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Combustion characteristics of n-heptane spray combustion in a low temperature reform gas/air environment

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Abstract

This paper presents a large eddy simulation study of n-heptane spray combustion in an n-heptane low temperature reform (LTR) gas environment in a constant volume combustion chamber, under conditions relevant to single-fuel reactivity controlled compression ignition (RCCI) combustion engines. The LTR gas is made up of partially oxidized intermediate species from rich n-heptane/air mixture in an external constant temperature reformer. It is found that a higher reform temperature results in a longer ignition delay time of the n-heptane spray and a higher liftoff length, due to the chemical effect of the LTR gas and the difference in the reaction zone structures. A significantly different spray flame structure is identified in the RCCI case from that of single-fuel spray combustion. After the onset of high temperature ignition, a double-layer flame structure is established in the RCCI

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case, with a diffusion flame layer and a lean premixed flame layer. The lean premixed flame affects the flow field, which significantly suppresses the mixing around the spray tip. As a result, the RCCI case exhibits a lower NO_x formation but a higher soot formation than the single-fuel case.

Keywords: spray combustion, fuel reform, dual fuel, Engine Combustion Network, Eulerian stochastic fields

1 1. Introduction

2 To reduce the impact of greenhouse gas and pollutant emissions from internal
3 combustion engines (ICE) on the environment, intensive research has been carried
4 out on developing advanced ICE combustion concepts [1–5]. The use of reform
5 gas is one novel approach [2], in which the exhaust gas heat can be used to reform
6 the fuel to smaller hydrocarbons and syngas (CO and H₂), by which the engine
7 exhaust heat can be recovered in the endothermic fuel reform reactions and the
8 engine efficiency can be improved. Tsolakis *et al.* [6] investigated exhaust gas
9 assisted fuel reform in diesel engines and reported that diesel fuel can be reformed
10 to LTR gases consisting of a high amount of H₂ (up to 16%) at the exhaust gas
11 temperature of 563 K with the assistance of a metal catalyst. It was shown that
12 when the engine exhaust gas recirculation (EGR) was replaced by the LTR gases
13 the engine-out emissions of soot and nitrogen oxides (NO_x) could be reduced.
14 Alger and Mangold [7] demonstrated an onboard reform approach to generate a
15 "dedicated EGR" in a spark-ignition gasoline engine, in which one of four engine
16 cylinders was used to generate the EGR under fuel-rich conditions. The EGR was
17 then used in the other three cylinders, which resulted in a significant improvement
18 of the fuel efficiency (by 10% at light load) and a significantly decreased CO and

19 unburned hydrocarbon (UHC) emissions, due to the existence of H_2 in the EGR
20 that enhanced near-wall combustion [7].

21 Dual-fuel Reactivity controlled compression ignition (RCCI) is another novel
22 advanced engine combustion concept [1, 8], which has the potential to achieve
23 simultaneously high engine efficiency and low emissions. In RCCI engines, a low
24 reactivity fuel is introduced into the cylinder to create a well-mixed charge of low
25 reactivity fuel, air and EGR. A high reactivity fuel is then injected before ignition
26 of the low reactivity fuel. RCCI engines suffer from the high sensitivity of ignition
27 delay time (IDT) to the incylinder charge conditions, and as such, the control of
28 ignition and heat release rate poses a challenge. This challenge could be mitigated
29 by combining the potential of both RCCI and reform gas [3, 9]. Geng *et al.* [3]
30 investigated a low temperature "single-fuel" RCCI engine. The fuel (n-heptane)
31 was reformed in an external reformer, under fuel-rich conditions, through low
32 temperature ignition reactions without the assistance of a catalyst. The reform gas
33 was introduced into the engine cylinder via the intake port where it was cooled by
34 mixing with intake air. Thus, the single-fuel RCCI process is conceptually similar
35 to that of dual-fuel RCCI, while it has the advantage of without having to use
36 two fuel tanks. In the baseline case of Geng *et al.* [3], the reformer temperature
37 was set to 423 K, under which the n-heptane in the reformer was vaporized but
38 not reformed. Thus, the end gas from the reformer was a mixture of gaseous n-
39 heptane and air. Compared with the baseline unreformed case, the reform gas case
40 exhibited a longer IDT, a lower heat release rate (HRR) and a lower soot emission.
41 These latter two properties are advantageous for the engine performance at high
42 load operation conditions, where the high values of peak HRR and soot emission
43 are of concern.

