Combustion and Flame 185 (2017) 75–81

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Extended flammability limits of *n*-heptane/air mixtures with cool flames

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ARTICLE INFO

Article history:
Received 5 January 2017
Revised 22 February 2017
Accepted 22 June 2017
Available online 20 July 2017

Keywords:
Flammability limit
n-Heptane
Premixed cool flame

ABSTRACT

A numerical and theoretical investigation has been conducted on the flammability limits of *n*-heptane/air mixtures by considering the role of the cool flame chemistry. It is found that the existence of the cool flame can substantially extend the lean and rich limits of the conventional high-temperature flame. Different levels of kinetic criteria based on the controlling branching and termination reactions at low temperatures are derived and shown to agree well with the numerical results at normal and elevated pressures. Furthermore, the critical temperature of cool flame flammability limits at normal pressure is found to be around 600 K and is insensitive to pressure variations.

1. Introduction

At low ($T < 650\,K$) and intermediate ($650\,K < T < 1000\,K$) temperatures, cool flames occur in many aliphatic hydrocarbon fuel–air mixtures dominated by low-temperature chemistry [1,2]. It is considered as a key factor responsible for engine knock [3], and is also closely related to the two-stage autoignition and the negative temperature coefficient (NTC) phenomena [4]. Consequently, extensive efforts have been made to observe cool flames in various combustion systems [2,5–15]. In particular, cool flames with oscillatory volumetric heat release and chemiluminescence have been observed in homogeneous mixtures such as those in heated closed vessels [5] and jet-stirred reactors [2]. In nonhomogeneous mixtures, which are the focus of the present study, there exists strong coupling between the cool flame chemistry and the transport processes involved in either nonpremixed or premixed systems. Specifically, for nonpremixed systems, Law and Zhao [6] and Zhao and Law [7] numerically investigated the ignition and extinction of diffusion cool flames at low strain rates and/or high pressures in the counterflow. The study demonstrated that low-temperature chemistry can be strongly coupled with transport to induce a secondary, cool-flame, S-curve, characterized by the existence of both ignition and extinction turnings, on the lower branch of the conventional primary S-curve for the hot flame. Subsequently, Deng et al. [8] experimentally observed the ignition and consequently existence of diffusion DME/air cool flames in the counterflow using infrared measurement. This was followed by a similar experimental observation of counterflow *n*-heptane diffusion cool flames with ozone sensitization by Won et al. [9]. Furthermore, Nayagam et al. [10,11] observed two-stage flame extinction in microgravity droplet combustion experiments, and hypothesized the presence of cool flame burning following extinction of the first-stage hot flame, while Farouk et al. [12,13] numerically modeled the two-stage extinction of *n*-heptane droplet and cool flame oscillation with radiative heat loss. In terms of premixed flames, Zhao et al. [14] computationally and experimentally observed premixed cool flames for $DME/O_2/N_2$ mixtures, and identified the finite residence time window for their existence in the counterflow. Furthermore, Ju et al. [15] numerically studied the premixed cool flame propagation speeds and flame structures of DME/O_2 mixtures, again with ozone sensitization.

Now that the physical existence of cool flames has been unambiguously established, it behooves us to examine its implications on the foundational concepts underlying various combustion phenomena and theory. Of particular importance is the concept of flammability limits of a combustible mixture, empirically defined as the lean and rich concentration limits of a fuel/oxidizer system beyond which steady flame propagation cannot be maintained [16]. Law and Egolfopoulos [17,18] postulated a chain-thermal theory indicating that, with the continuous reduction of the concentration of the controlling reactant and hence the associated flame temperature of a steadily-propagating planar flame in the doubly infinite domain, a state will be reached at which the temperature-insensitive three-body termination reaction overwhelms the temperature-sensitive two-body branching reac-

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http://dx.doi.org/10.1016/j.combustflame.2017.06.015
0010-2180/

tion, such as the $H + O_2 + M \rightarrow HO_2 + M$ and the $H + O_2 \rightarrow OH + O$ reactions in H_2–O_2 mixtures respectively, leading to a precipitous drop in the net reaction rate. This, together with the omnipresent radiative heat loss, leads to extinction of the flame [19]. Indeed, computational simulation demonstrated that the flame response exhibited the characteristic S-curve extinction turning point at the state where the sensitivity of the rate of the controlling termination reaction balances that of the controlling branching reaction. The predicted flammability limits of a variety of mixtures agree well with the observed values.

Since we have now established that steadily burning cool flames can be sustained with flame temperatures substantially below the adiabatic flame temperatures corresponding to the conventional hot flame, we shall re-visit the concept of the flammability limit, and explore if the limit, say in terms of the concentration of the controlling reactant, can be extended beyond that of the conventional limit based on the extinction of the hot flame. The practical implications, for example on enhanced combustion efficiency through ultra-lean combustion, and the extra precaution needed in the monitoring and prevention of fires and explosions, are obvious.

In view of the above considerations, we have conducted a computational study of the response of the near-limit, planar premixed *n*-heptane/air cool flames, using detailed chemistry and transport including radiative heat loss, and with emphasis on identifying the controlling mechanisms for the fundamental flammability limits and the dependence of these phenomena on the mixture properties. Specifically, we shall first investigate the rich and lean flammability limits of *n*-heptane/air cool flames, demonstrate the controlling low-temperature chemistry, and derive the associated kinetic criteria of these extended flammability limits. The effects of mixture temperature and pressure on these limits, and the flame regimes of the high-temperature flames and the cool flames, are also examined.

