Experimental and Numerical Investigation of n-Heptane/Air Counterflow Nonpremixed Flame Structure

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An experimental and numerical investigation of prevaporized n-heptane nitrogen-diluted nonpremixed flames is reported. The major objective is to provide well-resolved experimental data regarding the structure and emission characteristics of these flames, including profiles of major species (N\textsubscript{2}, O\textsubscript{2}, C\textsubscript{7}H\textsubscript{16}, CO\textsubscript{2}, CO, H\textsubscript{2}), hydrocarbon intermediates (CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, C\textsubscript{4}H\textsubscript{10}, and soot precursors (C\textsubscript{4}H\textsubscript{9}). A counterflow flame configuration is employed, because it provides a nearly one-dimensional flat flame that facilitates both the detailed measurements and simulations using comprehensive chemistry and transport models. The measurements are compared with predictions using a detailed n-heptane oxidation mechanism that includes the chemistry of NO\textsubscript{x} and polycyclic aromatic hydrocarbon formation. The measurements are compared with predictions using a detailed n-heptane oxidation mechanism that includes the chemistry of NO\textsubscript{x} and polycyclic aromatic hydrocarbon formation. Measurements and predictions exhibit excellent agreement for temperature and major species profiles (N\textsubscript{2}, O\textsubscript{2}, n-C\textsubscript{7}H\textsubscript{16}, CO\textsubscript{2}, CO, and H\textsubscript{2}), reasonably good agreement for intermediate species (CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, and C\textsubscript{4}H\textsubscript{10}), but significant differences with respect to benzene profiles. Consequently, the benzene submechanism was synergistically improved using pathway analysis and measured benzene profiles.

Introduction

LIQUID fuels are an important energy source due to their widespread use in various propulsion and energy-conversion applications such as internal combustion engines and gas turbine combustors. The various physical and chemical processes involved in liquid-fuel combustion have very complex interactions. In most practical devices, the liquid fuel is introduced into the combustion chamber in the form of a spray that consists of droplets that have a wide size and velocity distribution, resulting in disparate vaporization rates. Therefore, to avoid the complexities associated with the droplet/vapor transport and nonuniform evaporation processes, a fundamental investigation of liquid-fuel combustion in an idealized configuration that precludes vaporization is very useful. Also, although most practical liquid fuels are blends of several components, the investigation of an idealized fuel surrogate such as n-heptane can provide useful information about the combustion chemistry of heavier-hydrocarbon liquid fuels. In addition, n-heptane is also a reference fuel in the definition of the octane number and its oxidation chemistry has been extensively investigated [1–22].

Several investigations dealing with n-heptane flames have been reported in recent years. The combustion of n-C\textsubscript{7}H\textsubscript{16} has been investigated with reduced chemical mechanism for analyses of burning velocities [1], the structure and extinction of nonpremixed flames [2–4], and liquid-pool flames [5–7]. Semidetailed and detailed chemistry models have also been used to analyze n-C\textsubscript{7}H\textsubscript{16} combustion in various flame configurations [8–11]. A detailed mechanism describing C\textsubscript{7} pyrolysis and oxidation has been developed using extensive experimental data from a variety of experiments [12]. Experimental investigations of n-C\textsubscript{7}H\textsubscript{16} combustion have been performed using jet-stirred and plug-flow reactors [8,13], liquid pools [14–16], and droplets [17,18] and to determine premixed burning velocities [19]. In spite of the many previous investigations [20–22], there is a paucity of detailed measurements in well-characterized n-heptane flames, especially regarding the distribution of intermediate species such as C\textsubscript{1}–C\textsubscript{5} hydrocarbons, which are important from the perspective of validating the detailed reaction mechanisms and characterizing NO\textsubscript{x} and soot formation pathways. Moreover, a fundamental understanding of n-heptane flames under a wide range of conditions can assist in the design and optimization of various liquid-fueled combustion systems with respect to efficiency and overall emissions of NO\textsubscript{x} and particulate matter.

