A Continuation of Thermal Decomposition Product Testing With C_6 F-ketone, Increased Concentrations

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ABSTRACT

C_6 F-ketone is effective as a halon alternative for total flooding applications. As with other halon alternatives, exposure to fire causes the agent to decompose thermally into acid gas. Small-scale testing has been conducted utilizing on-line FTIR analysis to quantify the concentrations of thermal decomposition products (TDP). Agent concentrations equal to the minimum extinguishment value as well as that value plus a 20% safety factor were used. C_6 F-ketone was found to be, in terms of TDP, directly comparable to other commercially available halon alternatives.

Further testing in 3M's 1.28-m^3 enclosure includes increased agent concentrations of that initial minimum value plus 40% and 60%. The three variables in the test matrix are, fire size, discharge time, and agent concentration. TDP are quantified using on-line FTIR analysis. Data are compared with other commercially available halon alternatives previously tested.

INTRODUCTION

The need to find a sustainable alternative to halons is ever increasing. Commercially known as 3M™ Novec™ 1230 Fire Protection Fluid, C_6 F-ketone has proven to be effective for both total flooding and streaming applications.

In order to design any fire protection system properly it is important to investigate all the possible hazards associated with that system. Issues involving interaction of agent with flame front are particularly important. The thermal decomposition products (TDP) of main concern, resulting from the exposure of a halon alternative to fire, are hydrogen fluoride (HF) and carbonyl fluoride (COF_2). The effects of exposure to these compounds, mainly HF, have been well documented [1,2].

The three key factors affecting thermal decomposition production are the fire size-to-room volume ratio, the agent volumetric concentration, and the discharge time [3,4]. Previous testing has found a point of diminishing returns where further increases in agent concentration yield negligible reductions in TDP [5,6].

METHODOLOGY

TEST ENCLOSURE

Small-scale tests were conducted in 3M's 'box' [4]. This provides a 1.28-m^3 (45-ft^3) total floodable volume, 0.91x0.91x1.7-m^3 (3x3x5-ft^3). The box is instrumented with pressure transducers, for cylinder and discharge pressure, and thermocouples, for enclosure and agent temperatures. A complete schematic of the box is seen in Figures 1a and 1b.

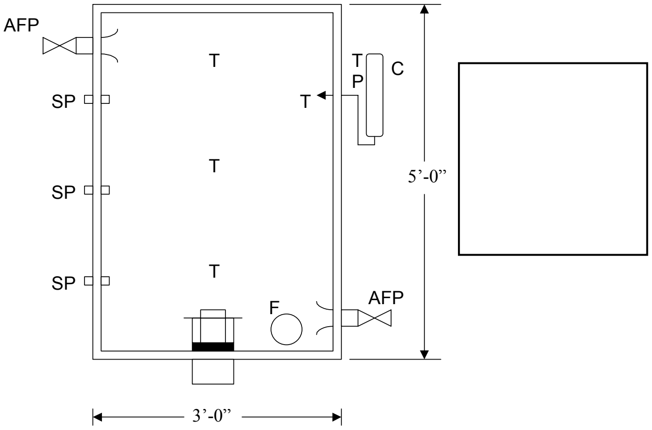

Figure 1a, Side View

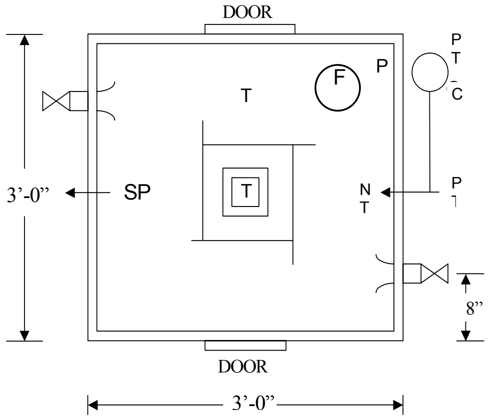

Figure 1b, Top View

AGENT CONCENTRATION CALCULATIONS

An update from previously reported agent concentrations is necessary [4]. Original agent concentrations were based on ideal gas law calculations for agent specific volume. This resulted in agent concentrations that vary slightly from those found using experimental data for C_6 F-ketone, Table 1. It is important to note that these do not affect the original quantities (mass) of agent used, only the corresponding concentrations (% v/v) are represented.

