

EVALUATION OF HALON ALTERNATIVES

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INTRODUCTION

Due to their implication in the destruction of stratospheric ozone, the production and use of the presently employed Halon fire extinguishing agents are being severely restricted. As a result, intense research programs have been undertaken in both the industrial and academic sectors to find replacements for these life-saving agents. Once a possible Halon alternative has been conceptualized, an evaluation of its properties is required to determine the actual performance of the agent.

Foremost, one is interested in the fire suppression properties of the candidate. These fire suppression properties are related to the chemical and physical properties of the agent. For example, physical properties such as latent heats and heat capacities determine the ability of the agent to absorb heat, and the presence of certain functional groups such as halogens or trifluoromethyl groups imparts good fire suppression properties due to the interactions of these species with radical species present in the flame. However, good fire suppression properties are by no means the sole requirement for a suitable Halon replacement. For example, in streaming applications other physical properties, especially volatility, are important. The toxicological properties of any alternative agent must also be considered, since human exposure is inevitable, to both the neat and decomposed agent, especially in the case of total flood systems in normally occupied areas. Finally, the environmental impact of any new agent, for example its potential for ozone depletion or greenhouse warming, must also be considered.

FIRE SUPPRESSION PROPERTIES

The fire suppression properties of an agent include its inerting properties, its ability to prevent ignition of a flammable mixture, and its extinguishing properties, its ability to extinguish a diffusion flame. Inerting properties are evaluated by determining the concentration of agent required to render nonflammable all mixtures of air, agent and the fuel under

investigation and are typically carried out in an explosion buret or explosion sphere. The extinguishing properties of an agent may be readily evaluated on a laboratory scale by determining the concentration of the agent in air required to extinguish a diffusion flame, employing the cup burner method. The ultimate test of any agents fire extinguishing abilities is of course its performance on large scale fires.

The inerting properties of an agent are evaluated by determining the concentration of agent required to prevent ignition of an air/agent/fuel mixture. Numerous air/fuel/agent mixtures are examined for flammability, with the goal of ascertaining the minimum concentration of agent required to prevent ignition of all air/fuel mixtures. Apparatus employed for the evaluation of inerting properties include the explosion buret [1,2], which is essentially identical in concept to the Bureau of Mines apparatus [3] used for the determination of flammability limits, and the explosion sphere [4].

The explosion buret is simply a long glass tube equipped with an ignition source and means for the introduction of air, agent and fuel. Air, agent and fuel are introduced into the tube to provide the desired mixture, and the ignition source activated. Mixtures are deemed flammable or nonflammable based upon how far a flame propagates along the length of the tube. Some investigators consider a mixture flammable only if propagation is along the entire length of the tube, whereas others consider a mixture flammable if the flame travels some fraction of the tube length.

A number of mixtures are examined in the explosion buret, and each mixture designated as either flammable or nonflammable, and the results summarized in the form of a flammability curve. The flammability curve depicts the flammability characteristics of the system as a function of its composition. The area inside the flammability curve corresponds to flammable mixtures, and points outside the curve correspond to nonflammable mixtures. The most important piece of information to be derived from this figure is the location of the peak in the flammability curve. This point represents the minimum concentration of agent in the system which will render all combinations of fuel and air nonflammable. For example, approximately 8.5 % by volume FM-100 is required to prevent ignition of n-heptane/air mixtures, as seen in the flammability curve for the n-heptane/air/FM-100 system (Figure 1). In practice a safety factor would be added to this value to ensure inerting.

An alternative method for evaluating the inerting properties of an agent employs an explosion sphere [4], The apparatus is shown in Figure 2, and consists of a spherical metal vessel

equipped with an ignition source and means for the introduction of air, agent and fuel. Air, agent and fuel are introduced into the explosion sphere to produce the desired mixture, and the ignition source activated. In this case the pressure is monitored, and a mixture is deemed flammable if the pressure increase following activation of the ignition source exceeds one psig. As for the case of the explosion buret, the results are summarized in the form of a flammability curve. Results for the FM-100/air/propane and FM-100/air/i-butane systems are shown in Figures 3 and 4, respectively. In both cases inerting properties were examined in an explosion sphere employing an ignition energy of approximately 70 Joules. The solid circles correspond to flammable mixtures, whereas nonflammable mixtures are represented by the open circles. Under these particular conditions, the flammability peak is seen to occur at 12 % by volume FM-100 for the FM-100/air/propane system and at approximately 11 % by volume FM-100 for the FM-100/air/i-butane system (Figures 3 and 4).

Inerting requirements as determined by various methods, including both explosion burets and spheres, have been found to vary with the fuel type, temperature, container volume and geometry, ignition energy, and, unfortunately, with the criteria of flammability established by the individual investigator. As a result, it is difficult, if not impossible, to judge which method, under what particular set of conditions, provides the most accurate evaluation of an agent's inerting properties. As a result, extreme caution must be used in attempting to extend these small scale results to full scale systems.

The more commonly encountered use of Halons is the extinguishment of diffusion flames, and the standard apparatus employed for the evaluation of extinguishing properties is the cup burner [1,5]. The cup burner is shown schematically in Figure 5, and consists of a Pyrex chimney, a metal or glass burner located inside the chimney, and inlets for fuel and air/agent mixtures. In the case of liquid fuels, the cup is filled with the fuel under investigation, and a leveling device employed to maintain the liquid level at the top of the cup. For gaseous fuels, the cup is replaced by a straight-bore tube of reduced diameter. A bed of glass beads is employed in the apparatus to ensure thorough mixing of the gas streams. The cup is filled with the fuel under investigation, the desired air flow is established, and the fuel ignited. After a suitable preburn period, the amount of agent in the air/agent stream is slowly increased until the flame just goes out. From the known flows of the air and agent, the extinguishing concentration of the agent may be calculated.

A number of factors affect the determination of extinguishing concentrations. In order to obtain reproducible results, it is important that laminar flow of the air feeding the flame be maintained, and precautions should be taken to prevent any disturbance of this flow [5]. Extinguishing concentrations are affected by the agent, the fuel, and the temperature of the agent and fuel, as well as by the rate of fuel and air supply. For tests involving liquid fuels, it has become standard procedure to adjust air flows so that the linear velocity of air past the cup is approximately 13 cm/s. For gaseous fuels, the linear velocity of the fuel is customarily matched to that of the air plus agent. By paying close attention to these and other factors, it is possible to obtain highly reproducible results in burners of various sizes, including scaled-down cup burners, which allow for the rapid determination of extinguishing concentrations and require a minimum of sample.

