CONSIDERATION OF LIQUID TO GAS PHENOMENA FOR A SUSTAINABLE, HIGH-BOILING, TROPODEGRADEABLE HALOCARBON

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ABSTRACT

The effectiveness of FK-5-1-12 has been demonstrated in flooding applications. OEMs' system listings and approvals demonstrate the progress made in developing FK-5-1-12 use as a gaseous, total-flooding clean-extinguishing agent. To a certain extent, this could also be realized with any high boiling tropodegradeable halocarbon. Despite this progress, there is not a universal appreciation of the ability to transform a high-boiling agent from a liquid into a gas in flooding applications. Understanding key physical properties of the compound will assist the researcher or fire protection engineer in application development and ultimate end use.

This paper examines the properties of FK-5-1-12 that most significantly augment its ability to vaporize from a liquid to a gas, but more importantly, to do so in the context of being a component of a standard conventional fire suppression system. Included are examples of actual data from tests conducted, as part of attestation test protocols.

INTRODUCTION

When a new and different technology is developed for an existing market, there is a learning curve in understanding, especially with a technology that departs in key ways from convention. FK-5-1-12 – CF3CF2C(O)CF(CF3)2 – is a fluid that is liquid at room temperature with a normal boiling point of 49°C(120°F). The properties of this halocarbon are unique, giving it certain advantages in end use, storage, handling, extinguishing and, of course, its environmental benefits. One aspect of the material is its ability to readily volatize when discharged from a properly designed and engineered fire suppression system. Unfortunately, it is not universally understood that this is so. But, a history of performance and significant data in rigorous systems approvals testing demonstrates this. So, it is important to understand how a high-boiling fluid simultaneously possesses the properties of a liquid and a vapor. Also important are properties, which exhibit useful characteristics that are key to these phenomena.

The following illustrates how the key components of FK-5-1-12 – such as its vapor pressure, latent heat of vaporization and heat capacity – produce air mixtures capable of extinguishing fires.

VAPOR PRESSURE

The vapor pressure of a pure liquid is defined as that pressure corresponding to the pure liquid-vapor equilibrium state at a specified temperature. Assuming ideal gas and ideal solution behavior, the vapor pressure of a pure liquid is equal to the partial pressure of its equilibrium vapor.

Figure 1 below shows a graph of the vapor pressure of water and FK-5-1-12. Water is shown for comparison, because the evaporative behavior of water, while uncharacteristic of many fluids, is a more common experience. The left-hand ordinate measures the vapor pressure of the pure liquids in atmospheres. The right-hand ordinate measures the gas-phase concentration of FK-5-1-12 or water assuming ideal solution and ideal gas behavior of a mixture with air at 1-atm total pressure (the liquid is considered a pure phase). In addition, boundary lines are drawn to represent a typical 4%-10vol% FK-5-1-12 concentration range for extinguishing or inerting applications. The plot shows that at room temperature liquid FK-5-1-12 will evaporate to create

