Kinetic effects of *n*-propylbenzene on *n*-dodecane cool flame extinction

Omar R. Yehia, Christopher B. Reuter, Yiguang Ju
Department of Mechanical and Aerospace Engineering, Princeton University
Princeton, NJ 08544, USA

1 Introduction

A fundamental understanding of low-temperature reactivity is crucial to the design and control of advanced engines [1–3] and the formulation of accurate transportation fuel surrogate models [4–7]. Since jet fuels and their surrogates contain significant amounts of *n*-alkanes and aromatics [8], an understanding of the low-temperature kinetic interactions between the different reactant classes and their influence on the combustion behavior of the mixture is necessary. Extensive work has been done to elucidate the nature of the kinetic influence of aromatics [9–11] and methyl esters [12,13] on the extinction behavior of *n*-alkane diffusion flames. The results showed that aromatics and methyl esters decrease hot flame reactivity primarily by the reduction of the H radical pool through reactions with the aromatic or ester fuels and their fragments, thereby preventing the H radicals from participating in the dominant chain-branching and major heat release reactions such as $H + O_2 = O + OH$ and $OH + CO = CO_2 + H$. For cool flames, the impact of the radical pool on flame extinction is more pronounced because of its low concentration and due to the slow chain-branching process. However, it is unclear as to whether similar interactions occur at low temperatures, given the fundamental differences between the high-temperature and low-temperature chain initiation and propagation mechanisms and the nature of the corresponding heat release [14]. Further, recent work [15] has demonstrated the ability of cool flames, at higher pressures and lower fuel concentrations, to surpass the reactivity of their hot flame counterparts. Therefore, it is necessary to understand the low-temperature kinetics that can govern flame extinction at these conditions. Therefore, the purpose of this work is to examine the kinetic interactions between *n*-alkane/aromatic blends, and to investigate the influence of such interactions on the reactivity of cool flames. Specifically, we investigate the influence of *n*-propylbenzene addition on *n*-dodecane/oxygen cool flame reactivity in a counterflow configuration by measuring the hot flame and cool flame extinction strain rates of the individual components and their blends.

2 Experimental and numerical methods

To examine the effects of the introduction *n*-propylbenzene on the extinction limits of *n*-dodecane/oxygen flames, we utilize a counterflow burner at atmospheric pressure. Details of the counterflow burner are

Correspondence to: oyehia@princeton.edu

described elsewhere [9], and a schematic of the experimental setup is shown in Figure 1. Briefly, the counterflow apparatus consists of two opposed temperature-controlled nozzles with 13-mm exit diameters. In the current work, a fixed separation distance of 22.5 mm was used. The upper burner was augmented with a fuel vaporization system, where liquid fuels were injected into a vaporization chamber using a controlled steel syringe pump (Harvard PHD 22/2000). Preheated nitrogen gas was used for liquid fuel vaporization and atomization through the chamber. The vaporized fuel/nitrogen mixture was then injected into the upper nozzle, maintained at 550 K, and met an oxidizer stream of pure oxygen from the lower burner, which was maintained at 300 K. Nitrogen guard flows were used to isolate the fuel/nitrogen and oxygen streams from the surrounding environment, and were maintained at the aforementioned temperatures. To ignite cool diffusion flames, an ozone generator (Ozone Solutions, TG-20) was used to initially populate the radical pool needed for low-temperature chain initiation reactions [16], and was switched off as the cool flame became self-sustaining. Given the weak chemiluminescent intensity characteristic of cool flames [17], planar laser-induced fluorescence of the formaldehyde molecule was employed to capture cool flame extinction. The formaldehyde laser-induced fluorescence was performed using the third harmonic of the output beam of a pulsed Nd:YAG laser (Quantel, Q-smart 850) at 5 Hz and 200 mJ/pulse. The fluorescence of the formaldehyde molecule was captured using an ICCD camera (Princeton Instruments, PI-MAX 4), and was filtered using a 390-nm low-pass filter. The experimental and numerical determination of flame extinction strain rates were performed by increasing the global strain rate while fixing the fuel mass flow rate and the location of the stagnation plane between the two opposed flows. The global strain rate, defined as the density-weighted gradient of the axial flow velocities [18], was varied by incrementally increasing the nitrogen and oxygen flow rates. Numerical computations were performed using the CHEMKIN OPPDIF module assuming plug flow conditions [19]. The Princeton second generation jet fuel surrogate chemical kinetic mechanism [12] was reduced to 591 species and 2745 reactions using a direct path flux analysis method [20].

