CUP-BURNER EXTINGUISHING CONCENTRATION CORRELATION WITH C_1 - C_8 CLASS B FUEL PROPERTIES

Joseph **A.** Senecal
Kidde-Fenwal, Inc.
Ashland, MA 01721 **USA**

ABSTRACT

The design of clean agent fire suppression systems requires minimum extinguishing concentration data as a basis for determining the minimum design concentration of the agent. Extinguishing concentrations determined by the cup-burner method are employed in **NFPA** 2001 and ISO 14520. In the absence of test data what is a designer to do? This paper reports on an examination of the relationship of cup-burner extinguishing concentration data to certain fuel properties, namely, autoignition temperature, oxygen content and hydrogen to carbon ratio. Data were evaluated for a number of aliphatic, aromatic and oxygenate fuels, and two HFC agents. The results indicated that a useful correlation exists between extinguishing concentration and H/C ratio. In the absence of test data this correlation could be **used** as the basis of system design. There was little correlation of extinguishing concentration with fuel AIT or oxygen content. The C_1 compounds (methane and methyl alcohol) have exceptional behaviors for which unproved hypotheses are offered.

INTRODUCTION

The development of standards for clean agent fire extinguishing systems suitable for use in occupied spaces has progressed steadily since the first issuance of **NFPA** 2001 in 1994. The second edition of that standard was issued only two years later [1] and the third edition [2], to be issued in 1999 *is,* at this writing, in an advanced stage of review and preparation by the 2001 committee. Other standards around the world have, to a great extent, used **NFPA** 2001 as a model. Important clean agent standards in development include Draft ISO 14520 **[3]** "Gaseous fire extinguishing systems - Physical properties and system design," in 15 parts; Draft CEA standard "Specifications for ***Halocarbon*** gas fire extinguishing systems, planning and installation"; and Draft LPCB (UK) standard "Requirements for LPCB System Approval Fire Testing of Fixed Gaseous Fire Extinguishing Systems." In Germany the VdS (Verband der Schadenversicherer e.v.) is taking the lead in promulgating a clean agent standard, and their work will likely be influential in the final form of the CEA document. In like manner, Underwriters Laboratories has advanced two revisions of the UL-1058 testing standard to be named UL-2166 for halocarbons and UL-2127 for inert gas systems.

A common and essential issue in these standards is the matter of fire extinguishing efficacy of gaseous agents. The approaches being taken by the standards authorities are quite different. Large-scale test data are generally required for system approval. Minimum safety factors range widely, from 20 to 70%, or more.

The user community, including both the end user and the manufacturers of gaseous extinguishing systems, want to keep costs to a minimum while maintaining a high level of fire protection. Further, other considerations having to do with space and weight of cylinders, installation issues and environmental stewardship have led to a high level of sensitivity relative to specifying

excessive quantities of either chemical or inert gas agents. **As** such, the technical community continues to investigate agent extinguishing issues to develop a higher level of confidence when specifying suppression systems for hazards and fuel types not specifically evaluated as part of an accepted large- scale test protocol.

The cup-burner method has been successfully used to develop minimum extinguishing concentration (MEC) values of agents for liquid and gaseous fuels. MEC values determined by the cup-burner method have been shown to be effective in extinguishing large-scale Class B fires where special re-ignition hazards are not present. **As** an example, the IMO protocol for acceptance of marine gaseous extinguishing systems calls for tests in a 500 m^3 chamber with fires of several megawatts intensity. Such fires have been extinguished using agents at the reported cup-burner MEC. It is not practical, however, to conduct large-scale fire extinguishing tests for every unknown fuel. Further, while the cup-burner method is approaching a high degree of standardization, the number of fuels evaluated is relatively limited. Again, it would he impractical to test every flammable liquid or gas and, further, mixtures of all sorts abound. The goal of this paper is to examine available cup-burner MEC data on two extinguishing agents with respect to some basic fuel properties to see if there is a basis of estimating MEC values in a simple yet reliable way that can serve as a basis of system design.