Gaseous polycyclic aromatic hydrocarbon (PAH) species and soot particles are undesirable pollutants because they reduce efficiency and have a detrimental health impact, particularly on the cardiopulmonary system [23]. Soot particles are formed inside hydrocarbon flames through the pyrolysis of hydrocarbon molecules and subsequent heterogeneous processes that are very complex [24,25]. However, because soot is formed through large benzene and larger PAH molecules, characterizing these species accurately is important to further improve the PAH formation chemistry. Seiser et al. [20] investigated the extinction of nitrogen-diluted n-heptane/air counterflow nonpremixed flames. Li and Williams [21] examined the structure of similar partially premixed flames But when the liquid fuel was introduced as a spray. Berta et al. [22,26] characterized the structure and emission characteristics of prevaporized n-heptane partially premixed flames. Liu et al. [27] reported a numerical study of the effect of strain rate on the transient autoignition of nonpremixed n-heptane at high pressures in a counterflow configuration.

Our primary objective is to provide useful experimental data for nitrogen-diluted n-heptane nonpremixed flames in a configuration that removes the complexities associated with droplet transport and vaporization. We measured temperature and species (including...
C_{1}\text{--}C_{6} and PAHs) concentration profiles for prevaporized n-heptane nonpremixed flames for different strain rates and nitrogen dilution. These flames have also been simulated using a detailed reaction mechanism that also considers soot precursors such as acetylene and benzene [12,28--30]. An improved mechanism to predict benzene and higher-PAH species is proposed based on the measurements and a sensitivity analysis.

**Experimental Apparatus**

A schematic diagram of the experimental setup in which the counterflow flames were established is presented in Fig. 1. The separation distance between the counterflow nozzles was varied from 10 to 15 mm. Both nozzle diameters were 27.38 mm. A mixture of prevaporized n-heptane and nitrogen fuel was introduced from the bottom nozzle. A nitrogen curtain was established through an annular duct surrounding the fuel jet to isolate the flames from ambient disturbances. This nitrogen and combustion products were vented and cooled through another annular duct around the oxidizer nozzle. The velocities of the two streams define the global strain rate [31]

\[
a_{g} = \frac{2|V_{O}|}{L} \left(1 + \frac{|V_{F}|}{|V_{O}|} \sqrt{\frac{\rho_{F}}{\rho_{O}}} \right)
\]

and were chosen to satisfy the momentum balance \(\rho_{O}V_{O}^{2} = \rho_{F}V_{F}^{2}\), where \(\rho\) represents density; \(V\) is the gas velocity; subscripts \(O\) and \(F\) refer to the oxidizer and fuel nozzles, respectively; and \(L\) is the separation distance between the two nozzles.

The oxidizer was air at room temperature and the fuel stream consisted of mixtures of nitrogen and prevaporized n-heptane. The fuel nozzle was heated and its temperature was controlled to maintain the fuel-containing stream at a 400-K temperature at the burner exit. The \(N_{2}/n\)-heptane mixture was formed in a pre-evaporizer, which was an electrically heated stainless steel chamber. The desired mass flow rate of \(n\)-heptane into the pre-evaporizer was maintained by a liquid pump while gaseous nitrogen was introduced through the chamber bottom. Approximately three-quarters of the chamber was filled with glass beads to impede the flow, thereby increasing its residence time and thus 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 a 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 [20]. The uncertainty in temperature measurements was less than 100 K. Species-concentration profiles were measured using a Varian CP-3800 gas chromatograph. Samples were drawn from the flame with a quartz microprobe that had a 0.34-mm tip diameter and 0.25-mm tip orifice. Constant vacuum was applied at the end of the line through a vacuum pump. The line carrying the sample to the gas chromatograph was made of fused silica and was heated to prevent condensation. A portion of the sample was injected into a Hayesep DB 100/120 packed column connected to a thermal conductivity detector to measure light gases (up to \(C_{2}H_{3}\)), and another portion was injected into a Petrocol DH capillary column that was placed inline with a flame-ionization detector to obtain hydrocarbon distributions up to \(C_{7}H_{10}\). The temperature in the gas-chromatograph oven was gradually increased 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 were converted into mole fractions with calibration constants that were obtained separately for every species from known standards. Water mole fractions were obtained through a mass balance of hydrogen atoms. Relative experimental errors associated with gas-chromatograph readings were within 10\%.