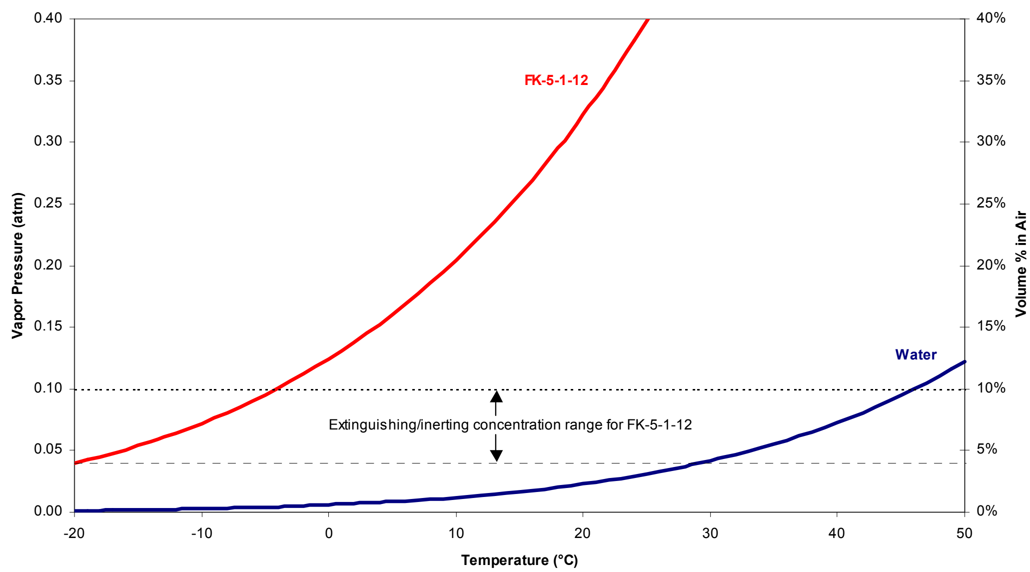

Figure 1: Vapor Pressure and Equilibrium Air Concentration of Liquids

a 32-vol% FK-5-1-12 vapor, well above that of typical extinguishing concentrations for the material. Once evaporated, there is no driving force for a vapor to condense into a liquid unless the vapor/air mixture is compressed or cooled below its dew point. In fact, the vapor pressure of FK-5-1-12 is such that it would support an extinguishing concentration of 5 vol% at a temperature as low as –16 °C. Water does not support a 5-vol% concentration in air until the temperature exceeds 33 °C.

The vapor-liquid equilibrium analysis above only considers the state of the system at a specific temperature. The evaporation of liquid into a gas requires an energy that is equal to its heat of vaporization. A spray of liquid agent will begin to cool as it evaporates.

Consider a liquid agent discharge into a room such that:

- the mass of agent introduced creates a "target" ideal-gas concentration once evaporated
- the room is adiabatic (no heat enters or leaves the room)
- the air and the agent are at the same temperature

The energy balance for the room then becomes:

{sensible heat of agent} + {sensible heat of air} = { heat of vaporization}

$$m^{agent}\int_{T_a}^{T} c_p^{agent}\,dT + m^{air}\int_{T_a}^{T} c_p^{air}\,dT = -m^{agent}H_{vap}^{agent} \qquad (1)$$

where T_a is the ambient temperature (20 °C) of the room and incoming liquid, m is the mass of the agent or air, and T is the final temperature of the room for complete evaporation. The equation above can be used to calculate the room temperature that would be achieved to totally evaporate the liquid introduced. Table 1 below lists typical properties, target concentrations, and adiabatic temperatures achieved as calculated from Eqn. 1 above for FK-5-1-12, HFC-227ea, and water. Although HFC-227ea would exist as a superheated liquid, Eqn. 1 is still applicable.

Property	FK-5-1-12	HFC-227ea	Water
H_{vap} (at bp. J/g)	63	75	2200
c_p (J/g/K)	1.003	1.247	4.18
Normal Boiling Point (°C)	49	-16.4	100
Gas Concentration vol% assumed	5	8	5
Adiabatic temperature for evaporation (°C)	-15	-21.7	-43

H_{vap}: heat of vaporization
c_p : specific heat capacity of the liquid at constant pressure

Table 1: Properties and Results for Adiabatic Evaporation in Air at 20 °C.

Table 1 shows that both FK-5-1-12 and HFC-227ea would reach temperatures of –15 (°C) or below in an adiabatic evaporation. For FK-5-1-12, the vapor pressure at –15 °C is 0.054 atm, which indicates that all of the FK-5-1-12 would evaporate. Temperatures below 0 °C have been measured in cold discharges of FK-5-1-12. An example of this is shown below in Figure 2, from the 2002 marine system approval testing using FK-5-1-12 at the USCG Fire & Safety Test Detachment, Mobile Alabama. Tested to the IMO MSC Circular #848 Test Protocol [1], the system actuation volatizes the FK-5-1-12 and distributes the agent to reach all portions of the test enclosure readily achieving the desired test concentration. This was a telltale fire test, which can be a challenge for any clean agent, not just a high boiling material such as FK-5-1-12. But, this shows that the heat transfer from a "cold" room is sufficient to completely convert the agent to a gaseous state suitable for extinguishing [2]. The water example is neither physically realistic nor obtainable, but does illustrate the difficulty in evaporating water. The water's high heat of vaporization and low vapor pressure makes it difficult to evaporate at room temperatures. Consequently, it is a poor analogy to apply experience for spray evaporation of water to these halocarbons.

