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Clean agents in explosion inerting.
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Clean agents in explosion inerting

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Highlights

- Single component fluorinated halon replacements enhance fuel lean explosions, but mitigate fuel rich explosions
- Adding N₂ does not improve performance; a full N₂ concentration is needed to suppress explosions
- A Halon 1301 / N₂ mix shows synergistic performance at sub-inert concentrations
- Testing candidate agents at below inerting concentrations provides a good indication for behaviour in real life situations.

Abstract

The US Federal Aviation Administration (FAA) observed during explosion tests that at low concentrations candidate halon replacement agents increased the explosion severity instead of mitigating the event. At UTC Aerospace Systems a test program was developed to assess the behaviour of alternative agents at values below inerting concentration. Two agents were selected, C₂HF₅ (Pentafluoroethane, HFC-125) and C₆F₁₂O (FK-5-1-12, Novec™1230). Baseline tests were performed with unsuppressed C₃H₈ (propane)/air mixtures and C₃H₈/air mixtures with CF₃Br (Halon 1301) and N₂ (nitrogen). Using CF₃Br or N₂ at below inerting concentrations mitigated the explosion. C₂HF₅ was tested against C₃H₈ at stoichiometric (4 vol%) and lower explosion limit (LEL) (2 vol%). Against 4 vol% C₃H₈ the combustion was mitigated, proportional to agent concentration; however, low concentrations of C₂HF₅ with 2 vol% C₃H₈ enhanced the explosion. Tests with N₂ against a volatile mixture of C₃H₈ with C₂HF₅ showed that N₂ mitigated the events. Final tests were performed with low concentrations of C₆F₁₂O against C₃H₈/air mixtures. This showed similar behaviour to that observed with the C₂HF₅ tests. Normally during

qualification tests for new agents the stoichiometric concentration of a fuel is deemed to be the worst case scenario and the baseline against which agents are tested. The above described test results show that this assumption may need to be reconsidered. This work shows that contrary to common assumption the agents investigated did not act chemically at the flame front, but mainly cooled the flame and changed the stoichiometry, i.e. the ratio of components of the flammable mixture.

Keywords: *gaseous suppressants, clean agents, inerting, mitigation, gas vapour explosions*

1. Introduction

The Montreal Protocol banned the production of Halon 1301 (CF₃Br) and Halon 1211 (CF₂ClBr) and limited their use to critical areas including aerospace applications^[1]. A number of halon replacement agents have been developed as acceptable alternatives for industrial fire protection applications. Some of these alternatives have been subjected to tests to assess their suitability for use in aerospace applications. During qualification tests at the test facilities of the US Federal Aviation Administration (FAA) unexpected agent behaviour occurred^[2]. It was observed during simulated aerosol can explosion testing that at low concentrations certain candidate agents increased the explosion severity instead of mitigating the event. CF₃Br mitigated these explosions at all tested concentrations.

1.1. Previous research into flammability of halon replacement agents

The US National Institute for Standards & Technology (NIST) carried out significant amounts of fundamental work on various halon replacements. Several of their publications refer to observed unusual behaviour. Experimental research into the efficacy of halon alternatives showed unusually high pressure ratios for a mixture containing CH₂F₂ and C₂HF₅ (HFC-125) and significant pressure increases at lean ethane/air mixtures^[3]. Further investigation into suppression of high speed flames led to the conclusion that the tested agents could either enhance or suppress combustion, depending on their volumetric concentration. C₂HF₅ at concentrations of 5 vol% showed the highest increase in severity of deflagration^[4].

The All-Russian Research Institute for Fire Protection (VNIIPO) investigated the influence of various fluorinated halocarbons on the combustion of gaseous fuel/air mixtures in closed vessel experiments. In some tests with lean fuel mixtures and low concentrations of fluorinated halocarbon an increase of explosion pressure was observed^[5].

Theoretical research into the possible causes for these phenomena included development of calculation models to describe and predict the mechanisms of the specific explosion events related to the simulated aerosol can explosion test^{[6] [7]}. This provided some possible explanations about the chemistry involved. More practical test work was required to investigate specific properties of the subject agents and verify calculation models as existing experimental test results did not provide information relevant for the specific conditions. The fire protection industry was requested to develop a test method to rapidly screen the exothermic reaction of candidate agents in the presence of a hydrocarbon flame^[8].

1.2. Test requirements

The FAA has defined a minimum performance standard for cargo compartment protection^[9]. The specific conditions of aircraft fire protection during flight are subject to altitude changes and ventilation losses. The consequence is that the agent concentration can vary over a prolonged period of time, in which a number of fire scenarios can occur. Requirements for the performance of aviation agents can differ from what is required from suppression agents in fixed ground-based industrial systems.

The simulated aerosol can explosion test procedure consists of a heated mixture of propane (C_3H_8), ethanol (C_2H_6O) and water (H_2O) being discharged across sparking electrodes, whereby the occurring combustion / explosion pressure is being measured.

At UTC Aerospace Systems a test program was developed based on previous test results and research performed by the FAA and NIST. The subject of investigation was the behaviour of alternative agents at values below their established inerting concentration against various concentrations of gaseous fuel.

