

Spring Technical Meeting
Eastern States Section of the Combustion Institute
March 6-9, 2022
Orlando, Florida

Radiation effects in hydrofluorocarbon/air flames: analysis and modeling

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Abstract: Hydrofluorocarbons (HFC), which are mildly flammable and pose potential fire risks, have received greater attention as a viable low global warming potential (GWP) alternative to traditional refrigerant and fire-suppressant compounds. Therefore, there is a demand to accurately quantify their flammability and reactivity to establish proper safety metrics. This study investigates the effects of radiation in slow-propagating HFC/air laminar flames. Planar 1-D simulations of R-32/air and R-1234yf/air flames show significant reductions in laminar flame speed due to radiative heat losses from the flame zone. Simulations of spherically expanding flames revealed that the radiation-induced flow needs to be considered when interpreting data from experiments. To this end, a radiation model was developed to circumvent the effects of radiation-induced inward flow in constant-pressure (CON-P) SEF experimental measurements, accounting for radiation heat loss using the optically thin limit model. Validation of the radiation model is currently underway, but preliminary results show that the model better predicts the inward flow velocity for most conditions compared to existing analytical models.

Keywords: *Hydrofluorocarbons, Laminar flame speed, Radiation heat loss, Radiation-induced inward flow*

1. Introduction

In the last decade, several major international conferences, such as the Twenty-Eighth Meeting of the Parties to the Montreal Protocol, have promoted the adoption of refrigerants and fire suppressant compounds with both lower ozone-depletion potential (ODP) and lower global warming potential (GWP) [1]. A group of hydrofluorocarbon (HFC) compounds have been identified with viable ODP and GWP characteristics. However, this particular group of HFCs are mildly flammable and pose potential fire risks [2]. Therefore, the flammability and reactivity of these compounds need to be quantified in order to establish proper safety metrics [3]. A mixture's flammability characteristics are often assessed through the laminar flame speed S_u^0 , a fundamental combustion parameter often used for kinetic model validation and turbulent combustion scaling [3]. However, derived S_u^0 measurements are often accompanied by large errors and uncertainties caused by the effects of radiation, which have been shown to significantly affect HFC/air flames due to their characteristically low propagation speeds [4]. Therefore, there is a need to study and quantify radiation effects in HFC/air flames.

Radiation effects have been quantified in flames using many different models, such as the optically-thin limit (OTL) model, which provides an analytical formulation for emission-dominated radiative heat loss [4-7, 11,12,16]. Results show that radiation has several major effects, specifically two relevant to weakly burning spherically-expanding flames (SEF): (1) radiation heat loss and conduction from the flame zone reduces the maximum flame temperature, consequently reducing flame propagation speeds [4-7], and (2) radiation-induced inward flow, generated by the burned gas contraction from radiative cooling, reduces burned flame speeds as the flame stretch rate decreases [4-7]. Santner et al. derived an analytical model to quantify radiation-induced inward flow u_b in hydrocarbon/air mixtures assuming a constant-pressure SEF configuration [6]. The radiation-induced inward flow velocity u_b can be subtracted from the measured flame expansion velocity (dR_f/dt), giving the burned flame speed S_b corrected for radiation-induced flow effects [6]. Hesse et al. extended Santner's analytical theory to HFC/air flames at elevated initial temperatures and pressures for stoichiometric CH_2F_2 (R-32) mixtures, showing decent agreement with Santner's analytical model for flame radii within the typical experimental range ($1\text{cm} < R_f < 3\text{cm}$) [4]. However, radiation losses have been shown to have a much more significant effect on weakly burning HFC/air flames, raising the question whether the assumptions utilized in Santner's model are valid for non-stoichiometric HFC/air flames at ambient conditions [7].