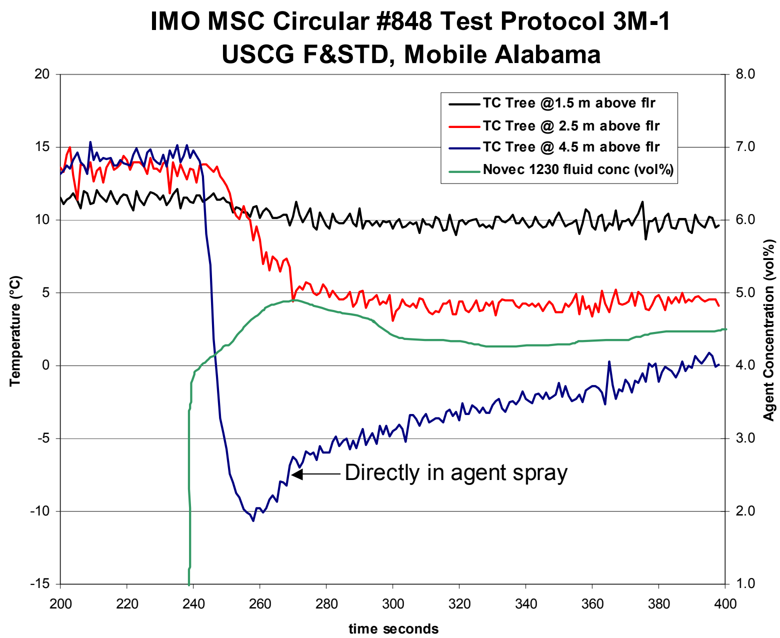

Figure 2: Actual 500m^3 Room Discharge Temperature Profile

HEAT OF VAPORIZATION, HEAT CAPACITY AND THE ASPEN PROCESS SIMULATION

The above analysis considered that the heat capacities and heats of vaporization for air and agent are temperature independent. A more complete analysis was performed using the Aspen Process Simulator, an analytical tool commonly used in the manufacturer of chemicals, which draws on a more complete set of physical property data. The discharge process was simulated as illustrated in Figure 3 as an adiabatic flash. FK-5-1-12 is mixed at a ratio to give a 5-mol% mixture in air.

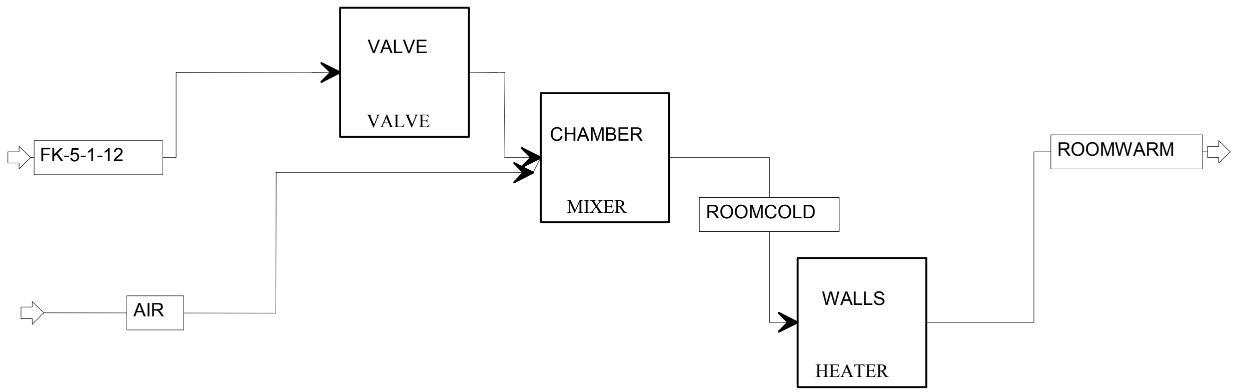

Figure 3: Aspen Process Simulation

Although not significant in this case, the flow rates where chosen to be equivalent to a 10 second agent discharge into a 100m^3 room. In the simulation, FK-5-1-12 flows through a valve reducing the pressure from a typical cylinder pressure of 374 psia to 14.7 psia. FK-5-1-12 and air are mixed in the chamber at 5:95 molar ratio (i.e. 5-vol% ideal gas). The ROOMCOLD-node lists the equilibrium state of the system following discharge. This is comparable to the adiabatic calculation above. The temperature of 1.6 °F (–16.8 °C) as compared to the –15 °C above indicating that the temperature effect on the heat of vaporization is negligible. In addition, the calculation shows that 99.9% of the mixture is in the vapor phase indicating that 97.3wt% of the liquid has been vaporized. The simulation also included heating to bring the mixed stream back to a typical end of discharge temperature of 50°F (10°C).

