Influence of Water Vapor on Hydrocarbon Combustion in the Presence of Hydrofluorocarbon Agents *

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Abstract
The effect of water vapor on hydrocarbon combustion (CH₄, C₂H₄, C₃H₈) was studied in the presence of an HFC agent (HFC-125). The effect depends on the F/H ratio of the initial mixture. A promotion effect was observed in mixtures with the F/H ratios ranging approximately from 0.9 to 2. The calculated maximum increase in peak flame temperature was in the range of 100 K to 150 K, and in burning velocity, in the range of 1 cm/s to 2 cm/s. The change of the ratio from F/H ratio < 1 to the conditions with the F/H ratio > 1 corresponds to the disappearance of H₂O and a substantial increase of CF₂O in the combustion products. Thermodynamic and laminar premix flame calculations demonstrate that “extra” fluorine, which is in excess of hydrogen (F/H > 1), reacts with added H₂O forming HF molecules. Calculations demonstrate that the equilibrium volume fractions of the fluorine atom can be as large as 0.5 % to 3 % for mixtures with an F/H > 1. The main reaction of H₂O conversion to HF is the F+H₂O=HF+OH reaction. Dependencies of the F/H ratio as a function of HFC-125 (C₂F₅H) concentration and showing the possible range of mixture compositions for a promotion effect, were generated for methane, ethylene and heptane at different equivalence ratios.

Key words: inhibition, promotion, fire suppression, water vapor, HFC 125, H₂O, HFC, halon replacement

1. Introduction
The promotion of combustion by some halon replacements has been observed in a required FAA qualifying test (the aerosol can test) for the use of fire suppressants in cargo bays of commercial aircraft [1, 2]. The aerosol can test simulates the explosion of a spray can (e.g. hair spray) contained in luggage during a cargo-bay fire. The simulated contents of the can (5.87 moles of ethanol, 2.05 moles of propane, and 5 moles of liquid water) have a high fraction of water, and hence, it is of value to explore the possibility of a promotion of combustion by water vapor. The effect of water vapor on the flammability limits [3, 4] has been demonstrated, and the importance of the halogen to hydrogen ratio of the reactants on the equilibrium products and overall reaction rate has been known for some time [5-7]. Nonetheless, there has been comparatively little done to understand the kinetic effects of water vapor in these systems.

In fires, added water is typically considered to be inert, and to reduce overall reaction rates thermally by increasing the latent and sensible heat of the mixture. In the case of flames with added HFCs (or flames of HFCs), however, chain-branching reactions are greatly reduced
by the radical trapping properties of the HFC (to form HF), and the systems are typically low in radicals [8]. Data of Takizawa et al [7] and our flame equilibrium calculations demonstrate that water should convert to HF if the initial composition corresponds to mixtures with [F]/[H]>1. Hence, added water can influence the reaction in a flame zone. Also, by allowing the formation of the very stable product HF, it can increase the temperature. Thus, it is of value to explore the kinetic effects of water vapor on combustion of hydrocarbon-air-hydrofluorocarbon mixtures. Sources of H$_2$O in fires include the fuel, water vapor in the ambient air, combustion products and added water. The goal of the present work was to explore the regimes of inhibition versus promotion by added water vapor, and in cases of promotion, identify the responsible reactions. We wanted to answer the questions: what is the effect of the H$_2$O conversion to HF, which reactions are responsible for this conversion, and are there any enhancement effects of the combustion process as a result of H$_2$O addition?

2. Kinetic model and calculation procedure

Modeling studies were conducted for methane, ethylene and propane combustion inhibited by C$_2$F$_5$H agent (HFC-125). The C1–C4 model of Wang et al [9] was used for the hydrocarbon flame, which was used in our previous work [10]. The mechanism to describe reactions of the hydrofluorocarbons (HFCs) in hydrocarbon flames is based on the C$_1$–C$_2$ NIST HFC mechanism [11], including modifications as summarized in ref. [10]. In addition, recent modeling of the combustion of pure fluorocarbon agents [12] suggests that relatively large concentrations of F atoms are observed in the reaction and post-flame zones. Thus, some formation of the F$_2$ species should be expected, and reactions related to the formation and consumption of F$_2$ as described in [13] have been added. The Chemkin set of programs of Sandia Laboratory was used for combustion equilibrium calculations and for modeling of laminar premix flames.