Table 1, Agent Concentration Calculations

Agent (% v/v)	Ideal Calculations (% v/v)	Corrected Calculations (% v/v)
Extinguishing*	4.86	4.56
Extinguishing+20	5.83	5.47
Extinguishing+40	6.81	6.38
Extinguishing+60	7.77	7.29

*C_6 F-ketone at initial n-heptane extinguishing value

Ideal Gas Law s-Value

$s = 0.071 + 0.0003T$

PRSV EOS* s-Value

$s = 0.0664 + 0.000274T$

*Peng-Robinson-Stryjek-Vera Equation of State

Increased agent concentrations were chosen as extinguishing + 40% and extinguishing + 60%. In accordance with the procedures for measuring extinguishment for n-heptane in NFPA 2001, the initial total volumetric agent concentration was determined as the cup-burner minimum extinguishing concentration for heptane, as established by a recognized testing lab. Agent mass required to produce the desired agent concentrations in the box were calculated as follows:

$$W = \frac{V}{s}\left(\frac{C}{100 - C}\right)$$

where, W is the mass of the agent in lb (kg), V is the enclosure volume in ft^3 (m^3), C is the agent design concentration (% v/v), and s is the agent specific volume at 1 atm. and ambient temperature [7].

DISCHARGE TIME

Discharge times of 3 s, 9 s, and 20+s were chosen for direct comparison with previous testing done [3,4,5,6]. Discharge time is controlled by the flow rate (orifice size) of the discharge nozzle. Initial testing was conducted to determine which nozzles were needed to produce the desired discharge time; the results of those tests are presented in Table 2.

Table 2, Nozzle Discharge Times

	Agent Discharge Time		
Agent Concentration	3 Seconds	9 Seconds	20+ Seconds
n-heptane extinguishing + 40% (6.4%)	Bete Company NF3000	Spraying Systems TP8007	Bete Company NF0300
n-heptane extinguishing + 60% (7.3%)	Spraying Systems TP8040	Spraying Systems TP8008	Spraying Systems TP8004

FIRE SIZE

The four different fires sizes used in this study were chosen to compare with previous work [3,4,5,6]. A cone calorimeter was used to determine the heat release rates of the four square pans, which measure, 2-cm (0.75-in), 4.5-cm (1.75-in), 7-cm (2.75-in), and 9.5-cm (3.75-in). The corresponding heat release rates for these pans when filled with heptane are, 0.1 kW, 0.6 kW, 1.7 kW, and 3.7 kW, respectively. For each test, the pans were filled to the top with fresh heptane immediately before the test. Fresh heptane was used for each test.

FTIR ANALYSIS PROCEDURE AND SETUP

Two MIDAC I-2000 Series Model FTIR spectrometers were used for this study. Each spectrometer was configured with a ZnSe beam splitter and a mercury cadmium telluride (MCT) detector. A 0.5-cm, unheated stainless-steel gas cell utilizing sulfur hexafluoride (SF_6) as a diluent was used to acquire C_6 F-ketone concentration data. TDP concentrations, which are orders of magnitude less than C_6 F-ketone concentrations, were acquired using an undiluted 10-cm, unheated, stainless steel gas cell. The spectrometers had an ultimate resolution of 0.5 cm^{-1} with triangular apodization. Sample gas extraction was accomplished with 110V gas sampling pumps. Portable computers were used for data acquisition.

