Suppression of Ignition over a Heated Metal Surface

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The effectiveness of various agents including N₂, C₂H₅F, C₂H₆F₂, CF₂Br, and CF₂I was compared in suppressing the ignition of stoichiometric mixtures of methane/air, propane/air, and ethene/air. Measurements were made of the critical ignition temperature of the reactants as they flowed over a heated nickel surface. The results showed that CF₂Br and CF₂I were both highly effectivesuppressants of ignition for all fuels studied. This was not the case for N₂, C₂H₅F, and C₂H₆F₂, which tended to have little effect on ignition unless very high agent concentrations were present, when ignition was not achieved. The effect of the average reactant velocity and the angle of approach of the reactants (relative to the heated metal surface) on the critical ignition temperature for stoichiometric ethene/air mixtures flowing over the heated nickel foil were also measured. © 1998 by The Combustion Institute

INTRODUCTION

Halon 1301, or trifluorobromomethane (CF₃Br), has been used as a fire extinguishing agent in many types of applications because of its many positive attributes. Due to its high ozone depletion potential, however, its production has been terminated. Many recent experimental studies have investigated the effectiveness of candidate replacement agents in suppressing premixed and nonpremixed flames [1]. The research presented here considers another aspect of the suppression problem, involving the impact of fire suppressants on the possible ignition of reactants flowing over a hot metal surface. This situation may be representative, for example, after suppression of a Class C fire by an agent, when electronics are still energized and the suppressant concentration is nonzero. In these cases, a condensed fuel may continue to vaporize, exist at flammable levels, and lead to the possibility of re-ignition. Although the fire may have been extinguished by a suppressant, re-ignition may still occur. Other scenarios associated with the "re-ignition" phenomena could involve a flame heated surface acting as an ignition source, such as the hot inner surface of an engine nacelle in a jet aircraft.

Conditions which lead to re-ignition are controlled by the time/temperature history of the reactive mixture and to a lesser extent by the type of metal surface and chemical composition of the fuel. Recent experiments in the Wright-Patterson Aircraft Engine Simulator show that when a liquid hydrocarbon fuel (JP-8 jet fuel or military hydraulic fluid 83282) was near a hot (700°C) metal surface, fire suppression and prevention of re-ignition required almost an order of magnitude more agent than if the hot surface were not present. Through observation, this was attributed to re-ignition [2]. Re-ignition was prevented only after very large amounts of agent were applied, presumably due to cooling of the hot metal surface.

Ignition, like flame extinction, is controlled by the Damköhler number criterion, where a critical value of the ratio of a characteristic flow time to a characteristic chemical reaction time controls the onset of ignition [3]. Ignition, however, is kinetically and phenomenologically distinct from flame extinction. The temperature regime is different, indicating likely differences in the controlling kinetic processes. For many applications, the re-ignition problem had been a concern long before the search for halon 1301 alternatives was undertaken. From a fire safety perspective, the re-ignition problem can be considered independent from the flame suppression problem, perhaps requiring a separate solution.

A standard test method for determination of auto-ignition temperatures of liquid fuels is ASTM-E 659-78 [4], which utilizes a heated 0.5 l borosilicate glass round-bottom short-necked
test flask. The auto-ignition temperature of a fluid is defined as the temperature at which its vapors will ignite in air at atmospheric pressure without an external ignition source. In the auto-ignition test, the ignition delay time varies for each experiment. The test is rather subjective and the ignition source strength is not well controlled. Because of long ignition delay times, decomposition of the original fuel molecule into a variety of intermediates may occur. In addition, the ASTM-E 659-78 test vessel may not be appropriate for use with halogenated compounds, because their decomposition products are known to react with borosilicate glass.

