Air Humidity Influence on Combustion of R-1234yf (CF$_3$CFCH$_2$), R-1234ze(E) (trans-CF$_3$CHCHF) and R-134a (CH$_2$FCF$_3$) Refrigerants

Valeri I Babushok[a], Gregory T. Linteris [a,*]

[a] National Institute of Standards and Technology, Gaithersburg, USA

* corresponding author, linteris@nist.gov 301-975-2283

Air Humidity Influence on Combustion of R1234yf (CF₃CFCH₂), R1234ze(E) (trans-CF₃CHCHF) and R134a (CH₂FCF₃) Refrigerants[1]

V.I. Babushok, G.T. Linteris*

National Institute of Standards and Technology, Gaithersburg, MD 20899 USA

Abstract

The influence of air humidity on flame propagation in mixtures of hydrofluorocarbons (HFCs) with air was studied through numerical simulations and comparison with measurements from the literature. Water vapor added to the air in mixtures of fluorine rich hydrofluorocarbons (F/H≥1) can be considered as a fuel additive that increases the production of radicals (H, O, OH) and increases the overall reaction rate. The hydrofluorocarbon flame is typically a two-stage reaction proceeding with a relatively fast reaction in the first stage transitioning to a very slow reaction in the second stage which leads to the combustion equilibrium products. The transition to the second stage is determined by the consumption of hydrogen-containing species and formation of HF. Despite a relatively small effect of water on the adiabatic combustion temperature, its influence is significant on the reaction rate and on the temperature increase in the first stage of the combustion leading to the increase in burning velocity. The main reaction for converting H_2O to hydrogen-containing radicals and promoting combustion is $H_2O+F=HF+OH$, as demonstrated by reaction path analyses for the fluorine rich hydrofluorocarbons R-1234yf, R-1234ze(E), and R-134a (F/H = 2). The calculated burning velocity dependence on the equivalence ratio ϕ agrees reasonably well with available experimental measurements for R1234yf and R-1234ze(E) with and without the addition of water vapor. In agreement with experimental data, with water vapor, the maximum of burning velocity over ϕ is shifted to the lean mixtures (near $\phi = 0.8$).

Keywords: Refrigerant flammability, Burning velocity, Low-GWP refrigerants, Kinetic model, Hydrofluorocarbons, Humidity, Moist air, R-1234yf; R-1234ze(E); R-134a

Novelty and Significance

Previous experiments by numerous authors have found that air humidity can have a strong effect on the measured burning velocity of refrigerants, sometimes increasing the burning velocity by a factor of three and bringing non-flammable refrigerants into the flammable regime. This is important for fire safety concerns in the use of new, low global-warming potential refrigerants. The present paper uncovers the mechanism responsible for the enhanced burning velocity for three

---

[1] Official contribution of NIST, not subject to copyright in the United States. Certain commercial equipment, instruments, and materials are identified in this paper to adequately specify procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology.

very important refrigerants and validates the kinetic model for varying levels of water vapor in the air through comparisons of measured and calculated burning velocity.

Author Contributions Statement

VIB: designed research, performed research, analyzed data, interpreted data, wrote the paper.

GTL: designed research, edited manuscript, interpreted data, modified presentation, wrote the paper.

1. Introduction

In accord with the Montreal Protocol many of the high ozone-depletion potential (ODP) hydrochlorofluorocarbons (HCFCs), have been largely phased out [1]. Many of the suggested replacement agents, hydrofluorocarbon compounds (HFCs), have a large global warming potential (GWP) (as did the high-ODP compounds). In general, the shortening of the atmospheric lifetime decreases the GWP but increases the molecule reactivity thus increasing the flammability, which creates design considerations with regard to fire safety. It is noteworthy that many fluorinated refrigerants become flammable, or their flammability limits are widened, in the presence of water vapor in the air. For example, Kondo et al. [2, 3] Yang et.al. [4] and Zhai et al. [5] were not able to ignite mixtures of R-1234ze(E) with dry air, but with moist air, the mixtures had measurable flammability limits.

Kondo et al. [3, 6, 7] indicated that for molecules in which the number of fluorine atoms is larger than that of hydrogen atoms, the humidity conditions can influence the flammability limits of HFC refrigerants and that the heat of combustion is larger in moist air than in dry air. The presence of water vapor increases the range of flammability or makes the air mixtures flammable for R-134a, R-1234yf, R-1234ze(E), R-410A, R-410B, R-245eb, R-245pc, R-245ca [6, 8]. The burning velocity (S_u) of R-1234yf and R-1234ze(E) was found to be higher in moist air than in dry air [9], and experiments showed that the quenching distance was decreased dramatically for R-1234yf when water vapor was added to the air. It is of interest that previous work for hydrocarbon-air flames with added fluorocarbon fire suppressants [10-12] has found that reactions of fluorine-containing species with water lead to the enhancement of combustion processes in those systems.

Recently, the combustion properties of C_1-C_2-C_3 fluorocarbons with differing ratios of fluorine to hydrogen atoms in the molecule have been studied [13-16], and the kinetic mechanism and findings from these studies provide the basis for the present work.

In the present work, the influence of water vapor on the combustion properties of R-1234yf, R-1234ze(E)and R-134a, which have a fluorine to hydrogen ratio (F/H) of 2, are studied through flame simulations, for a range of fuel-air equivalence ratio ϕ of 0.5 to 1.5 and standard conditions (298 K, 101 kPa). Comparisons with available experimental burning velocity data demonstrate reasonable agreement, and the experimentally observed trends are reproduced in numerical predictions. Nonetheless, the experimental measurement of low burning velocities of hydrofluorocarbons with high fluorine content are extremely difficult, being influenced by stretch, buoyancy, and radiation. Development of accurate methods for their measurement is an active area of research, and the existing burning velocity data in the literature for R-1234yf and R-1234ze(E) do not yet account for these effects. Recent work with R-32 [17-21] has indicated that radiation and stretch effects are important and imply that they will be even more important for R-1234yf [22] and R-1234ze(E). While it might seem premature to model the flames before good experimental data are available, it seems prudent to move forward in parallel in the experimental and modeling work and refine the kinetic mechanism as improved data become available.

2. Kinetic model and modeling procedure.

The kinetic model used in this work describes the combustion of several C_1-C_3 hydrofluorocarbons and has been presented in detail in [15, 16]. Briefly, four sub-mechanisms form the framework for the kinetic model: 1) GRI-Mech 3.0 [23], which includes reactions important for high-temperature oxidation of hydrocarbons up to C_3 species; 2) the NIST C_1-C_2 hydrofluorocarbon model [24] with modifications [25, 26], developed to describe hydrocarbon flames with added HFC fire suppressants; 3) the C_3-hydrofluorocarbon model based on that for flame inhibition by heptafluoropropane (R-227ea) [27]; and 4) the model for the decomposition of 2,3,3,3-tetrafluoropropene, 1,3,3,3-tetrafluoropropene, 3,3,3-trifluoropropene [13, 15]. Several rate constants of the model were adjusted, based on reaction pathway and sensitivity analyses, to obtain agreement between predicted and measured burning velocities for the set of HFC

refrigerants[2]. Comparison of modeling results with available experimental data for C_1-C_3 HFCs demonstrate reasonably good agreement [16] as described in the reference.

The open-source software package Cantera [28] was used to calculate combustion equilibrium and laminar flame structure. For the burning velocity calculations, the equations of mass, species, and energy conservation are solved numerically for the initial gas compositions, temperature (298 K), and pressure (101 kPa) corresponding to those in the experiments. The solution assumes isobaric, adiabatic, steady, planar, one-dimensional, laminar flow and neglects radiation and the Dufour effect, but includes thermal diffusion. Molecular diffusion is modeled with the multi-component transport equations. The boundary conditions, corresponding to a freely-propagating flame, are specified by inlet mass fraction fluxes, velocity and temperature (298 K), and vanishing gradients downstream from the flame. The number of active grid points was selected to assure that the solutions were grid independent.

3. Results and discussion

3.1. Flame equilibrium calculations

The stoichiometric reaction equation for combustion of $C_3H_2F_4$ (R-1234yf, R-1234ze(E)) in the presence water vapor can be written [9] as:

$$C_3H_2F_4 + xH_2O + 2.5O_2 = 2(1+x)HF + (1-x)CF_2O + (2+x)CO_2.$$
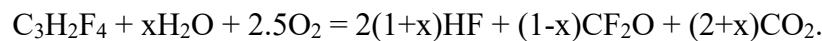
As discussed in [3, 6, 7, 10, 15], for HFCs with F/H ratio larger than 1, the air humidity increases the combustion temperature and increases HF concentration in the products. The stoichiometric equation indicates that the addition of H_2O to the system increases HF and CO_2 in products and decreases CF_2O. To some extent, water vapor behaves like a fuel additive to the system. Additionally, we can say that the presence of H_2O makes the mixture more oxygenated increasing the O/N ratio.