**Reaction Mechanism**

The reaction mechanism used in this study consists of the high-temperature reactions of a more comprehensive model that was previously developed and tested against a wide range of experimental data for different fuels [28,32]. Because of the hierarchical modularity of the mechanistic scheme, this model is based on a detailed submechanism of \(C_{1}\text{--}C_{4}\) species. Assuming analogy rules for similar reactions, only a few fundamental kinetic parameters are required for the progressive extension of the scheme toward heavier species. The resulting kinetic model of hydrocarbon oxidation from methane up to \(n\)-octane consists of about 170 species and 5000 reactions.

We selected this mechanism for our simulations because the subset of \(n\)-heptane oxidation reactions included in it has been extensively tuned by using experimental measurements for pure pyrolysis conditions, oxidation in jet-stirred and plug-flow reactors, and shock tube experiments [12]. Moreover, a relatively detailed model for PAHs that are soot precursors is contained in the mechanism. The formation of the first aromatic rings by the \(C_{2}\) and \(C_{4}\) chemistry and by the resonantly stabilized radicals such as propargyl and cyclopentadienyl (\(C_{3}H_{3}\)) has been carefully investigated [29,32]. Further growth of PAH species up to coronene (\(C_{24}H_{12}\)) is also modeled through the well-known hydrogen- abstraction/carbon-addition (HACA) mechanism [33], which has been extensively validated for counterflow flames burning a variety of fuels [34]. 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 [28,29,32].
Numerical simulations of counterflow flames were performed using the opposed diffusion flame (OPPDIF) code [35]. The code was modified to handle the complex reaction mechanism. The radiative heat transfer was modeled using an optically thin gas assumption, with CO₂, H₂O, CO, and CH₄ being the participating gaseous species. Further details are provided in [36,37]. The soot radiation is not included because the present study considers flames with moderate strain rates and significant nitrogen dilution in the fuel stream. This is further confirmed by the agreement between the measured and predicted peak flame temperatures. Most thermodynamic properties were obtained from Burcat and McBride [38] and unavailable properties were estimated using the group additivity and difference methods [39]. Transport properties were obtained from the CHEMKIN database [40] wherever available, and unavailable data were deduced through analogy with known species.

### Results and Discussion

We performed a detailed parametric investigation to characterize the effects of strain rate and nitrogen dilution on the structure and emission of n-heptane/air nonpremixed flames. We selected four of the cases that were investigated to characterize the flame structures for which the operating conditions in terms of strain rate, nitrogen dilution, and nozzle-separation distance are reported in Table 1. Flame A1 corresponds to a strain rate of 150 s⁻¹ and a nitrogen dilution of 85%, which are the conditions of Seiser et al. [20]. Their results were used for validation purposes. Flame B1 has a strain rate of 77 s⁻¹ and a nitrogen dilution of 50%. It is noteworthy that flame A1 is nearly nonsooting, whereas flame B1 is relatively more sooting.

Figure 2 presents digital images of flames A1 and B1 obtained for the same exposure conditions. Several differences are observed. The thickness of flame A1 is smaller, due to its larger strain. It has a bright blue color that is typical of CO oxidation. Flame B1 is thicker and exhibits an orange-red zone that is indicative of pyrolysis and soot-formation reactions. Although the soot formation is observable in this flame, it is not large enough to present difficulties for the gas sampling technique.

