

Fuel Unsaturation Effects on NO_x and PAH Formation in Spray Flames

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Abstract

The effect of fuel unsaturation on NO_x and PAH formation in spray flames is investigated at diesel engine conditions. The directed relation graph methodology is used to develop a reduced mechanism starting from the detailed CRECK mechanism². The reduced mechanism and spray models are validated against the shock tube ignition data and high-fidelity, non-reacting and reacting spray data from the Engine Combustion Network [26]. 3-D simulations are performed using the CONVERGE software to examine the structure and emission characteristics of n-heptane and 1-heptene spray flames in a constant-volume combustion vessel. Results indicate that the combustion under diesel engine conditions is characterized by a double-flame structure with a rich premixed reaction zone (RPZ) near the flame stabilization region and a non-premixed reaction zone (NPZ) further downstream. Most of NO_x is formed via thermal NO route in the NPZ, while PAH species are mainly formed in the RPZ. A small amount of NO is also formed via prompt route in the RPZ, and via N₂O intermediate route in the region outside NPZ, and via NNH intermediate route in the region between RPZ and NPZ. The presence of a double bond leads to higher flame temperature and thus higher NO in 1-heptene flame than that in n-heptane flame. It also leads to the increased formation of PAH species, implying increased soot emission in 1-heptene flame than that in n-heptane flame. Reaction path analysis indicate that the increased formation of PAH species can be attributed to the significantly higher amounts of 1,3-butadiene and allene formed due to β scission reactions resulting from the presence of double bond in 1-heptene.

Keywords: Fuel Unsaturation, NO_x and PAH emissions, N-heptane and 1-heptene spray flames, 3D simulations

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² <http://creckmodeling.chem.polimi.it/index.php/current-version-kinetic-mechanisms/low-and-high-temperature-complete-mechanism>.

25 1. Introduction

26 Liquid fuels used in propulsion and power generation applications are generally composed of a large
27 number of hydrocarbon compounds, with several containing one or more unsaturated C=C bonds. Numerous
28 recent studies have reported that the fuel reactivity and ignition behavior are strongly influenced by the degree of
29 unsaturation, i.e., the number and position of double bonds. Detailed kinetic models [1,2,3] have been developed
30 to examine the effects of the presence and position of double bonds on fuel reactivity and ignitability.
31 Experimental investigations have also been performed using shock tube [4,5,6], RCM [7,8,9], and flow reactor
32 [10]. An important finding from these studies is that the ignition delay time could increase significantly,
33 especially in the NTC (negative temperature coefficient) region, due to the presence of double bonds in the fuel
34 molecular structure. The fuel ignitability is also found to be strongly influenced by the length of the saturated
35 portion aside the double bond, with the longer alkyl chain yielding shorter ignition delay.

36 Engine experiments [11,12,13] using different biodiesel fuels have also reported longer ignition delays as
37 a consequence of unsaturated components in fuel composition. In addition, these and other engine experiments
38 [14, 15] with biodiesels have observed that due to the higher concentration of unsaturated components, some
39 biodiesels produce more PM and UHC compared to those containing smaller amount of unsaturated components.
40 In order to explain these trends in engine PM emission, fundamental investigations have been reported on the
41 formation of soot precursors during the combustion of unsaturated biodiesel components. Garner et al. [6]
42 observed from their shock tube experiments that 1-heptene (1-C₇H₁₄) produces more acetylene than does the n-
43 heptane (n-C₇H₁₆) over intermediate temperatures, 1100-1600K. Garner and Brezinsky [16] and Garner et al. [17]
44 subsequently extended the study to the oxidation of methyl octanoate and methyl trans-2-octenoate, and observed
45 longer ignition delay and increased acetylene (C₂H₂) formation in the case of unsaturated methyl ester. Note that
46 acetylene provides a major route for soot particle surface growth [18, 19]. Sarathy et al. [20] conducted flame
47 experiments and observed that compared to methyl butanoate, its unsaturated counterpart, methyl crotonate
48 produces higher amount of acetylene, propyne (1-C₃H₄), 1-butene (1-C₄H₈), 1,3-butadiene (1,3-C₄H₆), and
49 benzene (C₆H₆), indicating the potential of increased soot formation with unsaturated biodiesel fuels compared to

50 the saturated ones. Our previous studies [21,22] on n-heptane and 1-heptene partially premixed counterflow
51 flames (PPFs) revealed that 1-heptene produces higher amounts of acetylene and benzene compared to the
52 saturated fuel, n-heptane. Further analysis indicated that the dominant path for benzene formation involves the
53 recombination of propargyl radicals (C_3H_3), and the presence of the double bond in 1-heptene provides a
54 significant route for its production through the formation of allyl radical (C_3H_5). This path is not favored in the
55 oxidation of n-heptane, as it decomposes directly to smaller alkyl radicals.