3 Results and discussions

The experimentally and numerically determined hot flame extinction (HFE) limits of *n*-dodecane, *n*-propylbenzene, and their blends (by mole fraction) are shown in Figure 2, while the cool flame extinction (CFE) limits of their counterparts are shown in Figure 3. The computed extinction strain rate curves are shown in solid lines. While the reduced model qualitatively preserves the extinction behavior of the fuel blends, the model clearly overestimates mixture reactivity at every condition. Further work is needed to examine the kinetic model prediction accuracy over a wider range of strain rates and fuel mole fractions, while using nitrogen-diluted oxygen as the oxidizer as opposed to pure oxygen. Further, as seen in Figure 3, the cool flame reactivity is significantly overpredicted, and the discrepancy in model predictions and the experimental results are an order of magnitude larger for cool flames than for their hot flame counterparts. Further, by rescaling the results with the effective *n*-dodecane (nC12) mole fraction, it is obvious that the addition of *n*-propylbenzene (nPB) increases the reactivity of the

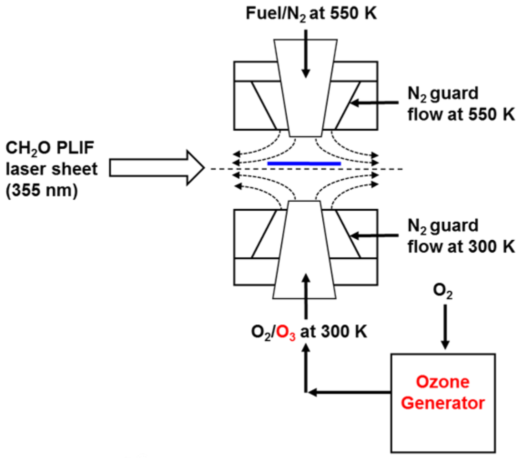

Figure 1. Counterflow burner experimental setup with ozone generator for cool flame ignition.

hot flame but significantly decreases the reactivity of its cool flame counterpart, which suggests that *n*-propylbenzene may have a kinetically inhibitive effect at low temperatures. It is interesting to note that the computed extinction strain rates also preserve such a trend. Therefore, to isolate such an effect, we examined the influence of *n*-propylbenzene addition on nitrogen-diluted *n*-dodecane mixtures while maintaining a constant mass fraction of *n*-dodecane.

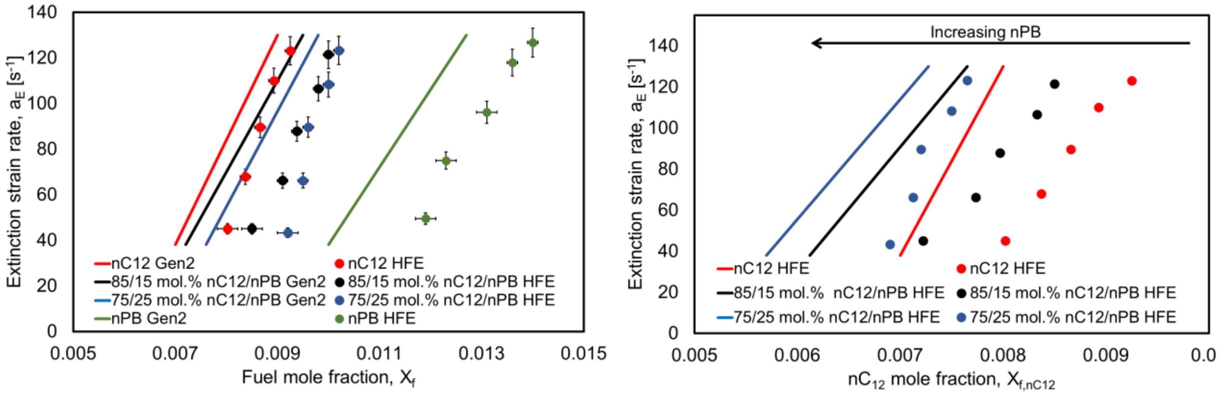

Figure 2. Hot flame extinction (HFE) strain rates as a function of fuel (left) and nC12 (right) mole fractions.