Experimentally, the final room temperatures are typically 0-10ºC, so the system is clearly non-adiabatic. The walls of the room represent a considerable amount of energy and surface for heat transport. For a typical UL test enclosure (specifically 3M's test room) the total volume is 103 m^3 and the wall surface area is 132 m^2. The energy in the room's wall represents an additional term on the left-hand side of Eqn. 1. The term is equal to

$$\{sensible\_heat\_in\_wall\} = m^{wall} \int_{T_p}^{t} c_p^{wall} dT = A^{wall} l^{wall} \rho^{wall} \int_{T_p}^{t} c_p^{wall} dT \qquad (2)$$

where m^{wall} is the mass of the wall, A^{wall} is the surface area for the wall, l^{wall} is the wall thickness, and ρ^{wall} is the density of the wall. Only the wall thickness remains to be specified. The energy accessible to the room will be considered the energy accessible during 10-s, a typical agent-discharge time. Using a boundary layer approximation for *l:*

$$l \approx \sqrt{\frac{k}{\rho c_p} t} \qquad (3)$$

where k is the thermal conductivity, and t is the time. Using the properties of white pine (ρ = 0.45 g/cm3, cp = 1.88 J/g/K, and k = 0.0035 J/s/cm/K) for this estimate, the thermal boundary layer is 2.1 mm and the mass of the wood in the room 119 kg. With the additional sensible heat of the room, the final temperature for a FK-5-1-12 discharge would be 10°C.

The thermodynamics indicate that FK-5-1-12 is capable of evaporating to produce useful fire extinguishing concentrations. In addition, adiabatic calculations show similar energy requirements for the evaporation of FK-5-1-12 and a superheated liquid such as 227ea. Also, this analysis has only considered no-fire scenarios. The energy introduced to the room by an actual fire would have a significant impact on the final temperature. For example, typical heptane pan-fires, used in agent tests for a 103-m^3 enclosure, provides a heating power of 300 kW; whereas, evaporation of the FK-5-1-12 mass for a 5-vol% concentration in a 10-s period requires a heating rate of 430 kW.

The dynamics of this process are much more difficult to analyze: droplet formation from jet, fluid dynamics of jets and droplets, mass and energy transport from the droplet to the vapor, and energy transport from the room. In particular, the energy transport mechanism, from the room to the gas at rates sufficient to achieve the final observed temperatures, is not obvious. Conductive, convective and radiative heat transfer all appear to contribute to this mechanism. The discharge through the nozzle needs to disperse the agent, creating sufficient surface area for this energy transfer to occur. Numerous discharge and extinguishing test attestations (i.e. UL, UK MCA) have demonstrated this can be achieved with FK-5-1-12. In addition, there is a considerable body of literature on sprays, spray cooling, and spray evaporation utilizing computational fluid dynamics to model the spray. One specifically relative article by Pitt et al. examined high-speed suppression discharges of halon alternatives. These authors note good agreement with initial experimental results but substantial work remains. They noted that physical data to validate these models are experimentally difficult or impossible [3].

In addition to NIST work on discharges, they analyzed (computationally and experimentally) droplet formation of liquid agents (water and Novec 7100 – a hydrofluoroether with physical properties similar to those of FK-5-1-12) and the transport of these droplets around objects. The work premise is based on the concept that dispersal and delivery of liquid droplets is more effective in fire extinguishment than vaporized agent alone. Optimization of the droplet size is critical. Presser et al. observed for turbulent flow around a cylinder, that specific droplet size could facilitate the droplet penetration around a solid cylinder. For example in their configuration using HFE-7100, 10-μm droplets evaporated before navigating the obstacle and 100-μm droplets had too great a momentum to penetrate behind the obstacle; however, 50-μm droplets were capable of penetrating behind the obstacle [4]. Judicious design of the discharge system may provide improved agent distribution for specific scenarios by optimizing droplet size, taking advantage of the properties of a higher boiling agent such as FK-5-1-12.

