCF_2CBrF_2$	99%	Interchim Company (France)
1-methoxy nonafluorobutane $CF_3CF_2CF_2OCH_3$	99.2%	Interchim Company (France)
1-bromo 1-propane $CH_3CH_2CH_2Br$	99%	Lancaster Synthesis Ltd. (Windham, NH)
Heptafluoropropyl 1,2,2,2 tetrafluoroethyl ether $CF_3CF_2CF_2COFCF_3$	97%	Syn Quest Laboratories (Alachua, FL)
N-heptane (HPLC grade)	99.9%	Fisher Scientific Inc. (Pittsburgh, PA)
Nitrogen	99.9%	Air Products (Columbus, GA)
Air	99.9%	Air Products (Columbus, GA)

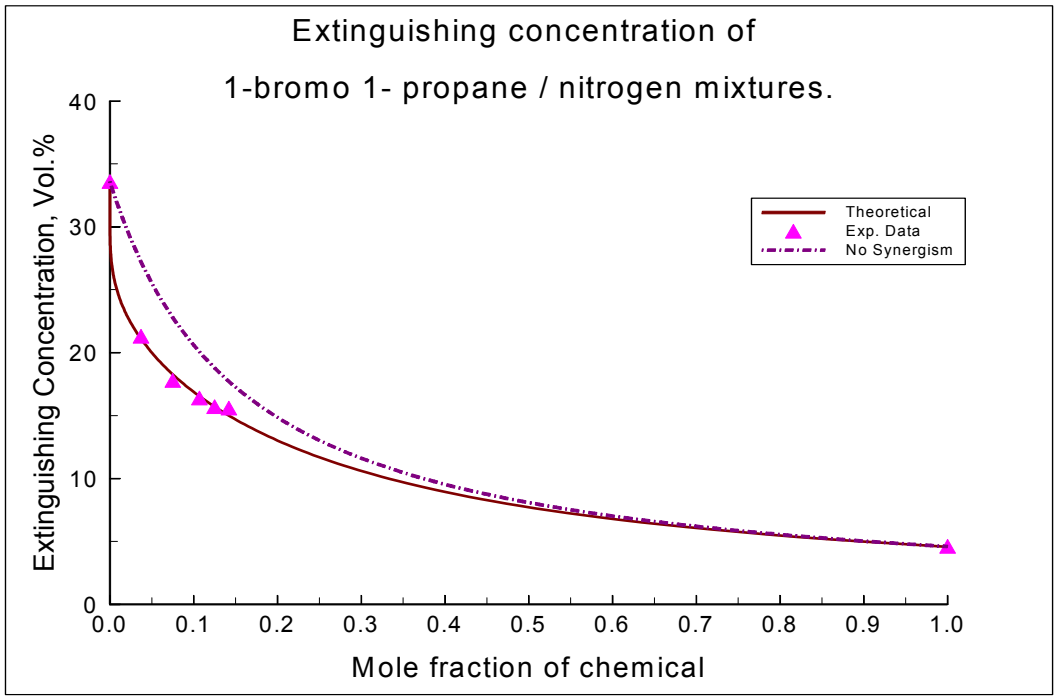
Table 2. Properties of fire suppressants

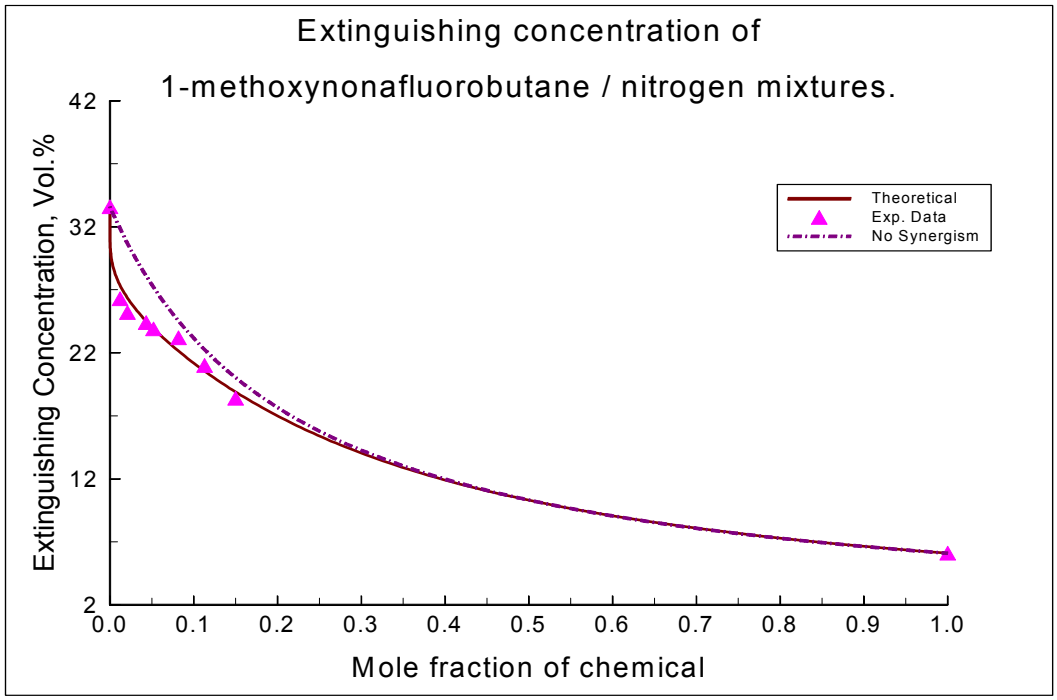
Compound	Boiling point °C	Density (1 atm, 25 °C) g/cm^3	Ext. Conc.* Vol.%
$CHBr=C(CF_3)_2$	63-64	1.749	2.6
$CH_2=CHCF_2CBrF_2$	55	1.622	3.5
$CF_3CF_2CF_2OCH_3$	60	1.500	6.1
$CH_3CH_2CH_2Br$	70-71	1.353	4.6
$CF_3CF_2CF_2COFCF_3$	40-42	1.538	3.7
N_2	-195.8	0.001	33.6