The extinguishing concentration required depends upon the fuel, and typical results are shown in Table 1 for FM-100. In general, flames of oxygenated fuels such as methanol, and unsaturated fuels require higher concentrations of agent for extinguishment than do simple alkanes such as n-butane or n-heptane. For an individual agent, the extinguishing concentration depends upon the fuel type, but the relative effectiveness of a series of agents is independent of the fuel, at least for the fuels and agents we have examined.

Fuel	Extinguishing Concentration, Volume %
n-heptane	3.9
n-butane	2.9
methanol	7.4
toluene	2.8
acetone	3.6
cyclohexane	4.0

Results for the extinguishment of n-butane diffusion flames with various agents are shown in Table 2. As expected, it is seen that those agents containing bromine are more effective than those containing only chlorine or fluorine. Table 2 shows the extinguishing concentrations on both a volume and weight percent basis, and it is worth noting that on a weight basis, FM-100 is observed to be more effective than Halon 1211 for the extinguishment of n-butane diffusion flames. This relative effectiveness has also been observed in the extinguishment of n-heptane diffusion flames in the laboratory cup burner, and also in large scale testing of Halon 1211 and FM-100 with various fuels.

TABLE 2: Extinguishment of n-Butane Diffusion Flames

Agent	Extinguishing Concentration, Volume %	Extinguishing Concentration, mg/L
FM-100	2.9	155
CF3Br	2.4	146
CF2BrCl	2.5	168
c-C4F8	5.0	408
CF3CF2Cl	5.6	352
CF3CF3	6.6	389
CF3Cl	7.1	301
CF3CF2H	8.0	392
CF2HCl	10.8	379

5.0 cm chimney; air velocity = 13.3 cm/s

Although the cup burner method is extremely useful for the evaluation of extinguishing properties, results have been reported in the open literature for relatively few compounds, and Table 3 summarizes the available information for extinguishment of n-heptane diffusion flames. Extinguishing concentrations have been determined for several noble gases [6], carbon dioxide [7], several hexavalent sulfur compounds [6] and a limited number of C1 through C4 compounds [5,7,8,9]. As was the case for n-butane

TABLE 3:

EXTINGUISHMENT OF n-HEPTANE
DIFFUSION FLAMES

Agent	Ext. Conc. Vol %	Ref.
Ar	41	1
Ne	37	1
He	32	2
N2	30	2
cO2	21	2
SF5Cl	13	1
SF6	11	1
S2F10	10.5	1
H2O (mist)	5.0	2
SF5Br	4.2	1
CF2Br2	2.4	2
CF3I	3.2	GLCC
CF3Br	3.5	3
CF2BrCl	3.8	3
CF2HBr	3.9	GLCC
CH2BrCl	4.5	3
CH3Br	5.1	2
CFC13	7.0	3
CF3Cl	7.8	2
CF2HCl	11.8	GLCC
CF3H	12.7	GLCC
CF4	14.2	GLCC
BrCF2CF2Br	2.1	3
CF3CHFBr	3.6	5
CF3CHCl2	6	4
CF3CHFCl	7.2	GLCC
CF3CF2Cl	7.4	2
CF3CF3	8.3	GLCC
CF3CF2H	9.3	GLCC
CF3CH2F	10	4
HCF2CF2H	11.5	GLCC
CF3CF2CF3	6.2	GLCC
CF3CH2CF3	7.0	GLCC
CF3CHF2	8.5	GLCC
c-C4F8	6.5	GLCC

1) Sheinson 2) Fire and Materials , 8, 148 (1984)

3) Hirst & Booth 4) NMERI

5) ICI

diffusion flames, it is observed that on a weight basis FM-100 is superior to Halon 1211 for the extinguishment of n-heptane flames. Again, those compounds containing bromine are observed to be more efficient extinguishing agents than those containing only chlorine or fluorine. The presence of a CF₃ group also enhances the fire extinguishing ability of an agent, as can be seen by comparing the tetrafluoroethanes, where the 134a isomer is observed to be a superior agent compared to the symmetrical 134 isomer.

The extinguishing efficiency of an agent can be estimated from its chemical structure. In the early 1950's, Malcolm [10] defined an atomic resistivity for the individual halogens and used these values to correlate chemical structure with inerting ability as determined in the explosion buret. In the late 1970's, Hirst and Booth [5] examined the extinguishing properties of a limited number of halogenated agents, and showed that the structure of the agent and its extinguishing ability were related by the expression

$$\log(\text{Conc}) = a \log(X) + b$$

where Conc is the extinguishing concentration in volume percent, X is the sum of the atomic resistivities, and the atomic resistivities of F, Cl and Br are 1, 2, and 10, respectively. Hence the extinguishing ability of an agent is related to its halogen content expressed as the sum of Malcolm's atomic resistivities, and a plot of the log of the extinguishing concentration versus the log of X is a straight line.

Figure 6 summarizes the results of the extinguishment of n-heptane diffusion flames. Except for CF₄, which is very thermally stable, all the points lie close to the line, demonstrating the constant relation between the extinguishing concentration and the halogen content, expressed as the sum of Malcolm's atomic resistivities. This is observed for a number of compound classes, including perfluorocarbons such as octafluoropropane, hexafluoroethane and octafluorocyclobutane, hydrofluorocarbons such as Freons 23, 134 and 134a, hydrochlorofluorocarbons such as Freon 22 and 124, chlorofluorocarbons such as Freon 13 and 115, and also for bromine-containing compounds such as Halons 1301 and 1211, and FM-100.

Similar results are observed for other fuels, for example n-butane, as shown in Figure 7. An important item to keep in mind is the fact that cup burner tests are concerned entirely with the vapor phase performance of the agent being tested.

Hence, while cup burner test results correlate well with the agents' performance in flooding systems, they do not necessarily correlate with the agents' performance in streaming applications, where other physical properties are also important, particularly the volatility of the agent. The ultimate test of any agents extinguishing ability, whether in total flooding or streaming applications, is its performance on large scale fires such as those encountered in real-life situations. Large scale tests include the various pit and pan fires for flammable liquids, and wood-crib and wood-panel tests for Class A materials. These test methods have been described in the literature, and detailed descriptions of large scale tests with Class A and Class B materials can be found for instance in UL Standard 711 [11].