Results of calculations of adiabatic combustion temperature for R-1234yf and R-134a as the function of the equivalence ratio are presented in Figure 1 (upper curves labeled T_{ad}). Note that the lower curves marked T_H are discussed later. Curves for T_{ad} are shown for the dry mixture (dotted lines) and for the mixture with humid air (solid lines) (water volume fraction of 0.028 for

---

[2] It should be emphasized that the mechanism adopted for the present calculations should be considered only as a starting point. Numerous changes to both the rates and the reactions incorporated may be made once a variety of experimental and theoretical data are available for testing the mechanism.

R-1234yf and 0.031 for R-134a). The influence of H_2O on the adiabatic combustion temperature is relatively small, with a maximum increase of about 20 K for R-1234yf, and it is observed in the lean mixtures approximately at the equivalence ratio 0.8. The range of the equivalence ratios for which an increase of adiabatic temperature is observed is $0.5 \leq \phi \leq 1.1$. Outside of this range the addition of water vapor decreases the adiabatic combustion temperature. The presented results are in agreement with our previous results for R-1234ze(E), for which added water vapor ($X_{H_2O} = 0.03$) increases T_{ad} by 17 K and 6.3 K for lean ($\phi = 0.7$) and stoichiometric ($\phi = 1.0$) flames, and decreases T_{ad} by 8.1 K for rich ($\phi = 1.3$) flames [15]. In contrast, addition of H_2O (0.031 volume fraction in the air) to a R-134a-air mixture (red curves in Figure 1) does not increase T_{ad} for the examined range ($0.5 \leq \phi \leq 1.5$) but rather, decreases it by up to 11 K for the richer flames.
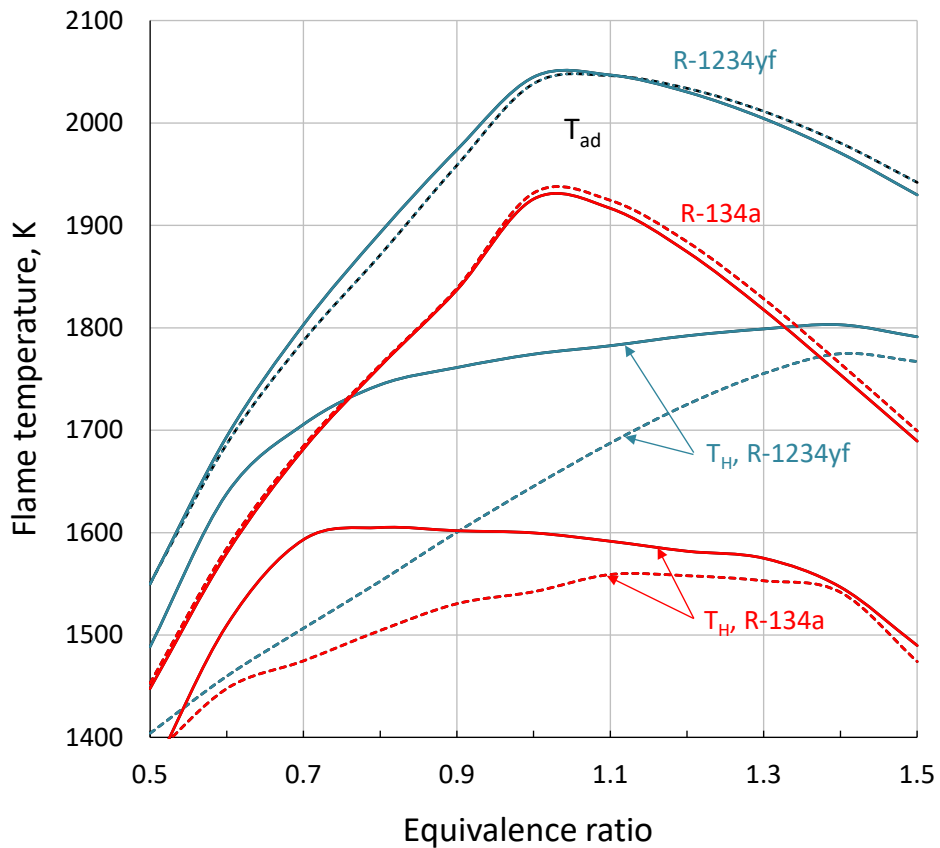

Figure 1. Adiabatic combustion temperature (T_{ad}) and flame temperature at the position of maximum H atom concentration (T_H) for R-1234yf and R-134a as a function of equivalence ratio for dry mixture (dotted line) and with moist air (solid line) containing 0.028 volume

fraction (R-1234yf) and 0.03 volume fraction (R-134a) of H_2O (initial conditions: 298 K, 101 kPa).

3.2. Flame propagation in moist air

The calculated dependencies of burning velocity on the equivalence ratio for R-1234yf and R-1234ze(E) are shown in Figure 2 together with the experimental data of Takizawa et al. [29]. The increase in burning velocity of R-1234yf flames with water vapor is dramatic, with the peak value (over ϕ) shifting to leaner conditions and roughly tripling for the data shown. The model captures the variation with ϕ, the difference between R-1234yf and R-1234ze(E), and roughly the effect of added water vapor, although the magnitude is off somewhat, especially for flames with lower burning velocity. As indicated, the predicted burning velocities at the highest water volume fraction (0.046) are slightly higher (about 10 %) than the measurements. Note, however, that the burning velocities in Figure 2 are likely to be affected by radiation.

Experimental burning velocities determined with spherically expanding flames, as in ref. [29], are affected by flame contraction in the burned gases due to radiative heat losses, which become increasingly important as the burning velocity decreases [30]. As discussed previously [19-21], radiation (and stretch) is important for R-32-air flames, which have similar products of combustion to the present flames and a radiation-uncorrected burning velocity of around 6 cm/s. Since the present flames have reported burning velocities in the range of 3 cm/s to 6 cm/s in the presence of moist air, they are likely affected by flame contraction. Similarly, the R-1234yf flames in dry air have a much lower burning velocity than predicted, and this is also likely due to the absence of radiation corrections in the experimental data reduction.

Calculated burning velocities for R134a/air mixtures as a function of ϕ are presented in Figure 3 for moist and dry conditions. The effect of water vapor is also largest (about 40 % at $\phi = 0.7$) for the lean flames (i.e., more added water relative to the fuel) and the effect of water on the peak burning velocity (over ϕ) is much less, only about a 25 % increase. There are no burning velocity data in the literature for R-134a/air mixtures at standard temperature and pressure, consistent with its "non-flame propagating" classification in the ASHRAE Standard 34 test [31]. Note, however, that water vapor has been shown to affect the ignition properties of R134a/air

mixtures [32], such that for some more stringent flammability metrics (e.g., ASTM-2079 [33]) it would be considered flammable.

Figure 4 shows the maximum measured [9] and calculated burning velocity (over all ϕ), for R-1234yf and R-1234ze(E) as a function of the water vapor volume fraction in air at elevated initial temperature (60 °C). Note that the higher initial temperature allows higher water vapor concentration. Experimental data for R-1234ze(E) were only presented at the highest water loading ([H_2O] = 0.11). Figure 4 illustrates a reasonable agreement considering the experimental difficulties of measurements at these conditions and the adiabatic one-dimensional model used to calculate burning velocity. The dependencies on the equivalence ratio are quite similar demonstrating an increase of burning velocity in the moist lean mixtures.
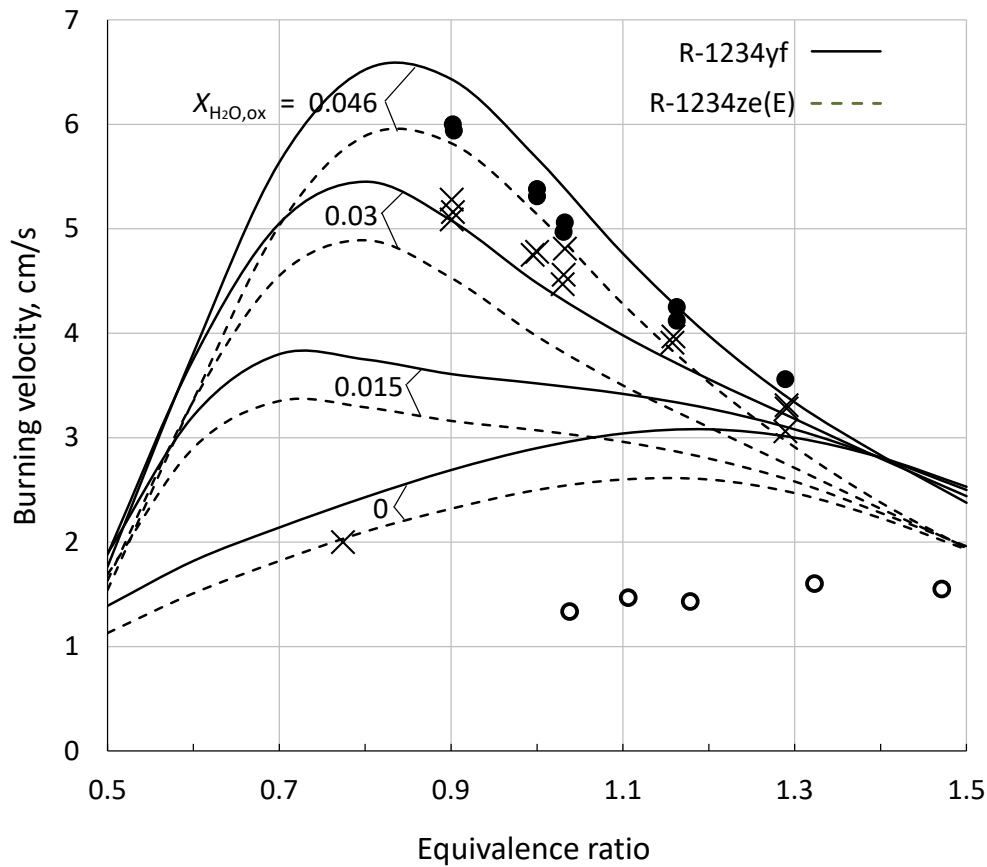