44 The fundamental physics behind the longer IDT, lower HRR and soot formation
45 in the reform gas single-fuel RCCI engine is unclear. It is expected that this is a
46 result of the LTR gas chemistry, e.g., the absence of the low temperature ignition
47 path in the LTR gas (that exists in the parent fuel, e.g., n-heptane), and the change of
48 the reaction front structure. The basic process of single-fuel RCCI combustion can
49 be identified to consist of three stages [10–12]: (a) onset of ignition in the mixing
50 layer of the directly injected fuel and the earlier injected reform gas/air mixture
51 (premixed charge), (b) reaction front propagation in the earlier injected reform
52 gas/air mixture, which can be either in the ignition wave mode or in the premixed
53 flame mode, and (c) combustion of the fuel-rich mixture of the directly injected
54 fuel in a diffusion flame mode. A recent experiment of Srna *et al.* [13] on n-
55 dodecane/methane RCCI combustion illustrated the transition process between the
56 different stages. Their results showed that a considerable amount of the directly
57 injected fuel (n-dodecane) was consumed in a flame-like propagation mode in
58 the mixing layer of n-dodecane and the surrounding lean premixed methane/air
59 mixture, followed by a premixed flame-like propagation in the lean premixed
60 methane/air mixture.

61 The combustion process of an n-heptane spray in a lean premixed n-heptane
62 LTR gas/air ambient environment in a constant volume chamber, under conditions
63 relevant to the single-fuel RCCI engine of Geng *et al.* [3], is studied in the present
64 work. The aim is to gain an improved understanding of (a) the effect of LTR
65 gas on the ignition of the parent fuel, (b) the structure of the reaction fronts in
66 the mixing layer of the directly injected parent fuel and the LTR gas, and in the
67 ambient lean LTR gas/air mixture, and (c) the NO_x and soot formation process in
68 LTR gas RCCI combustion. Since the RCCI combustion process involves multiple

69 modes, we chose to use large eddy simulation (LES) coupled with a finite rate
70 chemistry approach. This approach has been used to study spray combustion in
71 ambient methane/air mixtures [14, 15]. The approach offers detailed data for the
72 analysis of chemical reaction paths toward ignition and NOx/soot formation, and
73 for identification of the reaction front structures.

74 2. Numerical Method

75 A transported probability density function (PDF) is employed to model the
76 sub-grid scale (SGS) turbulence/chemistry interaction in the gas phase combustion
77 process. A Lagrangian particle tracking approach is used to model the liquid spray,
78 and the mass, momentum and heat transfers between the gas and liquid phases are
79 modeled using source terms in gas and liquid phase transport equations. Liquid
80 n-heptane is injected as spherical droplets, with the initial droplet size following
81 the Rosin-Rammler distribution [16]. Following previous works [17, 18], the
82 mean diameter of droplets is set as a half of the injector nozzle diameter, while the
83 maximum size is set as the diameter of the injector nozzle. The secondary break-
84 up process is modeled using a hybrid Kelvin Helmholtz-Rayleigh Taylor (KH-RT)
85 model [19]. The Frossling model and the Ranz-Marshall correlation are employed
86 to describe the droplet evaporation and heat transfer with the surrounding gas
87 phase, respectively. A detailed description of the spray sub-models for atomization,
88 breakup and evaporation is given in Ref. [20].