56 While the aforementioned studies have provided significant insight pertaining to fuel reactivity and
57 ignitability, relatively little research has been reported concerning the combustion and emission behavior of
58 unsaturated hydrocarbons in realistic flames. The present study examines the effect of the presence of a double
59 bond on NO_x and PAHs emissions in spray flames under diesel engine conditions. 3-D simulations are performed
60 for the fuel injection, ignition, combustion, and emission characteristics using saturated and unsaturated fuels,
61 namely n-heptane and 1-heptene, respectively. It extends our previous investigations [21, 22], which considered
62 quasi-1-D partially premixed flames in a counterflow configuration, to more realistic spray flames using the
63 Sandia constant volume reactor. This reactor has been extensively used at Sandia National Laboratories [23, 24,
64 25] to provide high-fidelity data for non-reacting and reacting sprays. The data can be downloaded from the
65 Engine Combustion Network (ECN) [26] website.

66 N-heptane and 1-heptene flames are simulated by developing a skeletal mechanism, by reducing it from
67 the detailed CRECK mechanism [27], using the Directed Relation Graph methodology with Error Propagation
68 and Sensitivity Analysis [28, 29]. The skeletal mechanism is validated using ignition delay measurements for n-
69 heptane and 1-heptene. The fuel oxidation model is then combined with the PAH and NO_x models, and
70 predictions for the n-heptane non-reacting and reacting sprays are validated against the ECN experimental data
71 [26]. Simulations are then performed to characterize the effects of fuel unsaturation or double bond on NO_x and
72 PAH emissions in spray flames at temperatures and pressures relevant to engine operating conditions. The
73 dominant NO_x and PAH species formation regions in these flames are identified using the scatter plots of relevant

74 species in ϕ -T space. Finally, a reaction path analysis is conducted to identify the dominant paths for the
75 formation of PAH species in n-heptane and 1-heptene flames.

76 **2. Computational Model**

77 Simulations are performed using a commercial CFD code, CONVERGE [30, 31], which incorporates the
78 state-of-the-art models for spray injection, atomization and breakup, turbulence, droplet collision and coalescence,
79 spray-wall interaction, and vaporization. Since the details of these models have been described elsewhere, only a
80 brief description is provided here. The 3D computational model for two-phase reacting flow is based on an
81 Eulerian-Lagrangian formulation. Gas-phase flow field is described by the Favre-averaged Navier-Stokes
82 equations in conjunction with the Reynolds-averaged Navier-Stokes (RANS)-based turbulence model [32], which
83 includes source terms for the effects of the dispersed phase on gas-phase turbulence. The turbulence combustion
84 interaction modeling (TCI) was not considered in the present study. As discussed by Pomraning et al. [33],
85 appropriate TCI models will reveal more small-scale details of flame structure compared to the well-mixed
86 models. However, such models are much more computationally expensive when implemented with detailed
87 mechanisms in engine-type simulations. On the other hand, the well-mixed models have been shown to be
88 accurate enough for predicting the basic two-phase flow properties, i.e., spray and vapor penetration, temperature
89 profile, ignition delay, and flame lift-off length, etc. Moreover, previous studies have demonstrated the validity of
90 such models for predicting combustion processes in both gasoline and compression ignition engines [26]. In
91 particular, Pomraning et al. [33] have provided a detailed assessment of the unsteady RANS-based approach, and
92 demonstrated that for well-resolved computations, the effects of mixing are accounted for using the RANS
93 turbulence model. Further improvements in the simulation results by implementing an appropriate TCI model will
94 be pursued in future work.

95 A finite volume methodology with a semi-implicit hybrid scheme is used to solve the governing equations
96 on the Eulerian grid for the gas-phase properties, which include 3 velocity components, temperature, pressure, and
97 species concentrations. The length and time scales associated with spray processes are too small to be resolved
98 computationally, necessitating the use of sub-grid scale models to describe the spray physics. The spray is

99 represented by a stochastic system of a discrete number of parcels, which are tracked computationally using a
100 Lagrangian scheme. The two phases are coupled through the mass, momentum, and energy exchange terms,
101 which are present in both the liquid- and gas-phase equations. The droplet breakup processes are modeled using
102 the Kelvin–Helmholtz and Rayleigh–Taylor (KH–RT) models [34]. Droplet collisions are modeled with the no
103 time counter algorithm [35]. A dynamic drag model [36] is used; it is based on the postulation that the drag
104 coefficient depends on the shape of the droplet, which can vary between a sphere and a disk. A droplet
105 evaporation model based on the Frossling correlation is used. Selected physical properties of n-heptane and 1-
106 heptene fuels at 20°C and 1atm are listed in Table 1 [37]. As indicated, the difference between the physical
107 properties of the two fuels is not significant. Moreover, since the focus here is on the chemistry effects of fuel
108 unsaturation, simulations for both fuels are carried out using the physical properties of n-heptane. The effects of
109 turbulence on the droplet are accounted for by using a turbulent dispersion model. Detailed kinetic modeling is
110 performed by using the SAGE chemical kinetic solver [5] in CONVERGE, which is directly coupled with the
111 gas-phase calculations through a well-stirred reactor model.

