



## Brief Communications

# Influence of water vapor on hydrocarbon combustion in the presence of hydrofluorocarbon agents <sup>☆</sup>



Valeri I. Babushok <sup>a,\*</sup>, Gregory T. Linteris <sup>a</sup>, Patrick T. Baker <sup>b</sup>

<sup>a</sup> National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

<sup>b</sup> The Boeing Company, Seattle, WA 98124, USA

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## ABSTRACT

The effect of water vapor on hydrocarbon combustion (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>) 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 100–150 K, and in burning velocity, in the range of 1–2 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 H<sub>2</sub>O and a substantial increase of CF<sub>2</sub>O 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 H<sub>2</sub>O forming HF molecules. Calculations demonstrate that the equilibrium volume fractions of the fluorine atom can be as large as 0.5–3% for mixtures with an F/H > 1. The main reaction of H<sub>2</sub>O conversion to HF is the F + H<sub>2</sub>O = HF + OH reaction. Dependencies of the F/H ratio as a function of HFC-125 (C<sub>2</sub>F<sub>5</sub>H) concentration and showing the possible range of mixture compositions for a promotion effect, were generated for methane, ethylene and heptane at different equivalence ratios.

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## 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 mol of ethanol, 2.05 mol of propane, and 5 mol 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<sub>2</sub>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<sub>2</sub>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<sub>2</sub>O addition?

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\* Corresponding author.

E-mail address: [vbabushok@nist.gov](mailto:vbabushok@nist.gov) (V.I. Babushok).

## 2. Kinetic model and calculation procedure

Modeling studies were conducted for methane, ethylene and propane combustion inhibited by  $C_2F_5H$  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<sub>1</sub>–C<sub>2</sub> 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

Figures 1a and 1b contains dependencies of equilibrium concentrations of major species and flame temperature for lean methane/air (0.71 equivalence ratio,  $C_2F_5H$  volume fraction of 7%, initial F/H = 1.06) and ethylene/air mixtures (0.6 equivalence ratio,  $C_2F_5H$  volume fraction of 5.1%, initial F/H = 1.25) as a function of  $H_2O$  concentration. It can be seen that the addition of  $H_2O$  (to mixtures with the F/H ratio >1) increases the combustion temperature, and the HF concentration in products, and decreases  $CF_2O$  concentration. In the vicinity of F/H = 1, significant decreases of  $CF_2O$  and F atom concentrations are observed with a simultaneous increase of equilibrium concentration of  $H_2O$  (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  $H_2O$  is converted to HF at the F/H ratio >1. The maximum temperature increase as a result of  $H_2O$  addition is about 110 K (Fig. 1b). It is of interest that flame equilibrium calculations demonstrate a large equilibrium concentration of the free fluorine atom with the addition of  $C_2F_5H$  agent to lean mixtures for ratios F/H > 1, e.g. F atom volume fraction is about 3% for ethylene at  $H_2O = 0$  (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)  $CO_2 + HF + H_2O$  at F/H < 1, and (2)  $CO_2 +$

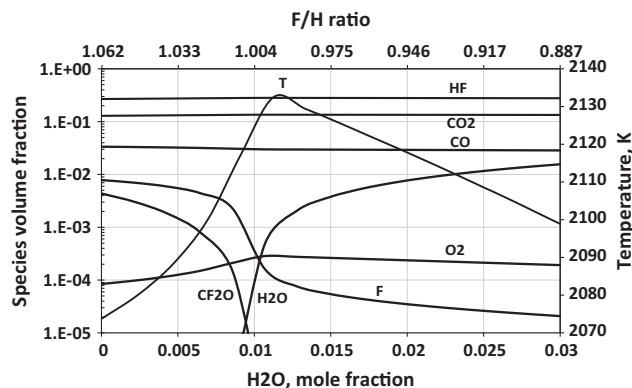


Fig. 1a. Flame equilibrium concentrations of the major species and temperature for methane flame as a function of  $H_2O$  concentration (0.71 equivalence ratio;  $C_2F_5H = 0.07$  volume fraction at  $[H_2O] = 0$ ;  $CH_4$ :air: $C_2F_5H$  ratio was kept constant, 298 K, 1 bar, F/H = 1.06 for dry mixture).

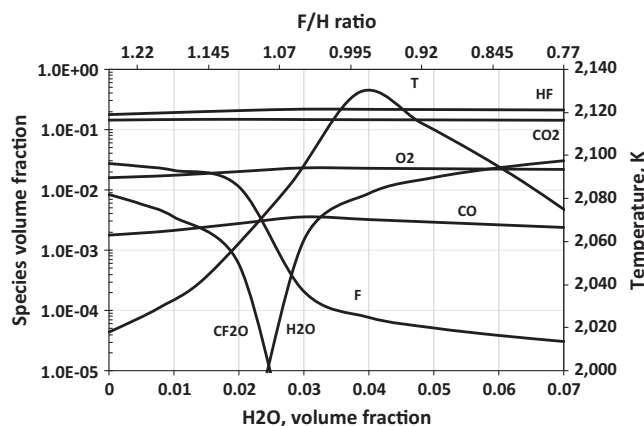
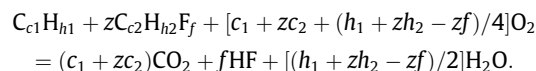


Fig. 1b. Flame equilibrium concentrations of the major species (volume fractions) and temperature for ethylene flame as a function of F/H ratio (0.6 equivalence ratio;  $C_2F_5H = 0.051$  volume fraction at  $[H_2O] = 0$ ;  $C_2H_4$ :air: $C_2F_5H$  ratio was kept constant, 298 K, 1 bar).

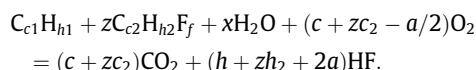
$HF + CF_2O(CF_4)$  at F/H > 1. Calculations show that the intermediate case, F/H = 1, roughly corresponds to the complete conversion of F atoms to HF acid with major combustion products  $CO_2$  and HF and with small amounts of  $H_2O$  and  $CF_2O$ . Combustion of the mixture of hydrocarbon ( $C_{c1}H_{h1}$ ) with added HFC ( $C_{c2}H_{h2}F_f$ ) in air corresponds to the following approximate stoichiometric equation at F/H < 1:



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

$$[HFC]_{st} = z / \{1 + z + 100[c_1 + zc_2 + (h_1 + zh_2 - zf)/4]/21\}.$$

Approximate stoichiometric equation at F/H = 1 with the addition of  $H_2O$  is as follows:



Stoichiometric amount of  $H_2O$  (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  $H_2O$  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 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  $H_2O$  concentration at different initial  $C_2F_5H$  concentrations, corresponding to different initial F/H ratios for dry mixtures (the corresponding ratio is shown in brackets). An increase of  $C_2F_5H$  concentration in the mixture decreases burning velocity. However, an increase of the HFC agent concentration increases the F/H ratio and, for  $C_2F_5H$  volume

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