For many applications, the minimum hot surface ignition temperature of a reactive mixture flowing over a hot metal surface may be a more appropriate test. This is because actual conditions may be very different than the ASTM-E 659-78 test. Surface material, system pressure, air temperature, surface size, air flow, stoichiometry, surface condition, contact or residence time, and even the geometry and location of a baffle can all be factors [7-8]. A large number of studies have investigated the ignition of (uninhibited) fuel vapor on hot metal surfaces [5-17]. Such measurements serve as a basis for comparison of the hazard of different fuels. For example, the surface temperature at ignition of alkanes generally decreases with chain length [7, 8]. A large number of experiments has focused on jet fuels and hydraulic fluids used specifically in aircraft applications [5, 9, 10]. The minimum hot metal surface ignition temperature was found to increase with increasing average reactant velocity, and decrease with increased air temperature [5, 14]. All of these results are dependent on the contact surface area, the flow field, and the boundary layer configuration which controls the contact or residence time and which has a strong influence on the ignition temperature through the Damköhler number.

Few experiments, however, have been conducted to study the effectiveness of halogenated agents in suppressing ignition. Finney studied the effect of halon 1301 on the auto-ignition of propanc in a static subatmospheric system [18]. Lemon et al. tested halogenated solid/liquid/binder mixtures which adhere to hot metal surfaces in an attempt to prevent re-ignition [19]. Generally, there is a scarcity of experimental information regarding the relative effectiveness of current halogenated fire suppressants in suppressing ignition.

Some studies have considered the detailed kinetics associated with inhibition by halogenated compounds on the ignition of fuel/air mixtures in well-stirred and plug-flow reactors [20-23]. Mulholland et al. conducted inhibition experiments using chlorinated compounds in well-stirred reactors and compared these results to detailed kinetic models [21]. Both ignition and extinction conditions were modeled. Griffiths et al. compared calculated and measured auto-ignition temperatures for alkanes in a closed vessel [24].

Other studies have considered the effects of both detailed kinetics and transport on ignition near a hot surface [25-27]. Kumar [25] and Vlachos et al. [26] modeled stagnation point flow, coupled with detailed kinetics, to predict the minimum surface temperature at ignition for H2/O2/diluent and CH4/air mixtures, respectively, in the vicinity of a hot surface. Sano and Yamashita [27] developed a two-dimensional laminar flow model to investigate the ignition of methane/air mixtures flowing over a hot surface. Their results showed that ignition over a hot plate is controlled by the diffusion of heat and mass as well as chemical reactions. The chemical-flow field structure associated with pre-ignition phenomena was related to increasing concentrations of radical species such as H atom and OH close to the hot surface. The equivalence ratio and the free stream velocity of reactants had little effect on the ignition delay, which decreased exponentially with increasing area of the hot surface. These model calculations were limited to very simple chemistry due to their computationally intensive nature. Sano and Yamashita’s investigation [27], for example, was limited to C1 chemistry. Detailed measurements in boundary layer flows by Pfefferle and co-workers emphasized the importance of radical species in the ignition phenomena [28, 29].

The objective of the studies described here was to measure the relative effectiveness of halogenated agents in suppressing the ignition
of flammable reactants flowing over a hot metal surface under well-controlled conditions.

EXPERIMENTAL METHOD AND APPARATUS

The agents tested were CF3I, HFC-125 (C2HF3), and HFC-227ea (C3HF7). These agents were selected based on their candidacy as replacement agents for halon 1301 in aircraft engine nacelle applications. Of particular interest is HFC-125, because it has been selected by the U.S. Air Force as a short term replacement for halon 1301 and CF3I which is favored by several U.S. aircraft manufacturers. Measurements were also conducted using halon 1301 (CF3Br) as a performance standard and in one case with inert N2.

Figure 1 is a schematic of the experimental apparatus based on a device previously described in detail [7, 8]. In these experiments, fuel, air, and agent were all mixed before contact with the heated metal surface. Experiments were performed to determine the temperature of the hot metal surface at ignition in the presence and absence of the halogenated agents. The apparatus included a direct current power supply, a foil holder, rolled thin (13 μm) metal foil strips, fast response subminiature ungrounded type-K thermocouples with 250 μm stainless steel sheaths, fuel gas cylinders (methane, ethene, and propane with purities of 99.97, 99.5, and 99.0% by volume, respectively), rotameters for fuel, air, and agent flow control, the mixing chamber, a quartz chimney (1.1 cm diameter), and a data acquisition system. The time response of the thermocouples was estimated to be 0.4 s.