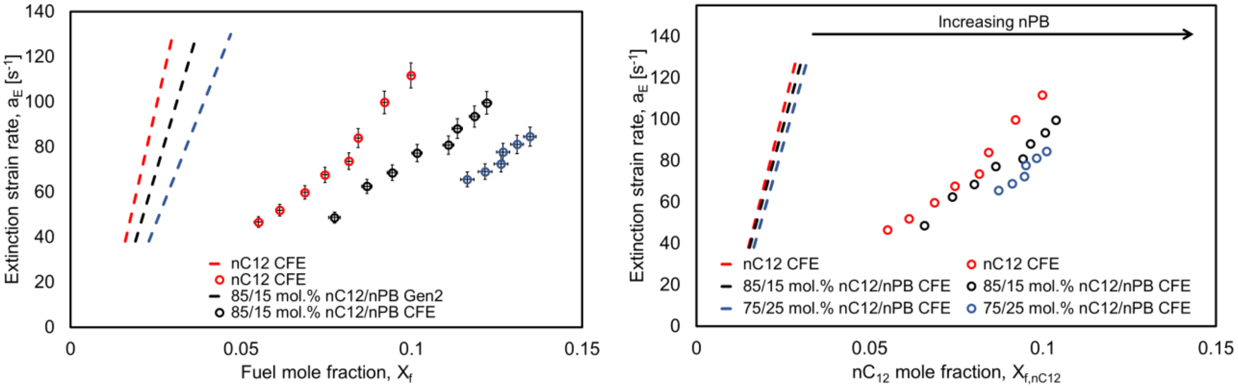

Figure 3. Cool flame extinction (CFE) strain rates as a function of fuel (left) and nC12 (right) mole fractions.

As seen in Figure 4, the introduction of *n*-propylbenzene, at a fixed mass fraction of *n*-dodecane, indeed inhibits *n*-dodecane consumption and decreases the rate of production of the hydroxyl radical (OH). Although not shown, such a trend is reversed in the case of hot flames, where the addition of *n*-propylbenzene promotes *n*-dodecane consumption and OH production. Since flame extinction is governed by the competition between heat release and heat loss, as well as radical production and quenching [9,21], the effect of *n*-propylbenzene on heat release rate and radical pool population must be considered. Pathway analyses of fuel consumption revealed that *n*-dodecane is consumed almost entirely (97%) by the H-abstraction reaction with OH ($nC_{12}H_{26} + OH = C_{12}H_{25} + H_2O$), which is effectively the only step for the low-temperature chain initiation process that leads to alkyl oxidation ($C_{12}H_{25} + O_2 = C_{12}H_{25}O_2$), subsequent alkyl peroxy radical isomerization ($C_{12}H_{25}O_2 = QOOH$) and oxidation ($QOOH + O_2 = QOOHO_2$), cyclic ether formation ($QOOH = QO + OH$) and further decomposition reactions to produce OH radicals and a variety of reactive intermediates, which is the known low-temperature chain branching process [22] that produces more than 50% of the OH radical pool. Further analysis of the OH consumption pathways revealed that, with the addition of *n*-propylbenzene (25 mol.% of the fuel), 8.8% of OH consumption occurs as a result of reactions with *n*-propylbenzene and its fragments in weakly exothermic reactions to produce stable intermediates that are unreactive at low temperature (below 750 K).

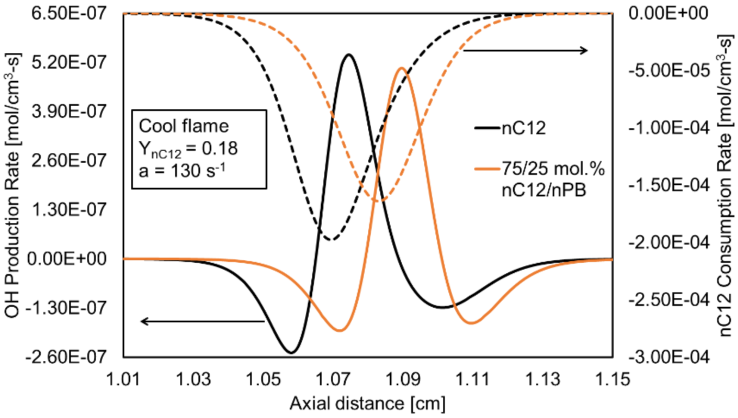

Figure 4. Cool flame nC12 consumption and OH consumption rates.

Heat release pathways for both cool flames and hot flames, shown in Figures 5 and 6 respectively, depict the difference between the effect of *n*-propylbenzene addition on heat release rates for both cool flames and hot flames. In cool flames, the scavenging of the OH radical by *n*-propylbenzene suppresses the chain initiation ($nC_{12}H_{26} + OH = C_{12}H_{25} + H_2O$), which in turn inhibits the alkyl oxidation reaction ($C_{12}H_{25} + O_2 = C_{12}H_{25}O_2$), both of which are major heat release reactions. It is clear that the inhibition of the initiation reaction suppresses heat release from all subsequent pathways. Conversely, in hot flames, the addition of *n*-propylbenzene increases the OH radical pool, as is evident by the significant enhancement in heat release, particularly in reactions involving OH consumption. Hence, we see that at high temperatures *n*-propylbenzene fragments can participate in the chain-propagation processes and contribute to overall heat release and radical pool population. However, at low temperatures, such reactions promote cool flame extinction by decreasing the OH radical population needed for chain initiation. Therefore, the inability of