- The two agents selected for the tests were HFC-125 (C_2HF_5) and Novec™1230 ($C_6F_{12}O$).
- The fuel selected was C_3H_8 , being the most volatile component in the FAA test fuel mix.
- The test apparatus selected was a standard spherical explosion test vessel.

2. Experimental

2.1. Test materials

The following materials were used: Propane, C_3H_8 , (99.5%) supplied by BOC. Nitrogen, N_2 , (99.9%) supplied by BOC. Halon 1301, CF_3Br , (Recycled: 99.6% minimum) supplied by Kidde Graviner. HFC-125, C_2HF_5 , (99.9%) supplied by Kidde Aerospace. Novec™1230, $C_6F_{12}O$, (99.9%) supplied by Kidde Fire Protection. Air, in-house compressed, filtered, dried to laboratory standard.

2.2. Methodology

The test method was based on European standard EN 1839:2012^[10], following the protocol as set out in European standard EN 15967:2011^[11], to ensure a recognised and reproducible test set-up. The test apparatus used in this program was a spherical 43 l explosion test vessel, fitted with a spark ignition unit with tungsten electrodes positioned at the centre of the vessel. The spark discharge time was 0.5 s during all tests. The apparatus was fitted with pressure sensors and thermocouples to measure pressure rise and flame propagation during explosion tests, shown schematically in Figure 1. The positioning of the three thermocouples in the vessel in line above the ignition source gave the advantage of measuring flame propagation during explosion in the vessel, and signs of flame detachment at incomplete combustion events.

In the charts in this work the temperatures are expressed in °C ($0\text{ °C} \equiv 273.15\text{ K}$); the pressures are expressed in bar ($1\text{ bar} \equiv 100\text{ kPa}$)

2.3. Measuring equipment

2.3.1. Pressure

The pressure was monitored with piezoresistive transducers, Kistler type 4045 A2, for low pressure (0-200 kPa) during filling of the apparatus and type 4045 A20, for high pressure (0-2000 kPa) during the explosion event. The signal from the transducers was conditioned via a Kistler type 4603 amplifier to the data acquisition equipment. The measuring accuracy of the combination was better than 1% of the full scale output. All tests were performed at an initial absolute pressure of 103 kPa (\approx 1.03 bar).

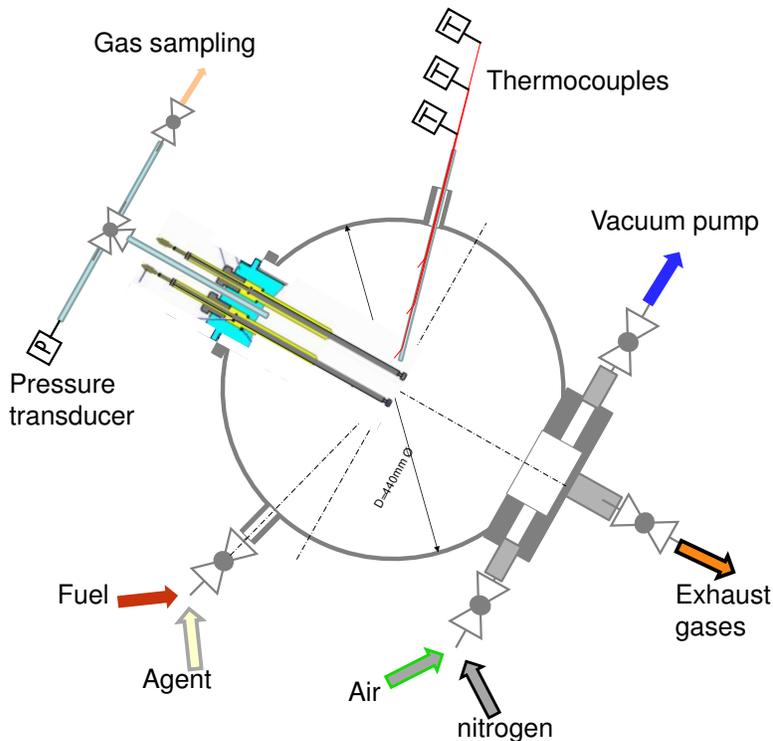


Figure 1: Schematic test vessel

2.3.2. Temperature

The internal temperature measurement was provided by three thermocouples, inserted 65 mm apart in a 6 mm stainless steel tube into the vessel. A fourth thermocouple was placed on the outside wall to monitor the skin temperature and regulate the heating. The vessel was fitted with a 270 W trace heating element for temperature control. All tests were performed with a start temperature of $307 \text{ K} \pm 4 \text{ K}$. The thermocouples used were Type K; mineral insulated, metal sheathed thermocouples with 0.5 mm sheath diameter and compliant with BS EN 60584-2 with a tolerance value according class 2^[12]. The overall diameter of 0.5 mm of the thermocouples ensures a typical response time of 0.03 s to achieve a value of 63% of the actual temperature when subjected to an instantaneous step change in temperature.

2.3.3. Data acquisition

Data logging was provided by a Dell PC, Type Optiplex 780 with Dual CPUs E8500 @ 3.16 GHz, in combination with a Data Translation module DT9805. The data acquisition software was a LabVIEW derived datalogging application. During this test series the data were captured at a frequency of 1 kHz.

2.3.4. Gas composition analysis

The gases were introduced into a vacuum vessel using their partial pressure during filling as a measure of the volumetric percentage of the components.