2. Numerical model

The planar one-dimensional premixed flame was simulated using the PREMIX code developed by Kee et al. [20] coupled with the CHEMKIN and TRANSPORT packages [21], with appropriate modifications to include the radiative heat loss in the energy equation. The flame was assumed to be optically thin and the Planck mean absorption coefficients were calculated for CH_4, CO_2, H_2O, and CO using the model given in [22]. The reaction mechanism for *n*-heptane, involving 88 species and 326 elementary reactions, was taken from Yoo et al. [23] with the RO_2 termination reactions from [24]. Adaptive gridding was used to resolve the detailed flame structure. Discretization in both time and space was reduced until no change was observed in the solution to ensure convergence.

Steady calculations were performed by omitting the time derivative terms in the conservation equations. For these calculations, the governing equations were solved in a coordinate system moving with the flame. As such, mass flux becomes an eigenvalue of the problem. In order to investigate the turning point behavior expected for the non-adiabatic, radiative flame, we employed the flame continuation technique of Nishioka et al. [25]. Specifically, in each of the calculations, the mass flux through the flame was prescribed as a parameter, and the boundary condition on the equivalence ratio ϕ of the mixture was relaxed. The code was then used to determine the unburned fuel/air mixture that satisfied the prescribed mass flux. This technique yields efficient solutions to near-limit flames where a slight change in ϕ yields a large change in the mass flux. The Dirichlet boundary condition was specified at the left, unburned boundary of the computational domain. Furthermore, an elevated initial temperature ($T_i = 500$ K) was used to promote the low-temperature chemistry for cool flames, especially in view of the interest in engine applications. Consequently the flammability limit investigated in the present system is not the conventional one based on having the room temperature as the ambient temperature, for either the high- or the low-temperature chemistry, being wider for the present hotter ambience. A zero-gradient condition for species was applied at the right, burned boundary, and the computational domain was chosen to be sufficiently large to allow cooling of the radiative flames.

3. Demonstration of extended flammability limits

We first examine the flame regimes of the steadily-propagating premixed *n*-heptane/air flames. Figures 1a and b respectively show the dependence of the maximum flame temperatures on the normalized equivalence ratio [16], $\Phi = \phi/(1+\phi)$, for lean and rich mixtures. It is seen that two flame solutions are possible, namely those corresponding to the conventional hot flames with flame temperatures close to the adiabatic flame temperatures, and those corresponding to the low-temperature flames with flame temperatures close to those of the cool flames. It is also noted that, while the flame propagates in the doubly-infinite domain, radiative cooling suppresses the transition of the cool flame to a hot flame in the downstream.

Figure 1a then demonstrates that, for the lean mixtures, there exists a critical, minimum value of $\Phi = 0.247$ beyond which the hot flame does not exist, and as such corresponds to the conventional flammability limit (for $T_i = 500$ K). At such a condition, the flame temperature is so low ($T_f = 1250$ K) that the important high temperature branching reaction, namely $H + O_2 \rightarrow HO + O$, is slower than the corresponding termination reactions, $H + O_2 + M \rightarrow HO_2 + M$. Consequently a freely-propagating hot flame could not sustain itself with radiative heat loss [17,18], as mentioned earlier. Beyond this state, no solution for the hot flame exists.

Cool flames, however, persist beyond this state to much leaner conditions. Similar to the hot flame branch, the cool flame also has a turning point, at $\Phi = 0.202$ and no solution exists below this limit, thereby representing an "absolute" lean flammability limit which is much lower than the hot flame limit of $\Phi = 0.247$. This lean flammability limit corresponds to the conventional equivalence ratio of $\phi = 0.256$, with the corresponding critical flame temperature of only around 600 K.

For rich mixtures, Fig. 1b shows that the cool flame can exist in a much broader range, up to $\Phi = 0.987$, which is corresponding to the conventional equivalence ratio at $\phi = 75.96$. For the hot flame, the conventional flammability limit does not exist as the characteristic turning point degenerates to an inflection transition because of the higher initial mixture temperature. While such a loss of distinct criticality is well recognized in the study of ignition–extinction phenomena [16], the implications of the present result on the mixture flammability is of both fundamental and practical interest, meriting further study.

Figure 2 shows the corresponding flame speed dependence on Φ for the lean and rich mixtures, demonstrating the substantially lower flame speeds for the cool flames, as expected. These excessively small values of the flame speeds also suggest the susceptibility of these weak flames to buoyancy and other accelerative body forces, thereby imposing further complications in assessing the fire and explosion propensities, as well as the performance of high-intensity burners undergoing accelerative maneuvers, as induced by these cool flames.

To validate the results from and quantify the uncertainties of the chemical kinetic as well as the radiation models, the predictions with different kinetic models and radiation intensities are shown in Fig. 3. The present results are compared with the predictions using another skeletal mechanism with 188 species [23]. It was found that both mechanisms could predict the current second cool flame limit with only small differences. Furthermore,