The number of studies that have carried out HFC/air flame experiments has greatly increased within the last decade. Many of these studies have reported empirically-derived S_u^0 for HFC refrigerants, such as R-32 and R-1234yf, using the constant-pressure (CON-P) [4,7-9] and constant-volume (CON-V) [8-12] SEF methods, as well as the tube method [13,14]. However, few studies have quantified flame speed reductions due to effects of radiation [4,7,11,12], causing considerable errors and uncertainties [15]. Burgess et al. conducted flame experiments for R-32/air mixtures using the CON-V SEF method and derived S_u^0 accounting for radiation heat loss [11]. Radiation losses were calculated using a Hybrid-ThermoDiffusive Radiation (HTDR) model, which calculates the reduction in burned gas temperature assuming the optically-thin limit [16]. Hegetschweiler et al. conducted flame experiments for R32/air mixtures using the CON-P SEF method and highlighted the effects of radiation-induced inward flow on stretched burned flame speeds, especially at very low stretch rates [7].

This study aims to investigate important aspects of radiation significant to HFC/air flames. First, 1-D, steady-state, planar flame simulations are performed using Cantera to investigate flame zone heat loss and flame speed reduction, lean flammability limits, and heat loss contributions from major radiating species. In addition, a spherical radiation model, which quantifies and corrects for radiation effects using experimental flame radius measurements, is developed.

2. Numerical approach

2.1 Quantifying heat losses in HFC flames

To explore aspects of radiation heat loss in HFC/air flames, 1-D, steady-state, freely propagating flame simulations were performed using the reacting flow code Cantera [17]. For various initial compositions of R-32/air and R-1234yf/air mixtures, both adiabatic and OTL radiation cases were performed, allowing flame zone heat losses to be quantified through the reduction in S_u^0 . Chemical

models for R-32 and R-1234yf combustion were obtained from Babushok et al. [3, 18,19]. To properly quantify the heat loss from major radiating species, the Cantera source code was modified to include Planck mean absorption coefficients (radiation coefficients) for the fluorinated compounds HF and CF₂O, obtained from Fuss & Hamins [20]. Adaptive gridding with strict refinement criteria was used to ensure that all solutions were grid-independent.

2.2 Spherical flame radiation model development

A radiation model was developed to quantify the radiation induced flow in CON-P SEF experiments, thereby enabling accurate determination of S_u^0 . The model is inspired by the Hybrid-ThermoDiffusive Radiation (HTDR) model developed by Xiouris et al., which interprets CON-V SEF experimental data to quantify the effect of radiative cooling on S_u^0 [16]. The HTDR model employed the following assumptions:

- The flame front is smooth, spherical, and infinitely thin
- The gas temperature and composition of unburned gas shells are frozen until combusted
- Combusted gas shells are equilibrated to the adiabatic flame temperature
- Radiative cooling for burned gas shells is performed using the OTL assumption

The HTDR model was modified to instead interpret experimental data for the CON-P SEF configuration. The total gas volume, equal to the spherical chamber volume, is initially divided into layers of thin spherical shells of equal width. To achieve constant pressure, the spherical chamber volume is allowed to expand as the volume of burned gas increases, circumventing the unburned gas compression step. In addition, the inward flow effect was quantified by isolating the burned gas contraction after the radiative cooling step. Each algorithm step corresponds to the combustion of the next unburned gas shell, for which the following sub-steps are performed:

1. Using the equilibrium capabilities of Cantera, dissociation is performed for each previously burned gas shell. This step holds enthalpy and pressure constant during equilibration to extract new shell volumes and species compositions from the previous radiative cooling step.
2. Similarly, combustion is performed for the currently burning gas shell, causing this shell volume to increase significantly.
3. The change in temperature per unit time due to radiative cooling is calculated for each burned gas shell. The radiative heat loss is calculated using the OTL radiation model, in which individual heat loss contributions are calculated for major product species using Planck mean absorption coefficients.
4. The radiative cooling time is found through linear interpolation between the experimental time-radius data and the simulated gas shells. Simulation data was used as the time-radius input for validation purposes.
5. Gas inflow velocity is calculated by dividing the total burned gas contraction by the radiative cooling time.

This algorithm is repeated for each subsequent shell until either all shells have been burned or simulated burned gas radius exceeds the final radius of the input experimental data.