The portable containers with individual gases were weighed before and after use to measure the consumed mass of gas.

After filling, gas samples of the mixture were taken. These gas samples were analysed with:

- *FTIR analysis*, Bruker Equinox 55 Fourier Transform Infrared Spectrometer
- *Oxygen analyser*, Servomex Xentra 4100 paramagnetic oxygen analyser

The data of the partial pressures, mass of gas and gas analysis were collected in a spreadsheet. The combination of the three methods provided a good control mechanism to establish the accurate gas ratios.

2.3.5. Data analysis

The captured data were transferred to a self-developed MS-Excel™ spreadsheet to process and analyse the data per test. An example of data measured during an explosion test can be found in figure 2. Significant data such as explosion pressure rise ($F = P_{max}/P_0$), dP/dt , rate of pressure rise (K_g) etc. were transferred to a summary spreadsheet with the collected test results.

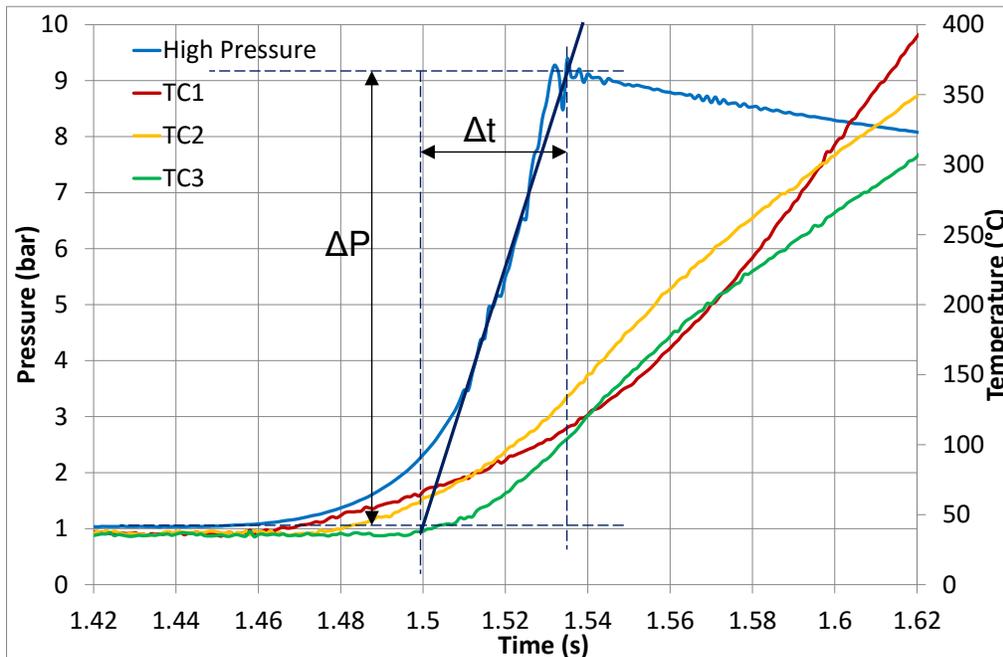


Figure 2: test result unsuppressed 4.15 vol% C₃H₈ explosion

3. Test results

Note: All points depicted in the graphs and charts showed signs of combustion, i.e. a pressure increase or heat generation more than produced by the ignition source alone.

Baseline C₃H₈/ air unsuppressed explosions were used to characterise and validate the test apparatus. Further validation was carried out using CF₃Br and N₂, two well-known gaseous suppressants with documented inerting concentrations. Two candidate agents were then evaluated: C₂HF₅, and C₆F₁₂O. In addition, tests were carried out with mixtures of C₂HF₅ and N₂. Table 1 provides an overview of the amount and type of tests performed.

Table 1, Overview Test series

Test Type	No. of Tests
Unsuppressed C ₃ H ₈ baseline tests	37
C ₃ H ₈ and CF ₃ Br baseline tests	7
C ₃ H ₈ and N ₂ baseline tests	11
C ₃ H ₈ + C ₂ HF ₅	41
C ₃ H ₈ + C ₆ F ₁₂ O	6
C ₃ H ₈ + C ₂ HF ₅ + N ₂	8

3.1. Validation Experiments

The baseline unsuppressed results agreed with published values, see Table 2. Figure 3 and 4 show graphs of the results. Inerting with N₂ provided the limiting oxygen concentration (LOC). The differences between the lower explosion limits (LEL) and the upper explosion limits (UEL) from the various sources can be explained by the differences in test standards, methods and apparatus used by the data sources. Using the observation of flame detachment in the “tube” method will detect signs of flammability at concentrations where the “bomb” method will not measure a sufficiently high pressure rise to meet the requirements [10]. Other factors are related to the dimensions of the test vessel, sensitivity of the pressure transducers and threshold for pressure increase applied. At values near the flammability limits the actual achieved pressure increase is strongly dependent on the size of the vessel. Under influence of buoyancy the flame will rise to the top of the vessel and will be quenched upon contact with the vessel wall. With increase of the size of the vessel the volume of gas mixture consumed relative to the total mixture available will diminish. The result in a larger vessel is a lower pressure rise than in a small vessel, with the same near limit fuel concentration.