CUP BURNER ANALYSIS

When determining extinguishing concentrations, a high boiling material like FK-5-1-12 introduces several new challenges in the cupburner apparatus. While it is straightforward that vaporization of FK-5-1-12 is readily achieved when discharged from a properly designed system, using nitrogen for superpressurization, a cupburner requires a different approach. Section B.4.3 of ISO 14520 states that a liquid agent must be provided as a pure extinguishant, as pressurizing with nitrogen could erroneously lower the cupburner value [5]. For low boiling extinguishants, which are gases at room temperature, this does not pose a challenge, as the extinguishant itself is introduced into the air stream under its own vapor pressure. However with a high boiling extinguishant, there is insufficient vapor pressure and must be heated to achieve a vapor pressure high enough to properly introduce it into the air stream. All parts of the cupburner apparatus, from the supply reservoir until the extinguishant is introduced into the air stream, must be heated to maintain a sufficient vapor pressure. Once in the air stream, the FK-5-1-12 will not partition back to the liquid phase, because it is well below its saturation concentration. A liquid bath is favorable to an oven to achieve these elevated temperatures, as the heat transfer from the liquid into the extinguishant is much greater than that of air. This increase in heat transfer should be able to overcome any cooling effects due to the vaporization of the extinguishant.

Another challenge introduced in the cupburner apparatus is the analysis of the air/extinguishant mixture. A measure of the remaining oxygen concentration in the air/extinguishant stream is not acceptable. The oxygen atom in FK-5-1-12 will interfere with many oxygen-analyzing devices. Measuring the flow rates of both the air and extinguishant also proves to be troublesome with high boiling point chemicals. The flow of gaseous agent is that of a saturated vapor. Any drop in pressure or temperature through a rotameter or other flow calculation instrument would result in condensation of the extinguishant. The preferred methods of analysis of the air/extinguishant mixture are infrared spectroscopy and gas chromatography. Gas analysis is favorable as it measures the amount of agent present rather than a difference between an initial and final value, such as with oxygen analysis. See Figure 4.

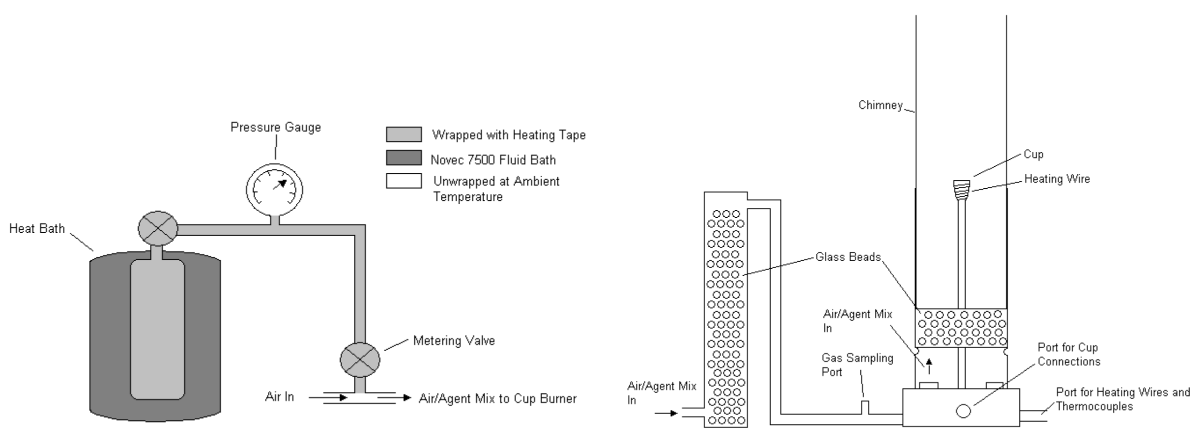

Figure 4: Agent/air supply to cupburner apparatus

CONCLUSIONS

FK-5-1-12 has sufficient vapor pressure, combined with its low heat of vaporization, to create and sustain gas concentrations several times that required for useful extinguishing concentrations. Adiabatic calculations show that sufficient sensible heat is present in the room air and incoming liquid agent to vaporize sufficient agent for extinguishment. This is comparable with another known clean agent, which shows similar energy requirements for evaporation to that of FK-5-1-12. The unique properties of a high-boiling agent enable use of additional methods for agent delivery. Finally, reliable delivery methods and consistent analytical tools are available to determine extinguishing concentrations of a high boiling material like FK-5-1-12 via the standard cupburner.

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