Tests were conducted using stoichiometric mixtures of premixed gaseous fuel and air. Although liquid fuels are important for many applications, use of a gaseous fuel represents a most dangerous case, i.e., when a liquid fuel has completely vaporized. Various amounts of agent were added to the mixture. The reactant mixture flowed over a heated metal foil which was held in a spring-loaded support [7], preventing warping of the foil with heating. A thin calcium silicate sheet was used to thermally isolate the foil from the brass foil holder.

A data acquisition system obtained temperature data at a rate of 2–4 Hz from the thermocouple which was situated on the back side of the hot metal foil (see Fig. 1). Forced contact was used to physically locate the thermocouple on the foil surface, opposite to the side on which the reactants flowed. Using the same apparatus, Smyth and Bryner compared the thermocouple temperature measurement technique with measurements using an optical py-
rometer [7, 8]. Their findings showed that the pyrometer measurements were typically 50-60°C more than the thermocouple measurements. The objective of this study was not to obtain absolute ignition temperature results, but was to determine the relative effect of fire suppressants on ignition temperatures.

The distance from the chimney edge to the hot metal surface was maintained at 6 mm for all tests. The flow of reactants was 912 ml/min (equal to an exit velocity of 16 cm/s from the quartz chimney), except in one series of experiments using stoichiometric ethene/air mixtures, when the flow was varied to determine its effect on the measured ignition temperature.

The nickel foil was nearly rectangular with dimensions 10.2 × 2.5 cm and a thickness of 0.013 cm. Each foil was notched, trimmed, and folded in a systematic manner such that the foil was preferentially heated along a strip 2 cm in width [7]. The effective heating area of the heated foil was thus approximately 2 × 2 cm. Approximately 40 A was necessary to heat the foil to 1000°C. Before ignition experiments were conducted, a standard burn-in procedure for the foils was executed [7, 8] using ethene/air mixtures. This procedure optimized reproducibility of the measurements.

The experiment proceeded as follows. To achieve ignition, the current through the foil was slowly increased to a value of 30-40 A at a rate of ≈ 0.2 A/s, causing a change in the metal surface temperature on the order of 7°C/s. As the current was increased, the measured thermocouple temperatures increased, and the central portion of the foil began to glow a dull red. Some local cooling of the foil was evident by the appearance of dark spots at the position of the thermocouple. Foil emission became brighter as the current was increased further. Ignition was evident when a thin blue flame was observed, appearing first near the foil surface and then flashing upstream toward the quartz chimney, where it stabilized. Upon observation of the flame, a voltage signal was manually sent to a second channel of the data acquisition system, marking the moment of ignition. The flame was then extinguished by shutting the fuel and the agent flows. The current through the metal foil was rapidly decreased by 20 A, decreasing the surface temperature by 100°C to 200°C. The same foil was used for many (> 30) ignition experiments before it failed. Failure was evident when high temperatures could not be achieved. The rate of foil failure was higher for the high temperature experiments.

The reactant mixture flowed near the heated metal surface for approximately 130 ms [8]. The angle of the flow impinging on the hot metal surface was maintained at 45°, except in one series of experiments using stoichiometric ethene/air mixtures, when the angle was varied to determine its effect on the measured ignition temperature.

Uncertainty for each measurement series was estimated to be 11°C based on a propagation of error analysis, with the uncertainty dominated by measurement variance. The average uncertainty associated with day to day variation in the measurements was much higher (nearly 40°C), possibly due to the positioning of the thermocouple with respect to the foil surface. For that reason, experiments were conducted in a systematic manner with each data point reported in Figs. 6–8 actually representing several series of measurements. Ignition measurements were first performed without an agent to establish a performance reference. A second series of experiments were performed with an agent added to the fuel/air mixture. The tests without agent addition were repeated to insure that foil oxidation did not affect the results with agent addition. In each of these series of tests, measurements were repeated at least five times to assure reproducibility. The reported values of the ignition temperature for tests without agent addition represent averages of many measurements (> 100), whereas the reported ignition temperatures for the tests with agent addition represent the difference of the average measured ignition temperatures with and without agent for that particular test series plus the average temperature with no agent for all tests.