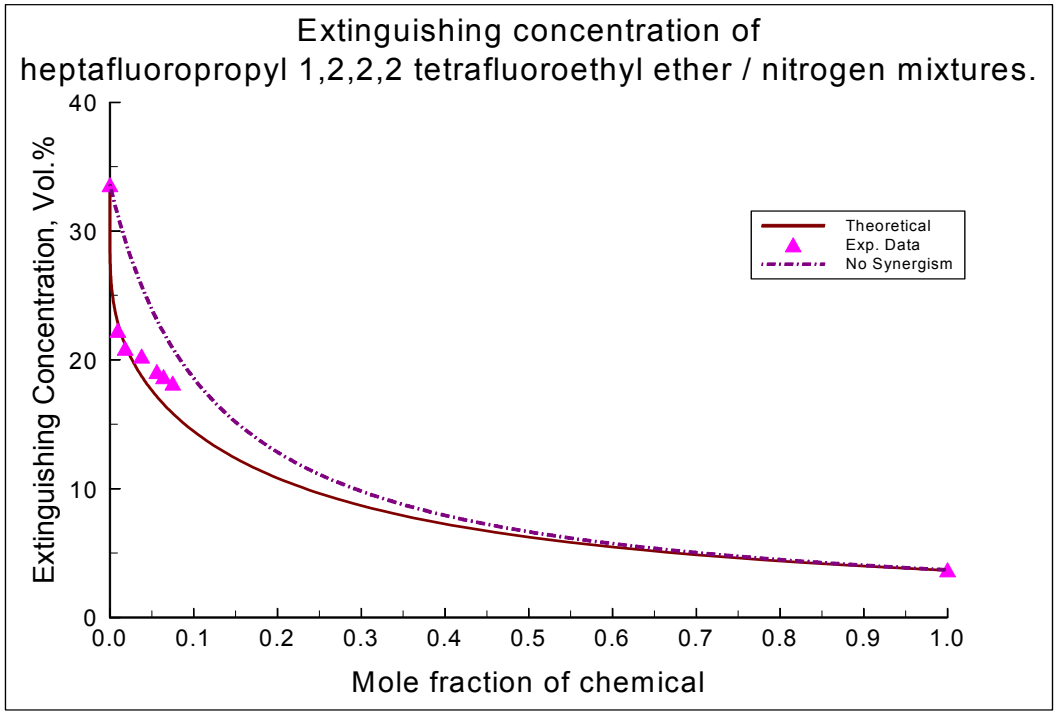
*Extinguishing Concentration


Extinguishing concentration of
4-bromo 3,3,4,4 tetrafluoro 1-butene / nitorgen mixtures.
Extinguishing Concentration, Vol.%
Mole fraction of chemical
Theoretical
Exp. Data
No synergism
0
10
20
30
40
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0


Extinguishing concentration of
1-bromo 2 (trifluoromethyl) 3,3,3 trifluoropropene / nitrogen mixtures.
Theoretical
Exp. Data
No Synergism
1
2
3
4
5
6
7
8
9
10
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0


Extinguishing concentration of
1-bromo 1- propane / nitrogen mixtures.
Extinguishing Concentration, Vol.%
Mole fraction of chemical
Theoretical
Exp. Data
No Synergism
0
10
20
30
40
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0


Extinguishing concentration of
1-methoxynonafluorobutane / nitrogen mixtures.
Extinguishing Concentration, Vol.%
Mole fraction of chemical
Theoretical
Exp. Data
No Synergism
2
12
22
32
42
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0


Extinguishing concentration of
heptafluoropropyl 1,2,2,2 tetrafluoroethyl ether / nitrogen mixtures.
Extinguishing Concentration, Vol.%
40
30
20
10
0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Mole fraction of chemical
Theoretical
Exp. Data
No Synergism