Table 2, Overview C₃H₈ explosion baseline data

Parameter	LEL	UEL	P _{max}	K _G	LOC
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Data Source	vol%	vol%	bar(abs)	bar m/s	vol% O ₂
GESTIS substance database ^[13]	1.7	10.8	9.4		9.8
Senecal and Beaulieu ^[14]			8.2	76	
Bartknecht ^[15]	2.4	8.5	8.9	100	
Kuchta ^[16]	2.1	9.5			11.5
This work	2.1	10.0	9.4	92	11.3

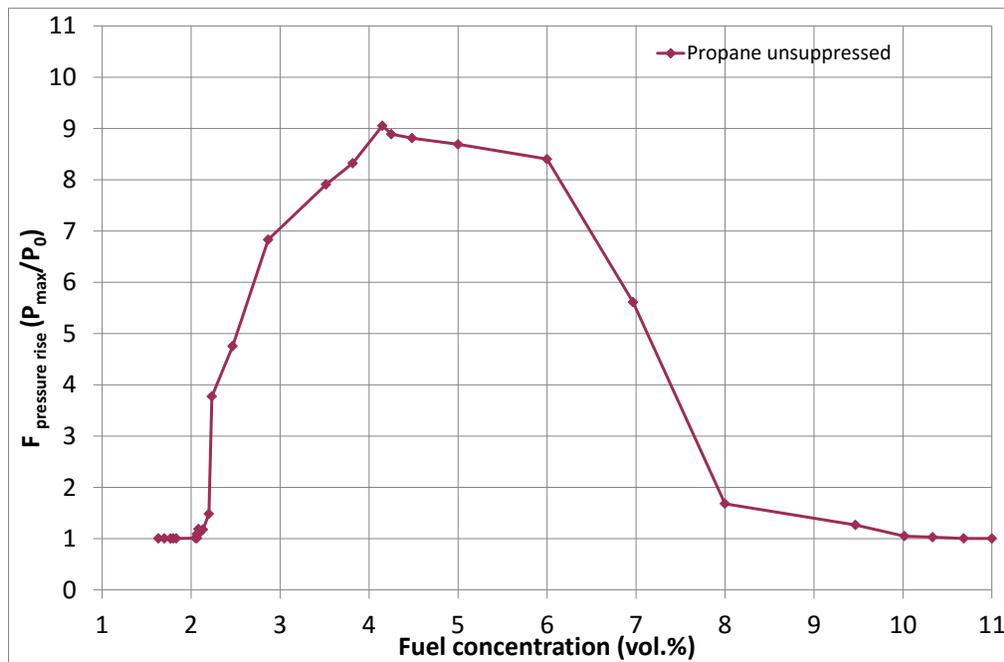


Figure 3: Pressure rise (F) unsuppressed C_3H_8 explosions

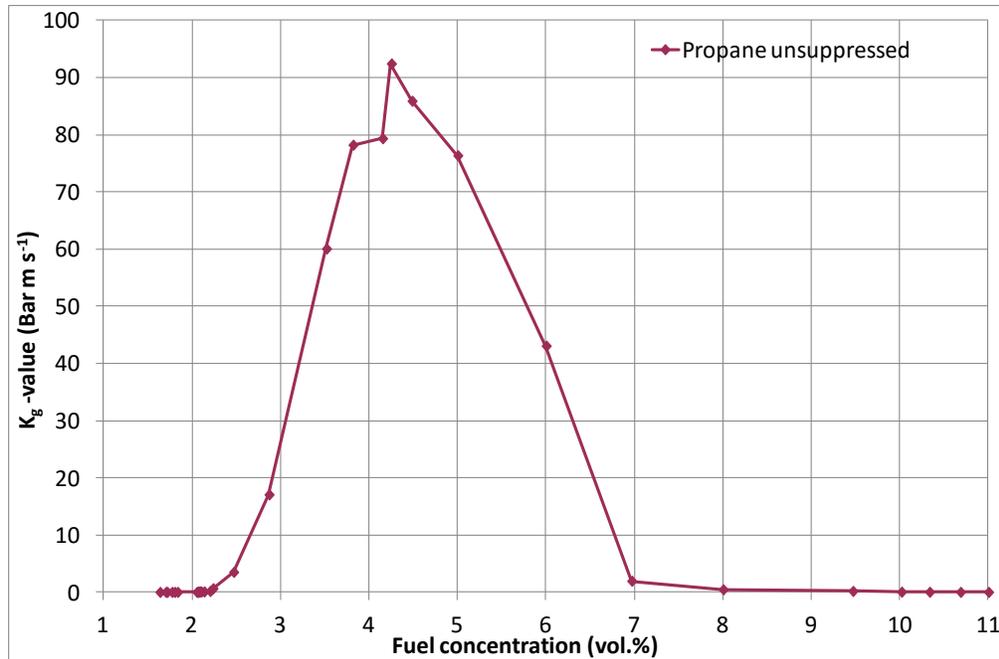


Figure 4: Rate of pressure rise (K_g) unsuppressed C_3H_8 explosions

3.2. Tests at sub-inerting concentrations

3.2.1. CF_3Br and N_2

Inerting concentration CF_3Br against C_3H_8 = 6.1 vol% (Coll, NFPA 12A, 2004) ^[17] [17]

Inerting concentration N_2 against C_3H_8 = 42 vol% (Zabetakis, NFPA 2001, 2004) ^[18] [18]

CF_3Br or N_2 when below inerting concentrations mitigated the explosion pressure in all test configurations. A combination of 2 vol% CF_3Br and 10 or 20 vol% N_2 resulted in enhanced suppression, as shown in figure 5.