CUP-BURNER APPARATUS AND PROCEDURE

The cup-burner apparatus consists of two basic elements: (I) the "cup" which is a fuel reservoir, and (2) a vertical chimney in which the cup is placed and permits a stream of air, or more importantly, a mixture of air and agent, to flow in a streamline manner upward past the cup (Figure 1). The cup burner, in its current form, was first described by Hirst and Booth in 1977 [4], and their design became referred to as the "ICI" cup burner and later as the "full-scale" cup burner. The use of this test system was largely dormant until the late 1980s when chemicals began to be studied as alternatives to Halon 1301 as clean gaseous total-flooding agents. A number of authors have since reported on the various aspects of the design and use of the cup burner. Moore et al. [5] developed and used reduced scale variants (5/8-scale and smaller) of the full-scale design which were found useful in conducting screening tests on agents that were available in only small quantities. Saso et al. [6] reported on the sensitivity of measured extinguishing concentration to variations in design and operating parameters. Growing worldwide interest and attention to details in the selection, evaluation, and use of gaseous extinguishing agents have led to adoption of the full-scale design as the standard apparatus.

Additionally, the procedures used in carrying out extinguishing concentration measurements have been specified in great detail and have been adopted as standards in ISO 14520 and in NFPA 2001 [2]. The basic procedure for liquid fuels is as follows: Admit fuel to cup such that the meniscus is just below the top edge of the cup. Establish flow of air in the chimney (40 liters/min is typical but can be different). After a prebum period of 90 to 120 sec, add agent vapor to the air stream in discrete steps until the flame is extinguished. (Consult the references for greater detail.) The agent concentration in the agent-air mixture at the point of flame extinguishment is recorded. The procedure is repeated several times and the results averaged. The accuracy of the test method, based on comparison of inter-laboratory results [7] is excellent with an apparent error of about 2% (relative) and the test-to-test repeatability (author's experience) is observed to be about 1% (relative).