3. Results and discussion

Figure 1 (1a, 1b) contains dependencies of equilibrium concentrations of major species and flame temperature for lean methane/air (0.71 equivalence ratio, C$_2$F$_5$H volume fraction of 7 %, initial F/H=1.06) and ethylene/air mixtures (0.6 equivalence ratio, C$_2$F$_5$H volume fraction of 5.1 %, initial F/H=1.25) as a function of H$_2$O concentration. It can be seen that the addition of H$_2$O (to mixtures with the F/H ratio > 1) increases the combustion temperature, and the HF concentration in products, and decreases CF$_2$O concentration. In the vicinity of F/H=1,
significant decreases of CF\textsubscript{2}O and F atom concentrations are observed with a simultaneous increase of equilibrium concentration of H\textsubscript{2}O (an increase of the equilibrium of H, O and OH radical concentrations is also observed). The ratio F/H =1 (Fig.1b) approximately corresponds to saturated concentration of water vapor (about 2.5% volume fraction). It can be seen that added H\textsubscript{2}O is converted to HF at the F/H ratio >1. The maximum temperature increase as a result of H\textsubscript{2}O addition is about 110K (Fig.1b). It is of interest that flame equilibrium calculations demonstrate a large equilibrium concentration of the free fluorine atom with the addition of C\textsubscript{2}F\textsubscript{5}H agent to lean mixtures for ratios F/H >1, e.g. F atom volume fraction is about 3\% for ethylene at H\textsubscript{2}O = 0 (Fig. 1b).

Results of Takizawa et al [7] and our flame equilibrium calculations demonstrate that the products for hydrocarbon combustion with HFC additives can be approximately described by two sets of major products: (1) CO\textsubscript{2}+HF+H\textsubscript{2}O at F/H<1, and, (2) CO\textsubscript{2}+HF+CF\textsubscript{2}O(CF\textsubscript{4}) at F/H>1. Calculations show that the intermediate case, F/H=1, roughly corresponds to the complete conversion of F atoms to HF acid with major combustion products CO\textsubscript{2} and HF and with small amounts of H\textsubscript{2}O and CF\textsubscript{2}O. Combustion of the mixture of hydrocarbon (C\textsubscript{c1}H\textsubscript{h1}) with added HFC (C\textsubscript{c2}H\textsubscript{h2}F\textsubscript{f}) in air corresponds to the following approximate stoichiometric equation at F/H <1:

\[
C_{c1}H_{h1} + z C_{c2}H_{h2}F_{f} + \left[ c_{1}+z c_{2}+(h_{1}+zh_{2}-zf)/4 \right] O_{2} = (c_{1}+z c_{2}) C O_{2} + f HF + \left[ (h_{1}+zh_{2}-zf)/2 \right] H_{2}O
\]

Stoichiometric HFC concentration (volume fraction) is determined by the relationship (similar to the relationship of Takizawa et al [7])

\[
[HFC]_{st} = z / \{1+z+100[c_{1}+z c_{2}+(h_{1}+zh_{2}-zf)/4]/21\}.
\]

Approximate stoichiometric equation at F/H=1 with the addition of H\textsubscript{2}O is as follows:

\[
C_{c1}H_{h1} + z C_{c2}H_{h2}F_{f} + x H_{2}O + (c+zc2-a/2)O_{2} = (c+zc2) C O_{2} + (h+zh2+2a)HF.
\]

Stoichiometric amount of H\textsubscript{2}O (volume fraction) is determined by the relationship:

\[
x_{st} = (zf-h_{1}-zh_{2})/2.
\]

Combustion temperatures and equilibrium products of HFC inhibited hydrocarbon flames show a significant dependence on the F/H ratio. For F/H<1, there is not enough initial fluorine to convert available hydrogen into HF, and the remaining hydrogen reacts with the formation of H\textsubscript{2}O as a main product. For mixtures with ratio F/H>1, formation of water is not observed; HF is the main hydrogen containing product. The maximum increase in temperature was about 100-150\degree K for considered cases. The maximum temperature is observed at F/H ratios slightly less
than 1. Note that Takizawa et al [7] discussed the composition of combustion products of HFC agents in air and experimentally measured the composition of products (HFC/air systems).