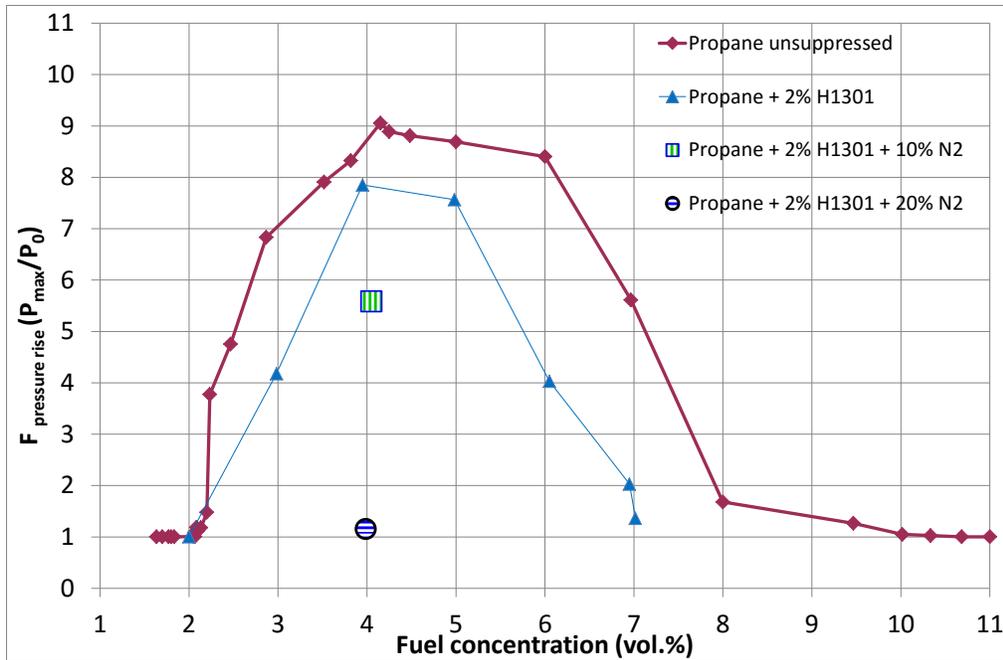


Figure 5: Pressure rise (F) partial inerting with 2 vol% CF_3Br

3.2.2. C_2HF_5 with C_3H_8

3.2.2.1. C_2HF_5 at 5%

Inerting concentration C_2HF_5 against C_3H_8 = 15.7 vol% (Senecal, NFPA 2001, 2004) ^[19] [19]

C_2HF_5 was tested in a concentration of 5 vol% against C_3H_8 . At fuel rich concentrations the explosion was mitigated, at fuel lean mixtures the explosion was enhanced, as shown in figure 6.

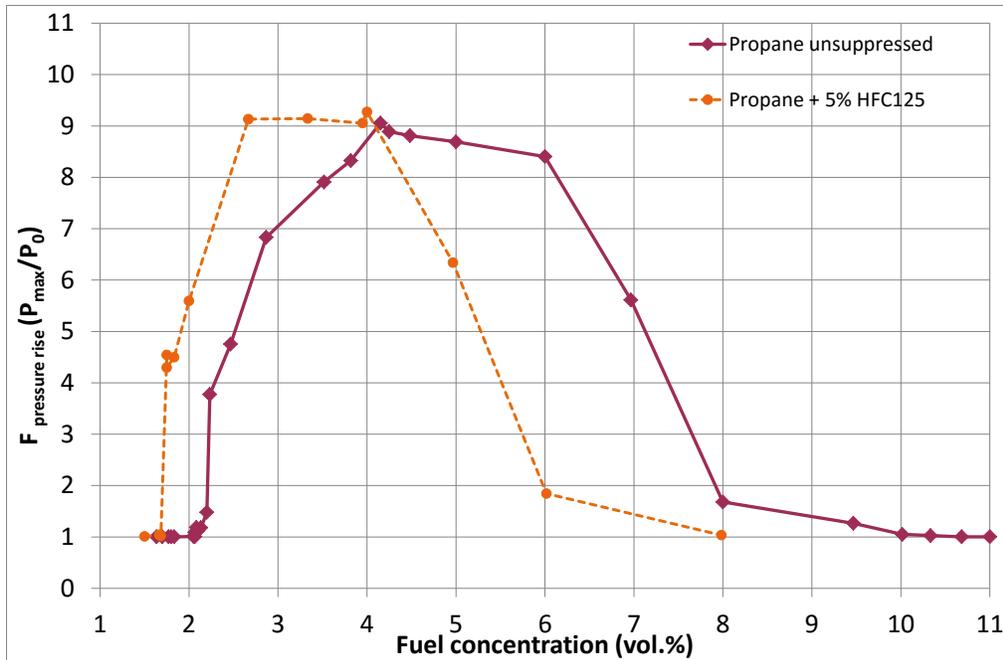


Figure 6: Pressure rise (F) partial inerting with 5 vol% C_2HF_5

3.2.2.2. C_3H_8 at 4% and 2%

N_2 and C_2HF_5 varying from 0.1x up to 0.9x of their full inerting concentration were tested against C_3H_8 /air mixtures with 4 vol% (stoichiometric) C_3H_8 and 2 vol% (2.1 vol% = Lower Explosion Limit) C_3H_8 .