112 The CFD solver uses an innovative modified cut-cell Cartesian method for grid generation [38]. The
113 adaptive mesh resolution (AMR) technique enables local mesh refinement in regions of high curvatures. For the
114 results presented here, the base (largest) grid size is fixed at 2mm. In order to resolve the flow near the injector, a
115 local refinement area with 0.125mm grid sizes are used, along with AMR based on the curvature in the velocity
116 and temperature fields. As discussed in the next section, these grid sizes were found to be sufficient to capture the
117 spray droplet break up, vaporization and combustion processes.

118 **3. Reduced Mechanism Generation and Validation**

119 In order to perform well-resolved simulations for both n-heptane and 1-heptene spray flames at diesel
120 engine conditions, a skeletal or reduced CRECK mechanism was developed to model the oxidation chemistry of
121 these two fuels, and the NO_x and PAH formation. The skeletal mechanism (207 species and 4094 reactions) was
122 obtained by reducing it from the detailed CRECK mechanism, based on the Directed Relation Graph with Error
123 Propagation and Sensitivity Analysis (DRGEP-SA) [28, 29]. The detailed CRECK mechanism (482 species and

124 19072 reactions), which has been developed and validated by Ranzi et al. [39, 40, 41, 42] for the simulations of
125 both low- and high-temperature combustion phenomena.

126 The DRGEPSA algorithm consists of two phases: (1) directed relation graph error propagation (DRGEP),
127 and (2) sensitivity analysis (SA). The mechanism reduction procedure has been reported by Lu and Law [28].
128 Since it is difficult to identify and eliminate an unimportant species because of the coupling between species, the
129 following rule is employed to determine whether a species can be removed. Considering that species A directly
130 forms species B, the species B can be removed if and only if its removal will not induce a significant error in the
131 production rate of species A. This error is determined by a normalized contribution of reaction $A \rightarrow B$ among all
132 the reactions dependent on species A. Also key species are specified to keep certain important reaction routes
133 such as the detailed PAH and NO_x formation routes. In the present study, CH_3 , acetylene (C_2H_2), benzene (C_6H_6),
134 pyrene ($\text{C}_{16}\text{H}_{10}$), ethylene (C_2H_4), propargyl (C_3H_3), cyclopentadiene (C_5H_6), naphthalene (C_{10}H_8), styrene
135 ($\text{C}_6\text{H}_5\text{C}_2\text{H}_3$), NO, N_2O , NNH, CH, CO, OH, HO_2 , H_2O_2 and heptylhydroperoxy ($\text{NC}_7\text{-QOOH}$) species are
136 specified to be kept in order to accurately account for the C1-C4 oxidation chemistry, n-heptane and 1-heptene
137 ignition behavior, and NO_x and PAH formation routes. The resulting reduced mechanism also contains all those
138 species that are related to the above key species. Once the optimal mechanism is obtained from the DRGEP step,
139 sensitivity analysis is performed to further reduce the size of the mechanism. All the species after DRGEP step are
140 arranged in ascending order based on the error in ignition delay induced by removing this species. The sensitivity
141 analysis removes the species identified from the top of the list one by one until the error generated by the resulting
142 skeletal mechanism with the remaining species reaches the user-defined tolerance for ignition delay.

143 **The operating conditions used during the reduction and testing of the reduced mechanism**
144 **include pressures of 30, 40, 50 atm, temperatures of 800, 900, 1000, 1100, 1200 K, and equivalence**
145 **ratios of 0.5, 1.0, 1.5, 2. Fuels used include 100% n-heptane, 100% 1-heptene, 100% methane,**
146 **50%n-heptane/50%methane, 50%1-heptene/50%methane, 90%n-heptane/10%methane, and**
147 **90%1-heptene/10%methane by volume.**

148 **3.1 Validation Using the Ignition and Spray Data from Experiments**

149 The reduced CRECK mechanism was validated against the shock tube ignition data for n-heptane and 1-
150 heptene, as well as the non-reacting and reacting spray data from ECN. Figure 1a presents a comparison of the
151 predicted ignition delays against the measurements of Gauthier et al. [43] for n-heptane/air mixtures. Simulations
152 were performed in constant-pressure, homogeneous reactor using the CHEMKIN software and four different
153 mechanisms, namely, the reduced CRECK mechanism, Chalmers mechanism [44, 45], detailed CRECK
154 mechanism, and detailed Lawrence Livermore National Laboratory (LLNL) mechanism [46]. Overall, there is
155 good agreement between the various predictions and measurements. At high temperatures ($T > 1100$ K), all the
156 four mechanisms overpredict ignition delays. However, at lower temperatures, relevant for ignition in diesel
157 engines, there is reasonably good agreement. Moreover, the reduced mechanism reproduces the experimentally
158 observed negative temperature coefficient (NTC) regime, wherein the ignition delay increases with temperature.
159 Figure 1b compares the ignition delays for 1-heptene/air mixtures predicted using the reduced and detailed
160 CRECK mechanisms against the measurements of Garner et al. [16]. Both the mechanisms are able to reproduce
161 the experimental data, although the values are somewhat overpredicted. Note that due to limited experimental
162 data, simulations only considered temperatures greater than 1300K. Moreover, for temperatures below 1300, the
163 ignition delays for 1-heptene become significantly higher compared to those for n-heptane.