The metals tested included stainless steel, titanium, and nickel. However, both titanium and stainless steel failed in the presence of even small agent concentrations (0.5% by volume) for temperatures below the ignition temperature, precluding any testing with these
metals. Failure was probably due to acid gas corrosion of the thin metal foils. Thus, all measurements reported here are for nickel surfaces.

RESULTS AND DISCUSSION

A number of experimental observations were made which were consistent with the concept of mixture flame speed. Under conditions of high agent loading for $\mathrm{C}_2\mathrm{HF}_3$ and $\mathrm{C}_2\mathrm{HF}_5$, instead of a blue flame flashing back upstream from the hot metal surface and stabilizing on top of the quartz chimney, a flame propagated downstream and stabilized on the downstream portion of the hot metal surface. For example, in stoichiometric ethene/air flames with the average exit velocity equal to 16 cm/s, flame stabilization occurred downstream for agent (volume based) concentrations of 3, 4, 10, and 15% for $\mathrm{CF}_3\mathrm{Br}$, $\mathrm{CF}_3\mathrm{I}$, $\mathrm{C}_2\mathrm{HF}_3$, and $\mathrm{C}_2\mathrm{HF}_5$, respectively. This was consistent with flame speeds of stoichiometric ethene/air mixtures where calculated flame speeds of 16 cm/s were achieved for agent concentrations of 3.5, 4.0, and 7.0% for $\mathrm{CF}_3\mathrm{Br}$, $\mathrm{CF}_3\mathrm{I}$, and $\mathrm{C}_2\mathrm{HF}_3$, respectively [30]. Flame speeds for $\mathrm{C}_2\mathrm{HF}_5$ have not been measured or calculated, so a comparison is impossible.

Further increases in agent concentration led to conditions where flame ignition was not achievable, even for high metal surface temperatures ($\approx 1200^\circ\mathrm{C}$). Instead, smoke was observed to roll off the hot metal surface. For example, in stoichiometric ethene/air mixtures, ignition did not occur for agent (volume based) concentrations of 4, 5, 15, and 20% for $\mathrm{CF}_3\mathrm{Br}$, $\mathrm{CF}_3\mathrm{I}$, $\mathrm{C}_2\mathrm{HF}_3$, and $\mathrm{C}_2\mathrm{HF}_5$, respectively. To prevent ignition under conditions of exposure to a hot surface required higher agent concentration than suppression of cup burner or opposed flow diffusion flames burning typical hydrocarbon fuels [1]. Experiments using propane and methane yielded nearly identical results. It is possible, however, that ignition can occur at higher foil temperatures (greater than $1200^\circ\mathrm{C}$).

Figure 2 shows a typical temperature/time data set measuring the critical (or minimum) surface temperature required to obtain ignition for a stoichiometric methane/air mixture. The results in Fig. 2 were for a stoichiometric methane/air mixture flowing over a heated nickel foil. The temperature was slowly increased ($\approx 7^\circ\mathrm{C}/\mathrm{s}$) until ignition was observed, as indicated by the arrow in the figure. Immediately after ignition, the temperature increased due to flame heating of the metal surface. A few seconds later (at time $\approx 217$ s in the figure), the power through the metal foil was rapidly decreased.

The data in Fig. 2 are a subset of the data shown in Fig. 3, which shows a series of ignition experiments for stoichiometric methane/air mixtures with and without the addition of 1% (by volume) halon 1301 ($\mathrm{CF}_3\mathrm{Br}$) flowing over a hot nickel surface. The plate temperature was increased until ignition was
observed, indicated by the arrows in the figure. The flame was then extinguished, the metal surface temperature reduced, and the experiment repeated. A significant difference due to the presence of even a small halon 1301 concentration was observed. Repeatability of the experiment is indicated by the results shown in Fig. 3.