AGENT DECOMPOSITION

In addition to its fire suppression properties, another important property of any alternative agent is the extent of decomposition occurring upon extinguishment. The production of high levels of toxic decomposition products during extinguishment, such as the halogen acids, could prevent the practical use of an otherwise attractive agent, as it could result in a health hazard to personnel, as well as damage to the assets being protected. Determination of decomposition products is typically carried out in an apparatus such as that shown in Figure 8. This consists of an enclosure fitted with a discharge nozzle for agent introduction, a fire pan containing the fuel, various thermocouple probes to allow for monitoring of, for example, fuel and flame temperatures, and suitable probes for extracting samples. In a typical experiment the fuel is ignited, and after a specified preburn period the agent is delivered at a given discharge rate in amounts sufficient to extinguish the fire. Samples are then taken at different locations at different time intervals following extinguishment, and are then analyzed for the halogen acids.

Typical results are shown in Table 4, comparing FM-100 and Halon 1301 for the extinguishment of n-heptane fires at agent concentrations of 4 % by volume. In this particular test, the discharge time was 10 seconds, and the fire size was 0.077 square feet of fuel surface area per 1000 cubic feet of enclosure volume. HF was monitored at two locations, and HBr at a single location, and Table 4 indicates the peak levels observed. The observed levels of HF were similar for the two agents, whereas much less HBr was produced in the case of extinguishment by FM-100. The high effectiveness of agents such as Halon 1301 and FM-100 leads to very low levels of decomposition products formed

upon extinguishment. For the case of less effective agents, the extent of decomposition can lead to the production of dangerous levels of toxic decomposition products.

Agent	HF (ppm)		HBr (ppm)
	Top	Bottom	
H-1301	12.7	0.2	25.6
FM-100	9.5	4.3	< 4

PHYSICAL AND THERMODYNAMIC PROPERTIES

Physical properties of importance for any Halon alternative include those shown in Figure 9. As pointed out previously, in streaming applications the physical properties of the agent, especially its volatility, can be as important as its extinguishing properties in determining its actual performance. For the determination of system design pressures and burst disc ratings for extinguishment systems, knowledge of the vapor pressure of the agent is required. Determination of fill ratios and flooding factors requires knowledge of the liquid and vapor densities as a function of temperature. Latent heats and heat capacities determine the agent's ability to absorb heat, and for flow modeling, the general thermodynamic properties of the agent are required.

Thermodynamic properties are generated by representing the experimental data algebraically with an equation of state, from which the thermodynamic properties are derived by the exact relations of thermodynamics. Required experimental data includes vapor pressures, saturated liquid and vapor densities, critical properties, PVT behavior and ideal gas heat capacities. Vapor pressures, liquid and vapor densities and PVT behavior may be determined in a constant or variable volume cell [12] and the ideal gas heat capacity is typically derived from infrared and Raman absorption measurements. The experimental data is typically smoothed by fitting to the appropriate equations, and the equation of state is then fitted to the smoothed experimental data. The Carnahan-Starling-DeSantis (CSD) equation of state for

example, has been shown to represent well the properties of small, nearly spherical molecules, examples of which include the commonly employed refrigerants and the Halon fire extinguishing agents [13]. The CSD equation of state is convenient as it can represent a fluid with a minimum of data, consisting of vapor pressures, saturated liquid and vapor densities, critical properties and ideal gas heat capacities. The standard or modified Benedict-Webb-Rubin (BWR) equation of state is also applicable, and can produce more accurate results, but at the expense of much greater complexity in fitting the equation of state to the experimental data. For example, the CSD equation of state involves 9 adjustable parameters, whereas the modified BWR equation of state has 32 adjustable variables for fitting the equation of state to the experimental data.

The thermodynamic properties of interest to the Halon systems designer are best summarized in the standard thermodynamic table familiar to those in the refrigeration industry. These tables list, as a function of temperature, vapor pressures, liquid and vapor densities, heats of evaporation (latent heats), liquid and vapor enthalpies, and liquid and vapor entropies. Various computer programs are available or may be designed to allow tabulation of superheated vapor properties, including densities, enthalpies and entropies, as well as liquid and vapor phase heat capacities, at both constant volume and constant pressure.

MATERIALS COMPATIBILITY

Determining the compatibility of an agent with the materials of construction of extinguishing systems is also an important part of any Halon alternative program. New agents which can serve as complete drop-in replacements, or those requiring only minor changes to existing systems would naturally be preferred over agents whose use would require extensive redesign of existing systems. Some of the materials found in typical Halon systems are listed in Figure 10, and these include stainless steels, carbon steels, aluminum and brass. Commonly encountered plastics include Viton, Buna N and neoprene as examples. Tests of the compatibility of a new agent with these materials and others is required to ascertain whether or not the agent may be employed in existing systems, and if not, what changes to the existing system must be made.

Corrosion testing of metals is preferably performed for both the dry agent and the agent in the presence of small amounts of water, since there is always the possibility that water may be inadvertently introduced into a system. These tests are typically performed by immersing the metal sample in the agent of interest for a certain time period at an elevated temperature,

and determining the corrosion rate from the weight loss of the test coupons. ASTM standards [14] are available which describe the various corrosion test procedures, and the tests may be performed in sealed glass ampoules, or for accelerated testing at elevated pressures, autoclaves may be employed. Elastomeric materials are evaluated for both weight gain and swelling following exposure to the agent, and ASTM methods are again available for such evaluations [15]. As is the case for metals, tests are typically performed at elevated temperatures by immersing the sample in the agent contained in a sealed glass tube, or for higher pressures, in an autoclave.

TOXICOLOGICAL PROPERTIES

Human exposure to any extinguishing agent is inevitable, and hence the toxicological properties of any replacement agent are important. The list in Figure 11 is not meant to be a list of required toxicity tests for extinguishing agents, but is simply a list of toxicity tests, in general order of testing, which might be required for any chemical for which human exposure might be expected. In the case of extinguishing agents, the most important screens are those corresponding to single, high dose exposures, for example the LC50 acute inhalation test and the acute dermal and oral tests. The average persons exposure to any extinguishing agent is likely to be a one-time brief exposure during a life-threatening fire event, during which any number of toxic combustion products from the fire itself may be present in high concentration.