Figure 2 demonstrates the dependencies of burning velocity of lean methane flame (0.71 equivalence ratio) on H2O concentration at different initial C2F5H concentrations, corresponding to different initial F/H ratios for dry mixtures (the corresponding ratio is shown in brackets). An increase of C2F5H concentration in the mixture decreases burning velocity. However, an increase of the HFC agent concentration increases the F/H ratio and, for C2F5H volume fractions of 6%, 6.5%, 7% and 7.65%, the addition of H2O increases the burning velocity. Thus with the increase of initial F/H ratio (increase of C2F5H concentration), the effect of water is changed from suppression to promotion.

The maximum burning velocity increase was approximately 1 cm/s for these conditions. The maximum velocity was observed at approximately the F/H ratio of 0.9 and at adiabatic temperatures slightly less than the maximum adiabatic temperature. Modeling results show that in the range of F/H ratios of 0.9 to approximately 2 (depending on the system), added water vapor increases burning velocity and temperature. Figure 3 contains concentration profiles of the major species in C2F5H inhibited methane flame with added water at F/H>1. It demonstrates again that the main H-containing product is HF, and that the initially added water reacts to form HF in the flame reaction zone. The reaction pathway analysis (laminar premixed flame calculations) shows that the main reaction contributing to the conversion of water to HF is the reaction of the fluorine atom with H2O

\[ \text{F} + \text{H}_2\text{O} = \text{HF} + \text{OH}. \]

This reaction leads also to the formation of the OH radical participating in further reactions of fuel conversion. The main source of F atoms is the decomposition of the FCO radical,

\[ \text{CFO} + \text{M} = \text{CO} + \text{F} + \text{M} \]

The FCO radical is mostly formed in the reactions:

\[ \text{CF} + \text{O}_2 = \text{CFO} + \text{O} \]
\[ \text{CF}_2\text{O} + \text{H} = \text{CFO} + \text{HF} \]
\[ \text{CF}_2 + \text{O} = \text{CFO} + \text{F} \]
\[ \text{CF}_2 + \text{OH} = \text{CFO} + \text{HF}. \]

As noted above, the equilibrium concentration of the F atom can be as high as 0.005 to 0.03 volume fraction at F/H >1. However, the observed typical F atom volume fraction in the
flame reaction zone are in the range $10^{-4}$ and $10^{-3}$ at these F/H ratios. A gradual increase of the F atom concentration is observed in the post-flame zone as a result of further slow post-flame reactions of fluorinated products with F atom formation. Naturally at this level of F atom concentrations, the contribution of reactions with F is increased substantially.

Favorable conditions to observe the promotion effect of H$_2$O are lean mixtures and fuels with reduced hydrogen content (low H/C ratio, unsaturated hydrocarbons), thus the ratio F/H=1 is reached at a smaller concentration of HFC agent. Figure 4(a-c) shows the dependencies of the F/H ratio on C$_2$F$_5$H concentration for methane, ethylene and heptane at different equivalence ratios (H$_2$O=0). These dependencies provide an initial estimate of conditions where the promotion effect of the addition of water vapor can be expected. The line F/H=1 shows the mixture composition corresponding approximately to the limit of H$_2$O promotion. The promotion effect disappears below this line. Addition of water decreases the F/H ratio for the same equivalence ratio, and a promotion effect should be observed for mixture compositions with F/H>1.

It might be considered that the promotion effect is relatively small. However, it is important that the promotion effect of water vapor is observed in a rather large range of H$_2$O and HFC concentrations. Additionally it is possible to speculate that in the vicinity of flammability limits for the suitable F/H ratios, an initially non-flammable mixture might become flammable with the addition of water vapor. Thus assuming that the 5 cm/s level of adiabatic burning velocity corresponds to flame extinction [14, 15], the addition of H$_2$O for C$_2$F$_5$H volume fraction of 7.65 % (Fig.2) shifts the mixture from the initially non-combustible conditions to flammable conditions. Note that Kondo et al [3, 4] recently found experimentally that the increase of water vapor pressure increases the flammability range of several fluorohydrocarbon refrigerents (e.g. R-410A, which is the mixture of CH$_2$F$_2$ and C$_2$F$_5$H) in air. It was also demonstrated that a non-combustible mixture of several HFC refrigerants with air may become combustible with the addition of water vapor [3].