3. Results and Discussion

To quantify the radiative heat loss from the flame zone in HFC/air flames, S_u^0 was computed for 1-D planar R-32/air and R-1234/air flames varying equivalence ratio, using both the adiabatic and OTL assumptions. An unburned gas temperature of 400K was used for all R-1234yf/air mixtures, as 1-D flame solutions did not exist for OTL radiation cases at 300K – the mixture was not flammable. Results for S_u^0 are shown in Fig. 1a. and Fig. 1b. for R-32/air and R-1234/air flames, respectively. In addition, percent reductions in S_u^0 are drawn to highlight the regions of smallest and largest radiative heat losses. Flame speed reductions are shown to be substantial, with percent reductions as great as 40% for the equivalence ratio range of interest. The reduction in S_u^0 is greatest near the estimated lower flammability limit, at which a Cantera grid-independent solution is no longer achievable with any further decrease in equivalence ratio. For comparison, percent reductions in lean methane/air flames were shown to be no greater than 3% for the same range of equivalence ratio. Therefore, the effect of radiative heat loss on S_u^0 is much greater for HFC/air flames compared to typical hydrocarbon/air flames for the same equivalence ratio.

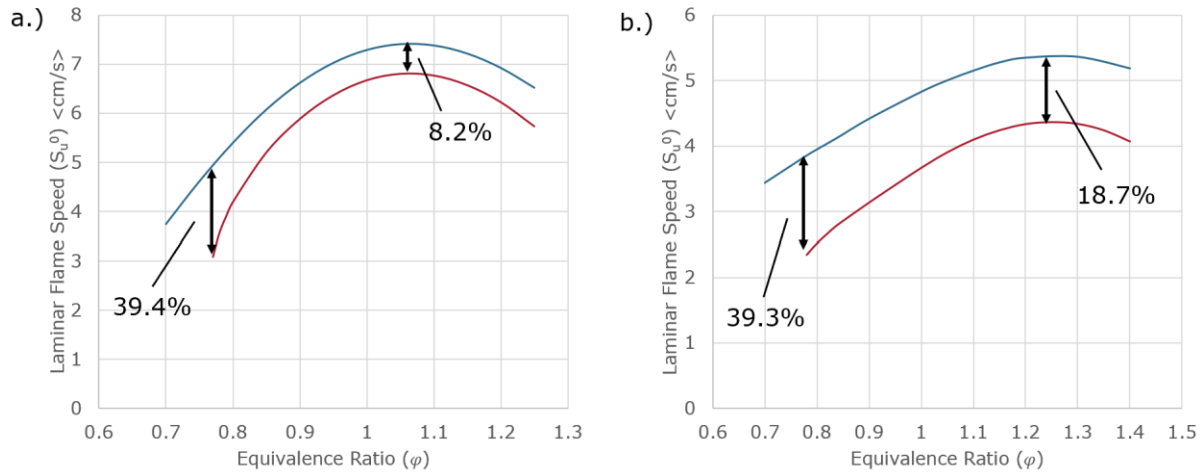


Figure 1: Laminar flame speed vs. equivalence ratio for a.) R-32/air at $P_0=1\text{atm}$ and $T_u=300\text{K}$, b.) R-1234yf/air at $P_0=1\text{atm}$ and $T_u=400\text{K}$.

The accuracy of S_u^0 , whether derived through flame simulation or data reduction methods, depends on the governing radiation model's ability to predict the total radiative heat loss. For the optically-thin limit (OTL) model, Planck mean absorption coefficient data must be included for all major burned gas products, as well as intermediates with large potentials for radiative emission. The major radiating species of HFC/air flames remain an important topic of study, as fluorinated burned gas products have been shown to vary across different HFC refrigerants due to factors such as a refrigerant's hydrogen-to-fluorine ratio. However, Planck mean absorption coefficient data currently available for fluorinated species is quite limited. Nevertheless, calculations for radiative heat loss contribution, using available Planck mean absorption coefficients, can offer insight into which species have the greatest potential for radiation heat loss. To this end, burned gas species mole fractions and percent contribution to total radiative heat loss was computed for R-1234yf/air flames varying equivalence ratio, as shown in Fig. 2a and Fig. 2b. The burned gas composition was taken to be that at the adiabatic flame temperature, as the burned gas location is ambiguous in