Figure 2. Dependencies of burning velocities on the equivalence ratio at different volume fractions of water vapor, solid lines: R-1234yf, dashed lines: R-1234ze(E). Experiment of Takizawa et al. [29]; R-1234yf, 0.046 volume fraction of H_2O in air: filled circles ●, dry: open circles ○ ; R-1234ze(E), 0.046 volume fraction of H_2O in air: X. (Initial conditions: 298 K and 101 kPa).
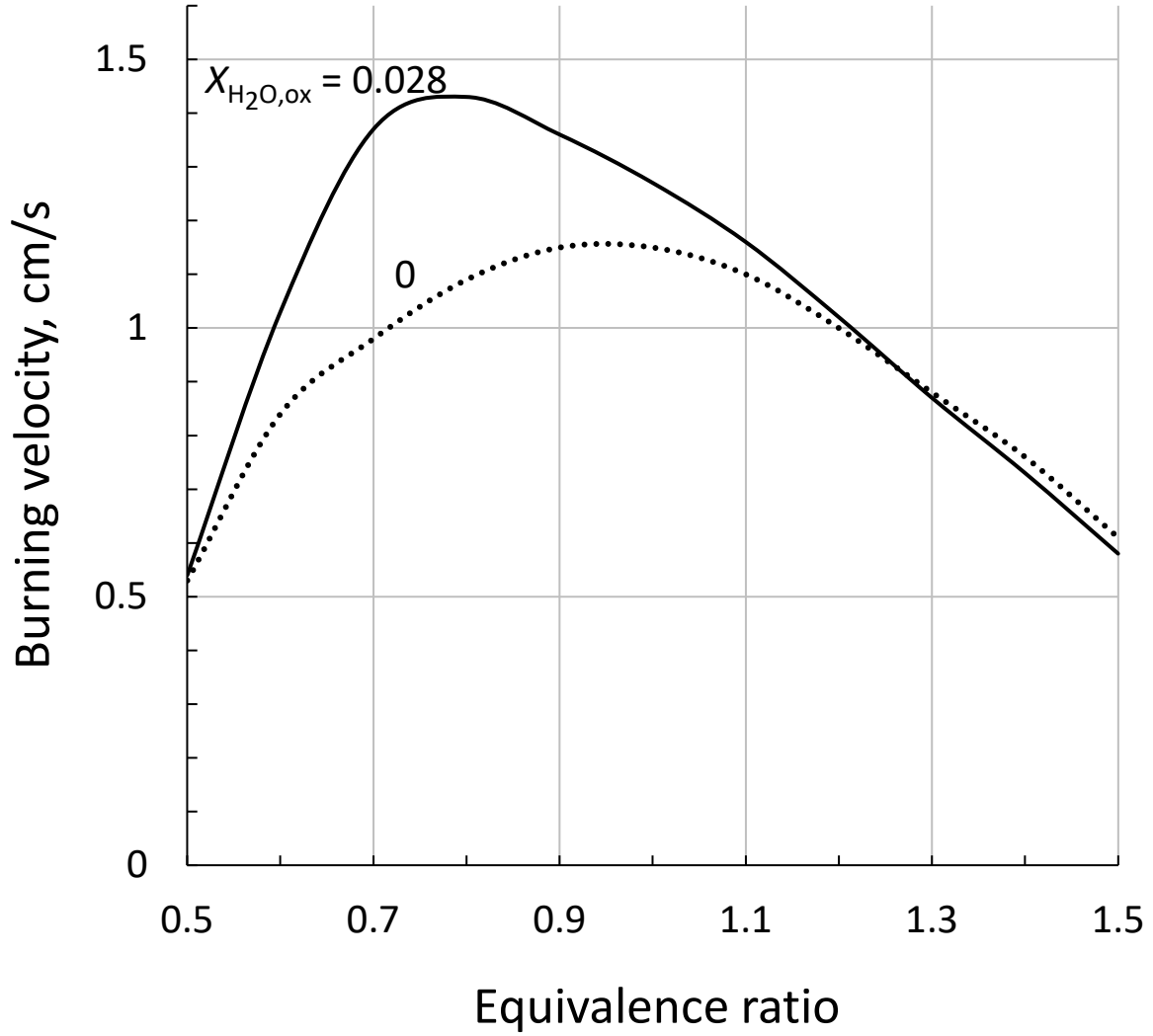
Figure 3. Calculated dependencies of burning velocity on the equivalence ratio for R-134a for dry and moist air (Initial conditions: 298 K, 101 kPa).
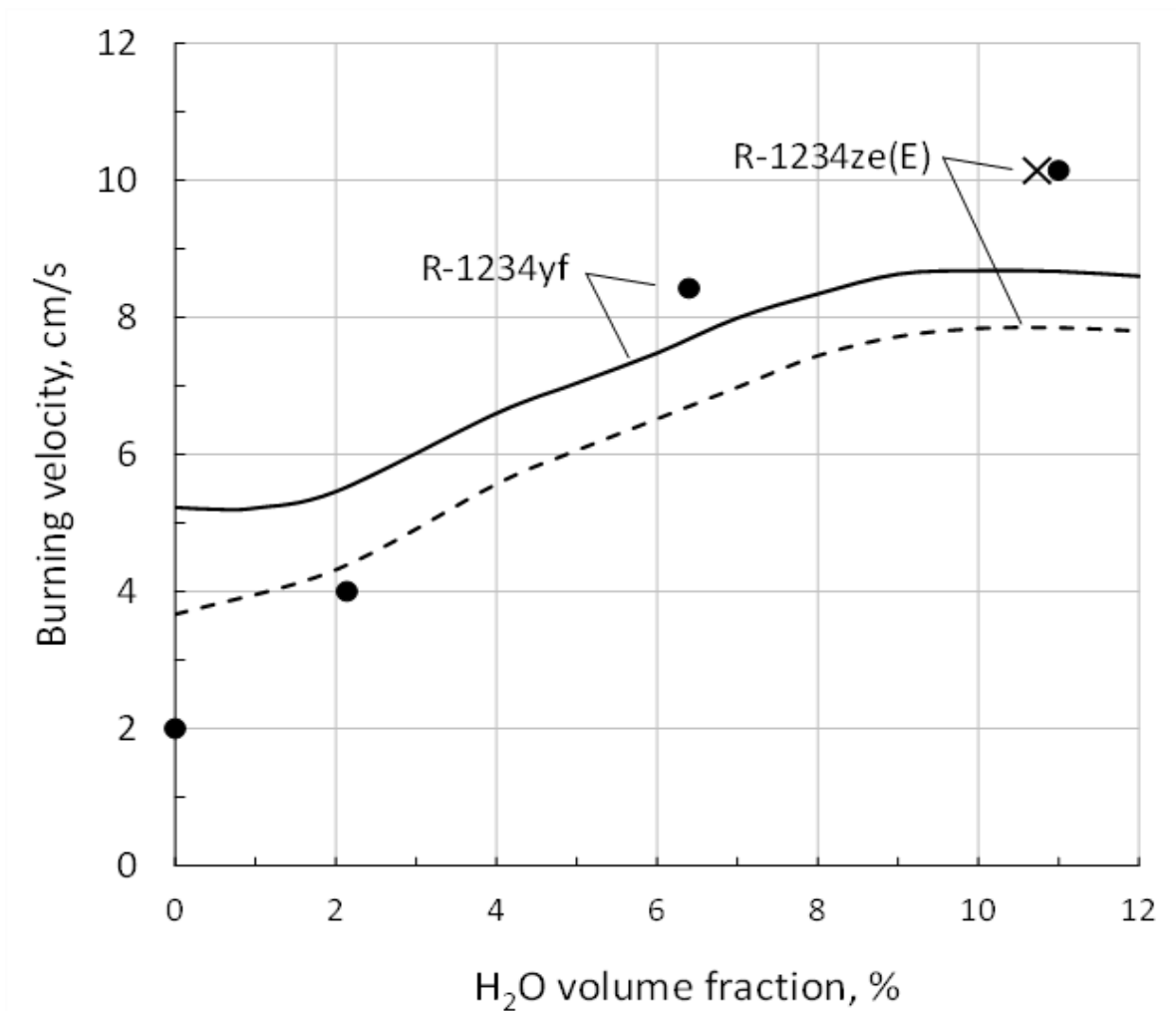
Figure 4. Dependence of maximum burning velocity of R-1234yf/air and R-1234ze(E)/air flames on the volume fraction of water in air. Experimental data, symbols [9]; R-1234yf: ●, R-1234ze(E): X. Numerical simulations, lines, R-1234yf: solid, R-1234ze(E): dashed. (Initial conditions: 60° C, 101 kPa).

