ABSTRACT
Laboratory tests have been conducted to determine the effects of nitrogen addition on the required propane inerting concentrations of CF$_3$CHFCF$_3$ and of CHF$_3$. Tests were conducted in a 6 liter spherical vessel equipped with an igniter with a 11 joule spark discharge energy. Using a 1 psig pressure rise inerting criterion, the baseline inerting concentration for CF$_3$CHFCF$_3$ was 11.7 v%, and for CHF$_3$ was 20.2 v%. Nitrogen addition increments of five v% caused the required CF$_3$CHFCF$_3$ concentrations to decrease by 1.0 to 1.4 v%, and the required CHF$_3$ concentration to decrease by 2 v%.

INTRODUCTION
Two commercially available, zero Ozone Depletion Potential, replacement agents for Halon 1301 total flooding fire and explosion suppression systems are CF$_3$CHFCF$_3$ (ASHRAE designation HFC-227ea) and CHF$_3$ (ASHRAE designation HFC-23). HFC-227ea has a relatively lower vapor pressure (458 kPa at $25^\circ$C) and, like Halon 1301, is pressurized with nitrogen to produce the required rapid discharge in fire and explosion suppression systems. HFC-23 has a much higher vapor pressure (4200 kPa at $25^\circ$C) and therefore does not require nitrogen pressurization for fire suppression, but may require it for explosion suppression applications.

According to NFPA 2001 [1], the design concentration for a clean agent fire extinguishing system should be based on the required inerting concentration "where conditions for
subsequent reflash or explosion could exist.” These conditions include the presence of sufficient flammable gas to develop a concentration of at least one half the lower flammable limit throughout the enclosure. In the case of petroleum production and processing facilities, the most commonly used flammable gas for inverting tests is propane. The propane inverting requirement for HFC-23, as given in the Appendix of NFPA 200, is 202 vol%. This value is slightly higher than the 19.8 vol% obtained by Heinonen and Skaggs [2] for HFC-23. Heinonen and Skaggs' reported propane inverting requirement for HFC-227ea is 12.0 vol%.

Nitrogen pressurization of HFC-227ea and HFC-23 agent containers in suppression systems will create a nitrogen-agent liquid phase blend in the container, and this blend will be discharged into the enclosure during agent discharge. The solubility of nitrogen in HFC-227ea has been measured by Yang [3] for a limited number of conditions. In the case of liquid HFC-227ea filling about one third of a vessel pressurized to 4.16 MPa by nitrogen, the nitrogen/HFC-227ea mass ratio was 0.068, which corresponds to a mole ratio of 0.41. Halon replacement agent fire suppression systems are expected to be pressurized to 4.2 MPa in some cases, and to 2.5 MPa in other cases. The latter would have a correspondingly lower nitrogen mole fraction in the container. On the other hand, explosion suppression systems could have container pressures above 4.2 MPa both for HFC-227ea and for HFC-23.

In view of the inevitable presence of a nitrogen-agent blend when these clean gaseous agent suppression systems are discharged, the effect of nitrogen on the required inverting concentrations can affect the design and/or performance of these systems. This is the subject of the experiments summarized below and described in more detail in the M.S. thesis [4].

EXPERIMENTAL APPARATUS AND TEST PROCEDURE

Inerting tests were conducted in a 6.4 liter spherical vessel previously used to measure inverting concentrations of Halon 1301 using different spark ignition energies [5-7]. The vessel, which is shown schematically in Figure 1, is equipped with a 150 psig (1035 kPa gage) rupture disc and a 50 psig (241 kPa) pressure relief valve.
Experimental Setup

FIGURE 1
APPARATUS SCHEMATIC
After the vessel was evacuated, fuel, air, nitrogen, and either HFC-227ea or HFC-23 were loaded monitoring partial pressures with a mercury manometer. The propane and air partial pressures were selected to maintain a stoichiometric equivalence ratio of 0.98 ± 0.025. When the desired component partial pressures were achieved, the manometer was disconnected and gases were mixed by rocking the vessel such that a 58 cm$^2$ paddle swings back and forth. The estimated induced gas motion corresponding to a 30 degree paddle swing is equivalent to about 14 air changes per minute. The paddle motion persisted for 20 to 40 seconds (five to ten air changes), and was followed by a 20 second quiescent period to allow gas motion to subside.