The extractive gas sampling system used for the enclosure testing consisted of approximately 8-ft of ¼”-dia PTFE tubing leading into the gas cells. Each spectrometer and its sampling system were operated independently. Samples were continuously pumped through the sample line and the gas cells at a flow rate of 1 and 2 lpm for the 0.5-cm and 10-cm gas cells, respectively. Flows were verified on site using a Dry Cal™ flow meter. FTIR sampling was initiated when the fuel was ignited. After extinguishment (5-20s), the enclosure remained sealed and was monitored until HF levels reached a maximum concentration and slowly began receding. The TDP and C_6 F-ketone concentrations in the enclosure were checked for residual quantities before each test.

TEST PROCEDURE

Immediately before each test began the test pan was filled to the top with heptane. The test began when the fuel was ignited, at which time the access door was sealed and the FTIR machines were turned on. The 60-s pre-burn occurred with both the box inlet and outlet valves open, minimizing combustion product buildup and oxygen depletion. The valves were then closed, and 5 seconds later the agent was discharged. After extinguishment, the fan inside the enclosure was turned on to mix the enclosure volume thoroughly. The box remained sealed during the FTIR analysis cycle.

RESULTS

As seen in Figure 1, a decrease in the discharge time result in decreased TDP. Decreasing the discharge time from 9 seconds to 3 seconds results in up to a 65% reduction in hydrogen fluoride production (ppm). Consistent with previous results, HF production is a monotonically increasing function of fire size [3,4,5,6,8]. This shows the importance of discharge time in system design. Figure 1 shows that TDP appears to level off as the fire size increases. This effect, previously reported by Linteris, may be attributed to kinetic limitations on the rate of agent consumption [9].

Note, at smaller fire sizes the concentration of TDP fell below the minimum detection limit (MDL) for the FTIR system. In these instances, a value of 0 ppm was chosen for comparison. For actual system design, a value equal to the MDL of the system should be used. That would represent a more conservative value important when safety is the major concern.