89 The PDF transport equations are solved using an Eulerian stochastic fields
90 (ESF) method [21]. In the ESF method, the mean and moments of a random
91 vector $\phi = (\phi_1, \phi_2 \cdots \phi_{N_s+1})$ are approximated by N_F number of stochastic fields,
92 $\xi_\alpha^{(n)}$, where the vector ϕ represents the N_s number of chemical species (species

93 mass fractions) and the mixture enthalpy. $\tilde{\phi}_\alpha = \frac{1}{N_F} \sum_{n=1}^{N_F} \xi_\alpha^{(n)}(\mathbf{x}, t)$. The equation
 94 for the n^{th} stochastic field is:

$$95 \quad \bar{\rho} d\xi_\alpha^{(n)} = C + D + M + W + S \quad (1)$$

96 where

$$97 \quad C = -\frac{\partial \bar{\rho} \tilde{u}_i \xi_\alpha^{(n)}}{\partial x_i} dt, D = \frac{\partial}{\partial x_i} \left(\Gamma_t \frac{\partial \xi_\alpha^{(n)}}{\partial x_i} \right) dt,$$

$$98 \quad M = -\frac{1}{2} \bar{\rho} C_\phi \left(\xi_\alpha^{(n)} - \tilde{\phi}_\alpha \right) \omega^{sgs} dt, W = \bar{\rho} \sqrt{2 \frac{\Gamma_t}{\bar{\rho}} \frac{\partial \xi_\alpha^{(n)}}{\partial x_i}} d^{(n)},$$

$$99 \quad 100 \quad 101 \quad S = \bar{\rho} S_\alpha^r \left(\xi^{(n)} \right) dt + \bar{\rho} S_\alpha^s \left(\xi^{(n)} \right) dt \quad (2)$$

102 with $1 \leq \alpha \leq N_s + 1$ and $1 \leq n \leq N_F$.

103 The above equation implies invoking the gradient transport hypothesis to model
 104 the turbulent eddy transport fluxes. Here Γ_t is the sum of total molecular and sub-
 105 grid scale diffusivities. $\bar{\rho} S_\alpha^r \left(\xi^{(n)} \right) dt$ and $\bar{\rho} S_\alpha^s \left(\xi^{(n)} \right) dt$ are the increment in $\xi_\alpha^{(n)}$
 106 due to chemical reactions and spray injection, respectively. $\bar{\rho}$ is the filtered gas
 107 density. C_ϕ is set to 2, which is a model constant in the micro-mixing model IEM
 108 (interaction with exchange to the mean) [22]. ω^{sgs} is the SGS scalar turbulent
 109 frequency, $\omega^{sgs} = \frac{\mu + \mu^{sgs}}{\bar{\rho} \Delta^2}$, with Δ being the filter width modeled as the cube root
 110 of the volume of the mesh cell. μ and μ^{sgs} are the laminar and SGS viscosity,
 111 respectively. The SGS diffusivity is modeled by one equation eddy-viscosity
 112 model. $d^{(n)}$ is approximated by time-step increments $dt^{1/2} \eta_i^n$, where η_i^n is a
 113 $\{-1, 1\}$ dichotomic random vector [21]. The random vector η_i^n is independent of
 114 space but different for each field. A factorization scheme [23] with three steps is
 115 adopted to solve the stochastic fields equation. Specifically, Step 1 involves the
 116 process of convection, diffusion, spray and Wiener term:

$$\bar{\rho} d\xi_{\alpha}^{(n)} = C + D + W + \bar{\rho} S_{\alpha}^s (\xi^{(n)}) dt \quad (3)$$

Step 2 is the micro-mixing process with analytical solution:

$$\xi_{\alpha}^{(n)} = \widetilde{\phi}_{\alpha} + \left(\xi_{\alpha}^{(n)} - \widetilde{\phi}_{\alpha} \right) * \exp (\omega^{sgs} dt) \quad (4)$$

The final step deals with the integration of the chemical reaction rates. To reduce the computational time of this step, the chemistry coordinate mapping (CCM) [24] acceleration method is coupled with the stiff ordinary differential equation (ODE) solver Seulex [25]:

$$\xi_{\alpha}^{(n)} = \xi_{\alpha}^{(n)} + S_{\alpha}^r (\xi^{(n)}) dt \quad (5)$$