The DC spark ignition source was generated by charging a 1,000 microfarad capacitor to 148 volts, such that the capacitor discharge energy is 11 joules. Electrodes situated near the center of the vessel had a gap spanned by carbon rods 1.9 mm in diameter and 19 mm long, thus allowing an energetic spark without generating high voltages. Carbon rod igniters (with varying spark energies) have been used extensively by Fenwal Safety Systems in numerous inerting experiments referenced in NFPA 2001 [1].

Instrumentation consisted of a 2 mm diameter chromel-alumel thermocouple in the upper hemisphere of the vessel, and a 0-50 psia pressure transducer flush mounted to a vessel port as illustrated in Figure 1. Output signals from the thermocouple and pressure transducer went to a two channel recording chart that was typically set for 100°C full-scale thermocouple output and 25 psia full-scale pressure transducer output. The estimated accuracy of the temperature and pressure measurements are ± 0.5°C and ± 0.05 psi, respectively.

In most cases two or three replicate tests were conducted for each gas composition. The scatter between replicates was within 1 psi for most compositions, but occasionally larger differences were observed. The occasionally significant scatter was probably due to decomposition product residue on the electrodes, which were typically cleaned after every other test, unless visual inspection dictated cleaning between tests.
RESULTS FOR HFC-227ea WITH NITROGEN

One hundred forty one tests were conducted with HFC-227ea and either zero, five, ten, fifteen, or twenty volume percent added nitrogen in the gas mixture. The pressures measured are shown in Figure 2 as a function of the vol\% CF$_3$CHFCF$_3$ (HFC-227ea) in the gas mixture. The slopes of the five curves representing various percent nitrogen additions appear to be similar for pressures less than about 4 psig. A horizontal line representing 1 psig is also shown in Figure 2 since that is the nominal pressure rise to determine the required inerting concentration in most previous studies.

![Graph showing pressure versus volume % HFC-227ea for various nitrogen additions.](image)

**Figure 2.** Pressure Versus % HFC-227ea for Various Nitrogen Additions.

The one psig line intersects the zero nitrogen addition curve in Fig 2 at a HFC-227ea concentration of 11.7 vol\%. This value is close to the 12.0 vol\% inerting concentration reported by Heinonen and Skaggs [2] for HFC-227ea. The fact that their value is slightly higher is consistent with their use of a higher spark ignition energy (70 joules) in a slightly larger test vessel.
It is apparent from Figure 2 that pressure increases less than one psig occur at HFC-227ea concentrations up to about one vol% higher than the nominal 1-psig inerting concentration. Temperature increases for this range of HFC-227ea concentrations were in the range 0 to about 50°C, indicating that the flame from the ignition source probably did not reach the thermocouple located near the top of the vessel. Thus, this combustion regime could be termed marginal with either no or only limited flame propagation away from the igniter.

If a more conservative criterion for inerting is needed, perhaps a measured temperature rise of 30°C could be utilized in order to preclude any significant flame propagation. The inerting concentrations based on this criterion and the one psig pressure rise criterion are compared in Table 1 for the various amounts of nitrogen added.

Table 1.