The measurements for flame A1 were compared with those reported by Seiser et al. [20]. Apart from small differences in the concentration profiles of minor species, which are attributed to differences in the experimental methods and associated errors, there was good agreement between the two measurement sets with respect to temperature and species mole fraction profiles. There was also good agreement with respect to the spatial shift observed between the measured and computed temperature profiles in the two studies.

Table 1 Operating conditions in terms of strain rate, nitrogen dilution (on a percent mole basis), and nozzle-separation distance for the cases investigated numerically and experimentally

<table>
<thead>
<tr>
<th>Flame</th>
<th>Strain rate, s⁻¹</th>
<th>N₂ dilution, %</th>
<th>Nozzle separation, cm</th>
<th>( V_o, \text{cm/s} )</th>
<th>( T_o, \text{K} )</th>
<th>( V_f, \text{cm/s} )</th>
<th>( T_f, \text{K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>150</td>
<td>85</td>
<td>1</td>
<td>37.50</td>
<td>300</td>
<td>32.52</td>
<td>400</td>
</tr>
<tr>
<td>A2</td>
<td>100</td>
<td>88</td>
<td>1.5</td>
<td>37.45</td>
<td>300</td>
<td>31.93</td>
<td>400</td>
</tr>
<tr>
<td>A3</td>
<td>50</td>
<td>90</td>
<td>1</td>
<td>12.57</td>
<td>300</td>
<td>10.98</td>
<td>400</td>
</tr>
<tr>
<td>B1</td>
<td>77</td>
<td>50</td>
<td>1</td>
<td>19.07</td>
<td>300</td>
<td>13.11</td>
<td>400</td>
</tr>
</tbody>
</table>

Flames A1 and B1 have similar structure, although flame B1 is spatially wider, due to its lower strain rate. For both flames, there is a single nonpremixed reaction zone on the oxidizer side of the stagnation plane, as indicated by the temperature and velocity profiles. As expected, the locations of the CO and H₂ concentration peaks precede those of the CO₂ and H₂O concentration peaks. All of these peaks are located in the high-temperature region. On the other hand, the C₂ and other intermediate hydrocarbon species have maximum concentrations on the fuel side of the flame, on which pyrolysis occurs [37]. The profiles for flame A1 exhibit sharper peaks because of the higher strain rate. The effect of nitrogen dilution can be seen in the peak temperature values. The flame-A1 peak temperature is 1798 K, and flame-B1 peak temperature is 1933 K, both values being much lower than the adiabatic-flame temperature (2274 K) of n-heptane/air mixture.

To characterize the effect of strain rate on the flame structure, we now discuss measurements and simulations for two other n-heptane/air nonpremixed flames. Figure 4 presents temperature, velocity, and species mole fraction profiles for flames A2 and A3, corresponding to strain rates of 100 and 50 s⁻¹, respectively. These cases, together with flame A1, are all relatively close to extinction, due to large nitrogen dilutions (ranging from 85 to 90%) of the fuel stream. There is also generally good agreement between measured and numerical data for these two flames, especially for temperature and major reactant and product species. Flame A3 is spatially broader than flame A2, due to the lower strain rate. The buoyant misalignment between measurements and predictions for it is larger than for flames A1 and A2, which provides evidence of the stronger buoyancy effect at low strain-rate values.

The peaks in the profiles of the C₃ species ethylene, acetylene, and methane are influenced by the strain rate, because it has an

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1 For clarity, different x scales were used for some of the species profiles.
effect on the stagnation-plane location relative to the hot region and the peak temperature. The peaks for these species lie near the stagnation plane, on which the residence time is relatively large. Going from flame A1 to flame A3, the separation between the stagnation plane and the peak temperature increases because the strain rate decreases, whereas the peak temperature decreases because the dilution of the fuel stream increases and the radiative heat loss increases at lower strain rates. Because this reduces the rate of heat transport from the flame toward the stagnation plane, pyrolysis reactions are diminished.