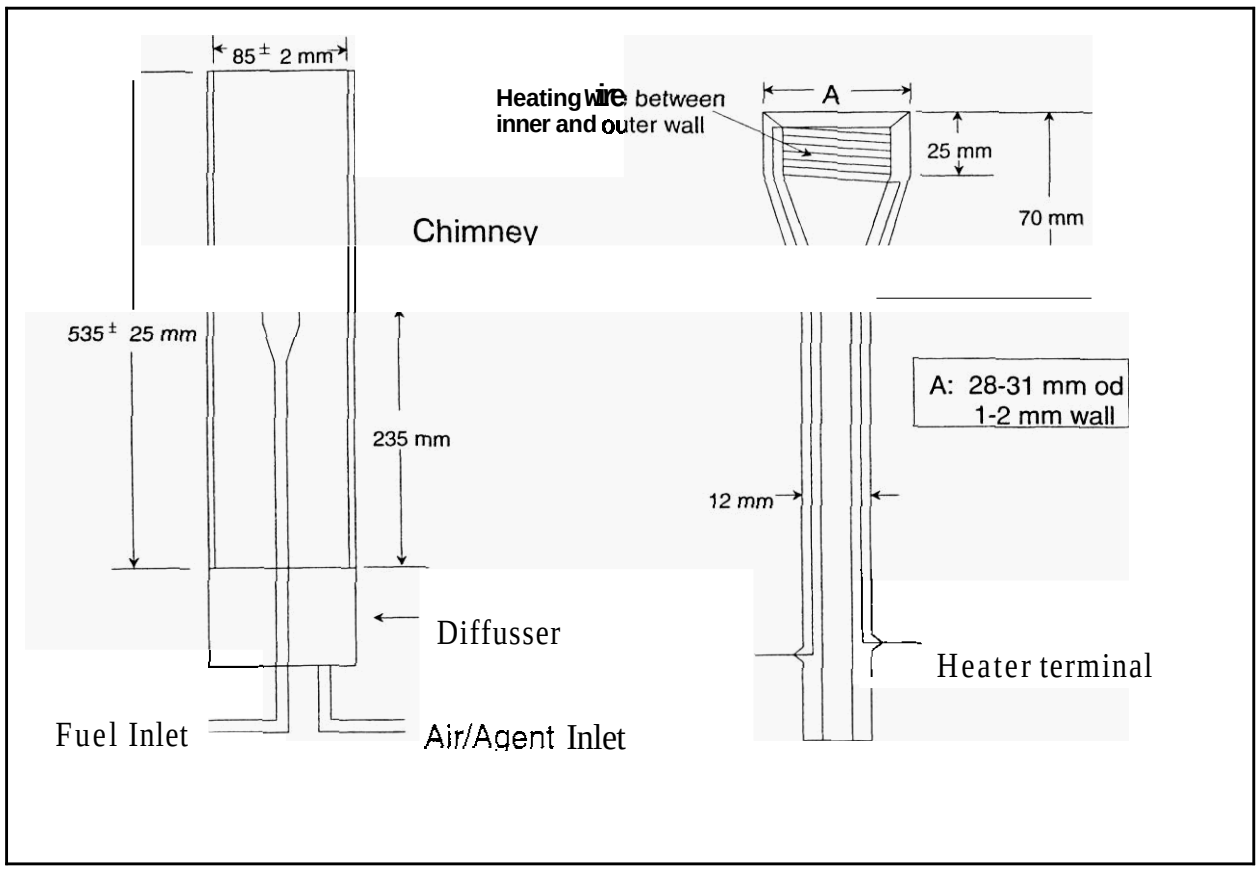

Figure 1. Standard cup burner. (Drawing courtesy of **Mark** Robin, Great Lakes Chemical Corp.)

DATA AND ANALYSIS

Cup-burner extinguishing concentration data are given in Table 1 for the two the HFC (hydrofluoro-carbon) agents HFC-227ea and HFC-23 and 34 Class **B** fuels. AIT values are given for those fuels for which data was available. The data were obtained from several sources (Great Lakes Chemical Corp.; NFPA 2001 Task Group on Cup Burner Data, 1998; Fenwal Safety Systems Combustion Research Center) all of which used the full-scale cup-burner apparatus and method. The relationships of the extinguishing concentration to the following fuel characteristics were examined

- Autoignition temperature
- Oxygen content
- Hydrogen to carbon ratio

Autoignition Temperature – AJT

One premise is that the amount of agent heat abstraction that might be required would be less for fuels having high AITs. The reason for this is that the minimum temperature in the flame reaction zone necessary to support combustion chemistry is approximately 1600K. To the extent that energy is required to preheat fuel to the AIT, it seemed feasible that there might be a reduction in the amount of heat abstraction required (i.e., less agent needed) to achieve flame quenching. Values of AIT, where known, are given in Table 1. The relationship of extinguishing

Table 1. Fuel AIT and Agent Cup Burner Extinguishing Concentration.

	AIT °C	HFC-227ea Vol.%	HFC-23 Vol.%
Acetone	465	6.6	12.1
Acetonitrile		4.3	
Aviation Gas		6.5	11.5
Benzene	560	5.2	10.5
Benzyl alcohol			12.0
n-Butane	405	6.6	13.2
1-Butyl alcohol			13.9
Diesel No. 2	225	6.7	11.4
Ethane	515	6.7	
Ethyl alcohol	365	8.1	15.6
Ethyl acetate		6.8	
Ethylene glycol	400	7.6	
Gasoline-NoLead		6.9	
Heptane, commercial		6.4	
n-Heptane	215	6.6	12.6
n-Hexane	225	6.7	12.7
Hydrogen	400	13.2	
Kerosene	210	6.9	12.5
Lube Oil @500F		7.1	
Methane	540	5.5	11.0
Methyl alcohol	385	9.7	18.7
Methyl ethyl ketone			13.6
Methyl isobutyl ketone		7.0	
Morpholine		7.9	
n-Octane	220	6.8	13.5
i-Octane		6.5	12.9
n-Pentane	260	6.6	13.7
Propane	450	6.7	13.0
i-Propyl alcohol		7.5	12.9
n-Propyl alcohol	440	7.7	
Tetrahydrofuran		7.4	
Toluene	480	5.2	10.1
Transformer Oil		7.0	
Xylene	508	6.0	9.8