Figure 4 shows the critical ignition temperature as a function of the velocity of the reactant stream for a stoichiometric ethene/air mixture. For comparison, the results of Smyth and Bryner [7, 8] are also shown. The measurements confirmed the results of Smyth and Bryner [7, 8], showing that changes in reactant flow had a very small impact on the measured ignition temperature for velocities from 8 to 24 cm/s. Because decreased velocities imply an increase in residence time for the reactants near the heated metal surface, decreased ignition temperatures may have been expected from these measurements. In their two-dimensional laminar flow model calculations, however, Sano and Yamashita [27] showed that the free stream velocity in methane/air mixtures had little effect on the ignition delay (which is a measure of the ease of ignition), consistent with our experimental results. This implies that the free stream velocity had little impact on processes occurring at locations close to the hot metal surface and within the boundary layer, where peak temperatures and radical concentrations are expected [28, 29].

Contrary to expectations, the measured ignition temperature increased somewhat (≈ 30°C) for decreased velocities (at 4 and 5 cm/s). This may have been due to air entrainment into the mixture for very low velocities, altering the mixture from stoichiometric to lean, requiring higher temperatures to achieve ignition. All further tests reported here were conducted for an average reactant velocity equal to 16 cm/s where the ignition temperature had little sensitivity to the mixture velocity.

Figure 5 shows the critical ignition temperature as a function of the angle of approach of the reactant stream toward the heated nickel surface for a stoichiometric ethene/air mixture. For all cases, the flow was laminar with Re varying from 0.001 to 0.01. The angle of the flow impinging on the hot metal surface was varied from 5 to 90° in stoichiometric ethene/air mixtures to determine its effect on the measured ignition temperature. For all of these measurements, the average reactant velocity exiting the chimney was 16 cm/s and the distance to the metal surface was maintained at 6 mm. Figure 5 shows that there was essentially no change in the measured ignition temperature with reactant approach angle relative to the metal surface until the reactant stream flowed at an angle equal to 90° in a stagnation point flow. Under those conditions, the ignition temperature was measured to be nearly 80°C less than for the other angles. In the stagnation point flow configuration, there was some uncertainty about the primary ignition location, which appeared to occur on the back side of the metal foil. A possible explanation for this is that a portion of the reactants diffused behind the foil and had long contact time with the back of the foil. A smaller ignition temperature would be expected in such a case. All other experiments were performed for a 45° reactant approach angle, where the ignition temperature showed little sensitivity to changes in the angle.

Figures 6–8 show the measured nickel surface temperature required to obtain ignition as a function of agent concentration for stoichiometric methane/air, ethene/air, and propane/air mixtures, respectively, as a function of agent concentration in the mixture. The dotted lines in the figures represent the ignition temperature in the absence of agent. For the agent addition tests, data points above the
dotted lines represent ignition suppression by the agent, whereas data below the lines represented ignition promotion. Methane required the highest ignition temperature followed by propane and then ethene. The measured ignition temperatures in the absence of agent were approximately 970, 910, and 760°C for the methane/air, propane/air, and ethene/air mixtures, respectively, consistent with the results of Smyth and Bryner [7, 8] and Laudenbauer [6].

The presence of the halogenated agents influenced measured ignition temperature depending on agent type. Figures 6–8 show that CF₃Br and CF₃I were consistently effective suppressants of ignition, significantly increasing the ignition temperature with small agent concentrations for all three fuels. Figure 7 shows that N₂ has little impact on the ignition temperature for even high concentrations (≈ 30%). C₂HF₃, on the other hand, behaved differently depending on fuel type. C₂HF₃ acted as a weak inhibitor of ignition in the ethene/air mixtures causing a moderate increase in the ignition temperature. For the alkanes, however, C₂HF₃ appeared to slightly promote ignition. C₂HF₅ also acted as a promoter, causing a decrease in the ignition temperature for methane/air mixtures (see Fig. 6).