A major objective of this work is to characterize the relative soot formation in n-heptane flames through the formation of major soot precursors such as acetylene and benzene, which lie along the growth process to PAH. Figures 2 and 3 indicate that flame B1 is sooting, whereas flame A1 is nearly nonsooting. However, both the predictions and measurements provide evidence that soot-precursor pathways are important for both cases. The measured and predicted profiles of acetylene and benzene mole fractions are presented in Figs. 3–5. The acetylene profiles for flames A1, B1, A2, and A3 are contained in Figs. 3 and 4, and those of benzene are shown in Fig. 5.
The measured and predicted acetylene profiles are in agreement with each other and with results from other investigators, but benzene measurements in n-heptane nonpremixed flames have not been previously reported, and so a definitive comparison could not be made. The predictions are unable to reproduce the measured benzene profiles. We also observed a similar disagreement between the measurements and prediction for benzene in n-heptane/air counterflow partially premixed flames [22,26]. Benzene mole fractions have also been measured by El Bakali et al. [41] in a laminar premixed flame.

To examine these discrepancies further, the dominant reactions associated with benzene formation were identified through a pathway analysis. Results are summarized in Fig. 6 and Table 2. Figure 6a shows the most important pathways of benzene formation in flame A1 at a location corresponding to the peak benzene mole fraction (0.428 cm from the fuel nozzle). The kinetic rates of the dominant reactions are listed in Table 2. The most important formation pathway is the recombination of propargyl radicals to form either benzene (R1) or phenyl (R2). The most important reaction for the formation of propargyl radical is the H abstraction on propadiene.
(R3), which is formed from the reaction of allyl radical C3H5 with H
(R4). Other pathways of benzene formation are the reaction between
C2 and C4 species and that of toluene with H. Toluene is formed by
the recombination and H-abstraction reactions of benzyl radical,
which is formed by phenyl and also by C2H2 and cyclopentadienyl.
The only significant consumption pathway of benzene is the H-
abstraction reaction to form phenyl, which reacts with acetylene to
form phenylacetylene as a first step of the well-known HACA
mechanism [33]. A similar analysis was also performed at x =
0.46 cm from the fuel nozzle, where the temperature is higher. At this
location, the interactions between C2 and C4 species are not
important anymore, whereas the recombination of propargyl radicals
becomes more important.

The dominant pathways of benzene formation in flame B1 are
shown in Fig. 6b. Both the temperatures and benzene peak locations
are similar in flames A1 and B1. Although all the reactions associated
with benzene formation have noticeably higher rates in flame B1
(due to higher fuel concentration) than those in flame A1, the relative
importance of the different pathways is quite similar; that is, the
recombination of propargyl is the most important reaction, but the
interactions between C2 and C4 also have an significant impact on
the formation of benzene. At 0.495 cm from the fuel nozzle, only the C3
pathway is important, and the reaction of toluene with H is less
important. For this case, toluene is formed by phenyl and by the
reaction of propargyl with C2H2, whereas the reaction of C2H2 with
cyclopentadiene occurs in the reverse direction (i.e., it consumes
toluene). At this location, the oxidation reactions of benzene start to
become important. In particular, benzene is consumed not only by H
abstraction, but also by reaction with OH to form cyclopentadienyl or
phenol.

The results of the sensitivity analysis indicate that reaction 4
(see Table 2) has the strongest influence on benzene formation.
Although the C3H4 concentration measurement could have
provided useful information regarding the accuracy of the reaction
rate constants for this reaction, the gas-chromatograph sampling
technique could not resolve all of the C1– hydrocarbons. The kinetic parameters reported by Tsang [42] for reaction 4 are about
times lower than those contained in the original mechanism
(see Table 2). Benzene predictions in the four flames with Tsang’s
kinetic parameter are compared in Fig. 5 with the experimental
measurements and the predictions of the original mechanism.