CONCLUSION

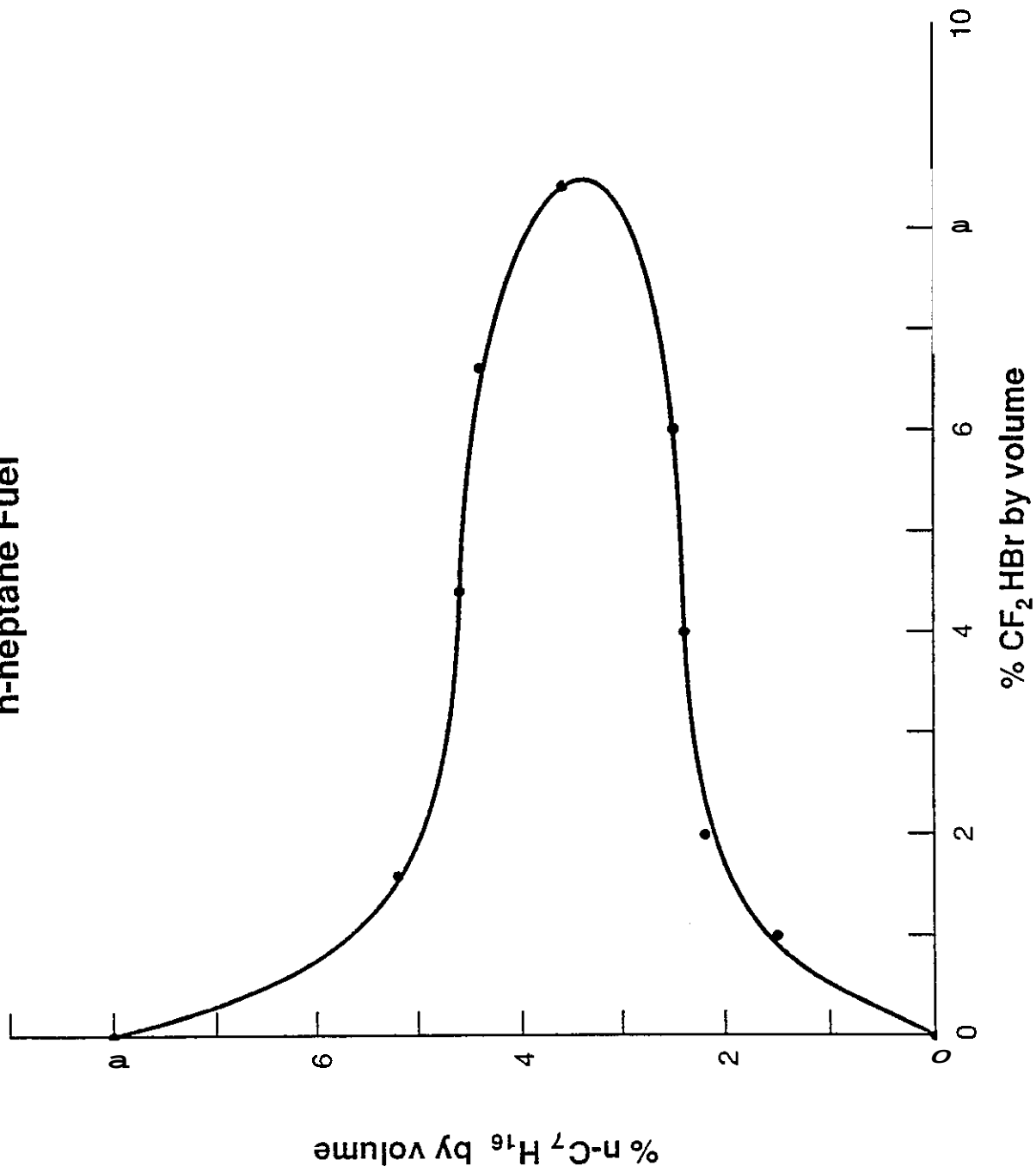
In closing, it is seen that the evaluation of any Halon alternative involves much more than a simple evaluation of its ability to extinguish an n-heptane flame in a cup burner. Physical properties, toxicological properties, material compatibility and environmental acceptability are also important to the potential user or manufacturer. In addition to those evaluations discussed above, and of utmost importance to any potential manufacturer, an evaluation of the cost of manufacturing any replacement agent must also be made. The challenge we are faced with is to devise a replacement agent that is highly efficient, clean, nontoxic, environmentally acceptable, and that can be manufactured at a reasonable cost, and this by no means a small challenge.

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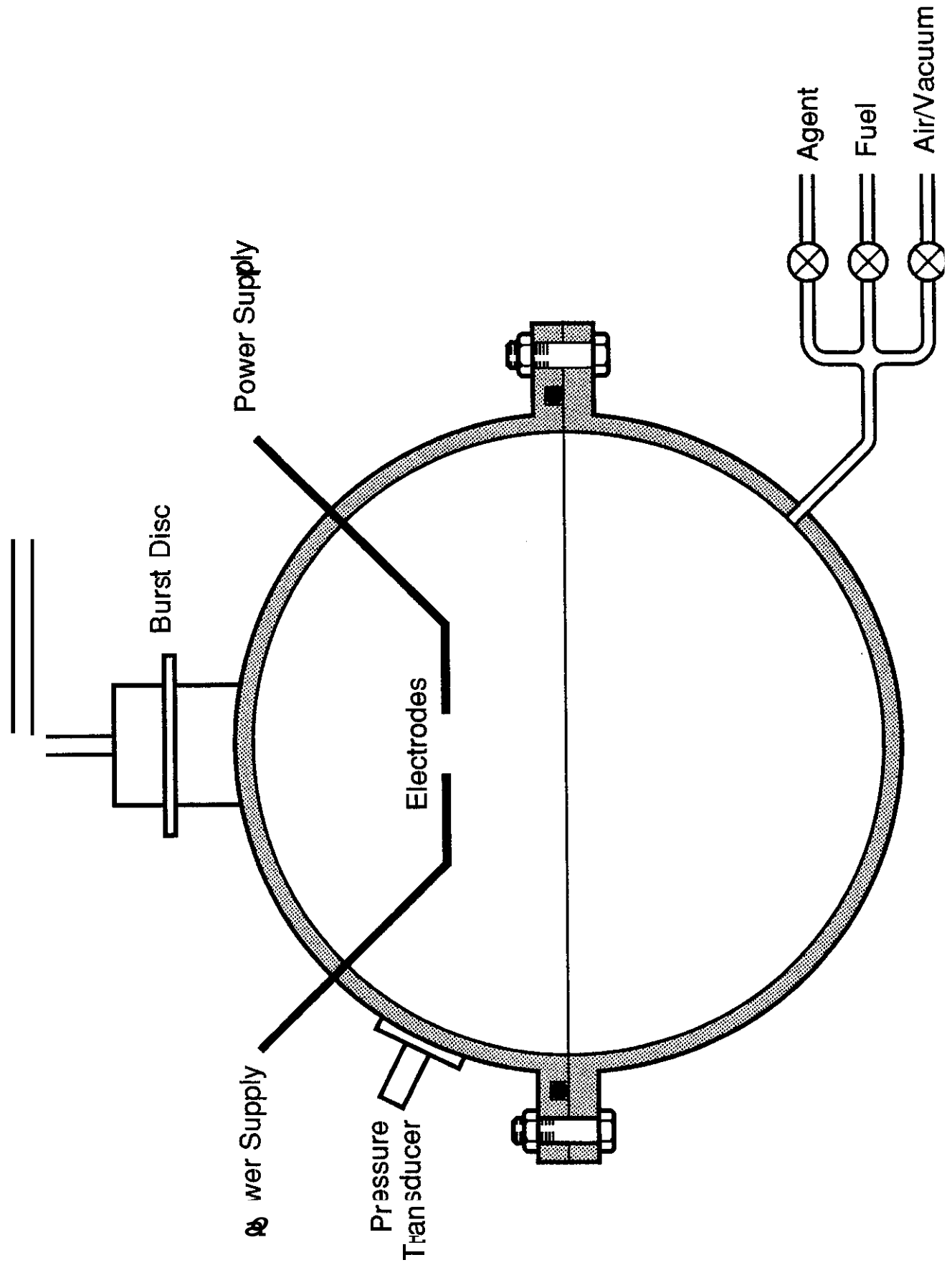
FIGURE 1:

**FM-100: Flammability Curve
n-heptane Fuel**



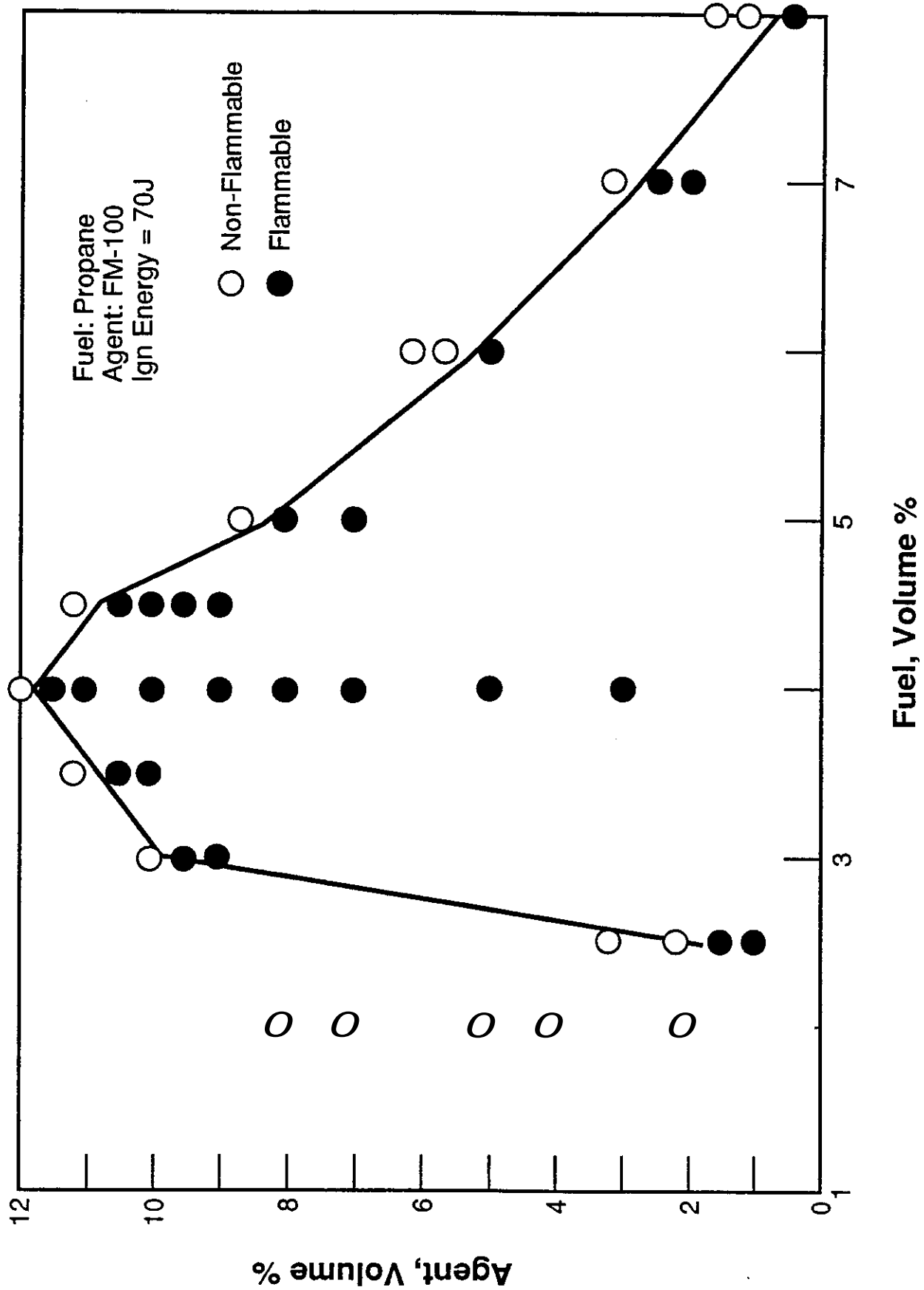
Fenwal Explosion Sphere

FIGURE 2:



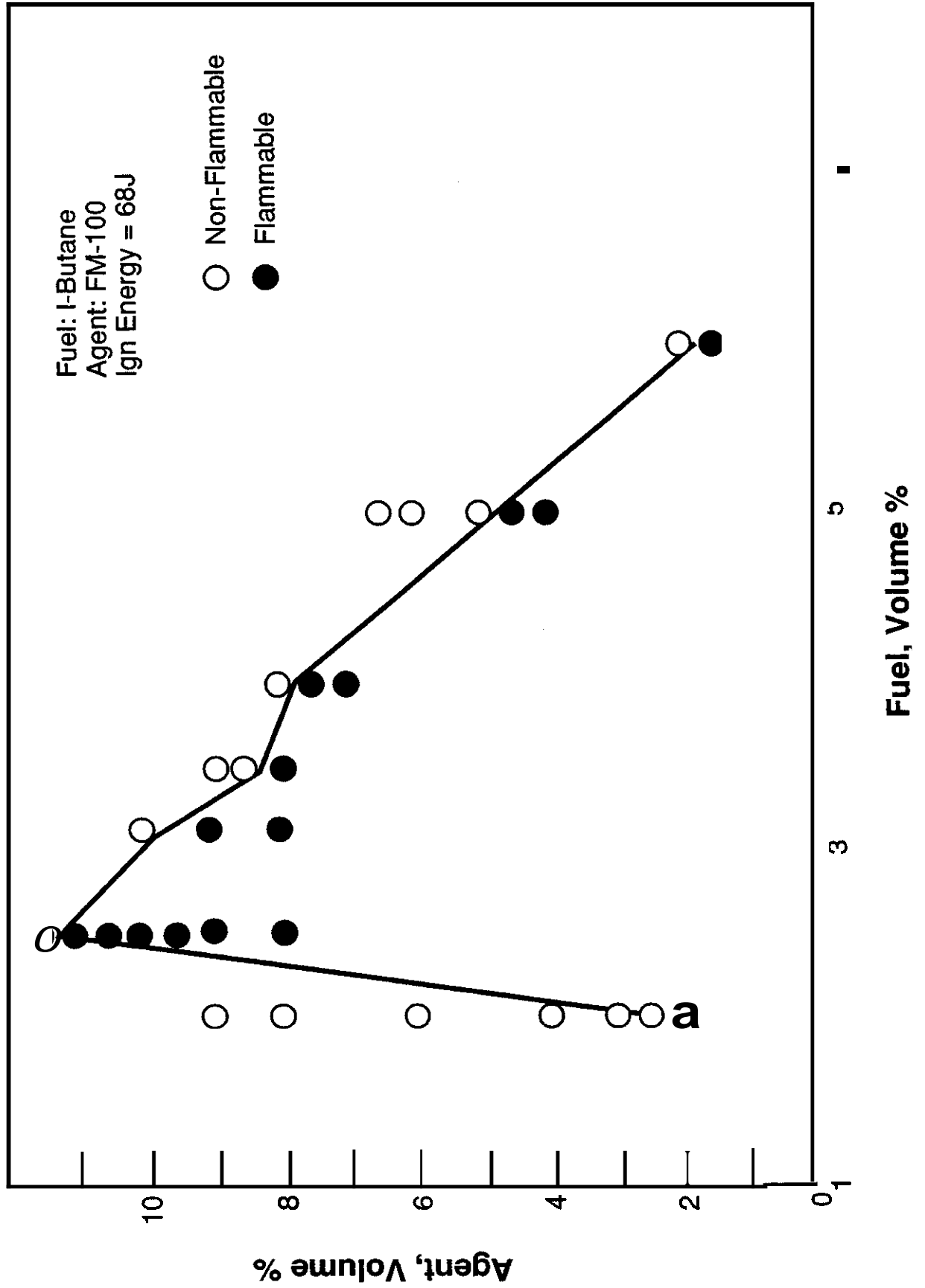
Halon Alternative Evaluation Flammability Diagram

FIGURE 3:



Halon Alternative Evaluation Flammability Diagram

FIGURE 4:



Cup Burner

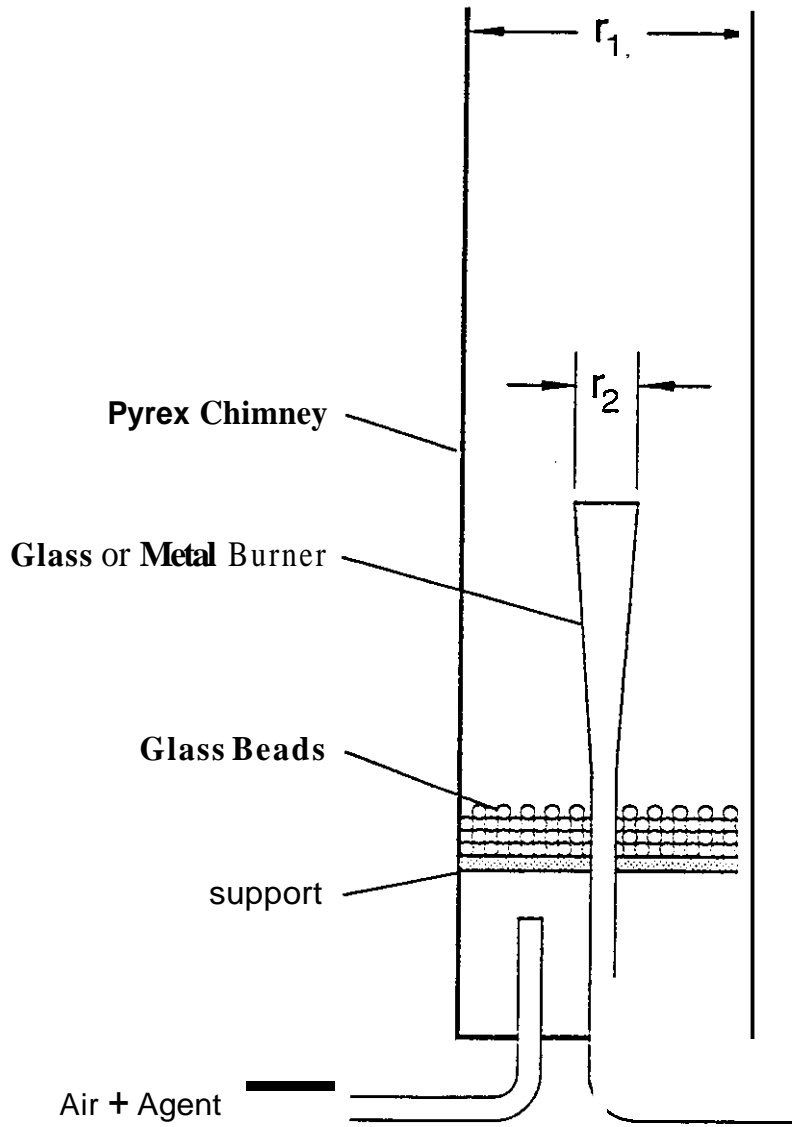


FIGURE 5.