164 Further validation of the reaction mechanism and spray models was performed using the high-fidelity
165 experimental data from the ECN [26] for turbulent non-reacting and reacting sprays. Validation for the non-
166 reacting spray is useful as it establishes that the spray models accurately predict the spray development and
167 fuel-air distribution. A schematic of the combustion vessel used in experimental studies at Sandia can be
168 found in Refs. [26]. **A cubical geometry of 108 mm on each side is used to represent the vessel geometry**
169 **in simulations. The vessel has a common-rail fuel injector that is mounted in a metal side-port such that**
170 **the spray is directed into the center of the chamber. The well-characterized engine relevant (high**
171 **temperature and pressure) initial conditions are created by burning a premixed fuel-air mixture. For**
172 **spray experiments, a range of ambient conditions in terms of density, temperature, and oxygen**
173 **concentrations can be provided. Further details of the vessel and injector are provided in Refs. [23, 47].**
174 For the results presented here, the base grid size is 2mm except for the grid convergence cases. In order to

175 resolve the flow near the injector, a fixed grid embedding is employed such that the minimum grid size is
176 0.125mm. In other regions, four levels of adaptive mesh refinement are employed based on the velocity and
177 temperature fields. The simulations are performed on the High Performance Computing Cluster at UIC using
178 up to three nodes. Each node has an Intel® Xeon® CPU at 2.60GHz with 16 cores and 20MB cache.

179 Figure 2 presents the liquid and vapor penetrations versus time for n-heptane non-reacting spray.
180 Predictions for the three grid sizes are compared with measurements. The experimental conditions used in the
181 simulations are listed in Table 2. Simulations use the same injection rate profile as experiments. The liquid
182 penetration distance is determined using the axial distance encompassing 97% of injected liquid n-heptane mass,
183 while the vapor penetration is calculated based on a fuel vapor mass fraction contour level of 1%. As indicated in
184 Fig. 3, the predicted liquid and spray penetrations are generally in good agreement with measurements. The liquid
185 penetration increases with time, and then stabilizes to a quasi-steady value. While the qualitative trends are
186 captured with all the three grid sizes, the quantitative agreement improves as the grid size is reduced, except for
187 the initial liquid penetration (for time below 0.5ms), which is overpredicted by the model. As discussed by Som et
188 al. [48], such differences may be attributed to several factors, including experimental uncertainties in near-nozzle
189 measurements, under-resolution of flow in the near-nozzle region, and inability to capture the effect of cavitation
190 and turbulence in the injector flow. It is also important to note that the predicted results are fairly grid-
191 independent for the grid sizes of 0.25 and 0.125mm, and the spray development and vaporization processes are
192 fairly well resolved using the RNG $k-\varepsilon$ turbulence model with the minimum grid size of 0.125mm. These results
193 are consistent with previous studies concerning grid convergence. Som et al. [48] performed computations of non-
194 reacting and reacting sprays for n-heptane and n-dodecane fuels, and observed good agreement between
195 measurements and predictions using the RNG $k-\varepsilon$ turbulence model with minimum grid size of 0.25mm. Xue et al.
196 [49] also performed simulations for the same two fuels using the RANS and LES turbulence models, and reported
197 grid convergence with grid sizes of 0.25mm and 0.125mm. Thus, the simulations in the present study were
198 performed using the minimum grid size of 0.125mm and four levels of adaptive mesh refinement (AMR) based
199 on the velocity and temperature fields, but a fixed grid embedding near the nozzle.

200 Validation results for the n-heptane reacting spray are presented in Figure 3, which compares the
201 measured and predicted ignition delays (τ_{ig}) and flame LOL for different initial temperatures. Additional
202 validation for the predicted τ_{ig} and LOL for different O_2 concentrations is provided in Ref. [50]. The experimental
203 conditions used in the simulations are listed in Table 2. **In experiments, τ_{ig} was determined using a criterion
204 based on a specific pressure rise, while in simulations, it was computed by using the time from start of
205 injection (SOI) to the instant when the maximum temperature (T_{max}) in the computational domain
206 exceeds a specified value (1500K). Using a different criterion based on the rate of change of T_{max} reaching a
207 peak value yielded essentially the same ignition delay. A specific OH mass fraction contour corresponding
208 to 2% of the peak value was used to determine the LOL in simulations, while it was measured using an
209 intensified CCD camera with a 310nm band-pass filter (10 nm FWHM) [51,52] in experiments.** There is
210 fairly good agreement between the predictions and experimental data. Both the experiments and predictions
211 indicate a decrease in ignition delay, and consequently in LOL, as the initial temperature is increased. It is also
212 important to note that both simulations and measurements do not indicate the existence of NTC region, which can
213 be seen in Fig. 1a for homogeneous n-heptane/air mixtures. This may be related to the temporally and spatially
214 evolving temperature and species fields for the spray case [53].