Data sources: AIT data from Zabatakis, Appendix A [8]; cup-burner extinguishing concentration data from Great Lakes Chemical Corp., Fenwal Safety Systems and NFPA-2001 Cup Burner Task **Group** (full-scale apparatus data **only).**

concentration and AIT is shown for the two agents in Figures 2 and 3. The data have been plotted using different symbols to distinguish basic fuel chemistries: aliphatic hydrocarbons (single carbon-carbon bonds); aromatics (benzene structure); and oxygenates.

1. Aliphatics: Fuels range from methane to octane in carbon chain length with AITs ranging from 215 to 540 "C. With the exception of methane, the extinguishing concentrations fall into **narrow** bands - 6.6 to 6.9 vol.% for HFC-227ea and 11.4 to 13.7 vol.% for HFC-23. There is no discernible correlation to **AIT.** The extinguishing concentration for methane is notably less than for the other aliphatics, **5.5** and 11 vol.% for HFC-227ea and HFC-23, respectively.

2. Aromatics: The fuels include benzene, toluene, and xylene. These and other aromatics are often important constituents in gasoline blends. Within this group there is no correlation of extinguishing concentration with AIT. The group **as** a whole has lower extinguishing concentrations than the C_2 to C_8 aliphatics.

3. Oxygenates: The AIT data are limited. Methyl alcohol is observed to have the highest extinguishing concentration of the liquid chemicals (and is exceeded only by hydrogen) and is followed by ethyl alcohol. The oxygenates as a group show **poor** correlation of extinguishing concentration with AIT for either agent.

Oxygen Content

Another premise is that fuels containing oxygen in their chemical structure might behave in a different and consistent way from non-oxygenated species. The oxygen content of each fuel was calculated as the oxygen atom fraction thereof. Extinguishing concentration was plotted against this parameter and are shown in Figures 4 and **5.** Methyl and ethyl alcohols, again, are exceptions to the general behavior of oxygenates. The extinguishing concentrations of the oxygenates, except for methyl and ethyl alcohol, are in the ranges of 6.8 to 7.7 vol.% for HFC-227ea (about 10%, relative, higher, at most, than observed for the aliphatics) and 12.0 *to* 13.9 vol.% for HFC-23, equivalent, within experimental error, to results observed for aliphatics.

Hydrogen to Carbon Ratio

The premise here is that hydrogen is a more active species than carbon and its intermediate species, and therefore a species having an WC value that is "high" would tend to require, other things being equal, a greater extinguishing concentration than other species. The plots of extinguishing concentration against WC ratio are shown in Figures 6 and 7. The C_1 compounds, methane and methyl alcohol, stand out as exceptions again. The extinguishing concentrations of the C_2 to C_8 species correlate well with H/C ratio. Linear regression analysis of the data (excluding the methane and methyl alcohol) yields:

HFC-227ea:	CB Conc. = 1.12 •(H/C) + 4.1	Correlation coefficient = 0.55
HFC-23:	CB Conc. = 2.1 • (H/C) + 8.1	Correlation coefficient = 0.72

