



Combustion inhibition and enhancement of premixed methane–air flames by halon replacements [☆]



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ABSTRACT

Apparent combustion enhancement by some halon replacement fire suppressants (proposed for use in aircraft cargo bays) has been observed in full-scale, constant-volume tests at the FAA. In order to explore the phenomena, laboratory-scale constant-volume combustion experiments were performed. The maximum explosion pressure and burning velocity were measured for methane–air flames with added CF₃Br (Halon 1301), C₆F₁₂O (Novec 1230), C₃H₂F₃Br (2-BTP), and C₂HF₅ (HFC-125). The explosion pressure, for initially stoichiometric flames, was increased mildly (up to 11% and 6%) with C₆F₁₂O and C₂HF₅ added at low concentrations, while at lean conditions ($\Phi = 0.6$), it was increased about 50% for added C₆F₁₂O, C₃H₂F₃Br, or C₂HF₅, at agent volume fractions $X_a = 0.02, 0.03,$ and 0.06 . The burning velocity for initially stoichiometric flames was always decreased with addition of any of the agents, whereas, for the lean conditions, it increased with added C₆F₁₂O or C₂HF₅ (32% and 14%, at $X_a = 0.01$ and 0.03). Burning velocities at higher initial pressure (3 bar) and temperature (400 K) showed lower inhibition effectiveness (than at ambient conditions) for the stoichiometric flames, and larger enhancement for the lean flames (and the effect was due primarily to the temperature increase). CF₃Br did not increase the explosion pressure or burning velocity for any of the tested conditions. Equilibrium calculations were used to interpret the experiments. The present work is consistent with the FAA results and previous analysis of the full-scale tests.

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1. Introduction

Halon 1301 (CF₃Br) is a very effective fire suppressant, but has been banned by the Montreal Protocol [1] because of its high ozone depletion potential (ODP). A critical-use exemption of recycled CF₃Br has been granted for aircraft crew compartments, engine nacelles, cargo bays, dry bays, and fuel tanks [2]. Nonetheless, the European Union is requiring replacement of CF₃Br in newly constructed aircraft by 2018 and in existing aircraft by 2040.

Three potential drop-in halon replacements were tested by the Federal Aviation Administration (FAA) for use in cargo bays, and all failed the FAA Aerosol Can Test (FAA-ACT) [3], which is one

component of the minimum performance standard for halon replacements [4]. The aerosol can test simulates the explosion of an aerosol can caused by a fire in the cargo bay. In the FAA-ACT, air and suppressant are premixed in a simulated cargo bay compartment (a pressure vessel, 11.4 m³ in volume), in which a fast-acting valve releases the simulated can contents (a two-phase spray of alcohol, propane, and water) past a continuous high-voltage DC arc. In the absence of suppressant, the pressure rise in the chamber is about 2 bar. Through repeated tests at different agent volume fractions X_a , the inerting concentration of an agent is determined as the value of X_a required to prevent significant pressure rise. The standard also requires that an agent, when added at sub-inerting concentrations, cannot produce a higher pressure rise than the uninhibited case. Unfortunately, all of the agents tested (C₆F₁₂O, Novec 1230, FK-5-1-12, CF₃CF₂C(=O)CF(CF₃)₂; C₃H₂F₃Br, 2-BTP, CH₂BrCF₃; and C₂HF₅, CHF₂CF₃, HFC-125), failed this element of the test, whereas Halon 1301 (CF₃Br) did not [3,5].

Experimental and numerical investigations of laboratory flames have described enhanced combustion with addition of halogenated suppressants, as outlined in Ref. [6]. The phenomena include

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increased total heat release, widened lean flammability limits, decreased ignition delay, and increased pressure rise. Most of the early work documented the effects, but did not analyze the causes. In more recent work [6–12], numerical combustion simulations have been applied to gain insight using recently developed (or updated) kinetic mechanisms [10,13–18]. The studies have concluded that exothermic reaction of the fire suppressants adds energy to the constant volume system, increasing the overpressure. To obtain the observed pressure rise in the FAA-ACT, agent reaction is shown to occur under very fuel-lean equivalence ratios (Φ , based on the aerosol can fuel only), nearly corresponding to pure agent and air. Kinetic calculations have indicated that addition of the agent to fuel-lean flames can increase not only the energy release, but the rate of reaction as well. Nonetheless, no laboratory-scale experiments have been conducted to validate the explanations or to explore the combustion enhancement observed in the FAA tests for the new agents $C_6F_{12}O$ and $C_3H_2F_3Br$ (and experiments for C_2HF_5 are limited [19,20]). Experimental studies of the influence of halogenated suppressants on laminar burning velocity exist [21–27], but very little data are available for agent addition to very lean hydrocarbon–air mixtures (which are of most interest with regard to the FAA tests). Previous work has shown the effectiveness of the agents $C_6F_{12}O$ and $C_3H_2F_3Br$ in standard tests for fire suppressant efficacy [28–31], but there are no data for their effect on burning velocity (a traditional method of quantifying flame inhibition effectiveness [32]).