215 Figure 4 compares the high speed soot luminosity images from ECN experiments with the soot contours
216 predicted using the RANS and LES models. The two-step soot model used in simulations is adopted from
217 Hiroyasu and Kadota [54]. The model assumes spherical particles formed by acetylene and, thus provides a
218 qualitative comparison with luminosity images. Note that while a two-step soot model based on acetylene is used
219 in the present study, the formation of PAHs is investigated in detail. The spray in the computed images (Fig. 4) is
220 shown by blue dots representing the size of liquid parcels, while the green contour line represents the OH mass
221 fraction contour corresponding to 2% of the peak value, and shows the flame envelope. Overall, there is good
222 agreement between the computed and measured flame images. As expected, the LES model provides more spatial
223 details or small-scale features compared to the RANS model. There is also good agreement between the measured
224 and predicted LOL values. Solid vertical lines at 0.017m in the computed images indicate the measured LOL.

225 4. N-Heptane Spray Flame Structure

226 Results here focus on the computed structure and emission characteristics of n-heptane and 1-heptene
227 spray flames in the Sandia combustor. Figure 5 shows the temporal evolution of n-heptane spray flame in terms of
228 temperature and mixture fraction contours at different times after the start of injection (SOI) for 1000K initial
229 temperature and 21% O₂. The black lines represent the mixture fraction or equivalence ratio ϕ ranging from 0.15
230 to 3, with ϕ defined as:

$$231 \quad \phi = \frac{2 \sum_i N_i \eta_{C,i} + \frac{1}{2} \sum_i N_i \eta_{H,i}}{\sum_i N_i \eta_{O,i}} \quad (1)$$

232 Here i represents all species except CO₂ and H₂O, N_i the number of moles of species i and $\eta_{C,i}$, $\eta_{H,i}$ and
233 $\eta_{O,i}$ the number of carbon (C), hydrogen (H) and oxygen (O) atoms, respectively, in i th species. The ϕ contours
234 are good marker of the reaction zones. Only the center part (0.04x0.08m²) of the computational domain
235 (0.108x0.108m²) is shown in the figure. The injector exit is located at the left boundary.

236 The processes of fuel injection, spray development, fuel-air mixing and ignition can be discerned from the
237 contour plots at 0.3 and 0.5ms. For instance, region within $\phi=3$ contour at 0.3ms indicates a fuel-rich zone
238 characterized by pre-ignition pyrolysis and oxidation reactions. Subsequently, the ignition occurs at 0.5ms, as
239 indicated by the high-temperature region between $x=30$ mm and $x=40$ mm. Note that the measured ignition delay
240 time in Sandia experiments for the same conditions was 0.53ms. The ignition process is more clearly depicted in
241 Fig. 6, which presents the heat release rate (HRR) contours (left) and scatter plots in ϕ -T space (right) at three
242 different times. Such scatter plots have previously been used to visualize the soot and NO_x formation regions in
243 IC engines, and also to provide insight into the ignition process [53]. The blue contours and scatter plots in Fig. 6
244 depict regions of negative HRR, indicating pre-ignition endothermic reactions. Moreover, prior to ignition event
245 (at $t=0.4$ ms), the peak HRR is only 1011J/s-m³, and located at $T \approx 900$ K and $\phi \approx 4$ in the scatter plot at $t=0.4$ ms.
246 However, at $t=0.5$ ms, a small region of high HRR can be visualized in the ϕ -T plot near $\phi=2.5$ and $T=1200$ K,
247 indicating the occurrence of ignition. Subsequently, a wide region with significant heat generation can be seen in

248 both the contour and scatter plots at 0.6ms, indicating self-sustained combustion with $T > 1200\text{K}$ and $0.1 < \phi < 5$. The
249 combustion process is more clearly indicated in Fig. 5 by the ϕ and T contours at $t = 0.7$ and 1.1ms . It is
250 characterized by distinct regions of rich premixed combustion and diffusion combustion. For the present case, the
251 rich premixed zone (RPZ) is indicated by region corresponding to $2 < \phi < 5$ and $2000\text{K} < T < 2500$, while the diffusion
252 or non-premixed zone (NPZ) corresponds to $0.15 < \phi < 2.5$ and high temperatures ($2500\text{K} < T < 2800$) due to
253 exothermic reactions forming CO_2 and H_2O species. The green vertical lines at $x = 17\text{mm}$ in Fig. 5 mark the
254 measured flame LOL, which matches with the predicted LOL indicated by the contours at $t = 0.7$ and 1.1ms .