Extinguishing Concentration vs. Halogen Content n-heptane Fuel

FIGURE 6:

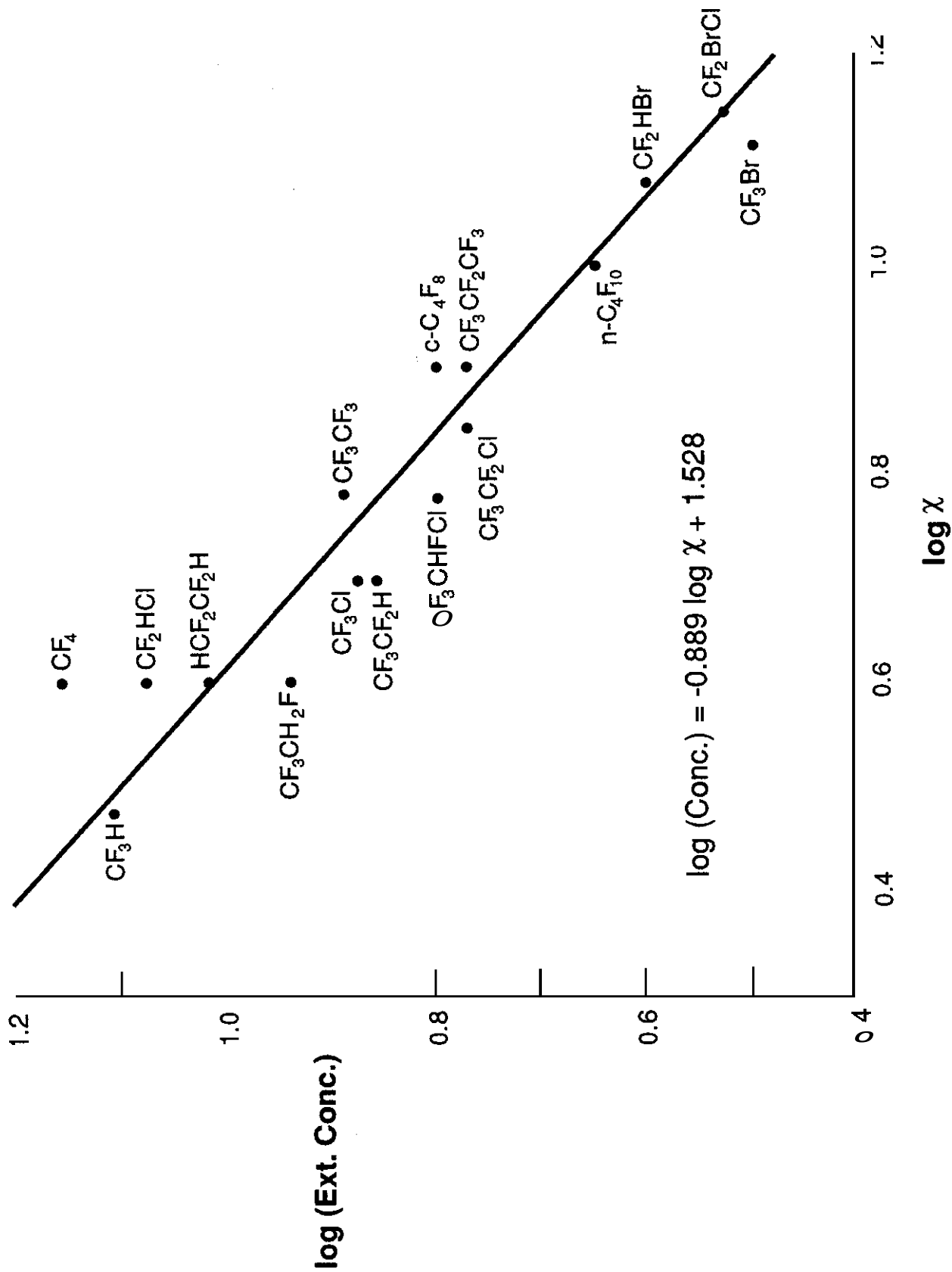


FIGURE 7: Extinguishing Concentration vs. Halogen Content
n-butane Fuel

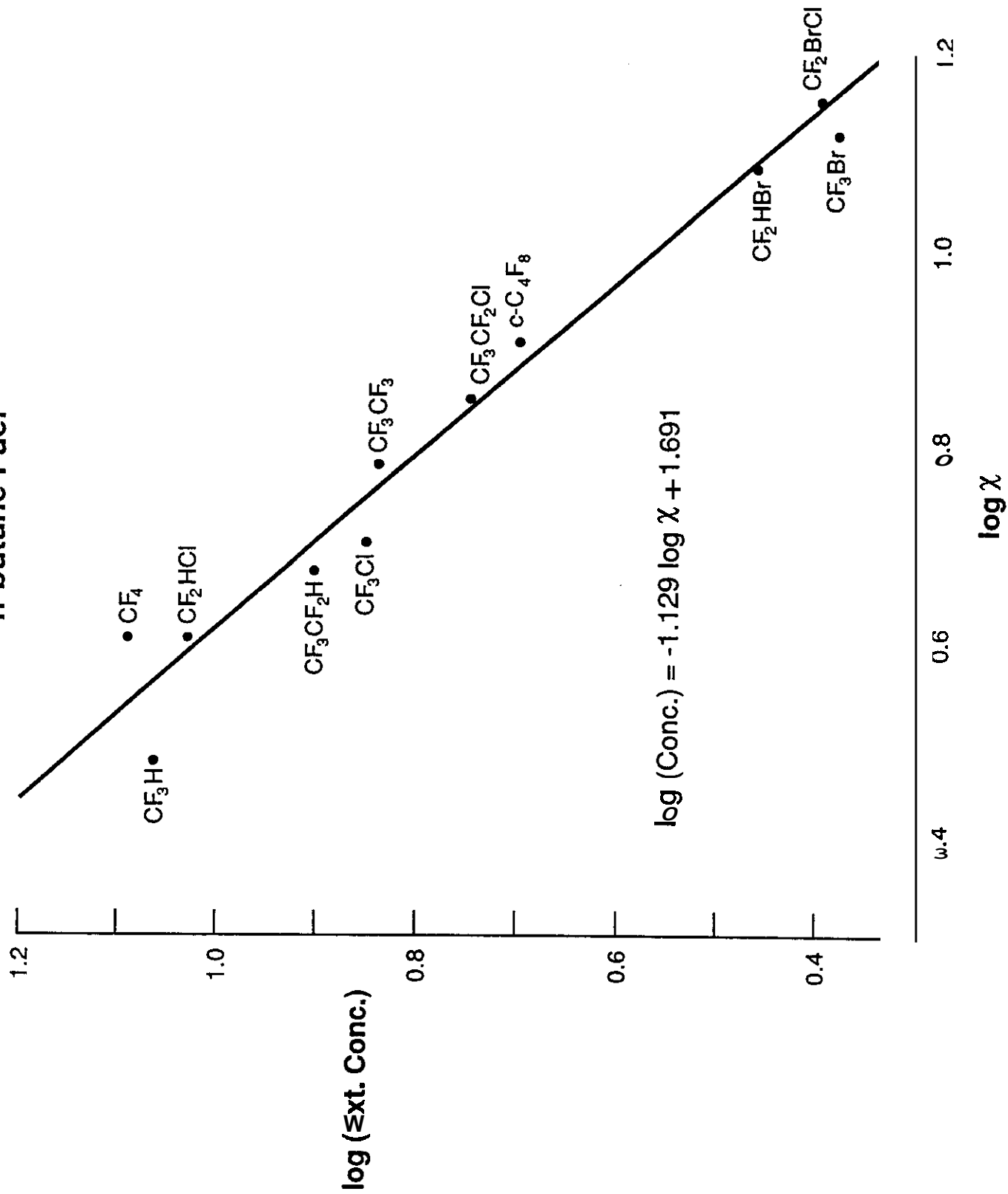
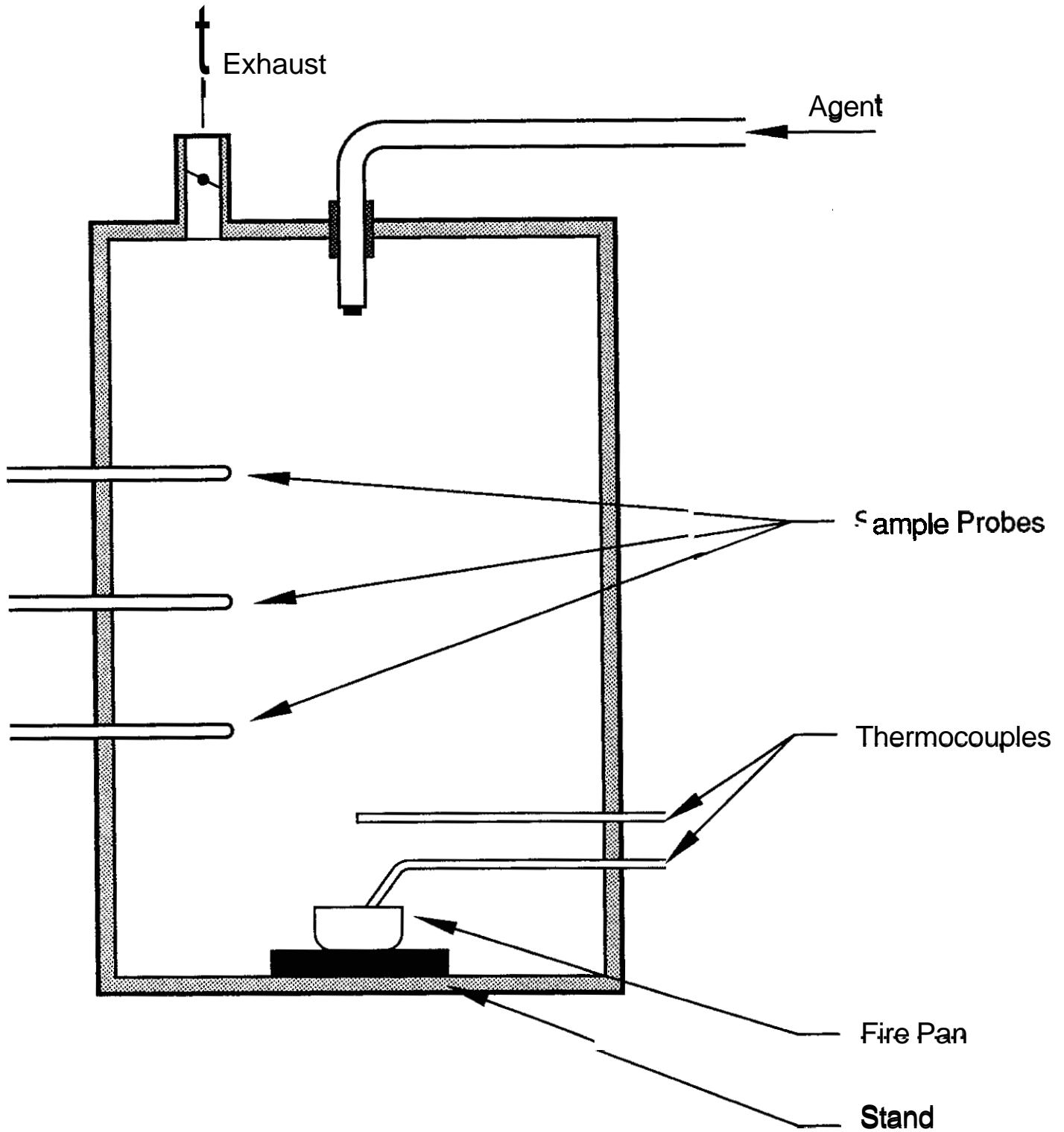


FIGURE 8:

Schematic of Apparatus for Determination of Decomposition Products



PHYSICAL PROPERTIES

Vapor pressure
Liquid density
Vapor density
Latent heat
Heat capacity
Enthalpy
Entropy
Conductivity
Nitrogen solubility

SYSTEM DESIGN

Design pressure
Fill ratio/fill density
Flooding factor
Flow modelling

FIGURE 9.

MATERIALS COMPATIBILITY

METALS

Stainless steel

SS302

SS304

SS316

SS321

Carbon steel

ASTM A-106-A

ASTM A-106-B

Brass

Aluminum

Copper

ELASTOMERS

Viton

Buna N

PTFE packing

Carboxylic nitrile butylamine

EDPM

Neoprene

FIGURE 10.

TOXICOLOGICAL PROPERTIES

Acute inhalation toxicity
Acute dermal toxicity
Acute oral toxicity
Primary eye irritation
Primary dermal irritation
Dermal sensitization
Acute delayed neurotoxicity
28-day oral
90-day oral
90-day dermal toxicity
90-day neurotoxicity
Chronic toxicity
Teratogenicity
Oncogenicity
Gene mutation (Ames Test)

FIGURE 11