3.3. Flame structures of R-1234yf and R-134a in dry and humid atmospheres.

Figure 5 shows the flame structures of R-1234yf in dry and moist air atmospheres for the equivalence ratio 0.8. This value of ϕ was selected because it is approximately that for which the maximum burning velocity occurs for moist air. While the flame coordinate of the x-axis is arbitrary, it is shifted for the moist case to align at the position of maximum H-atom volume fraction of the dry case. The top frame shows the volume fraction of major species (linear scale) and the bottom frame shows the volume fraction of chain-carrying radicals (log scale). The most

notable feature is that the temperature for the moist case rises much more rapidly and reaches a value about 200 K higher in the flame zone, while the temperature for the dry flame increases more slowly, followed by a continued increase in the region downstream of the main reaction zone to the equilibrium value. Thus, the temperature and species profiles for the dry flame exhibit a two-zone structure, as described earlier [13, 15, 34], but the moist flames less so because water increases the completeness of the reaction in the first zone.

Figure 5 shows that the two-zone structure is represented in the major species profiles as well. R-1234yf and water vapor are consumed rapidly, with the H_2O slightly slower. HF and CO_2 are major products, increasing rapidly in concentration for the moist flame but more slowly for the dry flame followed by continued increase far downstream. CO is an intermediate for both flames. Its concentration increases more rapidly in the dry flame than in the moist flame and is consumed slowly in both; in the moist flame, its concentration reaches a sharper peak within the flame zone and then decreases more rapidly downstream, although in the moist flame, both its production and consumption are faster. COF_2 is a product species in the dry flame (due to a shortage of H-atom to form the favored product HF), with little increase after the flame zone. In the moist flame, COF_2 is an intermediate and is consumed slowly downstream.

The two-zone structure is explained by the radical profiles shown in the lower frame of Figure 5. Peak H, O, and OH volume fractions in the flame zone of the moist flame are all more than an order-of-magnitude higher than in the dry flame. This supports the rapid reaction of R-1234yf and the heat release in the main reaction zone of the flame. In contrast, the equilibrium H, O, and OH volume fractions are only 2.4, 1.2, and 2.2 times higher in the moist flame than in the dry; i.e., the rapid buildup of radicals in the flame zone controls the flame propagation, not the behavior far downstream. As discussed below, reaction pathway analysis shows that the presence of water vapor leads to a significant increase of hydrogen containing radicals in the main reaction zone through the reaction $F+H_2O=HF+OH$. Although F atom concentration is generally higher in the downstream region of the moist flame as compared to the dry, at equilibrium it is about 20 % lower than in the dry flame. In the main flame reaction zone, F atom is both produced and consumed faster in the moist flame and its concentration serves as the driver of the flame acceleration with water vapor addition (via $F+H_2O=HF+OH$). At the location of maximum H atom concentration, the F atom concentration is about 40 % higher in the moist flame than at that location in the dry flame.
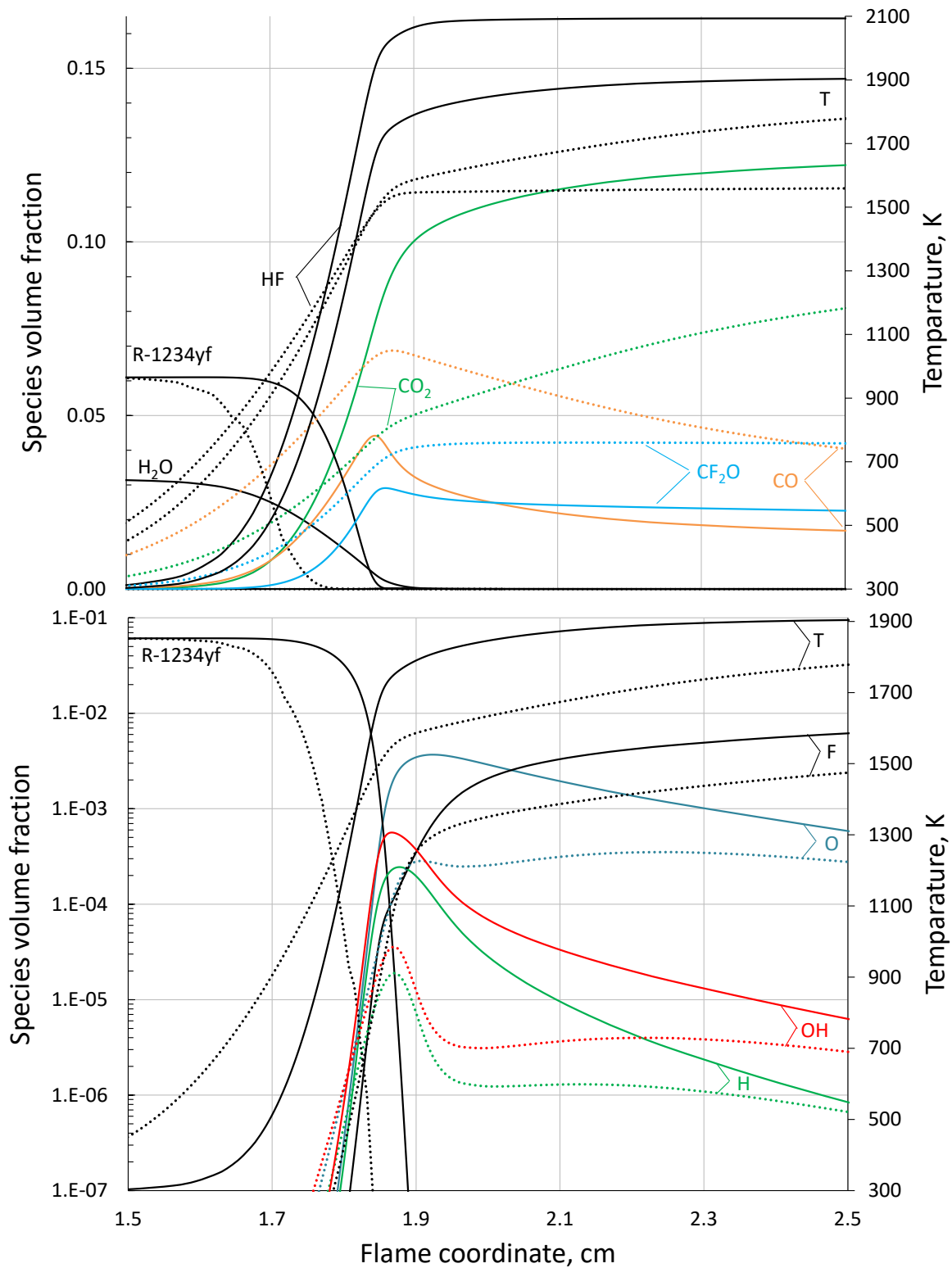
Figure 5. Flame structure of R-1234yf for dry (dotted lines) and moist (solid lines); air; (initial conditions: $\phi = 0.8$, 298 K, 101 kPa, volume fraction of H_2O in air: 0 or 0.03).