In the tests with 4 vol% C_3H_8 , the addition of 4 - 5 vol% C_2HF_5 resulted in a slight increase of explosion pressure, see figure 7, but at the same time a gradual decrease in the rate of pressure rise (K_g), see figure 8. The combustion process was slowed down. It was noticed that both N_2 and C_2HF_5 needed at least 0.6x of the full inerting concentration to achieve significant explosion mitigation.

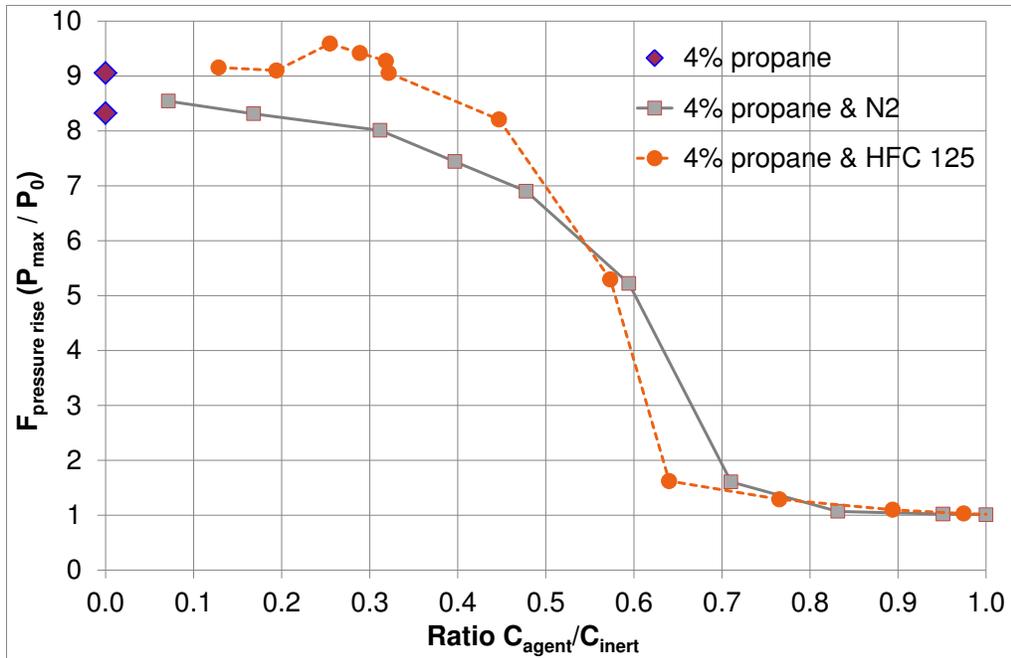


Figure 7: Pressure rise (F) partial inerting of 4 vol% C₃H₈

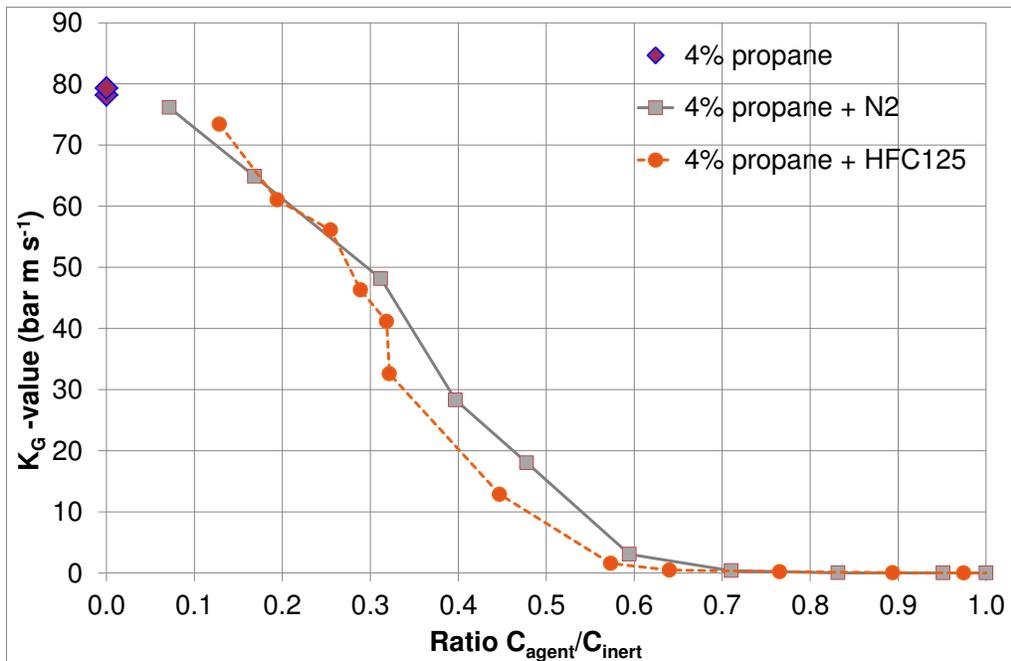


Figure 8: Rate of pressure rise (K_g) partial inerting of 4 vol% C₃H₈

In the tests with 2 vol% C₃H₈ a completely different behaviour was observed. The addition of various concentrations of C₂HF₅ turned a non-explosive C₃H₈/air mixture into a very reactive mixture with explosion overpressures up to 5 bar. The highest overpressures and rate of pressure rise were measured between 4 and 7 vol% C₂HF₅. See figure 9 and figure 10.