The CCM phase space variables are temperature $T^{(n)}$, equivalence ratio $\Phi^{(n)}$, scalar dissipation rate $\chi^{(n)}$, fuel mass fraction $Y_{fuel}^{(n)}$, and a fuel mass ratio of spray injection $\lambda_{fuel}^{(n)}$. The former four dimensions were adopted to describe the reaction progress, the fuel stratification, the mixing rate and the reaction progress in low temperature ignition [18]. The fifth variable, $\lambda_{fuel}^{(n)}$, is introduced to describe the mixing between the injected fuel and ambient LTR fuel. $\lambda_{fuel}^{(n)}$ is defined based on the mole numbers of C and H atoms:

$$\lambda_{fuel}^{(n)} = \frac{\widetilde{Z} * (4n_{C,fuel} + n_{H,fuel})}{\sum_{i=0}^{N_s} Y_i^{(n)} (4n_{C,i} + n_{H,i})} \quad (6)$$

where \widetilde{Z} is the mixture fraction, obtained from a transport equation:

$$\frac{\partial \bar{\rho} \widetilde{Z}}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_i \widetilde{Z}}{\partial x_i} = \frac{\partial}{\partial x_i} \left(\bar{\rho} \Gamma_t \frac{\partial \widetilde{Z}}{\partial x_i} \right) + \bar{\rho} S_{fuel}^S \quad (7)$$

where $\bar{\rho} S_{fuel}^S$ is the source term from the liquid n-heptane injection. $\widetilde{Z} = 1$ indicates the condition of pure n-heptane vapour in the mixture, whereas $\widetilde{Z} = 0$ indicates

137 the LTR gas/air ambient mixture. The CCM method was shown to have a speedup
138 rate of at least a factor of ten.

139 The n-heptane chemical mechanism of Lu *et al.* [26], which includes 68
140 species and 283 elementary reactions, is employed to describe the reform process
141 and spray combustion. The extended Zeldovich mechanism [27] is coupled with
142 the Lu *et al.* mechanism to predict the formation of NO_x. The multistep soot
143 model of Leung *et al.* [28] is used to predict the soot formation. The open-
144 source CFD code, OpenFOAM 4.x [29], is used in the LES. A finite volume
145 method with a second-order scheme is adopted for the spatial discretization and
146 an implicit second-order backward Euler scheme is used for the time integration.
147 Eight stochastic fields are used to capture the SGS PDF distributions, which have
148 been proven to provide reasonable accuracy [23] at an affordable computational
149 cost.

150 3. Case Specifications

151 The computational cases were selected according to the experiments of Geng
152 *et al.* [3]. The n-heptane/air LTR process took place in a constant temperature
153 channel reformer under atmospheric pressure with a residence time of 17.2 s, an
154 equivalence ratio of 8, and three reform temperatures (T_r) of 450 K, 550 K and
155 650 K. The reform process was modeled as a homogeneous reactor using the Lu *et al.*
156 mechanism [26]. The parent fuel conversion rate (FCR) and the mass fractions
157 of key species from the reformer are given in Table 1. The full list of species
158 mass fractions of LTR products is provided in the Supplementary data. After LTR,
159 the mixture was quickly cooled to 349 K, and the LTR gas was mixed with air
160 to form an LTR gas/air mixture with an equivalence ratio of 0.3. Case 1 acts as