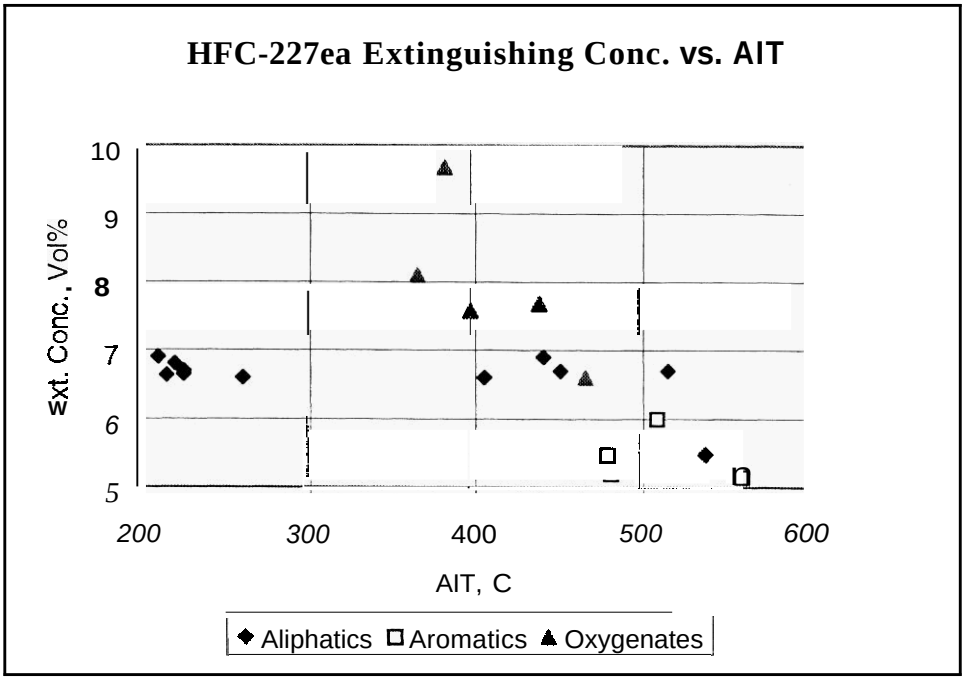

Figure 2. HFC-227ea extinguishing concentration vs. AIT

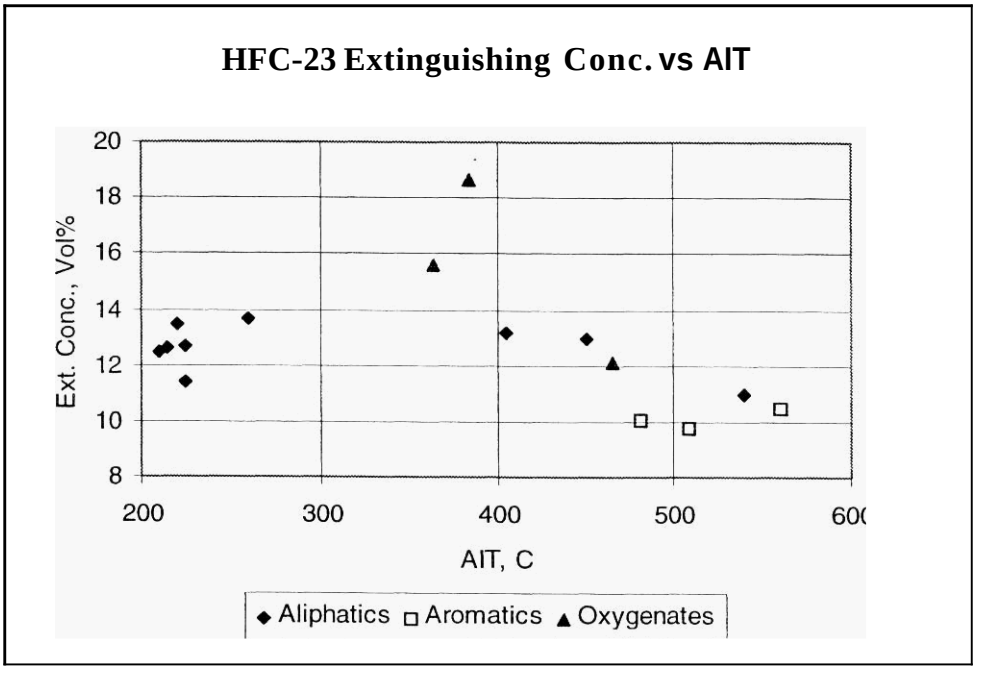

Figure 3. HFC-23 extinguishing concentration vs. AIT.