Figure 6 shows the flame temperature profiles at different moisture levels for flames of R1234yf (solid blue lines) or R134a (dashed red lines) at the equivalence ratio 0.8. These profiles are aligned at the position (zero on the x-axis) of maximum H atom concentration. For either fuel, the flame temperature increases faster and to a higher level in the first reaction zone with the added H_2O in comparison with the case with no added water (i.e., the flames are faster and thinner). Interestingly, the curves for each fuel all overlap at nearly the same temperature, around 1300 K, at a constant distance prior to the position of peak H atom, about 0.1 cm upstream for R-1234yf and 0.2 cm upstream for R-134a. The temperature increase due to water addition in the first zone is about 200 K for R-1234yf and about 100 K for R134a. The further temperature increase in the combustion products (second stage) is approximately 200 K to 400 K for R-1234yf and 100 K to 150 K for R-134a, and it is observed over a very long distance in comparison with the flame zone. That is, with water addition, the remaining increase in temperature in the second state is slower and increases less, and the reactions proceeding in the second stage (i.e., in the combustion products of first stage) have little influence on the burning velocity.

These trends are also illustrated in Figure 1 for the range of ϕ by the lower curves (label T_H), which show the temperature at the point of maximum H-atom concentration as a function of ϕ for flames of R-1234yf and R-134a with dry air (dotted lines) or moist air (solid lines). As indicated, the largest increase in T_H with added water vapor occurs in the lean flames (since more air implies more water vapor in the air relative to the fixed amount of fuel). As shown in Figure 2 and Figure 3, this value of ϕ also corresponds to that of the peak burning velocity for moist air. While this value of ϕ also corresponds to that of the largest increase in the equilibrium temperature (T_{ad}), the increase in T_{ad} is small. The present findings show that while the adiabatic temperature is increased for these compounds (due to the increase in heat of combustion), that effect is mild as compared to the effect on the two-zone structure and the temperature in the main reaction zone. The adiabatic condition occurs so far down stream that it likely does not affect the burning velocity.
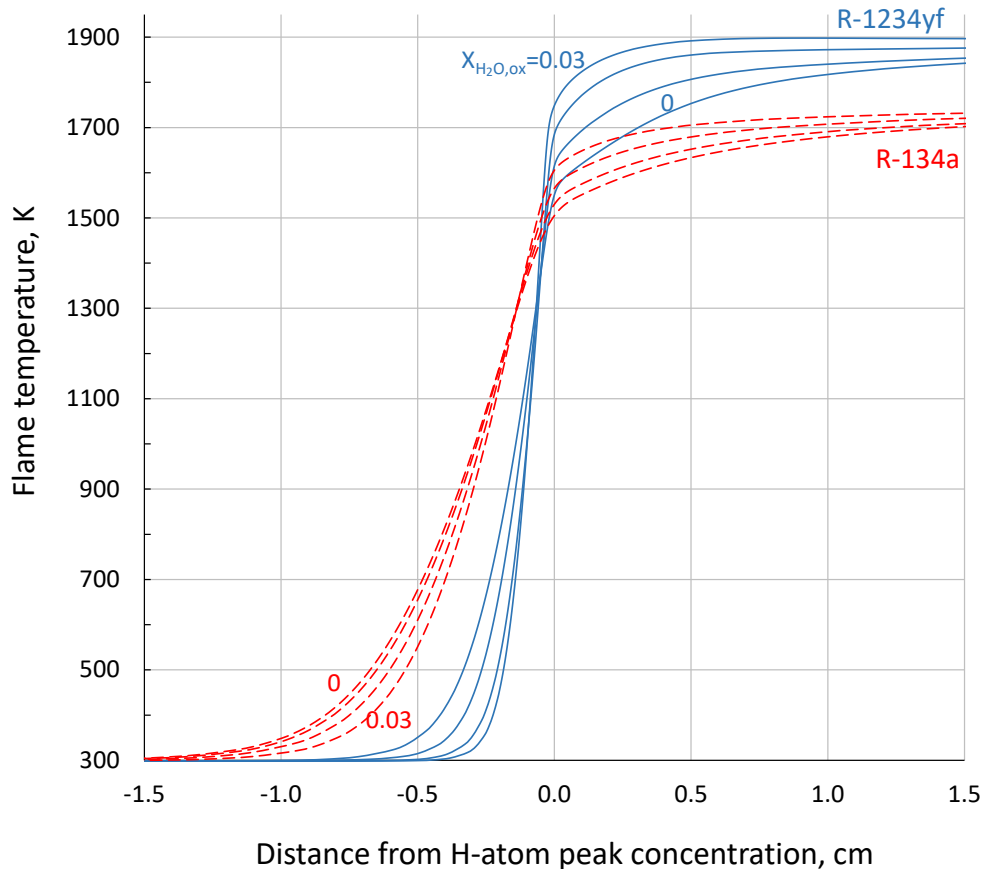
Figure 6. Temperature profiles in flames of R-1234yf or R-134a with air containing H_2O volume fractions of 0, 0.01, 0.02, and 0.03 (Initial conditions: $\phi = 0.8$, 298 K, 101 kPa).

Figure 7 presents the maximum radical concentrations (H, O, OH) and burning velocity as a function of the volume fraction of water vapor in air for the equivalence ratio 0.8 for R-1234yf (upper solid blue curves). As discussed with regard to Figure 5, the addition of water at 0.03 volume fraction leads to an increase in maximum radical concentrations of about an order of magnitude, 10.3, 12.3, and 12.8 for H, O, and OH, respectively, while burning velocity is increased slightly more than a factor of two. Figure 7 also shows the equivalent data for R-134a (lower dashed red curves) with 0 to 0.03 volume fraction of water, for which H, O, and OH are increased by a factor of 5, 4, and 7, respectively, with the burning velocity increased by a factor of 1.4. That is, the effects of water vapor on the radicals and burning velocity are much less for R134a due to its lower temperature in the main reaction zone and the high activation energy of the $H+O_2=OH+O$ chain-branching reaction. It should be noted however, that these are calculated flame speeds. Experimental measurements of flame speeds of R134a with air with or without water vapor have

not been made (propagating flames are not possible) for initial conditions at 23 °C temperature. Nonetheless, at 60 °C (and 50 % relative humidity at this condition), R134a has measurable flammability limits [29].
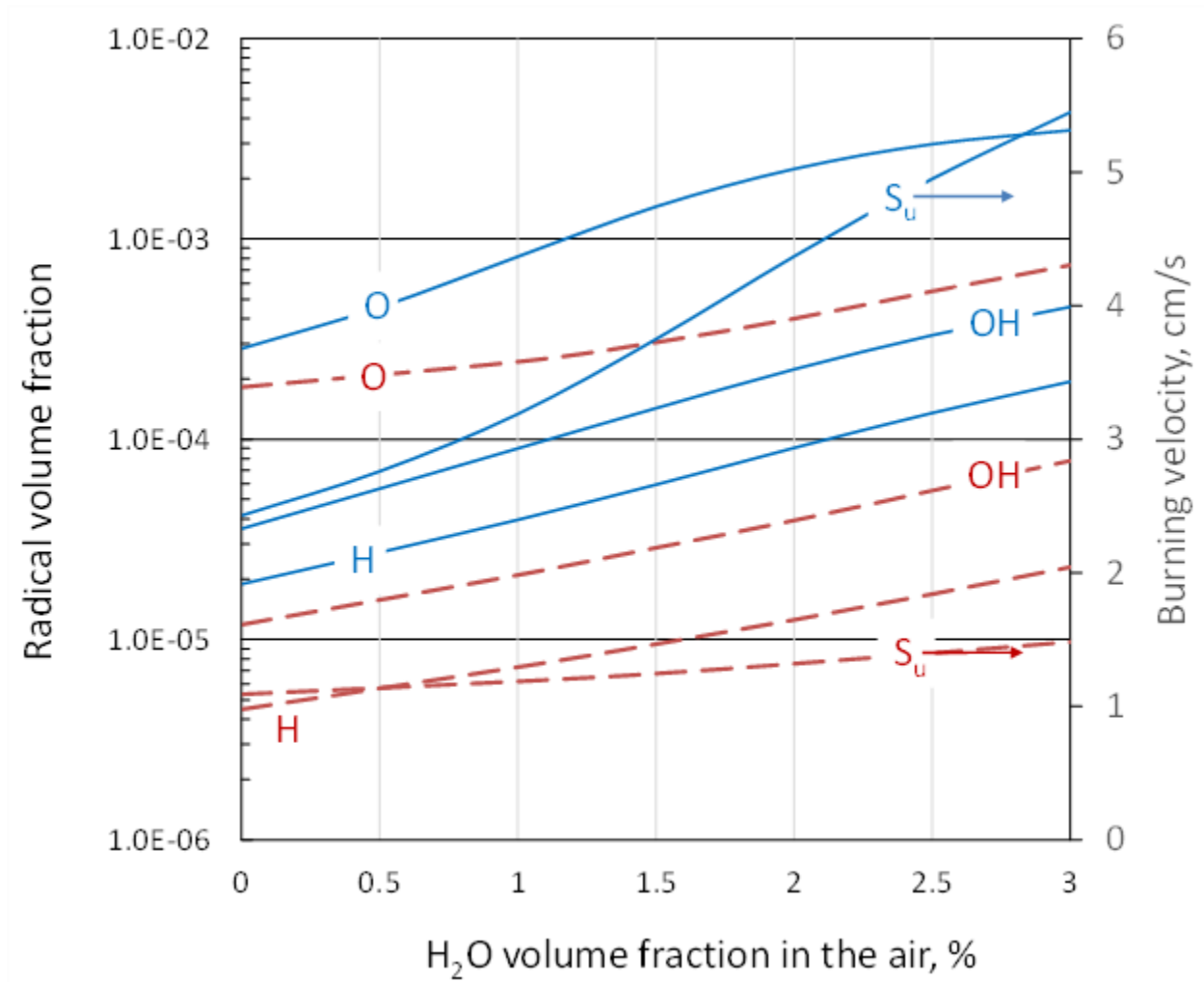