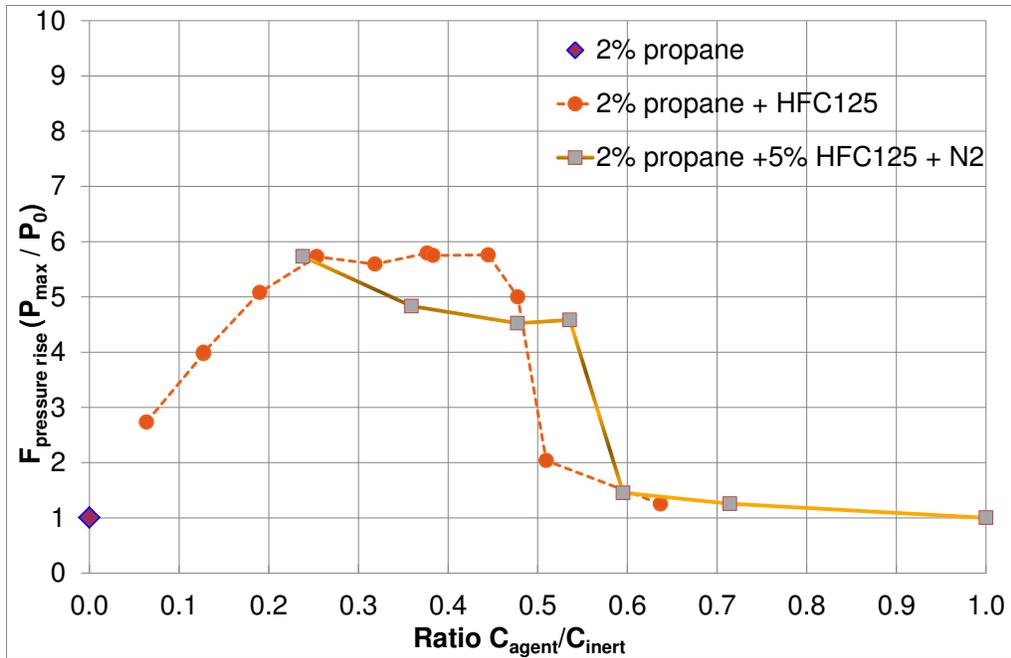


Figure 9: Pressure rise (F) partial inerting of 2 vol% C₃H₈

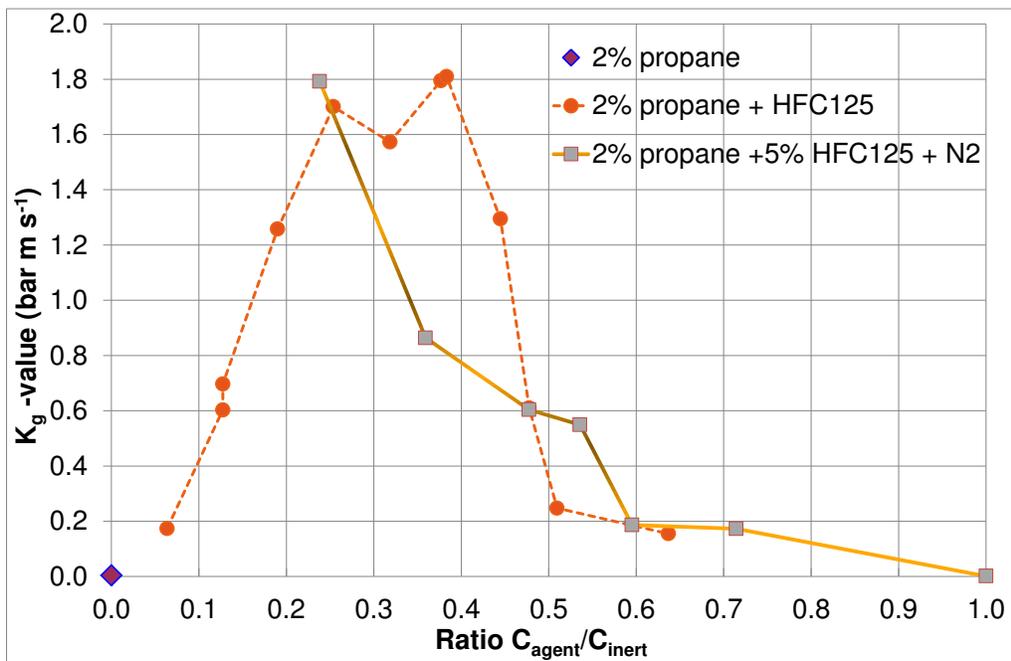


Figure 10: Rate of pressure rise (K_g) partial inerting of 2 vol% C₃H₈

Additional tests were performed to investigate the influence of N₂ on the explosion severity of the mixture of 2 vol% C₃H₈ with 5 vol% C₂HF₅. N₂ provided again significant mitigation of the event when used in concentrations of at least 0.6x of the full inerting concentration of 42 vol%. See figure 9 and figure 10.