<table>
<thead>
<tr>
<th>% Nitrogen Added</th>
<th>Required % HFC-227 for AT &lt; 30°C</th>
<th>Required % HFC-227 for AP &lt; 1 psig</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12.4</td>
<td>11.7</td>
</tr>
<tr>
<td>5</td>
<td>11.5</td>
<td>10.4</td>
</tr>
<tr>
<td>10</td>
<td>9.7</td>
<td>9.0</td>
</tr>
<tr>
<td>15</td>
<td>8.8</td>
<td>8.0</td>
</tr>
<tr>
<td>20</td>
<td>7.6</td>
<td>6.9</td>
</tr>
</tbody>
</table>

Results for the one psig inerting criterion in Table 1 show that the required HFC-227ea inerting concentration decreases by 1.0 to 1.4 vol% as 5 vol% nitrogen is added to the gas mixture. This is an indication of the relative inerting effectiveness of nitrogen and HFC-227ea, which has a significantly higher molar specific heat than nitrogen besides
having some chemical inhibiting effect upon decomposing.

Figure 3 shows the required HFC-227ea/nitrogen blend inverting concentration (based on the one psig criterion) as a function of nitrogen mole fraction in the blend. The all nitrogen point (42 vol% $N_2$ required to inert) is based on the data in Zabetakis [8]. The relatively large blend inverting concentrations required at high nitrogen mole fractions are again indicative of the reduced inverting efficiency of nitrogen compared to HFC-227ea.

![Blend Inverting Concentration vs N2 Mole Fraction in Blend](image)

**Figure 3.** Required $N_2$/HFC-227ea inverting concentrations as a function of $N_2$ mole fraction in the blend.

RESULTS FOR HFC-23 BLENDED WITH NITROGEN

Thirty two tests were conducted with HFC-23 and either zero or five vol % nitrogen added to the gas mixture. Resulting pressures as a function of vol % CHF, (HFC-23) are plotted in Figure 4. The one psig inverting threshold is also indicated in Fig 4. The inverting concentration indicated in Fig 4 for 0 % nitrogen is 20.1 vol % HFC-23 which is almost identical to the value in NFPA 2001 [1] based on Fenwal data.
When 5 vol % nitrogen is added to the mixture, the required CHF, inerting concentration is reduced by about 2 vol % to about **182 vol%**. This reduction is larger than the reduction previously observed with HFC-227ea because HFC-23 is less effective than HFC-227ea on a volume (molar) basis.

A comparison of the inerting concentrations corresponding to a 30°C temperature rise and a 1 psig pressure rise with HFC-23 is shown in Table 2. As with HFC-227ea, the 30°C temperature rise criterion requires a higher HFC-23 inerting concentration; in this case 0.6 to 0.7 vol % higher.

![Figure 4. N₂/CHF₃ Blend Concentration Required for Inerting as a Function of Nitrogen Fraction in Blend.](image)

Figure 4. N₂/CHF₃ Blend Concentration Required for Inerting as a Function of Nitrogen Fraction in Blend.
Table 2.
INERTING CRITERIA EFFECTS ON REQUIRED HFC-23 CONCENTRATIONS

<table>
<thead>
<tr>
<th>% Nitrogen Added</th>
<th>Required % HFC-23 for AT ≤ 30°C</th>
<th>Required % HFC-23 for AP &lt; 1 psig</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20.8</td>
<td>20.1</td>
</tr>
<tr>
<td>5</td>
<td>18.0</td>
<td>18.2</td>
</tr>
</tbody>
</table>

DESIGN APPLICATIONS

Results obtained here can be combined with nitrogen solubility data to determine inerting requirements for nitrogen pressurized HFC-227ea. For example, in the case of HFC-227ea pressurized to 42 MPa with nitrogen such that the nitrogen mole fraction in solution is 0.368. From Figure 3, the blend inerting concentration required at that nitrogen mole fraction is 165 vol %.

The HFC-227ea concentration in the blend inerted propane-air-blend mixture is 10.4 vol %. This is not only less than the required 11.7 vol % required without any added nitrogen; it is also less than the 105 vol % Lowest Observed Adverse Effect Level according to the toxicity data reported in NFPA 2001.

As additional solubility and fire/explosion suppression system specifications are developed, other applications of these results can be implemented.

REFERENCES