255 Figure 7 presents the integrated fuel vapor mass and HRR profiles with respect to time. The two-stage
256 ignition process can be clearly seen from the HRR profile. The first increase in HRR at 0.2ms is related to the 1st-
257 stage ignition while the second sharp increase at 0.5ms pertains to the 2nd-stage ignition, followed by the rich
258 premixed combustion and the diffusion combustion. The rich premixed combustion is also indicated by the sharp
259 decrease in n-heptane mass between 0.5 and 0.8ms , while the diffusion combustion is indicated by more moderate
260 and nearly constant rate of decrease of n-heptane mass. The RPZ and NPZ can be distinguished more clearly in
261 Fig. 8, which presents C_2H_2 , OH , NO , and C_6H_6 mass fraction contours. As indicated, the RPZ and NPZ are
262 characterized, respectively, by the high concentrations of C_2H_2 and OH species. In addition, most of NO is formed
263 in the NPZ where temperatures are high, while benzene (C_6H_6) is formed in the RPZ.

264 In order to identify the relative contributions of various NO_x (NO and NO_2) formation routes, Figure 9
265 presents contour plots for the mass fractions of NO , NO_2 , HCN , NH , N_2O and NNH . Note that HCN and NH
266 species are important for prompt NO , while N_2O and NNH species are associated with NO formed through the
267 N_2O intermediate and NNH intermediate routes, respectively. As can be seen in Fig. 9a, most of NO is formed in
268 NPZ, with a relatively a small amount also being formed in RPZ and the region outside NPZ. The NO formed in
269 NPZ is predominantly through the thermal NO route since temperatures are the highest (2600K to 2900K) there.
270 In indicated in Fig. 9b, most of NO_2 is formed in the region outside NPZ, where temperature is about 1500K and
271 abundant amount of O_2 is present. The prompt NO is mainly formed in RPZ as indicated by the HCN and NH
272 contours in Figs. 9c and 9d, respectively. Finally, N_2O is formed in the lean region outside the NPZ similar to

273 NO₂, (cf. Fig. 9e), while NNH is formed in the region between the RPZ and NPZ (cf. Fig. 9f), implying that NNH
274 intermediate route is important there.

275 **4.1 Effect of Fuel Molecular Structure on NO and PAH Formation**

276 In order to characterize the effect of fuel molecular structure or unsaturation on NO and PAH emissions,
277 n-heptane and 1-heptene spray flames were simulated at identical conditions in the Sandia reactor. Figure 10
278 presents the temporal variations of peak temperature and integrated NO mass for the two flames. Note that at
279 typical autoignition temperatures (800-1000K) in diesel engines, 1-heptene has much longer ignition delays than
280 n-heptane. Consequently, simulations were performed with an initial temperature of 1300K. At this temperature,
281 ignition delays for the two fuels are nearly the same (≈ 0.2 ms), as indicated in Fig. 10. These values also compare
282 well with the measured value of 0.26ms in Sandia experiments. More importantly, the peak temperature for 1-
283 heptene flame is 2870K compared to a value of 2840K for n-heptane flame. Consequently, 1-heptene flame
284 produces more NO compared to n-heptane flame. For example, at $t=1.4$ ms, the total NO in 1-heptene flame is 18%
285 higher than that in n-heptane flames, and the difference can be mostly attributed to increased thermal NO in 1-
286 heptene flame.

287 Since temperature is the important factor for thermal NO, the increased NO in 1-heptene flame can be
288 attributed to higher peak temperature in this flame. Note that the heating value of 1-heptene is (LHV=44.66MJ/kg)
289 is slightly lower than that of n-heptane (44.92MJ/kg). Thus the higher peak temperature in 1-heptene flame is not
290 related to the heating value, but to the fuel oxidation chemistry. In order to examine this aspect, homogeneous
291 reactor simulations were performed at similar conditions. Figure 11 presents the reaction path analysis for the two
292 fuels, based on constant volume simulations with initial conditions similar to those for spray flames, i.e.,
293 $T=1300$ K, $p=55$ atm, $\phi=1$. At these conditions, oxidation routes are significantly different for the two fuels. As
294 indicated in Fig. 11a, the dominant path for n-heptane is through H abstraction reaction forming alkyl radicals.
295 Here the more prominent reaction is $C_7H_{16} + OH \Rightarrow H_2O + C_7H_{15}$. A relatively small amount of n-heptane (12%)
296 also decomposes through the breaking of C-C bonds to form smaller alkyl radicals with 2 to 5 carbons.
297 Subsequently, about 82% of C_7H_{15} undergoes β scission reactions forming smaller ($C_2 \sim C_5$) alkyls and olefins,

298 while about 12% of C_7H_{15} undergoes oxidation with O_2 and isomerization to form heptyl-hydroperoxy radical
299 ($C_7H_{14}-QOOH$). However, the heptyl-hydroperoxy radicals directly dissociate into small hydrocarbons and
300 heptene (C_7H_{14}), and the latter gets oxidized to form $C_2\sim C_5$. In contrast, due to the presence of double bond, about
301 33% of 1-heptene undergoes β scission reactions, mainly through reactions $C_7H_{14}+OH\Rightarrow CH_2CHCH_2+C_4H_8+H_2O$
302 and $C_7H_{14}\Rightarrow CH_2CHCH_2+C_4H_9$, to form allyl radicals (CH_2CHCH_2). The rest 67% of 1-heptene is oxidized to
303 form smaller hydrocarbons. All these oxidation reactions are faster compared to the dissociation reaction of 1-
304 heptene. Consequently, the ignition delay is shorter for 1-heptene compared to that of n-heptane.

