

Spring Technical Meeting
Eastern States Section of the Combustion Institute
March 4-7, 2018
State College, Pennsylvania

Predicted Burning Velocities of C₁ and C₂ Hydrofluorocarbon Refrigerant Flames with Air

Gregory Linteris¹, Valeri Babushok¹

¹*Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, 20899*

Abstract: Due to their high global warming potentials, many existing working fluids for heating, cooling and refrigeration equipment are being phased out. Their replacements will often be flammable or slightly flammable, and the burning velocity of refrigerant-air mixtures is being used as a metric to rank their flammability. To allow industry to estimate the flammability of new blends of agents, predictive tools for the burning velocity of refrigerants are being developed, which requires a kinetic mechanism. The NIST hydrofluorocarbon HFC mechanism was developed 20 years ago to describe hydrocarbon-air flames with added trace amounts of hydrofluorocarbon fire retardants (primarily CH₂F₂, CF₃H, CF₄, C₂H₂F₄, C₂HF₅, and C₂F₆). The mechanism has been modified to include new HFC compounds, more recent rate data, and rate data for new species. The modified mechanism is used to predict steady, planar, 1D, unstretched burning velocities for mixtures of each refrigerant with air, over a range of fuel-air equivalence ratio ϕ , for comparison with the available experimental data. Agreement is good, and major kinetic pathways and radical populations are explored to uncover the general reaction properties of these new flames.

Keywords: *Refrigerant flammability, burning velocity, low-GWP refrigerants, hydrofluorocarbons*

1. Introduction

Existing refrigerant working fluids in vapor-compression heating/cooling equipment have high global warming potential (GWP), and are being phased through international treaties (i.e., the Kigali Agreement, an addendum to the Montreal Protocol.). Low-GWP replacements have been developed, primarily by adding double bonds or hydrogens to the molecules, which makes them break down in the troposphere. Unfortunately, these properties also make them more flammable. Flammable refrigerants are a new challenge for the Heating, Ventilation, and Air-Conditioning industry, and new building standards are required for the safe use of the new compounds. Burning velocity has been adopted as part of the standard to characterize the new refrigerants.

To meet the challenges of high efficiency, good volumetric capacity, low toxicity, zero ozone depletion potential, low GWP, and low flammability, industry will use blends of compounds. Analytical methods exist for optimizing the blends for all these properties except for flammability. To allow industry to estimate the flammability of new blends of agents, predictive tools for the burning velocity of refrigerants are being developed, which requires a kinetic mechanism. The NIST hydrofluorocarbon (HFC) mechanism was developed 20 years ago to describe the addition of HFC fire suppressants to hydrocarbon-air flames. It is currently being updated and extended to apply to new refrigerants added at high concentrations in air, and will likely require additional

reactions and species. As a first step in this process, the existing NIST HFC mechanism was applied to predict burning velocities of some pure C₁ and C₂ HFC compounds in air. Agreement was initially good for some compounds and poor for others. Consequently, some improvements were made, including addition of new HFC intermediates and their reaction rates, more recent rate data, and updated thermodynamic data. The modified mechanism is then used to predict steady, adiabatic, planar, 1D, unstretched burning velocities for mixtures of each refrigerant with air, over a range of fuel-air equivalence ratio ϕ , for comparison with experimental data in the literature. The compounds of interest are the saturated C₁ and C₂ HFC compounds with varying fluorine to hydrogen atom ratio in the reactant stream, which is characterized by F/(F+H), or the (moles F)/(mole F + moles H).

2. Kinetic Modeling

The starting kinetic model is from the NIST C₁-C₂ HFC model [1, 2], which was combined with GRI2.0 [3]. The mechanism has been updated and expanded to include larger HFC's, C₃H₂F₃Br, and C₆F₁₂O, as described in Ref. [4]. Since the original work, a rather large amount of new kinetic data on the reactions of fluorine containing species has been published. The kinetic model has been modified to include new species and recent reaction rate data. The thermodynamic data for fluorine-containing species has been also updated using the data of Burcat et al. [5]. The CHEMKIN and Cantera packages were used for combustion equilibrium calculations and for modeling of laminar flame propagation in mixtures of the C₁-C₂-HFCs in dry air. It should be noted that the present kinetic model should be considered as a starting point for further development and refinement. Numerous changes to both the rates and the reactions may be made once a variety of experimental data and theoretical results are available for testing the mechanism.