3.2.3. C₆F₁₂O

Inerting concentration $C_6F_{12}O$ against $C_3H_8 = 8.1 \text{ vol\%}$ (Schmeer, NFPA 2001, 2004)

A final test series was performed with a low concentration, 2.5 vol% $C_6F_{12}O$ against C_3H_8 /air mixtures at various concentrations. This showed similar behaviour to that observed with the C_2HF_5 tests. At rich fuel/air mixtures (above stoichiometric concentrations) the $C_6F_{12}O$ mitigated the explosion pressure; at lean fuel/air mixtures the agent exacerbated the explosion. See figure 11.

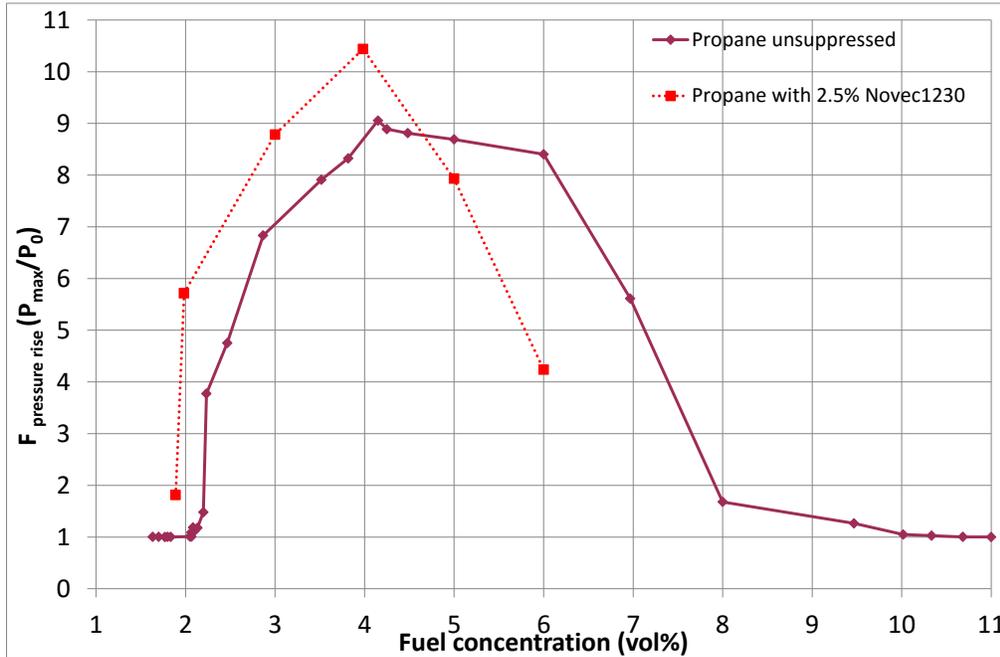


Figure 11: Pressure rise (F) partial inerting with 2.5 vol% $C_6F_{12}O$

4. Discussion

The fire suppressing property of fluorinated agents is mainly based on heat absorption, thereby cooling the flammable mixture^[20]. During this process the agent decomposes and the fluorine reacts with the hydrogen component of the fuel in an exothermic reaction, replacing the hydrogen-oxygen reaction with a hydrogen-fluorine reaction. Effectively this means that a low concentration hydrocarbon fuel combined with low concentration fluorine based suppression agent can result in a reactive flammable mixture. This was clearly demonstrated with the tests with 5 vol% C_2HF_5 and the tests with C_2HF_5 against 2 vol% C_3H_8 and further confirmed with the results of the tests with 2.5 vol% $C_6F_{12}O$. At fuel concentrations from stoichiometric and upward a low concentration fluorinated agent will aid in creating an over-rich fuel mixture with diminished combustion as a result. In this scenario the agent shows a similar suppression behaviour as an inert gas which solely acts by cooling the flammable mixture, this can be seen when comparing both N_2 and C_2HF_5 against 4 vol% C_3H_8 .

One of the objectives of this work was to develop a laboratory scale experiment to investigate specific agent properties at critical limits to provide data for validation of calculation models and to provide a rapid screening tool for candidate agents for aviation applications. The chosen test methodology and apparatus can fulfil this requirement.

5. Conclusions

Normally during qualification tests for new agents, the stoichiometric concentration of a fuel is deemed to be the worst case scenario and the baseline against which agents are tested. The above described test results show that this assumption may need to be reconsidered.

Testing candidate agents in the controlled environment of a standard spherical explosion test vessel against various fuel ratios, at a range of low agent concentrations and in combinations provides a good indication for possible behaviour in non-ideal / real life situations.

In real fire scenarios fuel air mixtures are rarely homogeneous. This means that during discharge of alternative agents in an enclosure with flammable vapours a situation may occur where the agent enhances the fire. A critical situation may occur as well when a protected enclosure is vented after successful suppression of a fire involving a fuel rich mixture.

It is important to keep this in mind during the design of a fire suppression and smoke venting system.

Acknowledgements

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