305 Figure 12 compares the temporal profiles of temperature and NO mole fraction for the two fuels. These
306 simulations were performed in a well-stirred reactor using the Chemkin software. Consistent with the reaction
307 path analysis, the ignition delay times are 0.014ms and 0.018ms, while the peak temperatures are 3241K and
308 3217K for 1-heptene and n-heptane, respectively. The higher temperature is responsible for the 6.1% higher in
309 NO for 1-heptene compared to that for n-heptane. Similar differences are observed for the NO formed through the
310 prompt, N_2O and NNH intermediate routes for the two fuels. Figure 13 compares the total amounts of HCN, N_2O ,
311 NNH, and CH species in n-heptane and 1-heptene flames at 1.4ms. The CH_2 plot is similar to CH plot, and not
312 shown. The amounts of HCN, N_2O , and NNH are higher in 1-heptene flame compared to those in n-heptane flame,
313 indicating that the NO formed through these routes is also higher in 1-heptene flame. Amongst the three routes,
314 the contribution of prompt NO is more significant compared to the N_2O and NNH intermediate routes. This is
315 based on the fact that the total mass of HCN is noticeably higher than those of N_2O and NNH. It is also important
316 to note that the amounts of CH and CH_2 (not shown) produced in n-heptane and 1-heptene flames are similar,
317 implying that the prompt NO route depends less on these species, and more on the higher temperature in 1-
318 heptene flame. Figure 14 presents the scatter plots of HCN, N_2O and NNH in ϕ -T space for the n-heptane and 1-
319 heptene flames. Consistent with the plots of these species in Fig. 9, most of HCN and thus prompt NO is formed
320 in RPZ, i.e., in the region $2<\phi<6$ and $1700<T<2200$, while N_2O is formed in the lean region outside NPZ with
321 $1500<T<2000$, and NNH is formed between RPZ and NPZ, in the region $2<\phi<3$ and $2400<T<2700$.
322 Quantitatively, 1-heptene produces significantly higher HCN and thus higher prompt NO compared to that of n-

323 heptane, as indicated by a wider range of red dots. The contributions of N_2O and NNH intermediate routes are
324 also higher in -1-heptene flame than those in n-heptane flame, but the differences are not as significant.

325 Figure 15 presents the benzene mass fraction contours for 1-heptene and n-heptane flames at $t=1.4$ ms.
326 While the benzene formation region is located within the rich premixed zone for both flames, the amount of
327 benzene formed in 1-heptene is significantly higher. The peak mass fractions are 0.0118 and 0.0087 for 1-heptene
328 and n-heptane, respectively, i.e., 36% higher benzene for 1-heptene. Similar trends were observed for the
329 formation of heavier PAH, such as pyrene ($C_{16}H_{10}$). Figure 16 compares the temporal variation of integrated mass
330 of benzene and pyrene in n-heptane and 1-heptene flames. As expected, 1-heptene flame produces significantly
331 more benzene and pyrene compared to n-heptane flame, with the differences being 22.0% and 21.9% for benzene
332 and pyrene, respectively, at $t=1.4$ ms.

333 Since benzene is an important aromatic species for pyrene and subsequent soot formation, it is important
334 to identify the dominant path for benzene formation. The path analysis is presented in Fig. 17, based on well-
335 stirred reactor simulations for the combustion of the two fuels at the same conditions as those of Fig. 11. Two
336 major routes to form benzene involve reactions methyl-cyclo-pentadiene (MCPTD) \Rightarrow benzene and
337 $C_3+C_3\Rightarrow$ benzene, where C_3+C_3 represent reactions involving either two propargyl (C_3H_3) radicals or a propargyl
338 reacting with allene (AC_3H_4) or propyne (PC_3H_4). While these two routes appear to be similar for the two fuels,
339 the amount of benzene formed is higher in 1-heptene due to the higher concentrations of allene and C_4H_5 species.
340 This is due to the fact that the presence of double bond in 1-heptene opens an additional route (highlighted with
341 red) for allene formation through 1,3-butadiene (C_4H_6) and 3-butenal (C_3H_5CHO). In addition, the contribution of
342 C_4H_5 route to form allene in 1-heptene is increased to 14% compared to 8% for n-heptane. Since these two routes
343 are both associated with 1,3-butadiene, further analysis was done to identify the reason for the increased
344 formation of 1,3-butadiene in 1-heptene. As highlighted by red lines in Fig. 17, this can be attributed to the
345 presence of double bond in 1-heptene, which leads to its direct decomposition to form two C_4 hydrocarbons, C_4H_8
346 and $CH_2C_3H_5$, through β scission reaction. These two C_4 species lead to the formation of 1,3-butadiene and C_4H_7
347 in 1-heptene. In contrast, there are fewer routes to form 1,3-butadiene and C_4H_7 in n-heptane. Moreover, the two
348 routes involving C_4H_8 and C_5H_{10} produce much less 1,3-butadiene compared to the direct decomposition reactions