In the present work, the agents used in the FAA-ACT (CF_3Br , $C_6F_{12}O$, $C_3H_2F_3Br$, and C_2HF_5) are added at various sub-inerting concentrations to stoichiometric and lean methane–air flames in a laboratory-scale constant volume combustion chamber to determine their influence on the maximum pressure rise and burning velocity. The effects of compressive heating on the burning velocity are also determined. The goals of the present work are to test the concepts developed via numerical simulations and analysis of the FAA tests [6,7,10], reproduce the phenomena observed in the complex full-scale FAA experiments, and explore if the laboratory-scale experiment can be used as a screening tool for cargo bay halon replacements. Although the FAA-ACT fuel is composed of propane, ethanol, and water, methane was used to simplify the experimental procedure, and to reduce the potential influence of flame stretch and radiative heat loss from soot formation. Additionally, since the experimental data are among the first to examine the effect of added $C_6F_{12}O$ and $C_3H_2F_3Br$ on premixed flames, performing experiments with a simple hydrocarbon seems appropriate (previous work showed the inhibition effectiveness of halogenated suppressants to be relatively insensitive to the hydrocarbon fuel type [33]).

2. Experimental

2.1. Apparatus and procedure

A schematic diagram of the constant volume apparatus is shown in Fig. 1. The stainless steel (316) spherical vessel is similar to previous designs [34–37], with an inner diameter of 15.24 cm, volume of 1.85 L, wall thickness of 2.54 cm, and is equipped with electrodes, an absolute pressure gage, a dynamic pressure sensor, and a thermocouple. The experiment can provide the flammability limits, explosion pressure (constant-volume), and rate of pressure rise; further processing of the latter can be used to obtain the laminar burning velocity (1-D spherical) as a function of initial pressure and temperature (which increase as the unburned gases are compressed).

A vacuum pump reduces chamber pressure below 0.1 Torr prior to reactant addition. Test mixtures are prepared in the chamber

using the partial pressure method, following injection of first liquid then gaseous reactants. Component partial pressures are determined with an absolute pressure transducer (Omega, PX811; claimed accuracy of 0.1% of reading) that is periodically calibrated against a Baratron 627D (claimed accuracy of 0.12%) and a Wallace & Tiernan 1500 pressure gage (claimed accuracy of 0.066%). Liquid suppressants ($C_6F_{12}O$ and $C_3H_2F_3Br$) are injected using a syringe and a gas-tight septum separated from the chamber by a ball valve (to ensure leak-free operation during the experiment).

The ignition system initiates reaction either via an electrical spark, or hot-wire heating. The present work uses only the former (a capacitive discharge ignition system, based on the work of Shepherd et al. [38]). A 1–15 kV power supply (Acopian) and custom-made capacitor banks (1–50 nF) provide variable ignition energies, with an estimated operating range of 0.05–500 mJ. Two tungsten electrodes form a gap in the center of the chamber. Thin electrodes (0.4 mm diameter) minimize heat loss from the flame, and the spark gap is adjustable (2 mm, typical).

The sample gases are CH_4 (Matheson Tri-Gas, 99.97% purity), CF_3Br (Great Lakes Chemical Corp., 99.6% purity), $C_6F_{12}O$ (3M, >99% purity), $C_3H_2F_3Br$ (American Pacific Corp., >99% purity), and C_2HF_5 (Allied Signal Chemicals, 99.5% purity). The air is house compressed air (filtered and dried) that is additionally conditioned with a 0.01 μm filter, carbon filter, and a desiccant bed to remove small aerosols, organic vapors, and water vapor before use. The relative humidity of the air, measured with a humidity gage (TSI VELOCICALC, 8386), is less than 2% for all tests.

For a test, the reactants are added, followed by a 5 min mixing and settling time [34]. Ignition is attempted several times, while gradually increasing the capacitor charging voltage, until ignition occurs. This ensures the ignition energy is within an order of magnitude of the minimum value. (Note that for stoichiometric iso-octane–air mixtures, Marshall et al. [39] found that the burning velocity was insensitive to the ignition energy for values up to 1000 times the minimum ignition energy.) The explosion pressure is recorded at 4000 Hz. with a dynamic pressure sensor (PCB Piezotronics, 101A06; claimed accuracy of 0.1% of reading). The product gases are immediately purged to vacuum via a large flow of N_2 (to minimize acid gas exposure to, and heating of, the experiment), and the chamber is allowed to cool for 20 min before the next experiment. Laminar burning velocity is determined from the pressure trace using a thermodynamic model, developed by Metghalchi and Keck [34,40] and further refined by others [35,41]. A brief overview of the method follows.

2.2. Burning velocity from the pressure trace

The contents of the chamber are divided into burned and unburned zones separated by a reaction sheet, assumed to be of zero thickness, spherical, and smooth (no instabilities). Initially, the unburned gas is considered mixed and at rest. As the unburned gases react, a spatially uniform increase in pressure occurs. The burned gas is in chemical equilibrium and both the burned and unburned gases are considered as ideal, semi-perfect gases. Both zones are adiabatic, and the unburned gas is isentropically compressed as the mixture reacts in the flame sheet.

With these assumptions, the instantaneous flame radius and burning velocity can be expressed in terms of the chamber pressure by applying conservation of mass. The results are given in Eqs. (1) and (2) (detailed formulation of the equations can be found in Refs. [34,41]),

$$r_f = R[1 - (1 - x_b)(P_0/P)^{1/\gamma_u}]^{1/3} \quad (1)$$

$$S_L = R/3(R/r_f)^2(P_0/P)^{1/\gamma_u}(dx_b/dt) \quad (2)$$

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