3. Results and Discussion

Figure 1 and Figure 2 show, for a range of stoichiometries, the adiabatic flame temperature T_{aft} (upper curves), and the steady, adiabatic, 1D, planar, laminar, unstretched burning velocities S_u^0 (lower curves) calculated with the Sandia EQUIL and PREMIX codes. The figures also show the experimental data (points) of Takizawa and co-workers from outwardly propagating spherical flames in constant volume and constant pressure experiments [6-8]. Table 1 summarizes for each compound the peak T_{aft} and S_u^0 from the experiments and simulations. Also shown are the stoichiometric volume fraction of each compound and the ratio of fluorine to hydrogen atoms, expressed as F/(F+H).

The stoichiometric concentration of the agents is generally higher than that for hydrocarbons, and increases as the fluorine loading in the molecule increases. The temperatures are similar for the flammable HFCs (R161, R41, R152, R152a, R143, R143a), with the peak flame temperatures in the range 2100 K $\leq T_{aft} \leq$ 2300 K, which is comparable, sometimes higher, than that of hydrocarbons. For the non-flammable refrigerants (R23, R134a, R134, and R125), the peak T_{aft} is somewhat lower (< 1960 K). As illustrated, the agreement in the measured and predicted burning velocity is reasonable for most refrigerants. For R143 and R143a, the simulations predict the peak burning velocity fairly well, although they show a peak value at leaner values of ϕ than measured in the experiments. It should be noted that agreement between predictions and measurements for fluoromethane (CH₃F) and fluoroethane (C₂H₅F) using the original NIST model was poor. Modification of the enthalpy of formation for these compounds and kinetic data for several reactions was required to improve the predictions. Nonetheless, it should also be noted that stretch

and radiation have not been included in the simulations or in the reduction of the experimental data, and these might affect the results [9].

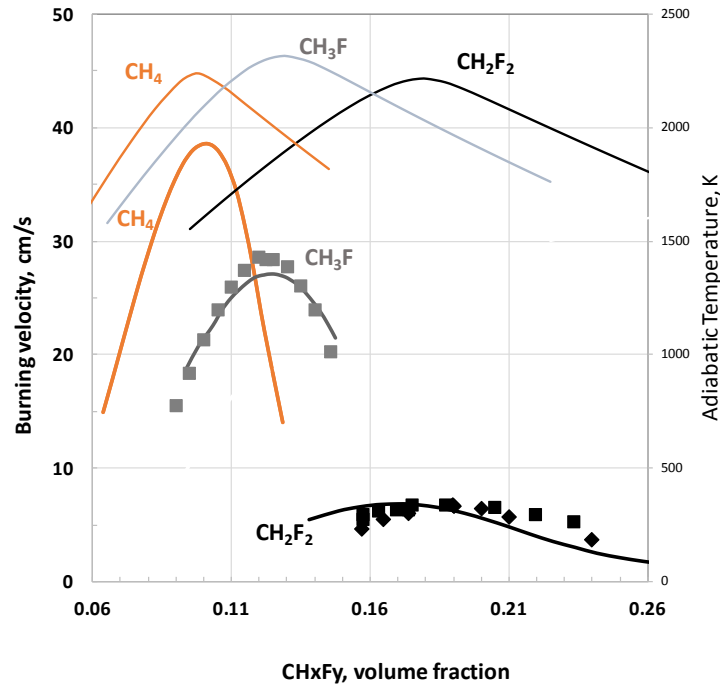


Figure 1: Burning velocity (left scale) and adiabatic flame temperature (right scale) for C₁ hydrofluorocarbons in air.