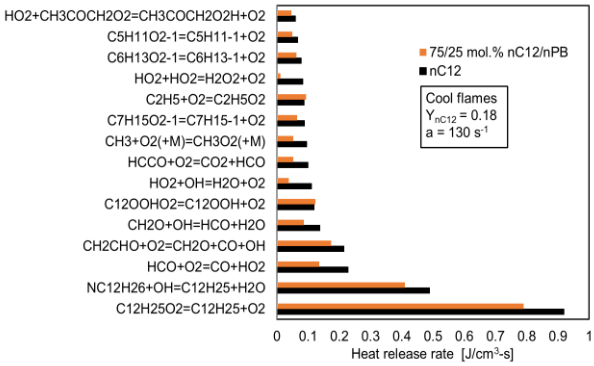

Figure 5. Cool flame major heat release rate pathways

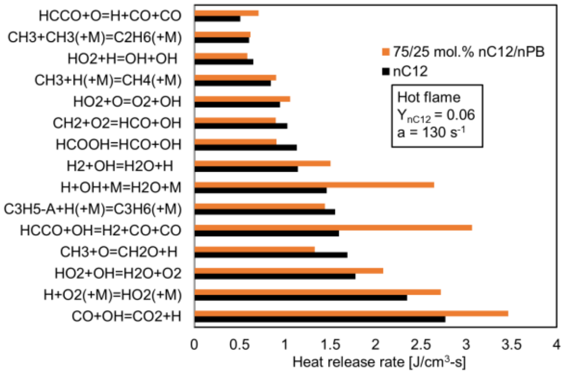

Figure 6. Hot flame major heat release rate pathways.

aromatic molecules to participate in the low-temperature chain propagation process highlights a fundamental difference between *n*-dodecane/*n*-propylbenzene kinetic coupling in hot and cool flames.

Cool flame extinction strain rate sensitivity analysis, shown in Figure 7, further highlights the importance of the radical pool population on cool flame extinction. It is evident that cool flame extinction is particularly sensitive to the chain initiation reaction and the alkyl peroxy radical isomerization for its propagation of the low-temperature chain reaction, as was discussed previously. It is also evident that reactions that do not participate in the low-temperature chain branching mechanism, even if strongly exothermic (such as CH_2O + OH = HCO + H_2O), decrease cool flame reactivity.

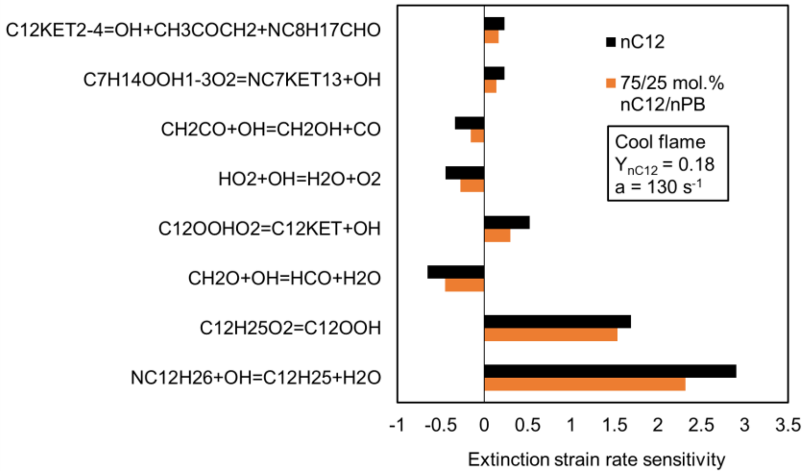

Figure 7. Cool flame extinction strain rate sensitivity.

4 Conclusions

The kinetic effect of *n*-propylbenzene on *n*-dodecane hot flames and cool flames was examined. It is demonstrated that *n*-propylbenzene addition increases the reactivity of the *n*-dodecane hot flame but decreases the reactivity of its cool flame counterpart, at fixed mass fractions of *n*-dodecane. The increase in hot flame reactivity was attributed to the increase of enthalpy and flame temperature and hence to net heat release, while the decrease in cool flame reactivity was attributed to the kinetic termination of the OH radical by aromatics and its fragments, which delays the consumption of *n*-dodecane. The addition of *n*-propylbenzene fundamentally interferes with the primary low-temperature chain initiation process by precluding the *n*-dodecane H-abstraction reaction with the OH radical. The decrease in cool flame reactivity is therefore due to the effective kinetic termination of the OH radical owing to the relative stability of *n*-propylbenzene fragments at low temperatures and their inability to participate in the low-temperature chain propagation mechanism. Finally, we note that while the reduced chemical mechanism was able to reasonably predict the extinction strain rates for the hot flames, significant discrepancies exist between the predicted and measured cool flame extinction limits. Further work is needed to examine the kinetic model prediction capability.

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