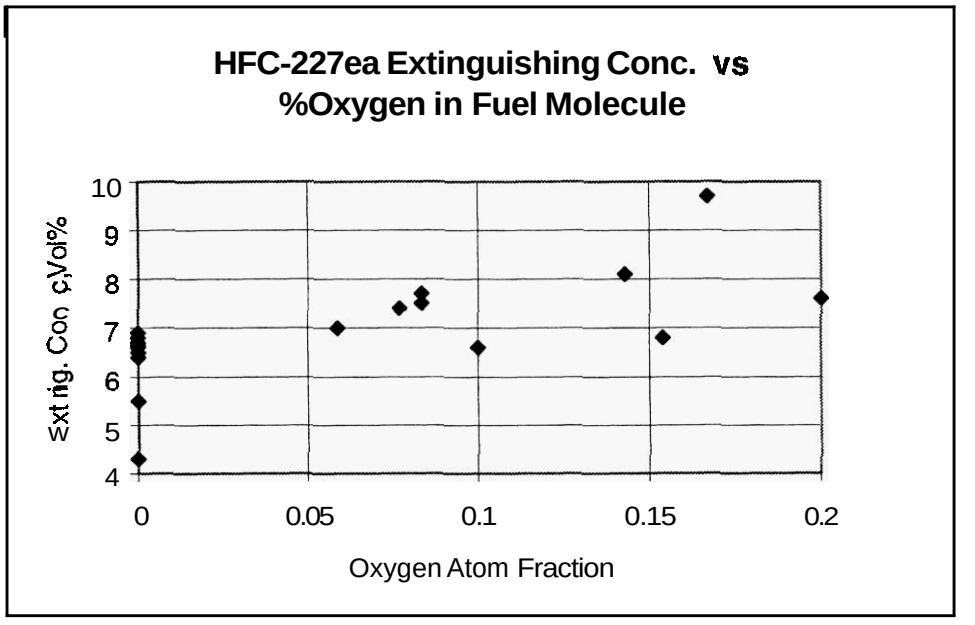

Figure **4.** HFC-227ea extinguishing concentration vs. oxygen content.

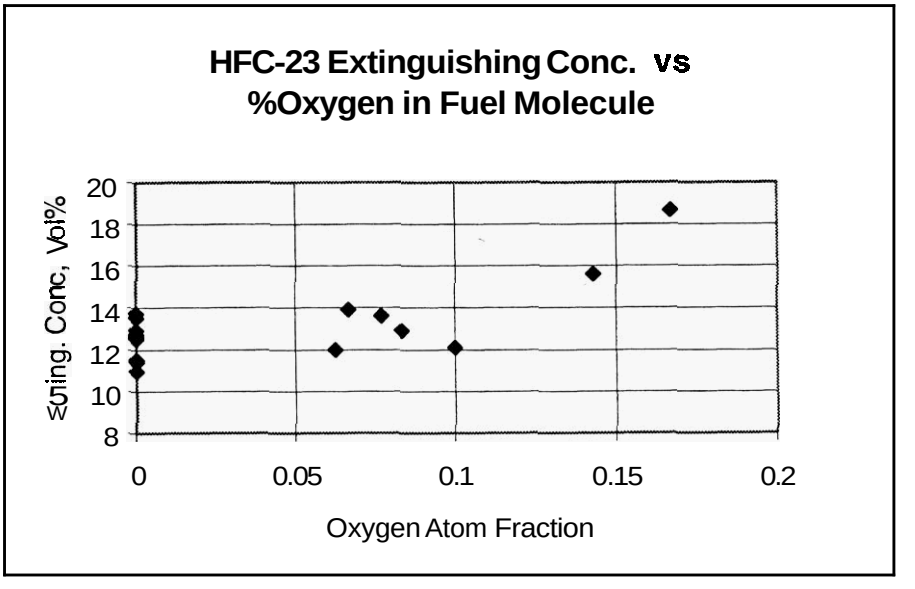

Figure *5.* HFC-23 extinguishing concentration vs. oxygen content.