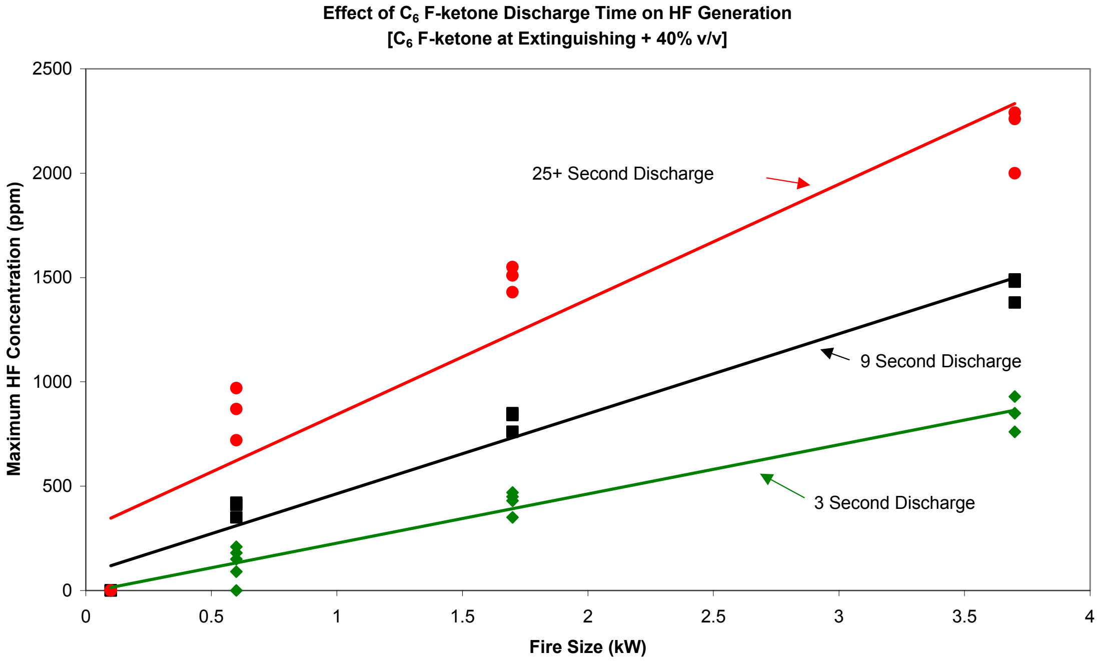

Figure 1

As shown previously C_6 F-ketone is effective in extinguishing class A fires, Figure 2. The HF production from class A fires is lower than for class B fires. This is consistent with previous work and shows that heptane was a good choice for a “worst-case” scenario for HF production [3,4]. The variability on the wood test is evident by the range in reported results.

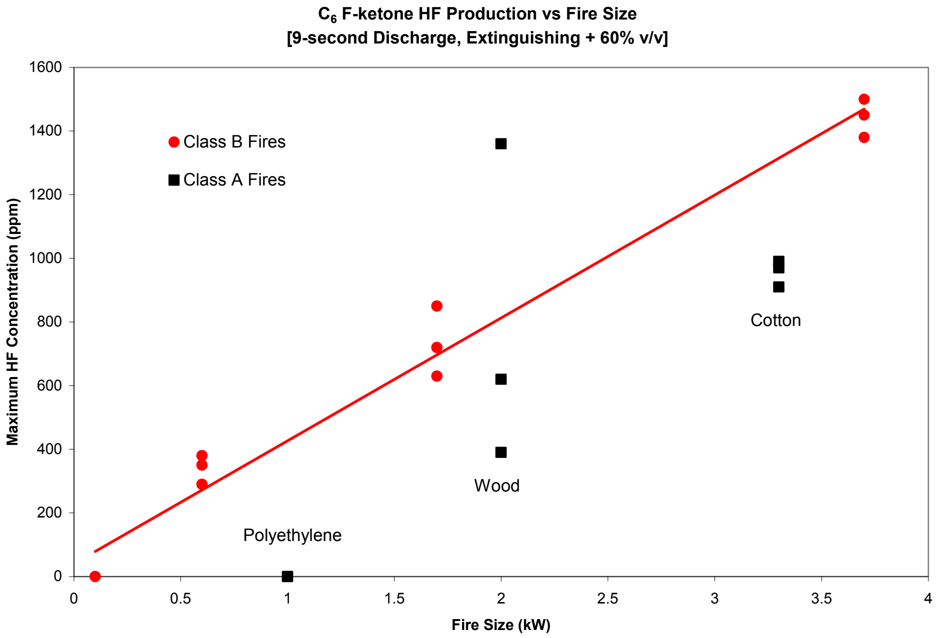

Figure 2

Increasing the agent concentration reduces the quantity of HF produced. A point of diminishing returns is reached where any further increases in agent concentration yield negligible reductions. This effect is irrespective of fire size and has been demonstrated for other agents as well. As seen in Figure 3, at extinguishing plus 40% (v/v) concentration HF production is at a minimum.

