Partially Premixed n-Heptane/Air Counterflow Flames

P. Berta, I. K. Puri, and S. K. Aggarwal

Department of Mechanical and Industrial Engineering
University of Illinois at Chicago, Chicago IL 60607 - USA

INTRODUCTION

Liquid fuels are an important energy source, since they are used in numerous propulsion and energy conversion applications. The characteristics of liquid fuel combustion are very complex. In order to avoid the complexities associated with the droplet/vapor transport and nonuniform evaporation processes, a fundamental investigation of liquid fuel combustion in idealized configurations is very useful. Such an investigation can also facilitate the validation of fundamental theoretical/computational models through measurements in flames. However, there is a paucity of such measurements in the literature [1,2]. We report on such an investigation. Although most practical liquid fuels are blends of several components, we have examined n-heptane for its role as a surrogate liquid fuel for sake of simplicity. It is also a reference fuel in the definition of the octane number, and its oxidation chemistry has been extensively investigated.

Due to their diverse applications and relevance, partially premixed flames have been investigated extensively in recent years. The bulk of the fundamental studies have focused on methane-air flames (e.g.,3,4), motivated perhaps by the fact that detailed reaction mechanisms are available to model the chemistry. With the exception of a few recent investigations [1,5 ,6 ,7 ,8], the literature regarding the burning of higher hydrocarbon fuels, especially liquid fuels, in partially premixed flames is relatively sparse. In this investigation, we report on an experimental-computational investigation of n-heptane partially premixed flames established in a counterflow burner. Our objective is to provide detailed experimental data that can be subsequently used for the validation of computational models and reaction mechanisms involving simulations of liquid fuels in general, and n-heptane in particular.

EXPERIMENTAL APPARATUS

The separation distance between the nozzles of the counterflow burner was 15 mm and their diameter was 27.38 mm. The fuel was introduced from the bottom nozzle. A nitrogen curtain was established through an annular duct surrounding the fuel jet in order to isolate the flame from ambient disturbances. The nitrogen and burned gases were exhausted and cooled through another annular duct around the oxidizer nozzle. The velocities of the two streams were chosen to conform to the global strain rate [9],

\[ a_g = \frac{2V_O}{L} \left( 1 + \frac{V_F}{V_O} \frac{\rho_F}{\rho_O} \right) \]

and to satisfy the momentum balance, \( \rho_F V_O^2 = \rho_O V_F^2 \).

The oxidizer was air at room temperature while the fuel stream consisted of mixtures of air and prevaporized n-heptane. The fuel nozzle was heated and the temperature was controlled to maintain the fuel-containing stream at a 400 K temperature at the burner exit. The air/n-heptane was mixed in a prevaporizer, which consisted of a stainless steel chamber that was electrically heated. The desired mass flowrate of n-heptane into the prevaporizer was maintained by a liquid pump, while gaseous nitrogen was introduced through the bottom of
the chamber. Approximately one-half of the chamber was filled with glass beads to impede the flow, thereby increasing its residence time in the chamber and, hence, enhancing the heat transfer to the liquid fuel. The temperature of the fuel vapor–gaseous nitrogen mixture exiting the chamber was monitored by a thermocouple. Temperature profiles of various flames were measured using a Pt-Pt 13%Rh thermocouple with a spherical bead diameter of 0.25 mm and wire diameter of 0.127 mm. The measured values were corrected for radiation heat losses from the bead, assuming a constant emissivity of 0.2 and a Nusselt number of 2.0 [1]. Species concentration profiles were characterized using a Varian 3800CP Gas Chromatograph. Samples were drawn from the flame with a quartz microprobe that had a 0.95 mm tip diameter and 0.39 mm tip orifice. Constant vacuum was applied at the end of the line through a vacuum pump. The line carrying the sample to the GC was made of stainless steel and heated to prevent condensation. A portion of the sample was injected into a Haysep DB 100/120 packed column connected to a thermal conductivity detector to measure light gases (up to C2H4) and another part into a Petrocol DH capillary column that was in line with a flame ionization detector to obtain the hydrocarbon distribution up to C7H16. Temperature programming was employed to minimize the analysis time. The temperature and pressure in the sampling loops were controlled to ensure that the same volume of gas was sampled for each analysis. The chromatogram peaks have been converted into mole fractions with calibration constants that were obtained separately for every species from known standards. Water molar fractions were evaluated through a mass balance of hydrogen atoms.