349 for 1-heptene. Finally, 1-heptene also produces higher amount of cyC_5H_5 through C_5H_8 , which further increases
350 the amount of benzene formed through methyl-cyclo-pentadiene route. Thus, while the relative contributions of
351 the two benzene formation routes are similar for the two fuels (21% for MCPTD route and 79% for C3 route vs.
352 20% and 80% for n-heptane and 1-heptene, respectively), the amount of benzene formed is higher in 1-heptene
353 due to the significantly higher amounts of 1,3-butadiene and allene. This is further confirmed in Fig. 18, which
354 compares the integrated amounts of acetylene, propargyl, 1,3-butadiene and allene formed in n-heptane and 1-
355 heptene flames. While the amounts of acetylene and propargyl formed in the two flames are similar, significantly
356 higher amounts of 1,3-butadiene (about 117% higher) and allene (48% higher) are formed in 1-heptene flame
357 compared to those in n-heptane flame. Thus the pathway analysis based on well-stirred reactor simulations
358 confirm the 3-D CFD results that the increased amount of benzene in 1-heptene flame is associated with the β
359 scission reactions due to the presence of double bond in 1-heptene. This result is generally consistent, except for
360 the methyl-cyclo-pentadiene route, with the reaction path analysis for benzene formation reported in a previous
361 study [55] dealing with 1-heptene and n-heptane counterflow flames.

362 5. Conclusions

363 We have examined the effect of fuel unsaturation on NO_x and PAH formation in n-heptane and 1-heptene
364 spray flames at diesel engine conditions. The directed relation graph with error propagation and sensitivity
365 analysis has been employed to develop a reduced kinetic mechanism (with 207 species and 4094 reactions),
366 starting from the detailed CRECK mechanism [42] containing 482 species and 19072 reactions. The mechanism
367 and spray models have been validated against the shock tube ignition data and high-fidelity spray data in a
368 constant-volume combustion vessel from the Engine Combustion Network (ECN) [26]. The 3-D CONVERGE
369 software has been used to examine the structure and emission characteristics of n-heptane and 1-heptene spray
370 flames in the same vessel. Important observations are as follows.

371 (1) Validation of the reduced mechanism for the ignition of n-heptane/air and 1-heptene/air mixtures indicates
372 fairly good agreement between the predictions and measurements. The mechanism also shows good
373 agreement with other detailed and reduced mechanisms, and reproduces the experimentally observed negative

374 temperature coefficient (NTC) behavior for n-heptane/air mixtures. In addition, results indicate that at
375 moderate temperatures ($800 < T < 1100$), ignition delays for 1-heptene are significantly higher than those for n-
376 heptane, but similar at high temperatures. Validations of the 3-D simulations against the ECN data for n-
377 heptane sprays also show good agreement between the predicted and measured spray penetration lengths,
378 ignition delays, flame liftoff lengths, and global flame structure.

379 (2) Simulation results for n-heptane and 1-heptene spray flames indicate that the combustion under diesel engine
380 conditions is characterized by a double-flame structure with a rich premixed reaction zone (RPZ) near the
381 flame stabilization region and a non-premixed reaction zone (NPZ) further downstream. The RPZ and NPZ
382 are characterized, respectively, by the high concentrations of C_2H_2 and OH species.

383 (3) The scatter plots in ϕ -T space are used to identify the dominant NO_x and PAH formation regions in spray
384 flames. For the conditions investigated, most of NO_x is formed via thermal NO route in the NPZ, while PAH
385 species are mainly formed in the RPZ. Relatively small amount of NO is also formed via prompt route in the
386 RPZ, and via N_2O intermediate route in the fuel-lean region outside NPZ, and via NNH intermediate route in
387 the region between RPZ and NPZ.

388 (4) The presence of a double bond leads to higher flame temperature and consequently higher thermal NO in 1-
389 heptene flame than that in n-heptane flame. It also leads to the significantly higher amounts of PAH species,
390 implying higher soot emission in 1-heptene flame compared to that in n-heptane flame. Reaction path analysis
391 indicates that this can be attributed to β scission reactions due to the presence of double bond, which lead to
392 the significantly higher amounts of 1,3-butadiene and allene formed in 1-heptene compared to those in n-
393 heptane. Moreover, the presence of double bond in 1-heptene opens an additional route for allene formation
394 through 1,3-butadiene (C_4H_6) and 3-butenal (C_3H_5CHO) species.

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