Note that most of the present results are obtained for water concentrations up to approximately saturated water vapor concentration at ambient conditions. The use of preheated systems and the addition of water as a fine mist increases the range of added water concentrations and might enhance the promotion effects for corresponding concentrations of HFC agent. Thermodynamic calculations demonstrate that the effect is observed for both gas
and liquid phase water additions. The addition of water in a liquid phase (rather than gas phase) reduces the flame temperature increases by 30 K to 40 K. Several laminar flame calculations were performed for lean ethylene- and propane-air mixtures with added C₂F₅H and H₂O, and additionally for pure C₂F₅H- and 2-BTP-air compositions with added H₂O. These calculations also demonstrate that the addition of water vapor leads to an increase in burning velocities and flame temperatures for systems with initial F/H ratio >1. The observed maximum increases in burning velocity were approximately 2 cm/s with H₂O addition for the considered cases.

4. Conclusions

In this work we studied the promotion effect of water vapor addition on HFC inhibited flames. The influence is observed in a range of initial conditions close to lean flammability limits (where the ratio F/H is close to 1). The following conclusions can be drawn from this work:

1) A promotion effect of H₂O addition to the HFC inhibited flames was observed. The maximum increase of flame temperature was approximately 100 K to 150° K, and the maximum burning velocity increase was 1 cm/s to 2 cm/s as a result of H₂O addition. The promotion effect was observed in the range of F/H ratios between approximately 0.9 and 2.

2) The promotion effect is caused by the conversion of hydrogen atoms from water to HF, a thermodynamically preferable process which is important for mixtures with F/H ratios >1. With H₂O addition the maximum combustion temperature was observed in the vicinity of F/H=1 ratio and the maximum burning velocity was observed at F/H ratios close to 0.9.

3) Mixture compositions with F/H > 1 correspond to lean flames, systems close to lean flammability limits, and systems with the reduced H/C ratios (unsaturated hydrocarbons). Calculations of F/H ratios as a function of the HFC agent concentration for different systems, and equivalence ratios show that practically all lean HFC inhibited systems close to flammability limits should experience a promotional effect with the addition of water.

4) The main reaction responsible for the conversion of H₂O to HF is H₂O+F=HF+OH. The major source of the F atom is the decomposition of FCO radical. The change of ratio from F/H<1 to F/H>1 corresponds to the disappearance of H₂O and a substantial increase of CF₂O in the combustion products.

5) Flame equilibrium calculations demonstrate a rather large fluorine atom volume fraction (0.5% to 3%) at F/H>1. With the addition of H₂O, the F atom concentration decreases, with a large drop observed, particularly in the vicinity of F/H=1.
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5. References.

Figure captions:

Figure 1a. Flame equilibrium concentrations of the major species and temperature for methane flame as a function of H2O concentration (0.71 equivalence ratio; C2F5H=0.07 volume fraction at [H2O]=0; CH4:air:C2F5H ratio was kept constant, 298 K, 1 bar, F/H=1.06 for dry mixture).

Figure 1b. Flame equilibrium concentrations of the major species (volume fractions) and temperature for ethylene flame as a function of F/H ratio (0.6 equivalence ratio; C2F5H=0.051 volume fraction at [H2O]=0; C2H4:air:C2F5H ratio was kept constant, 298 K, 1 bar).

Figure 2. Burning velocity of inhibited methane flame as a function of added H2O at different C2F5H initial concentrations (F/H ratios are provided for dry mixtures in the brackets; 0.71 equivalence ratio; the CH4:air:C2F5H ratio was kept constant, 298 K, 1 bar).

Figure 3. Flame structure of methane flame inhibited by C2F5H and with added H2O (0.71 equivalence ratio; C2F5H – 7.5%; H2O-2.05%, 5.25 cm/s burning velocity, 300 K, 1 bar, F/H=0.96).

Figure 4(a-c). Dependence of F/H ratio on C2F5H concentration at different equivalence ratios (no H2O added; a) methane flame; b) ethylene flame; c) heptane flame)
Figure 1a.

![Graph showing F/H ratio vs. H2O mole fraction with temperature on the x-axis and species volume fraction on the y-axis.]

Figure 1b.

![Graph showing F/H ratio vs. H2O volume fraction with temperature on the x-axis and species volume fraction on the y-axis.]

Species:
- H2O
- CO2
- CO
- F
- CF2O
- HF
- O2
Figure 3.
Figure 4.

a) Methane flame

b) Ethylene flame
c) Heptane flame