Figure 7. Dependencies of maximum radical concentrations (H, OH, O) in flame zone of R-1234yf (left axis) and burning velocity (right axis) on the concentration of H_2O in air (Initial conditions: ϕ=0.8, 298 K, 101 kPa).

3.4. Reaction mechanism

Combustion of R-1234yf in dry air proceeds at a relatively low temperature (T_{ad} = 2050 K), or nearly 200 K lower than that of hydrocarbons. Table 1 shows the contributions of different

reactions to the decomposition of R-1234yf in dry and moist air (equivalence ratio 0.8). Reaction contributions were obtained by integration of reaction rates through the flame reaction zone, and they are presented as percent of their contribution to overall consumption rate of R-1234yf. The largest portion of R-1234yf consumption proceeds through the reactions with radicals. For the dry conditions, F-atom reactions dominate (37 %) followed by O (16 %), H (11 %) and OH (9 %). For moist conditions, F-atom reactions (11 %) are lower by a factor of three, H (15 %) are increased moderately and OH (19 %) is doubled. Interestingly, thermal decomposition reactions are not particularly important for either case, accounting for about 9 % for the dry condition and 14 % for moist, the latter increase due to the higher reaction zone temperature of the moist flames.

Table 1. Major reactions responsible for R-1234yf (CH_2CFCF_3) consumption in dry and most mixtures with air (101 kPa, 298K, equivalence ratio 0.8, 0 or 0.03 volume fraction of H_2O in air).
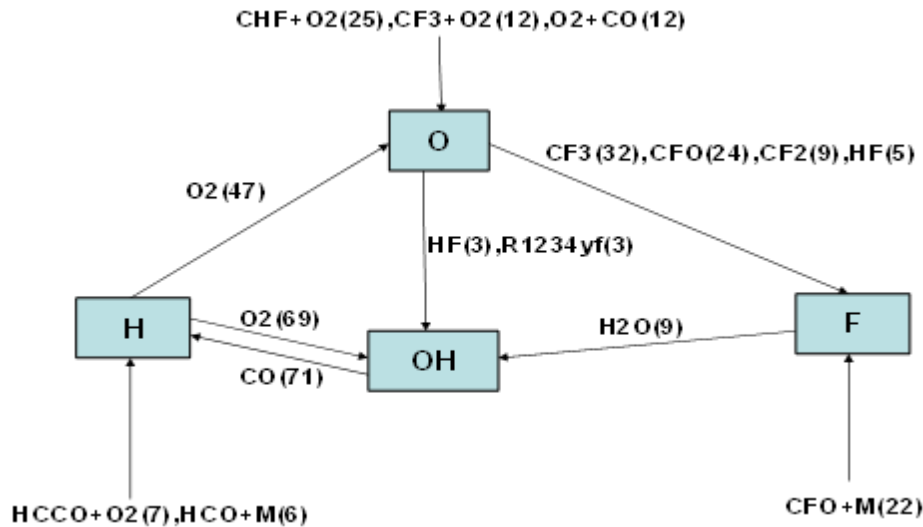
Reaction	Fraction of Total Consumption (%)	
	Dry mixture	Moist mixture
$CH_2CFCF_3+F=CH-CFCF_3+HF$	37	10.8
$CH_2CFCF_3+O=CF_3-CHF+HCO$	16	17.9
$CH_2CFCF_3+H=CH_2CHF+CF_3$	10.5	14.9
$CH_2CFCF_3+OH=CH-CFCF_3+H_2O$	9	18.6
$CH_2CFCF_3=CF_3CCH+HF$	8.7	13.7
$CH_2CFCF_3+O=CH_2F+CO+CF_3$	8.3	9.3
$CH_2CFCF_3+O=CH-CFCF_3+OH$	4.6	7.3
$CH_2CFCF_3+OH=CH_3+CF_3COF$		6.0

Examination of the reaction pathways of radical formation for the dry and moist cases demonstrates for the latter, an increase in the formation of the hydroxyl radical through the reaction of $F+H_2O=OH+HF$. This is followed by an increase in the consumption reaction for CO, $CO+OH=CO_2+H$ and an increase in the chain branching reaction $H+O_2=OH+O$, and thus an increase in H and particularly O. A decrease in the relative importance of the $H+O_2$ reaction for formation of OH results from an increase in the formation of OH from the reaction $F+H_2O$. These features are all consistent with the higher flame-zone temperature in the moist case.

Thus, the reactions with radicals control the rate of R-1234yf decomposition in flame. The addition of water vapor to the system increases the radical concentrations and the rate of R-1234yf

decomposition in flame reaction zone. The main reaction of cycles of radical formation (H,O,OH and F) are presented on Fig. 10 (a,b) which control the reaction rate on the flame zone.

8a. Dry mixture

CHF+O2(25),CF3+O2(12),O2+CO(12)

O

CF3(32),CFO(24),CF2(9),HF(5)

O2(47)

HF(3),R1234yf(3)

H

O2(69)

H2O(9)

F

OH

CO(71)

HCCO+O2(7),HCO+M(6)

CFO+M(22)

8b. Wet mixture

CHF+O2(18),CF3+O2(5),O2+CO(2)

O

CF3(26),CFO(15),CF2(9),HF(4)

O2(66)

R1234yf(3),HF(2)

H

O2(55)

H2O(29)

F

OH

CO(70)
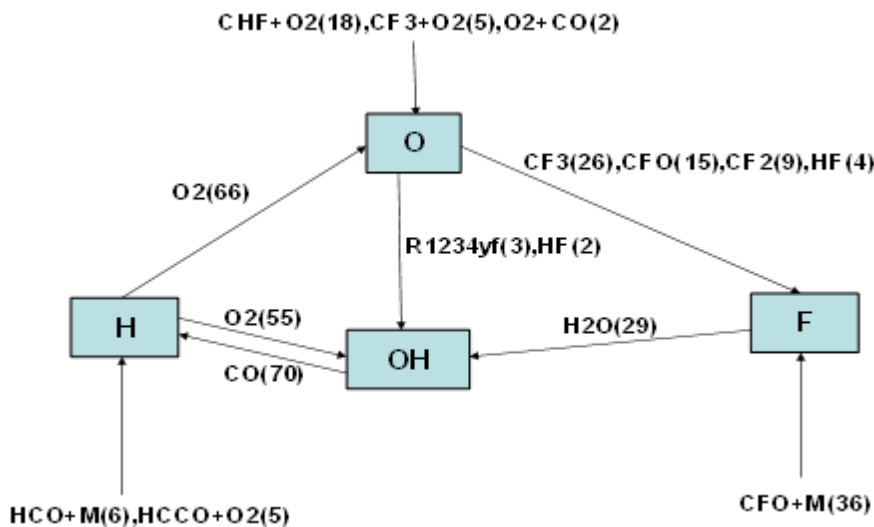
HCO+M(6),HCCO+O2(5)

CFO+M(36)

Figure 8(a,b). Reaction cycles of radical formation for dry (a) and wet (b) mixtures in the flame of R-1234yf (3 % of H_2O in air, equivalence ratio 0.8, 298 K, 101 kPa). Reaction contributions were obtained by integration of the corresponding reaction rates through the flame reaction zone. The number next to the reaction partner or to the reaction is the fraction (%) of the formation of the corresponding radical by that route.