161 a validation case for the present spray combustion model, and also as a baseline
162 reference case for the n-heptane spray combustion. Specifically, the ambient air
163 in Case 1 has a temperature of 900 K, an initial pressure of 40 bar, a density of
164 14.8 kg/m^3 , and a mole fraction of oxygen of 21%. The fuel injector nozzle is
165 $100 \text{ }\mu\text{m}$ with 150 MPa injection pressure and 6.8 ms injection time. This case is
166 known as the Engine Combustion network (ECN) Spray-H and well-documented
167 experiments are available [30]. Cases 2, 3, and 4 are LTR gas RCCI cases with
168 the same combustor and injector configuration, and ambient gas temperature, as in
169 Case 1, but with three different reform temperatures. Case 5 has the same reform
170 temperature as Case 4, but with an ambient equivalence ratio (Φ_a) of 0.5. The
171 ambient pressure is slightly different from Case 1, to maintain the same density of
172 14.8 kg/m^3 . The computational domain is a cube with a side length of 108 mm,
173 which is the same as the ECN rig [30]. The LES mesh is locally refined to 0.25
174 mm in the near injector region where spray evaporation, ignition and earlier flame
175 propagation take place. It is shown that the chosen grid yields a grid-independent
176 result, and the ignition and liftoff process of the n-heptane spray flame are captured
177 very well [17, 31]. The CFL number is limited to 0.1, resulting in a time step
178 of approximately $5 \times 10^{-8} \text{ s}$, which is enough to capture the unsteady motion of
179 spray combustion.

180 **4. Results and Discussions**

181 *4.1. Model Validation*

182 The non-reacting spray ECN Spray-H experiments [30] is studied to validate
183 the spray model. This case is referred here to as Case NR, which has an initial
184 ambient temperature of 1000 K with zero oxygen in the ambient mixture [30].

Table 1: Case setup and mass fractions of representative species of the reform gas.

Case	$T_r (K)$	FCR (%)	NC_7H_{16}	NC_7KET	CH_2O	CO	Φ_a	$T_\alpha (K)$	$\rho_\alpha (kg/m^3)$
1	-	-	0	0	0	0	0	900	14.8
2	450	0	0.3466	0	0	0	0.3	900	14.8
3	550	82	0.0611	0.0060	0.0088	0.0353	0.3	900	14.8
4	650	88	0.0412	0	0.0075	0.0482	0.3	900	14.8
5	650	88	0.0412	0	0.0075	0.0482	0.5	900	14.8

185 The initial pressure conditions and the spray setups are the same as that in Case
186 1, Table 1. Figure 1 shows a comparison between the measured and the predicted
187 liquid and vapor penetration lengths and radial profiles of mixture fraction. The
188 liquid length is defined as the farthest axial distance with 5% liquid volume and
189 the gas penetration is the maximum distance from the nozzle outlet to where the
190 mixture fraction is 0.1% [30]. All these quantities predicted in LES are in good
191 agreement with experimental data, cf. Fig. 1.

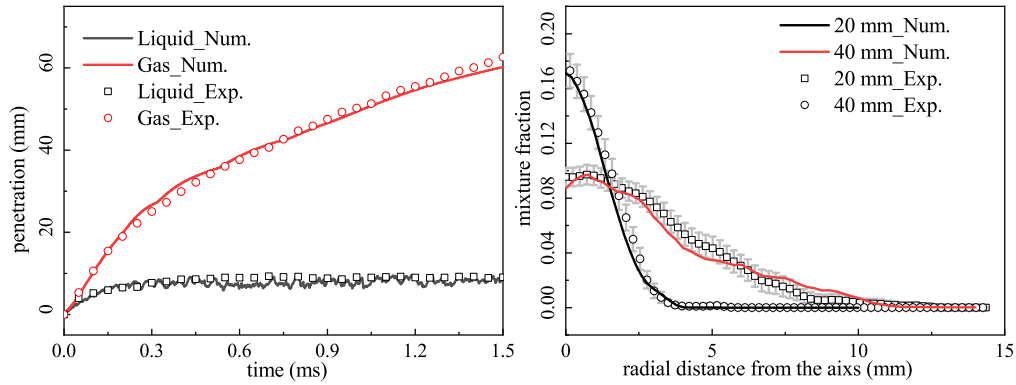


Figure 1: Liquid and gas penetration in the non-reacting case (left). Mixture fraction spatial distribution along the radius direction at two axial height of the non-reacting case (right). Symbols represent the ECN experimental results [30] and lines are the LES results.