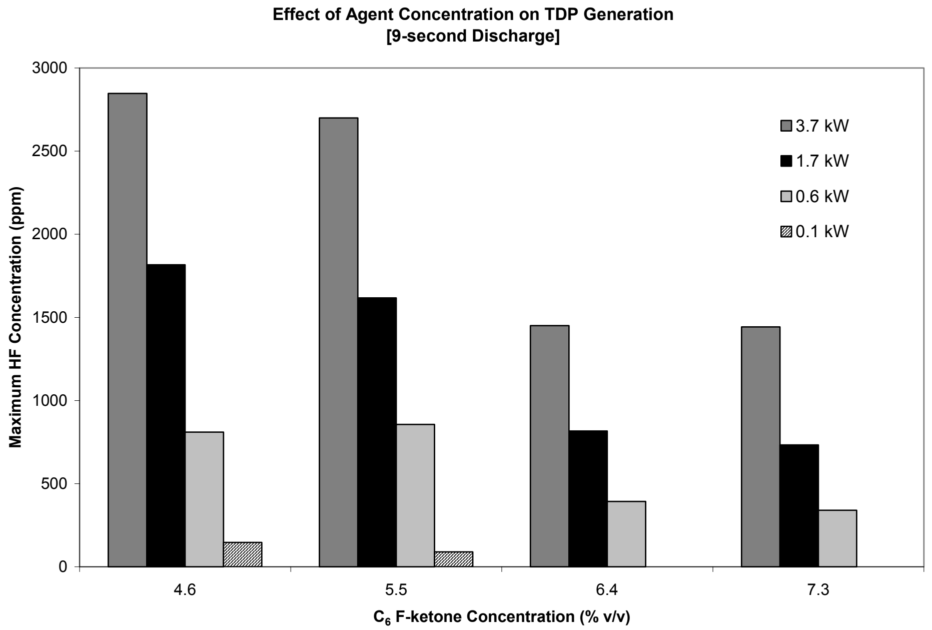

Figure 3

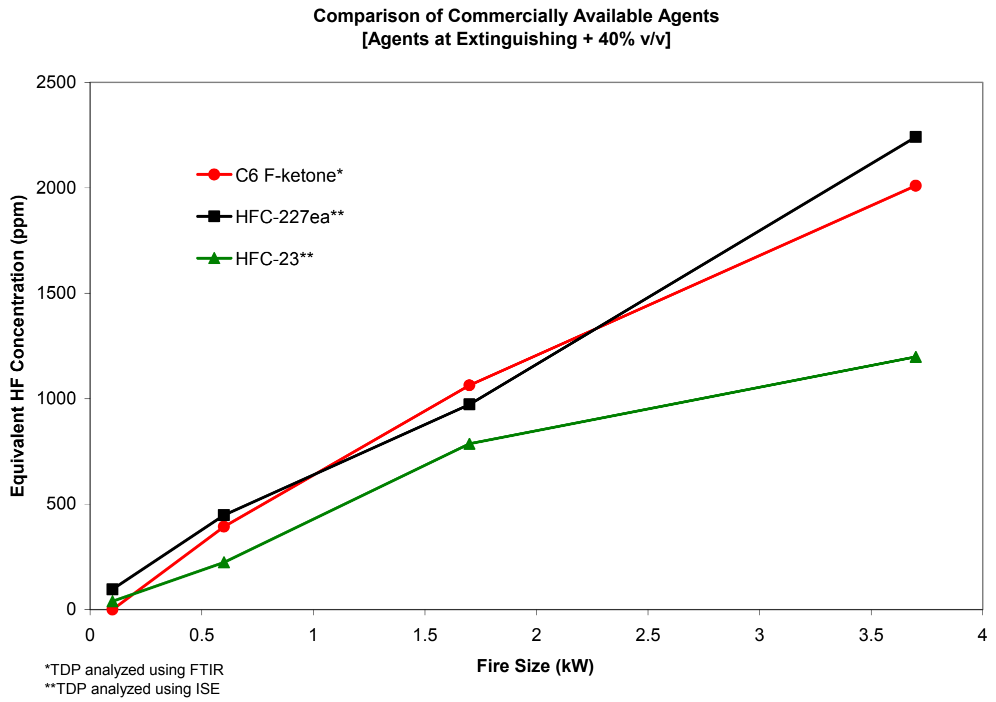

Figure 4

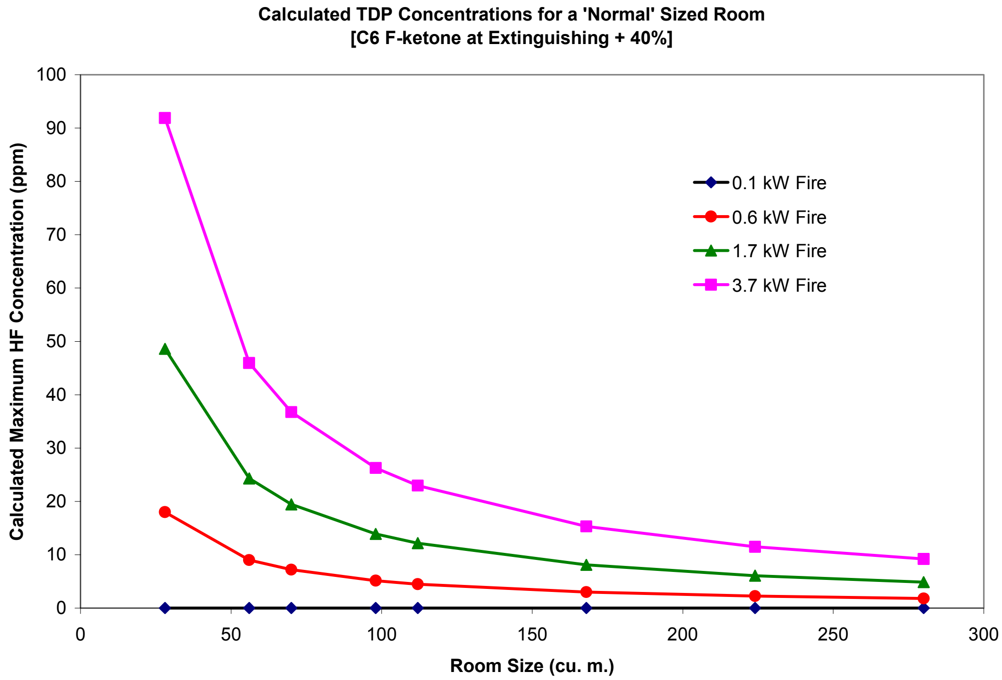

Figure 5

In terms of HF production, C_6 F-ketone in these test scenarios is directly comparable to other commercially available clean agents, Figure 4. Note that equivalent maximum HF concentrations are reported. TDP analyzed using an ion-selective electrode (ISE) only detects the presence of hydrolysable fluoride, which is then converted to an equivalent HF concentration. To be consistent TDP analyzed using FTIR are also reported as equivalent maximum HF concentrations. Since COF_2 is the only other significant contributor to hydrolysable fluoride, equivalent HF concentrations (ppm) are determined as the HF concentration (ppm) plus twice the COF_2 concentration (ppm). Doubling of the COF_2 concentration is due to the effect of hydrolysis, see Equation 1.

[Eq.1] $$COF_2 + H_2O \rightarrow CO_2 + 2HF$$

The Robens Institute indicates the highest tolerable HF concentration for a 1-min human exposure is 120 ppm. Figure 5 shows that when normal sized rooms and possible use concentrations are considered C_6 F-ketone produces tolerable levels of HF.

Discussion and Conclusion

Test results have shown, in terms of TDP, C_6 F-ketone is directly comparable to other commercially available halon alternatives. The maximum equivalent HF concentrations found are consistent with those for other in-kind halocarbon agents. Also, the three major factors affecting TDP are the fire size-to-volume ratio, discharge time, and agent concentration. The latter two have a direct effect on the fire extinguishment time. TDP is a monotonically increasing function of fire size.

Increasing the agent concentration is an effective way to reduce TDP. However, a point of diminishing returns can be reached where further increases in agent concentration yield negligible decreases in TDP. This is consistent with previous work [5].

As indicated previously, hazards such as those present in telecommunications facilities often result in fire sizes less than 10 kW at detection, with detection often desired at 1 kW [7]. When typical fire sizes and room sizes are considered, TDP concentrations fall below the dangerous toxic level (DTL) set by Meldrum [2].

Finally, through the use of effective system design, TDP concentrations can be maintained below dangerous levels. Among other methods, this can be accomplished through early fire detection, adequate agent concentrations, and system discharge time. An agent is only as effective as the system in which it is used.

References

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