Comparison of two reaction pathways of radical formation demonstrates the increase in the formation of the hydroxyl radical through the reaction of $F+H_2O=OH+HF$ leading to the increased formation of H and O in the wet mixtures. Particularly of interest is the increased contribution of the chain branching reaction $H+O_2$ in the formation of O atom. Figure 7 demonstrates the increase of maximum radical concentrations with the change of H_2O concentration in air. The relative decrease on the formation of OH in the reaction $H+O_2$ is the result of the increase in the formation from the reaction $F+H_2O$.

The main reactions of R-134a consumption are presented in Table 2. As indicated, for the dry condition, the consumption is primarily from thermal decomposition, reaction with F, and reaction with OH, in approximately equal proportions, with minor (about 5 % each) contributions from reaction with H and O. For the moist condition, the fraction proceeding through reaction with F is reduced by half, and thermal decomposition and reaction with OH are about 20 % higher, with other reactions about the same. Thus, as compared with the R-1234yf flame, the relative contribution of the decomposition reaction for R-134a is higher, although radical reactions are still high, still accounting for a fraction of about 0.60.

Table 2. Major reactions responsible for R-134a (CH_2FCF_3) consumption in dry and miost mixtures with air (01 kPa, 298K, equivalence ratio 0.8, 0 or 0.03 volume fraction of H_2O in air).

	Fraction of Total Consumption (%)	
Reaction	Dry mixture	Moist mixture
$CH_2F\text{-}CF_3+F=CF_3\text{-}CHF+HF$	31	16
$CH_2F\text{-}CF_3=CHFCF_2+HF$	29	37
$CH_2F\text{-}CF_3+OH=CF_3\text{-}CHF+H_2O$	28	35
$CH_2F\text{-}CF_3+O=CF_3\text{-}CHF+OH$	6	6
$CH_2F\text{-}CF_3+H=CF_3\text{-}CHF+H_2$	4	5
$CH_2F\text{-}CF_3+CF_3=CF_3\text{-}CHF+CHF_3$	2	1

3.5. Influence of air humidity on flame propagation of hydrofluorocarbons with F/H = 1 (R-32, R-143a, R-1243zf) and F/H = 0.5 (R-152a).

It is also of interest to investigate the effect of air humidity on the flame propagation in HFC mixtures with F/H ratios of 1 and 0.5. Equilibrium calculations for R-32 (CH_2F_2), R-143a

(CH$_3$CF$_3$), R-1243zf (CH$_2$CHCF$_3$) and R-152a (CH$_3$CHF$_2$) indicate that addition of water up to 0.03 volume fraction in air decreases the adiabatic combustion temperature for these compounds in the range $0.5 \leq \phi \leq 1.5$.   Figure 9 shows the calculated burning velocity as a function of ϕ for R-32, R-143a, and R-1243zf. As indicated, there is a mild increase in burning velocity (up to about 10 %) for R-32 and R-143a for $0.9 \leq \phi \leq 1.5$, and for R-1243zf for $0.8 \leq \phi \leq 1.5$. For leaner conditions the burning velocity is decreased slightly, up to around 10 % at the leanest condition. For R-152a (F/H = 0.5, and not shown in the figure), calculations show that water vapor decreases the burning velocity slightly for $0.5 \leq \phi \leq 1.5$. The maximum increase of burning velocity for compounds R-32, R-143a and R-1243zf (F/H = 1) occurs at about $\phi = 1.1$ as compared to $\phi = 0.8$ for R-1234yf, R1234ze(E), and R134a (F/H = 2) as described above.
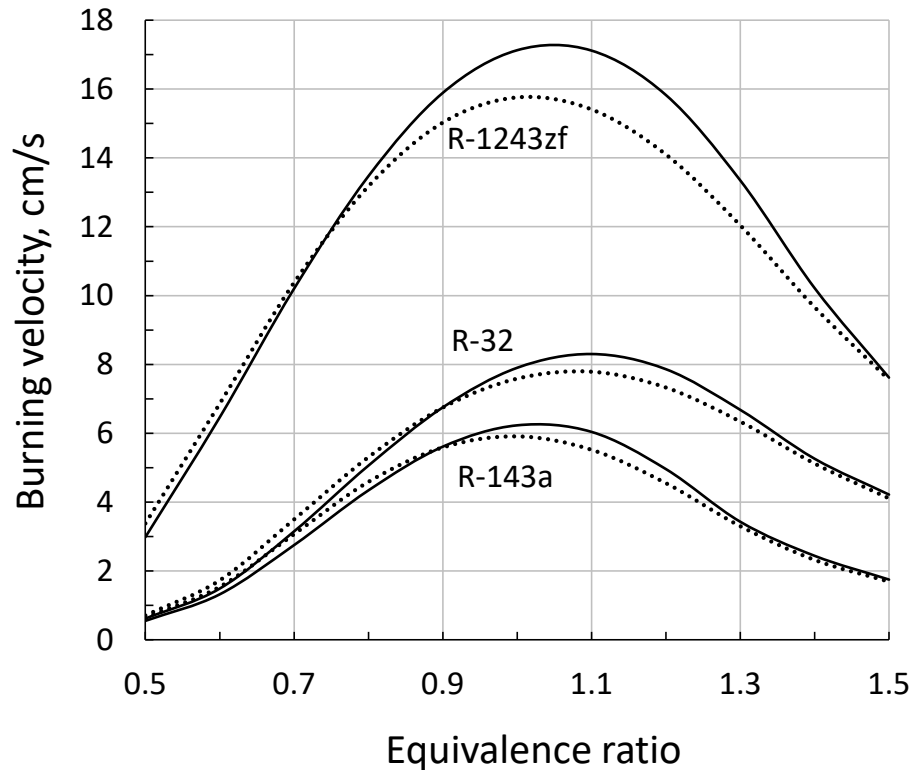

Figure 9. Burning velocity dependence on the equivalence ratio for R-32, R-143a and R-1243zf in air (solid lines: water volume fraction of 0.028 in air; dotted lines: dry air; 298 K, 101 kPa).

Analysis shows that the flames of R-32, R-143a and R-1243zf have a two-zone flame structure similar to that of R-134a, R-1234ze(E) and R-1234yf. Addition of water vapor to these

systems leads to the increase of radical concentrations (H, O, OH) and flame temperature in the first flame reaction zone despite the lower adiabatic flame temperature with the added water vapor for these compounds. Nonetheless, the effect of the water vapor for these fuels is relatively small because they have much lower F atom volume fraction at the point of maximum H atom.

4. Conclusions

The promotion effect of water vapor on combustion of hydrofluorocarbon refrigerants with F/H ratio of 2 (R-1234yf, R-1234ze(E), R-134a) in air was studied through flame propagation modeling. Calculations were also performed for hydrofluorocarbons with F/H = 1 (R-1243zf, R-143a, R-32) and F/H = 0.5 (R-152a). The main effect of air humidity is the increase of the radical pool in the flame reaction zone and thus a corresponding increase in the overall reaction rate. The main results are as follows:

1) Numerical calculations of the burning velocities for R-1234yf, R-1234ze(E) and R-134a (F/H = 2) in air over a range of equivalence ratio, with and without water vapor, predict the available experimental results reasonably well and capture the promotion effects of water vapor.

2) For HFCs with F/H = 2, water vapor behaves as an additional fuel, shifting the maximum burning velocity to leaner fuel compositions, with a peak at $\phi = 0.8$ at which the effects of the water vapor on chain-branching radical concentrations and main reaction zone temperature are also the greatest.

3) The main reaction responsible for the promotion is $H_2O+F = OH+HF$, which leads to an increase in the chain-branching radical concentrations in the flame. The addition of water near that for saturation at room temperature increases the maximum radical concentrations (H, OH, O) by about an order of magnitude in the flames of R-1234yf, R-1234ze(E) and about a factor of six for R-134a.

4) For dry HFC/air mixtures with F/H $\geq$ 1, the flames have a two-zone structure: the first zone is dominated by typical radical reactions for hydrocarbon systems, with near complete conversion of hydrogen in the system to hydrogen fluoride and a rapid increase in temperature. Beyond that point there is a second stage of reaction in which CO consumption and reactions of fluorinated species occur leading to additional temperature rise.

5) With water vapor addition, the chain-branching radical pool, overall reaction rate, extent of reaction, and temperature in the first stage all increase. For a water volume fraction of 0.03, the

temperature in the first stage is up to 200 K higher for R-1234yf and R-1234ze(E) and up to 100 K for R-134a.

6.) For R-32, R-143a, and R-1243zf (F/H = 1), addition of water (0.03 volume fraction) increases the burning velocity up to 10 % despite a lower adiabatic equilibrium combustion temperature. The water vapor has the maximum effect $\phi = 1.1$, near to the ϕ of peak S_u. For R-152a (F/H = 0.5), water addition up to 0.03 volume fraction in air decreased the adiabatic temperature and burning velocity for $0.5 \leq \phi \leq 1.5$.