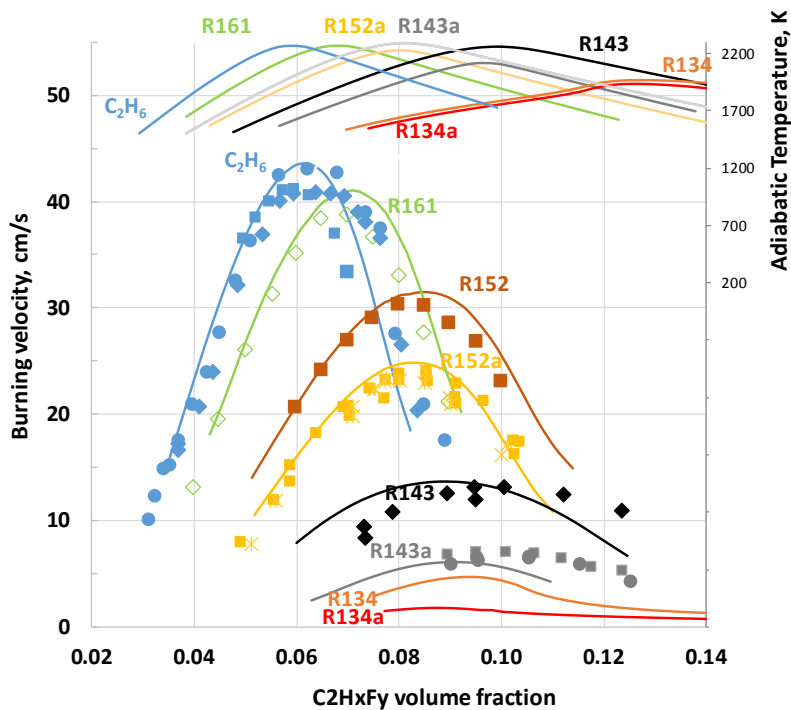


Figure 2: Burning velocity (left scale) and adiabatic flame temperature (right scale) for C₂ hydrofluorocarbons in air.

In Table 1, burning velocities and adiabatic flame temperatures are listed from highest value of S_u^0 to lowest; both T_{aft} and S_u^0 decrease with increasing fluorine loading in the refrigerant. This is also shown in Figure 3, which presents T_{aft} and S_u^0 as a function of the fluorine loading the system. Also, the asymmetrical isomers tend to be less flammable than the symmetrical ones, having both lower T_{aft} and S_u^0 .

Using the calculated flame structures, the variation in radical concentrations with fluorine loading is determined. Figure 4 shows the sum of the peak volume fraction of chain-carrying radicals (H, O, and OH) as well as that for F-containing radicals, as a function of the fluorine loading. As illustrated, the former drops off rapidly as the number of H atoms in the system becomes close to that of F atoms $F/(F+H)=0.5$, while the F radicals steadily increase. Hence, at higher fluorine loading, the chemistry becomes dominated by fluorine-containing radicals. Figure 5 shows that with increased fluorine loading, the volume fraction of both F-atoms (at the point of maximum OH volume fraction) and sum of the peak for F-containing radicals increases steadily, as does the equilibrium F atom volume fraction, which becomes higher than the value in the flame zone. For these flames equilibrium F atom volume fraction can be on the order of 1 %.

Table 1. Burning velocities and adiabatic combustion temperatures for stoichiometric refrigerant-air mixtures (initial temperature 298 K, 1 bar).

Refrigerant	Formula	T_{aft} K	S_u^0 max (Expt.) cm/s	S_u^0 max (Calc.) cm/s	$X_{stoic.}$ %	F/(F+H)
<u>Flammable:</u>						
R-170	C ₂ H ₆	2265	40.9	43.1	5.66	0.00
R161	C ₂ H ₅ F	2265	38.3	41	6.54	0.17
R-50	CH ₄	2230	36.5	38.6	9.5	0.00
R-152	CH ₂ F-CH ₂ F	2278	30.1	32.1	7.75	0.33
R-41	CH ₃ F	2273	28.3	27.2	12.3	0.25
R-152a	CH ₃ -CHF ₂	2220	23.6	24.9	7.75	0.33
R-143	CH ₂ F-CHF ₂	2248	13.1	13.7	9.5	0.50
R-32	CH ₂ F ₂	2207	6.7	7.3	17.4	0.50
R-143a	CH ₃ -CF ₃	2115	7.1	6.1	9.5	0.50
<u>Non-Flammable:</u>						
R-134	CHF ₂ -CHF ₂	1958		4.6	12.3	0.67
R134a	CH ₂ F-CF ₃	1927		1.8	12.3	0.67
R-125	CHF ₂ -CF ₃	1793		1.56 (at 400K)	17.4	0.83
R-23	CHF ₃	1713		0.57 (at 400K)	29.6	0.75
R-116	C ₂ F ₆	1389		0	29.58	1.00