**REACTION MECHANISM**

The kinetic mechanism (SOX) used to model the flames was developed by extending a detailed oxidation scheme for several fuels [2,10]. Due to the hierarchical modularity of the mechanistic scheme, this model is based on a detailed sub-mechanism of C1-C4 species. Assuming analogy rules for similar reactions, only a few fundamental kinetic parameters are required for the progressive extension of the scheme towards heavier species. The resulting kinetic model of hydrocarbon oxidation from methane up to n-octane consists of about 150 species and 3500 reactions.
We have selected this scheme for modeling since the subset of n-heptane oxidation reactions in the mechanism have been extensively tuned by validating experimental measurements for pure pyrolysis conditions, oxidation in a jet stirred and plug flow reactors, and on a large set of shock tube experiments [11]. The polycyclic aromatic hydrocarbons (PAHs), well known for being soot precursors, are described with large detail in the scheme. The formation of the first aromatic rings by the C2 and C4 chemistry and by the resonantly stabilized radicals like propargyl and cyclopentadienyl (C5H3 and C5H5) has been carefully investigated [12,10]. Further growth of PAH species up to coronene (C24H12) is also modeled through the well known HACA mechanism (Hydrogen Abstraction Carbon Addition) [13], which has been extensively validated for counterflow flames burning a variety of fuels [14]. The main consumption reactions of aromatics and PAHs are H abstraction reactions by H and OH radicals. The high temperature reactions have been validated against substantial experimental data [12,10]. Numerical simulations of counterflow flames were performed using with the OPPDIF code [15] that is capable of modeling combustion between two opposed jets. The code was modified to handle the complex reaction mechanism and to account for thermal radiation through the optically thin model [16]. Most thermodynamic properties were obtained from Burcat [17] and unavailable properties were estimated using the group additivity and difference methods [18]. Transport properties were obtained from the CHEMKIN database [19] wherever available, while unavailable data was deduced through analogy with known species.

RESULTS AND DISCUSSION

Several counterflow partially premixed flames were established at strain rates ag = 50 and 100 s\(^{-1}\) and fuel stream equivalence ratios \(\phi = 4, 6, 9, \) and 20. Fuel is introduced from the bottom nozzle. The double flame structure that is characterized by separate premixed and nonpremixed reaction zones becomes visually more distinct as ag decreases and \(\phi\) increases, which also increases the separation distance \(\phi\) between the two zones. The premixed reaction zone is established on the fuel-side of the stagnation plane at the location \(x_p\) where the local axial velocity \(V_x\) equals the burning velocity \(S_{L,a}\) of the stretched flame. Since \(S_{L,a}\) increases as \(\phi\) is reduced, the premixed flame moves away from the stagnation plane toward the fuel nozzle to satisfy the condition \(S_{L,a} = V_x\). The nonpremixed flame is established on the oxidizer side at the location \(x_n\) where the fuel and oxidizer fluxes meet in stoichiometric proportion. Therefore, the value of the reaction zone separation distance \(\phi\) increases as the fuel-side premixing approaches stoichiometric conditions. Increasing the strain rate has an opposite effect, since for larger flow velocities the location \(x_p\) is pushed toward the stagnation plane. Soot is formed in the \(\phi = 20\) and \(ag = 50\) s\(^{-1}\) flame for which the premixed reaction zone has a yellow-orange luminosity. This luminosity fades as \(\phi\) is decreased, and is absent for the \(ag = 100\) s\(^{-1}\) flames.

Table 1 compares our measurements of the peak temperatures and specific major and minor species mole fractions with those for n-heptane flames found in the literature [1,6]. The major species are the major products (CO\(_2\) and H\(_2\)O) and intermediates (CO and H\(_2\)), and C\(_2\)H\(_2\) and C\(_2\)H\(_4\) are chosen since they lie along the C\(_2\) decomposition pathway that leads to soot precursors. The first comparison pertains to our measurements of a nonpremixed flame with the results from Ref. 1. Our measured peak temperature is higher by 100 K, which is attributed to the lower ag value in our experiment (100 s\(^{-1}\) versus 150 s\(^{-1}\) in Ref. 1). Nonetheless, the peak concentrations of CO, H\(_2\), H\(_2\)O, and summed C\(_2\) species are in very good agreement, but there is a discrepancy in the CO\(_2\) measurements. The nonpremixed flame reported in Ref. 6 was enriched with oxygen in order to match the peak temperature of their \(\phi = 2.8\) partially premixed flame. In addition, liquid n-heptane was introduced in the
form of a spray. Therefore, it is difficult to make a direct comparison of the strain rate for that flame and our measurements. That flame contains larger concentrations of oxidation products. Our measurements of the peak amounts of C₂ species differ from theirs, but the summed values of the respective C₂ compounds are virtually identical. There is general agreement between various facets of our nonpremixed flame measurements and the results of Refs. 1 and 6. This provides some consistency to the three sets of data.