Because the present flames have quite low burning velocity, future work should investigate the effects of radiation, which have been neglected in the present work.

Acknowledgements:

References:

[1] UNEP, United Nations Environment Programme, Further Amendment of the Montreal Protocol,UNEP/OzL.Pro.28/CRP/10, Kigali, Rwanda, 2016.

[2] S. Kondo, K. Takizawa, A. Takahashi, K. Tokuhashi, J. Mizukado, A. Sekiya, Flammability limits of olefinic and saturated fluoro-compounds, Journal of Hazardous Materials 171 (2009) 613-618.

[3] S. Kondo, K. Takizawa, K. Tokuhashi, Effects of temperature and humidity on the flammability limits of several 2L refrigerants, J Fluorine Chem 144 (2012) 130-136.

[4] Z. Yang, X. Wu, T. Tian, Flammability of Trans-1, 3, 3, 3-tetrafluoroprop-1-ene and its binary blends, Energy 91 (2015) 386-392.

[5] R. Zhai, Z. Yang, B. Feng, S. Sun, Effect of environmental condition on the flammability limits of two isomers of tetrafluoropropene, Combust. Flame 207 (2019) 295-301.

[6] S. Kondo, K. Takizawa, K. Tokuhashi, Effect of high humidity on flammability property of a few non-flammable refrigerants, J Fluorine Chem 161 (2014) 29-33.

[7] S. Kondo, Y. Urano, K. Takizawa, A. Takahashi, K. Tokuhashi, A. Sekiya, Flammability limits of multi-fluorinated compounds, Fire Saf. J. 41 (2006) 46-56.

[8] K. Takizawa, Fundamental Flammability (Section 2), in: Risk Assesssment of Mildly Flammable Refrigerants. Technical report, Japan Society of Refrigeration, Heating, and Air-Conditioning Engineers, Tokyo, Japan, 2015, pp. 20-42.

[9] K. Takizawa, E. Hihara, C. Dang, M. Ito, 2. Fundamental flammibility. 2.3.1. Effect of humidity on burning velocity., in: Risk Assessment of Mildly Flammable Refrigerants. Final Report 2016., The Japan Society of Refrigerating and Air Conditioning Engineers, Tokyo, Japan, 2017, pp. 22-67.

[10] V. I. Babushok, G. T. Linteris, P. T. Baker, Influence of water vapor on hydrocarbon combustion in the presence of hydrofluorocarbon agents, Combust. Flame 162 (2015) 2307-2310.

[11] V. Babushok, G. T. Linteris, D. R. Burgess Jr, P. T. Baker, Hydrocarbon flame inhibition by C3H2F3Br (2-BTP), Combust. Flame 162 (2015) 1104-1112.

[12] F. Takahashi, V. R. Katta, V. I. Babushok, G. T. Linteris, Numerical and experimental studies of extinguishment of cup-burner flames by C6F12O, Proc. Combust. Inst. 38 (2021) 4645-4653.

[13] V. I. Babushok, G. T. Linteris, Kinetic mechanism of 2,3,3,3-tetrafluoropropene (HFO-1234yf) combustion, J Fluorine Chem 201 (2017) 15-18.

[14] G. Linteris, V. Babushok, Laminar burning velocity predictions for C1 and C2 hydrofluorocarbon refrigerants with air, J Fluorine Chem 230 (2020) 109324.

[15] V. I. Babushok, D. R. Burgess, M. J. Hegetschweiler, G. T. Linteris, Flame propagation in the mixtures of O2/N2 oxidizer with fluorinated propene refrigerants (CH2CFCF3, CHFCHCF3, CH2CHCF3), Combust. Sci. Technol. 193 (2021) 1949-1972.

[16] V. I. Babushok, D. R. Burgess Jr, D. K. Kim, M. J. Hegetschweiler, G. T. Linteris, Modeling of Combustion of Fluorine-Containing Refrigerants,NIST Technical Note TN 2170, National Institue of Standards and Technology, Gaithersburg, MD, 2021.

[17] M. J. Hegetschweiler, L. Berger, R. Hesse, J. Beeckmann, C. Bariki, H. Pitsch, G. T. Linteris, Data reduction considerations for the burning velocity of spherical constant volume flames of R32 (CH2F2) with air, Combust. Flame 254 (2023) 112807.

[18] R. Hesse, C. Bariki, M. J. Hegetschweiler, G. T. Linteris, H. Pitsch, J. Beeckmann, Elucidating the challenges in extracting ultra-slow flame speeds in a closed vessel—A CH2F2 microgravity case study using optical and pressure-rise data, Proc. Combust. Inst. 39 (2023) 1783-1792.

[19] M. J. Hegetschweiler, J. L. Pagliaro, L. Berger, R. Hesse, J. Beeckmann, C. Bariki, H. Pitsch, G. T. Linteris, Data reduction considerations for spherical R-32 (CH2F2)-air flame experiments, Combust. Flame 237 (2022) 111806.

[20] R. Hesse, L. Berger, C. Bariki, M. J. Hegetschweiler, G. T. Linteris, H. Pitsch, J. Beeckmann, Low global-warming-potential refrigerant CH2F2 (R-32): Integration of a radiation heat loss correction method to accurately determine experimental flame speed metrics, Proc. Combust. Inst. 38 (2021) 4665-4672.

[21] M. Hegetschweiler, J. Pagliaro, L. Berger, R. Hesse, J. Beeckmann, H. Pitsch, G. Linteris, Effects of stretch and radiation on the laminar burning velocity of R-32/air flames, Sci. Technol. Built Environ. 26 (2020) 599-609.

[22] C. Schwenzer, R. Hesse, R. Glaznev, J. Beeckmann, H. Pitsch, G. Linteris, Effects of stretch and radiation on the burning velocity of R-1234yf in zero-g, Proc. Combust. Inst. to be submitted for publication (2023).

[23] G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, B. Eiteneer, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, J. W. C. Gardiner, V. V. Lissianski, Z. Qin, GRI Mech 3.0 http://www.me.berkeley.edu/gri_mech, University of California Berkeley, Berkeley, CA, 2000.

[24] D. R. Burgess Jr, M. R. Zachariah, W. Tsang, P. R. Westmoreland, Thermochemical and chemical kinetic data for fluorinated hydrocarbons, Prog. Energy Combust. Sci. 21 (1995) 453-529.

[25] V. I. Babushok, G. T. Linteris, O. Meier, Combustion properties of halogenated fire suppressants, Combust Flame 159 (2012) 3569-3575.

[26] G. T. Linteris, D. R. Burgess, F. Takahashi, V. R. Katta, H. K. Chelliah, O. Meier, Stirred reactor calculations to understand unwanted combustion enhancement by potential halon replacements, Combust. Flame 159 (2012) 1016-1025.

[27] B. A. Williams, D. M. L'Esperance, J. W. Fleming, Intermediate species profiles in low-pressure methane/oxygen flames inhibited by 2-H heptafluoropropane: Comparison of experimental data with kinetic modeling, Combust. Flame 120 (2000) 160-172.

[28] D. G. Goodwin, H. K. Moffat, R. L. Speth, Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes. http:/www.cantera.org, Version 2.1.1, California Institute of Technology, Pasedena, CA, 2016.

[29] K. Takizawa, M. Tamura, Progress Report of Research Institute for Innovation in Sustainable Chemistry, in: E. Hihara, (Ed.) Risk Assessment of Mildly Flammable Refrigerants. 2013 Progress Report, The Japan Society of Refrigerating and Air Conditioning Engineers, Tokyo, Japan, 2014, pp. 58-62.

[30] Z. Chen, Effects of radiation and compression on propagating spherical flames of methane/air mixtures near the lean flammability limit, Combust. Flame 157 (2010) 2267-2276.

[31] ASHRAE, ANSI/ASHRAE Standard 34-2019, Designation and Safety Classification of Refrigerants, American Society of Heating, Refrigerating and Air-Conditioning Engineers,, Atlanta, GA, 2019.

[32] G. Linteris, J. L. Pagliaro, P. B. Sunderland, Test Results Prepared for Honeywell: Igniter Material Effects in the Japanese High Pressure Gas Law Test,NIST Technical Note 1902, National Institute of Standards and Technology, Gaithersburg, MD, 2016.

[33] ASTM, ASTM E2079-19:   Standard Test Methods for Limiting Oxygen (Oxidant) Concentration in Gases and Vapors, in: ASTM Fire Standards, American Society of Testing and Materials, West Conshohocken, PA, 20119, pp.

[34] C. D. Needham, P. R. Westmoreland, Combustion and flammability chemistry for the refrigerant HFO-1234yf (2,3,3,3-tetrafluroropropene), Combust. Flame 184 (2017) 176-185.