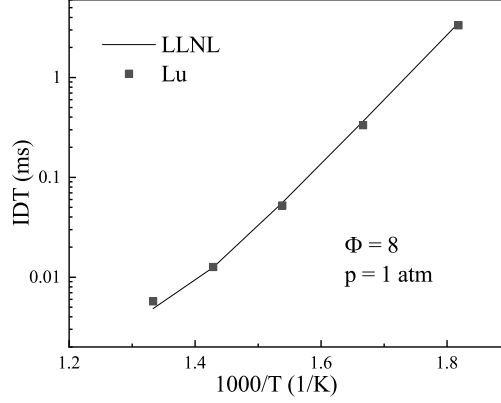


Figure 2: Predicted ignition delay time (IDT) of rich n-heptane/air mixture ($\Phi = 8$) using the Lu *et al.* mechanism and the LLNL mechanism under different initial temperatures and atmospheric pressure.

192 The performance of Lu *et al.* mechanism is examined under current fuel rich
 193 condition. Lu *et al.* mechanism is a skeletal mechanism based on the detailed
 194 LLNL n-heptane mechanism (version 2) [32] and it has been used in n-heptane
 195 spray combustion simulation [33]. Since the reform process is governed by the
 196 low temperature reaction path of n-heptane chemistry, and Lu *et al.* mechanism
 197 is validated against the detailed mechanism under the current reform condition
 198 ($\Phi = 8$). As seen in Fig. 2, the ignition delay time (IDT) predicted by Lu *et al.*
 199 mechanism is nearly the same as that by the detailed mechanism.

200 To validate the ESF model and the dependence of the results on the number
 201 of stochastic fields (N_F), the pressure rise history predicted using different N_F is
 202 compared with ECN experiments and LES predictions by the well-stirred reactor
 203 (WSR) model. WSR has been used in recent LES of n-dodecane spray flames
 204 [14]. Much finer grid may be needed with WSR (with one fourth of the current
 205 mesh size). With the current grid resolution, the pressure rise is significantly under-

206 predicted with WSR compared with ESF regardless the number of stochastic fields.
 207 Note that this is consistent with the results of Som *et al.* [33], in which similar LES
 208 filter size and mesh size were used. It was shown that Lu *et al.* mechanism with
 209 WSR always predicted a longer IDT. When increasing the number of stochastic
 210 fields from two to twelve, it is shown that the pressure rise profile converges,
 211 cf. Fig. 3. Marginal differences are found between the results from the eight and
 212 twelve stochastic fields for the onset time of pressure rise, and the slope of pressure
 213 rise profile.

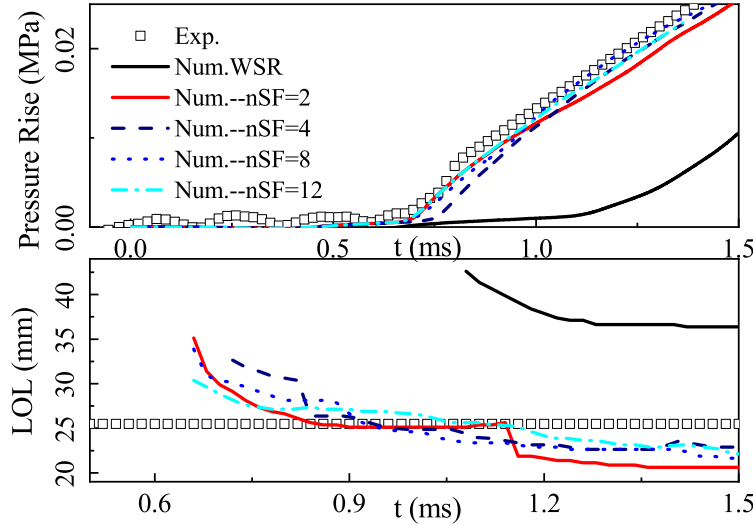


Figure 3: Temporal evolution of mean pressure (top) and liftoff length (bottom) in the combustor of Case 1 with different number of stochastic fields. Symbols represent the ECN experimental results [30] and lines are the LES results.