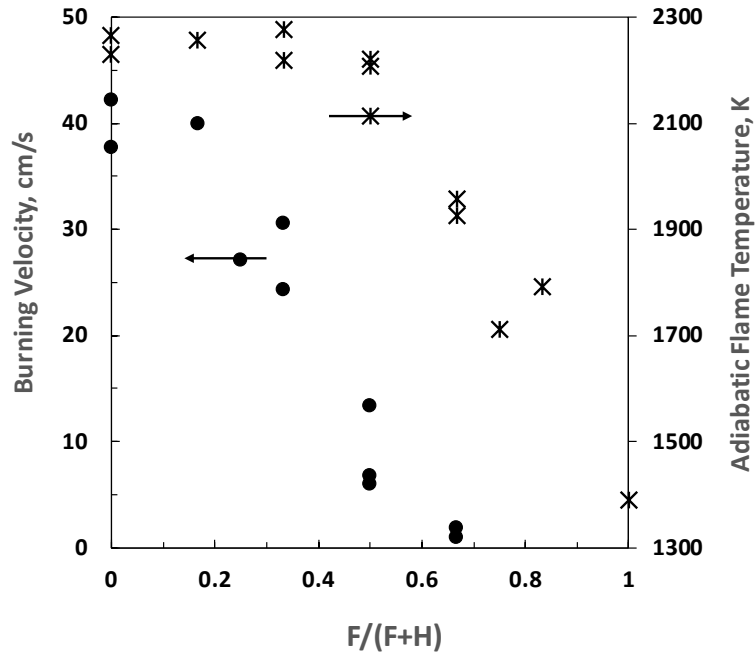


Figure 3: Burning velocity (left scale) and adiabatic flame temperature (right scale) as a function of the ratio of F atoms to F plus H atoms in the initial refrigerant-air mixture.

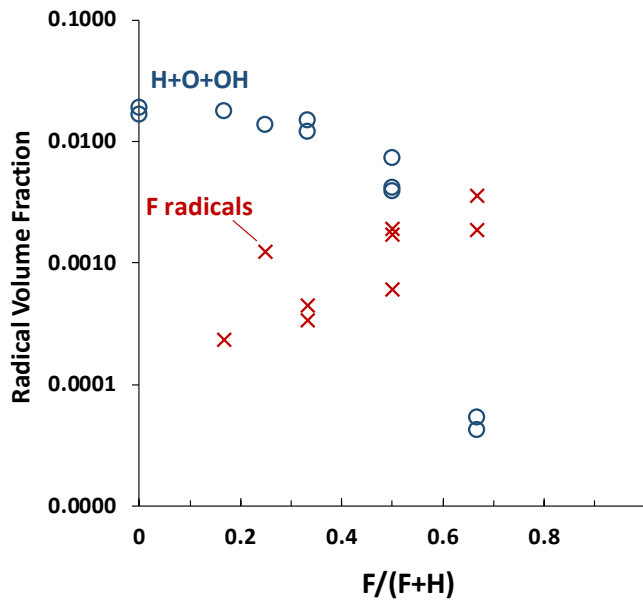


Figure 4: Volume fraction of total chain-branching radicals (H+O+OH) and F atoms as a function of the ratio of F atoms to F plus H atoms.

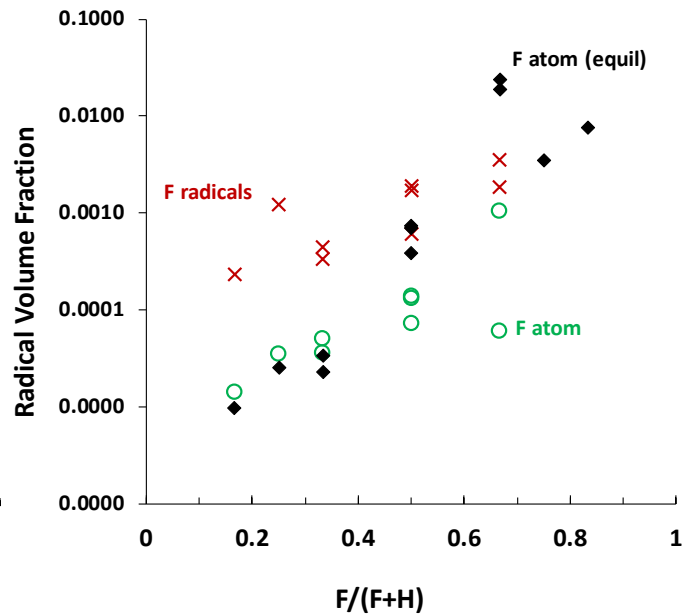


Figure 5: Volume fraction for fluorine radicals (F-radicals) and F atoms in the flame reaction zone, and for F atoms at equilibrium as a function of the ratio of F to F plus H atoms.