Based on the degree of data correlation it appears that a conservative estimate of extinguishing concentration would be obtained for untested species by applying the correlation to the known WC value of the fuel and then adding an extra quantity, say 1%,in each case. The upper lines in Figures **6** and 7 represent the estimated cup burner values plus 1%. Thus, in the absence of test data, the fuel WC value could be used **as** a reliable and conservative estimator of the extinguishing concentration of the agents HFC-227ea or HFC-23.

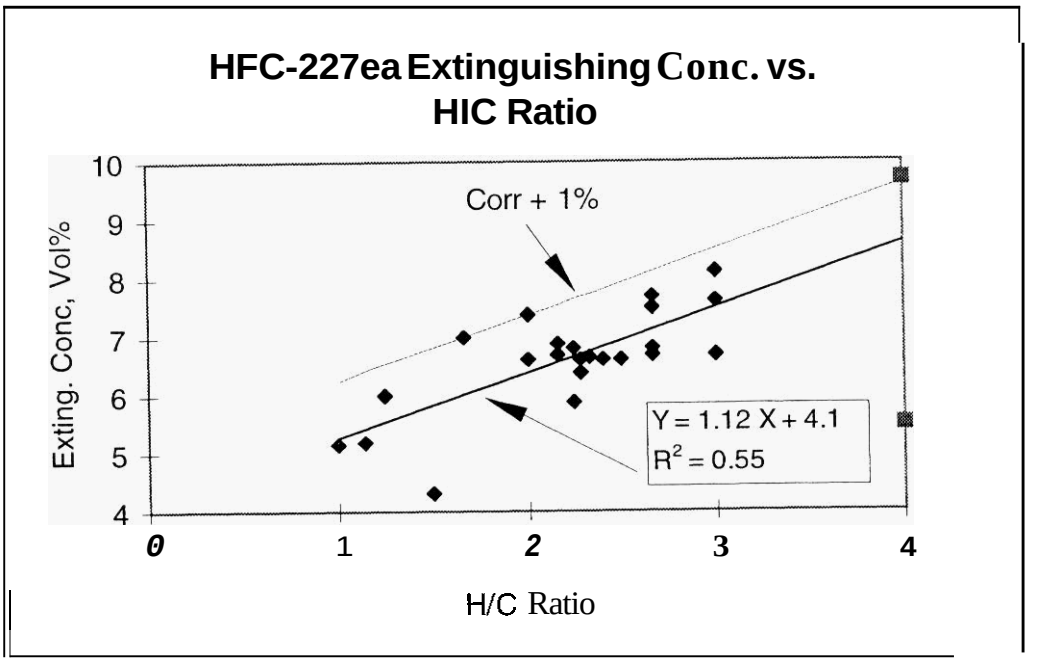

Figure 6. HFC-227ea extinguishing concentration vs. H/C ratio.
H/C = 4 species not included in the trend line.