radiative flames. For R-1234yf/air flames, CO_2 , HF, and CF_2O , make up over 90% of the contribution to the total radiative heat loss across all equivalence ratios. Although CF_2O mole fractions are considerably smaller than those of HF, CF_2O makes a similar radiative heat loss contribution to that of HF due to its large Planck mean absorption coefficient at high burned gas temperatures. These results highlight the potential for relatively minor species to be major radiation contributors.

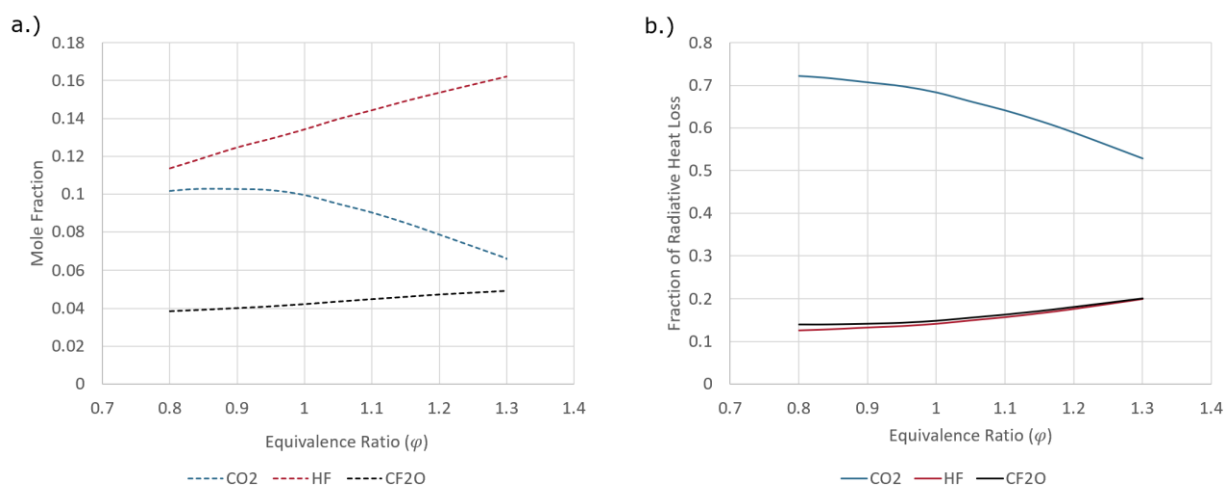


Figure 2: a.) R-1234yf/air burned gas mole fraction vs. equivalence ratio at $P_0=1\text{atm}$ and $T_u=400\text{K}$ and b.) R-1234yf/air burned gas species radiative heat loss contribution vs. equivalence ratio at $P_0=1\text{atm}$ and $T_u=400\text{K}$.

4. Conclusions

In this study, radiation effects were quantified for weakly-propagating HFC/air flames. 1-D, steady-state, planar flame simulations were performed to study the reduction in flame speed due to flame zone heat loss, as well as explore major species contribution to radiative heat loss. Flame speed reductions are shown to be greater for slowly-propagating HFC/air flames compared to typical hydrocarbon/air flames. Radiative heat loss results emphasize the importance of Planck mean absorption coefficient data for major product species, but suggest that additional fluorinated species may need to be considered in the radiation heat loss model for other HFC refrigerant/air flames. Furthermore, a spherical flame radiation model was developed to interpret CON-P SEF experimental measurements, circumventing the effect of radiation-induced inward flow. Validation of the spherical flame radiation model is currently underway, but preliminary results show that the model better predicts the inward flow velocity for most conditions compared to existing analytical models.

5. Acknowledgements

This research was funded by the NSF grant CBET-2053239.

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