4. Conclusions

The laminar, planar, 1D, adiabatic burning velocity of saturated C₁ and C₂ HFC refrigerants (R41, R32, R161, R152, R152a, R143, R143a, R134, R134a) were calculated using the NIST HFC mechanism available in the literature and compared to existing experimental data. The predictions were in significant disagreement for CH₃F and C₂H₅F, and mild disagreement for other compounds. Consequently, the NIST HFC mechanism was modified with additional reactions, using more recent rate data in the literature, and with updated thermodynamic properties. After the changes, the agreement for these refrigerants, over a range of equivalence ratio, was good. The mechanism was then used to examine the properties of the refrigerant-air flames. Adiabatic temperatures of the refrigerant-air flames were comparable to, and sometimes higher than, similar hydrocarbons, and were lower for the non-flammable refrigerants. Burning velocity and flame temperature decreased as the fluorine to hydrogen ratio in the reactants increased. The symmetrical isomers of the fluoroethanes (R152, R143, R134) have higher adiabatic flame temperature and laminar burning velocity than the asymmetrical isomers (R152a, R143a, R134a), consistent with differences in enthalpies of formation. Analysis of the flame structures revealed that with increasing fluorine to hydrogen ratio, the chain-branching radical concentrations in the flame decrease, and fluorine-containing radicals, particularly F atom, increase. At high enough F/H ratio, the F atom equilibrium values are even higher than those in the flame zone.

5. Acknowledgements

This work was supported by the Buildings Technologies Office of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy under contract no. DE-EE0007615 with Antonio Bouza serving as Project Manager.

6. References

- [1] D. R. Burgess, M. R. Zachariah, W. Tsang, P. R. Westmoreland, Thermochemical and chemical kinetic data for fluorinated hydrocarbons, *Prog. Energy Combust. Sci.* 21 (1995) 453-529.
- [2] D. Burgess, M. R. Zachariah, W. Tsang, P. R. Westmoreland, Thermochemical and Chemical Kinetic Data for Fluorinated Hydrocarbons, Report No. NIST Technical Note 1412, Gaithersburg, MD, 1995.
- [3] G. T. Linteris, L. Truett, Inhibition of premixed methane-air flames by fluoromethanes, *Combust. Flame* 105 (1996) 15-27.
- [4] V. I. Babushok, G. T. Linteris, D. R. Burgess, P. T. Baker, Hydrocarbon flame inhibition by C₃H₂F₃Br (2-BTP), *Combust. Flame* 162 (2015) 1104-1112.
- [5] E. Goos, A. Burcat, B. Ruscic, Extended third millennium thermodynamic database for combustion and air-pollution use with updates from active thermochemical tables. <[Ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics/BURCAT.THR](ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics/BURCAT.THR)> (August 2012).
- [6] K. Takizawa, A. Takahashi, K. Tokuhashi, S. Kondo, A. Sekiya, Burning velocity measurement of fluorinated compounds by the spherical-vessel method, *Combust. Flame* 141 (2005) 298-307.
- [7] K. Takizawa, A. Takahashi, K. Tokuhashi, S. Kondo, A. Sekiya, Burning velocity measurement of HFC-41, HFC-152, and HFC-161 by the spherical-vessel method, *J Fluorine Chem* 127 (2006) 1547-1553.
- [8] K. Takizawa, S. Takagi, K. Tokuhashi, S. Kondo, M. Mamiya, H. Nagai, Assessment of Burning Velocity Test Methods for Mildly Flammable Refrigerants, Part 1: Closed-Vessel Method, *ASHRAE Trans.* 119 (2013) 243-254.
- [9] R. Burrell, J. L. Pagliaro, G. T. Linteris, Effects of stretch and thermal radiation on difluoromethane-air burning velocity measurements in constant volume spherically expanding flames, *Proc. Combust. Inst.* 37 (2018) submitted.