Our investigation shows that the peak flame temperature increases with increasing premixing of the fuel stream. The peak temperature of the φ = 2.8 flame in Ref. 6 is lower than our measurement in a φ = 4 flame. Apart from measurement uncertainties and different fluid dynamic conditions at the boundaries [20] it is possible that the φ = 2.8 flame was established at a higher aₙ value. The peak temperatures of all partially premixed cases are ~2100 K, which are lower than the adiabatic flame temperature of 2274 K. All three measurements show that the value of φ increases as φ decreases, i.e., with greater partial premixing. The peak CO₂ and H₂O concentrations are relatively insensitive to partial premixing. The CO peak is on the premixed side and it increase as larger amounts of oxygen are supplied by decreasing the fuel side equivalence ratio. Likewise, the increasing amount of fuel-side oxygen reduces the peak H₂ concentration upstream of the premixed fraction zone. Not surprisingly, the increased oxidation with decreasing φ also reduces the peak concentrations of the C₂ species. This shows the influence of partial premixing on the formation of C₂ related soot precursors. It is known that partially premixed flames be less sooting than their nonpremixed or premixed counterparts [21,22].

Figures 2(a)-(h) present the structures of two n-heptane/air partially premixed flames with a high (φ = 4) and low (φ = 10) level of fuel/air premixing. The double flame structure is clear by observing the measured temperatures in Figs. 2(a) and (b), but not so through the simulations. The visually observed locations of the premixed and nonpremixed reaction zones are marked in the figures. The measured and simulated temperatures and major species concentration profiles are in relatively good agreement.

The premixed reaction zone, on the left in the figures (c) and (d), propagates upstream. It burns in the fuel-rich mixture and produces intermediate species such as CO and H₂. These species are transported to the nonpremixed reaction zone where they burn to produce CO₂ and H₂O. In a purely nonpremixed flame the CO formation is immediately followed by oxidation on the air-side of the flame. The carbon monoxide and carbon dioxide peaks are spatially closer in nonpremixed flames than for partially premixed flames. The separation between these peaks increases as the equivalence ratio is lowered and the flame transitions to two distinct, premixed and nonpremixed, interacting structures.

Figures 2(e) and (f) present the concentration profiles of light hydrocarbon species. The agreement between simulated and predicted profiles is good. For both flames the C₂ species

---

**Tab. 1** Comparison of experimental n-heptane counterflow flames various values of aₙ (s⁻¹) and φ. Temperatures are in K, peak concentrations are in molar fractions, flame spacing Δ is in mm. The subscripts F and O refer to the respective concentrations at the fuel and oxidizer nozzle. Similar conditions are highlighted.
have peaks in the premixed reaction zone, implying that the C₂-decomposition occurs there. These intermediate species are consumed before reaching the nonpremixed reaction zone. The peak concentrations of the species occur in the order CH₄ > C₂H₂ > C₂H₄ > sum of all C₃ species. The peak values of these species decrease with increasing oxidizer availability as the equivalence ratio is lowered.

Figures 2(g) and (h) can also provide some insight into the soot formation pathway for n-heptane-air partially premixed flames. Acetylene and benzene are considered to be soot precursors. In the $\phi = 4$ flame the acetylene peak concentration is three times lower than in...
the $\phi = 10$ partially premixed flame. The benzene peak concentration is likewise approximately halved. The oxidizer contained in the premixed fuel stream drives the reactions towards oxidation rather than pyrolysis. The oxidizer is present in partially premixed flames throughout the combustion system and there are no regions characterized by simultaneous high temperature and high fuel concentration. As a result pyrolysis reactions leading to soot formation are greatly diminished.

CONCLUSIONS

Experiments were performed to characterize the structure of n-heptane/air nonpremixed and partially premixed counterflow flames by varying the fuel stream equivalence ratio. A detailed comparison between measurements and simulations are provided for high and low premixing cases for the profiles of temperature and concentrations of CO, CO$_2$, H$_2$, CH$_4$, C$_2$H$_2$, C$_2$H$_4$, C$_3$ hydrocarbons, and C$_6$H$_6$. The measurements were compared with the experimental results reported in the literature and there is agreement regarding major facets of these data.

REFERENCES