The improvement in the predicted benzene profile is evident for all four
flames. In the relatively less sooting flames (i.e., flames A1, A2,
and A3), the predicted benzene is still high, but significantly
better, whereas in flame B1, the prediction becomes very good
within experimental uncertainties. Only the C6H6 mole fraction
profiles are shown with the modified mechanism, because no
differences were observed for the temperature and the other
species profiles. It is important to note that in the laminar premixed
flame of El Bakali et al. [41], the predicted benzene profile using
the modified mechanism also shows better agreement with the
measured profile.

| Table 2 | Dominant reactions associated with benzene formation |
| | Reaction | A, | β, | E, |
| 1 | C3H6 + C3H3 → C6H6 | 3.0 × 10^9 | 0 | 0 | Ranzi et al. [28] |
| 2 | C3H3 + C3H3 → C6H6 + H | 3.0 × 10^9 | 0 | 0 | Ranzi et al. [28] |
| 3 | OH + CH2 = C + CH2 → H2O + C2H3 | 2.0 × 10^4 | 2 | 1000 | Ranzi et al. [28] |
| | H + CH2 = C = CH2 → H2 + C2H2 | 5.0 × 10^4 | 2 | 5000 | Ranzi et al. [28] |
| | CH2 + CH2 = C = CH2 → H2 + C2H2 | 4.0 × 10^10 | 0 | 16,000 | Ranzi et al. [28] |
| 4 | H + CH = CH - CH2 + H2 + CH2 = C = CH2 | 1.81 × 10^10 | 0 | 0 | Tsang [42] |

*Three-parameter form of the Arrhenius equation k(T) = AT^n exp(-E_a/RT); units are kmol, m^3, kcal, and K
Fig. 6 Main pathways of benzene formation and consumption in a) flames A1 and b) B1 at 0.429 cm from the fuel nozzle; thickness of the arrows is proportional to the reaction rate; numbers are the reaction rates times $10^4$ kmol/m$^3$/s.

Conclusions

An experimental and numerical investigation was performed to examine the structure and emission characteristics of N$_2$-diluted nonpremixed n-heptane/air counterflow flames. Well-resolved experimental data for temperature and species-concentration profiles, including those of major species (n-heptane, O$_2$, N$_2$, CO, H$_2$, CO$_2$, and H$_2$O), intermediate hydrocarbon species (CH$_4$, C$_2$H$_4$, C$_3$H$_7$, and C$_4$H$_{10}$), and aromatic species (C$_n$H$_m$) have been reported for prevaporized n-heptane counterflow flames established at different levels of nitrogen dilution and strain rate. The measurements have been compared with simulations performed using a comprehensive reaction mechanism that includes detailed chemistry models for n-heptane oxidation and NOx and PAH species (up to C$_{14}$H$_{18}$) formation. Based on this comparison, the mechanism was modified to better predict the pyrolysis reactions associated with the formation of PAH species.

There is good quantitative agreement between measurements and predictions for temperature, major reactant/product species (n-heptane, O$_2$, N$_2$, and CO$_2$), and intermediate fuel species (H$_2$ and CO). There is also a fairly good agreement for intermediate hydrocarbon species (CH$_4$, C$_2$H$_4$, C$_3$H$_7$, and C$_4$H$_{10}$) as well as for benzene. For the conditions investigated, the reaction pathways analysis indicate that the major benzene formation reaction is the recombination of propargyl radicals, whereas the important reaction for the formation of propargyl radical is the H abstraction on propylene, which is formed from the reaction of allyl radical C$_3$H$_3$ with H. Other pathways of benzene formation are the reaction between C$_2$ and C$_3$ species and that of toluene with H. Toluene is formed by the recombination and H-abstraction reactions of benzyl radical, which is formed by phenyl and also by C$_2$H$_2$ and cyclopentadienyl. The consumption of benzene occurs mainly through the H-abstraction reaction to form phenyl, which reacts with acetylene to form phenylacetylene as a first step of the well-known HACA mechanism.

References


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