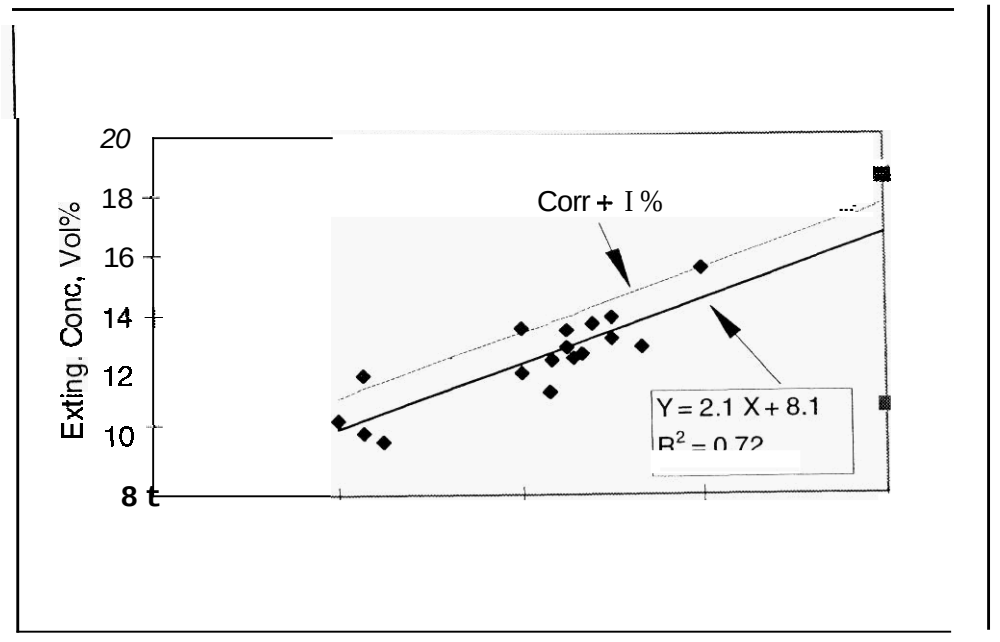

Figure 7. HFC-23 extinguishing concentration vs. WC ratio.
WC = 4 species not included in the trend line.

THE CASE OF METHYL ALCOHOL

The extinguishing concentration for methyl alcohol, and to a lesser extent for ethyl alcohol, is consistently greater than for other species. Why? No satisfactory explanation has been offered for this behavior by others. The following is offered as an unproved hypothesis: Methyl alcohol-air flames are essentially clean, i.e., essentially no in situ soot forms leading to very low IR emission rates from the reaction zone and, consequently, low radiative cooling rates. Thus, the basic thermal quenching burden on the agent is increased and is satisfied only at higher agent concentrations. If this hypothesis is valid, there is no reason to suspect that other "methyl alcohol-like" fuels are untested and are posing special risks. The above correlations could be applied, therefore, with reasonable confidence in establishing clean agent system designs for Class B hazards of other fuels.

THE CASE OF METHANE

The extinguishing concentration for methane is consistently lower than for other aliphatics for all agents. Why? This is a less interesting case from a safety standpoint. However, the following is offered: The extinguishing concentration for methane (and the aromatics) is relatively low because its molecular level degradation in flames leads to a reduction in hydroxyl radical population without adding to the total free radical population. Methane, a stable molecule, undergoes decomposition by energetic reactions as shown below [9]

$$CH4 + \bullet OH \rightarrow CH_3\bullet + H_2O \qquad (1)$$

Reaction **(1)** produces a non-reactive (or low reactivity) final product, H_2O, and exchanges a combustion-critical radical (OH) for one that is less efficient ($CH_3\bullet$) in propagation of flame chemistry. Higher aliphatic hydrocarbons, on the other hand, are thermally less stable and can readily decompose homogeneously by collision with energetic third (non-reactive) species as exemplified by the following propane reaction

$$C_3H_8 + M \rightarrow C_3H_7\bullet + H\bullet + M \qquad (2)$$

where M and M' are two different energetic states of a third body (for example, M could be an energetic nitrogen molecule). Reactions like (2) both add to the free radical population and do not reduce the population of $OH\bullet$. Thus, by this hypothesis, it should be expected that thermally stable species would have extinguishing concentrations lower than that of aliphatics as a group. This hypothesis is borne out in the observed behavior of the aromatic fuels.

CONCLUSIONS

1. Extinguishing concentration does not generally correlate with fuel autoignition temperature. Such correlation is completely absent for the aliphatic hydrocarbons.
2. **Fuel** oxygen content does not correlate to extinguishing concentration. In the case of HFC-23 the oxygenates and aliphatics are indistinguishable with respect to extinguishing concentration. In the case of HFC-227ea the extinguishing concentrations of the oxygenates, **as** a group, are about 10% (relative) higher than for the aliphatics.

3. Extinguishing concentrations correlate reasonably well with fuel WC ratio, sufficiently so that this correlation could be used as a basis of determining minimum agent design concentrations where test data are absent.
4. It is proposed that the elevated extinguishing concentration for methyl alcohol flames is due in part to low thermal emission thereby imposing a greater thermal quenching burden on the gaseous agent.
5. Lower extinguishing concentrations consistently observed for methane are likely due to a reduction in population of reactive free radicals consequent to the reaction steps involved in the initial dehydrogenation of the molecule.

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