Because gas-phase ignition is influenced by radical producing reactions [27–30], it is not surprising that CF₃Br and CF₃I influence ignition. These compounds are well known flame inhibitors, acting to decrease radical concentrations in flames through scavenging reactions associated with Br and I containing intermediates [30–32]. These molecules do not readily break down until they are exposed to moderate to elevated temperatures. For example, the characteristic time for CF₃Br decomposition at
Fig. 8. The critical ignition temperature as a function of agent concentration for stoichiometric propane/air mixtures flowing over a heated nickel foil.

730°C is 3 s [23]. This time decreases very rapidly with temperature [33]. The characteristic time for CF₃I breakdown is almost an order of magnitude faster than for CF₃Br [23]. Thus, I and Br containing intermediates will exist in the heated boundary layers of the experiments reported here. It is not unexpected that these intermediates participate in pre-ignition chemistry, impacting radical concentrations and thereby minimum ignition temperatures. It is left to future research to explain the details of the ignition suppression mechanism for the halogen containing compounds. Models of such systems will require consideration of both transport and detailed inhibition chemistry.

CONCLUSIONS

The effectiveness of various agents including N₂, C₂H₂F₃, C₂H₅F₂, CF₃Br, and CF₃I were compared in suppressing the ignition of stoichiometric mixtures of methane/air, propane/air, and ethene/air flowing over a heated nickel surface. CF₃Br and CF₃I are shown to be significantly more effective than N₂, C₂H₂F₃, or C₂H₅F₂ in suppressing ignition of the fuel/air mixtures. For small concentrations of these agents, ignition required substantially higher surface temperatures than the case with no agent added. The results were generally consistent for the three fuels except for the case of C₂H₅F₂, which behaved differently depending on fuel type. Whereas C₂H₅F₂ acted as a weak inhibitor of ignition in the ethene/air mixtures, it appeared to slightly promote ignition for the methane and propane mixtures. C₂H₅I also acted as a slight promoter for stoichiometric methane/air mixtures, causing a small decrease in the ignition temperature. In general, however, N₂, C₂H₂F₃, and C₂H₅F₂ tended to have little effect on ignition unless very high agent concentrations were present, in which case ignition was not achieved. In summary, CF₃I and CF₃Br were highly effective ignition suppressants, whereas HFC-227 and HFC-125 were very poor ignition suppressants.

The results reported here suggest that agent selection for a specific fire application should carefully consider possible hazards associated with fuel re-ignition when nearby electronics remain energized or when surfaces in the flow field are heated. In these cases, prevention of ignition requires a higher agent concentration than suppression of cup burner or opposed flow diffusion flames burning typical hydrocarbon fuels [34]. In addition, the re-ignition problem may be more severe with use of C₂H₂F₃, for example, as compared to CF₃Br. At best, C₂H₂F₃ has little impact on ignition suppression. A possible practical approach to deal with the Class C fire suppression problem is to consider using an agent target concentration in the fire zone which renders even the most flammable mixtures nonflammable. Under such conditions, both flame suppression and the prevention of re-ignition are assured. Flammability limits must be determined for the particular fuel/air/agent mixture of interest with consideration of the relevant flow and temperature field. If agent target concentrations are based on flammability limits, then it is anticipated that critical agent concentrations will be two to three times that required for suppression of simple nonpremixed flame such as cup burner or opposed flow diffusion flames [34, 35]. For systems with moderate ventilation, prevention of re-ignition may be sustainable only for a period of time on the order of the agent injection duration. When the agent concentration falls below the flammability limits, re-ignition will be possible and other prevention strategies should be considered.
SUPPRESSION OF IGNITION

The results reported here are pertinent to cases where the hot surface is on the order of 1 cm in diameter and the flow contact time is on the order of 100 ms. These measurements are valuable in comparing the effect of halogenated agents on ignition temperatures under well-controlled experimental conditions. Similar measurements are also of interest for applications where heated surface areas and contact times are larger, and where lower ignition temperatures are anticipated. At lower temperatures, different mechanisms are expected to dominate the ignition kinetics [30]. In this regime, it is of interest to determine if iodine and bromine containing compounds are as efficient suppressants of ignition as they are at elevated temperatures.

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