214 Figure 3 shows also comparison of measured and predicted liftoff length (LOL)
 215 with different models and N_F . Here, LOL is defined as the nearest axis distance,
 216 where OH mass fraction reaching its 2% of the maximum value [30]. The results
 217 are consistent with the pressure rise. The WSR model over-predicted the LOL,

218 while the ESF model yields a better prediction of LOL. The predicted LOL con-
219 verges as N_F increases from 2 to 12. In the following simulations eight stochastic
220 fields are adopted as a compromise between accuracy and CPU time.

221 The validation of the soot model has been done for an n-heptane spray flame
222 case similar to Case 1 (with a different ambient temperature of 1000 K). The results
223 were presented in our previous work [34]. The temporal evolution of experimental
224 and LES predicted soot optical thickness were compared at axial locations of 40
225 mm, 50 mm and 60 mm downstream the injector nozzle exit plane. The line-
226 of-sight extinction (KL) data were measured using Laser-induced incandescence
227 (LII), while the LES predicted KL was converted from the spatial integration of
228 soot volume fraction as suggested by ECN [30]. The onset of the soot formation
229 and the magnitude of KL value were well-predicted in the current LES model.

230 Fig. 4 shows the pressure rise for the Cases 1-4 and the corresponding ECN
231 experimental results for Case 1 [30]. The numerical results are in good agreement
232 with the experimental data, including the ignition delay time and the heat release
233 rate. For the LTR gas RCCI cases, the time at which pressure starts to rise shows a
234 non-monotonic dependence on FCR or reform temperature, whereas the pressure
235 rise rate appears to decrease with increasing FCR or LTR temperature. Further
236 details on the ignition process will be investigated below.

237 4.2. Ignition and Flame Liftoff

238 In n-heptane ignition, the low temperature ignition (LTI, also known as cool
239 flame) can be characterized with heptyl-peroxide (RO_2) or ketohydroperoxide
240 (NC_7KET), whereas high temperature ignition (HTI) is associated with a rapid
241 increase in temperature and the concentration of OH radicals. The temporal
242 evolution of the maximal temperature and mean mass fraction of OH radicals,

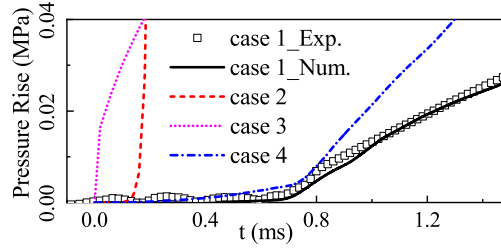


Figure 4: Temporal evolution of pressure in the combustor. Symbols represent the ECN experimental results [30] and lines are the LES results.

243 displayed in Fig. 5, indicates that the IDT (i.e., τ_{ig} , the time at the onset of HTI) of
 244 Case 2 is 0.46 ms, the shortest among all cases. Note that the mean temperature
 245 in Fig. 5 is mainly governed by combustion of the ambient gas; thus, the temporal
 246 evolution of the mean temperature (TMean) denotes the ambient fuel reactivity,
 247 because the injected fuel is much less than the ambient fuel due to the large
 248 domain. With the lowest LTR temperature, the ambient gas in Case 2 is a mixture
 249 of n-heptane and air. The ambient n-heptane/air mixture has a temperature of 900
 250 K, which, due to the negative temperature coefficient (NTC), gives rise to a longer
 251 IDT in the ambient mixture than that in the mixing layer of the ambient gas and
 252 the vapor n-heptane from the liquid jet, due to the lower temperature in the mixing
 253 layer. The ignition in both the mixing layer and the ambient mixture of Case 2
 254 undergoes two stages, LTI and HTI stages. The LTI stage (the cool flame stage)
 255 at 0.2 ms is indicated by the local peak mass fractions of OH, NC₇KET, and RO₂.
 256 The heat release from LTI in Case 2 is substantial, resulting in a 40 - 50 K increase
 257 in the mean combustor temperature, the highest increase among all cases, along
 258 with the highest mean mass fractions of OH, NC₇KET, and RO₂.

259 The LTR temperature in Case 3 is 550 K, which is high enough to reform
 260 the fuel into LTI products, including NC₇KET, with a small amount of unburned

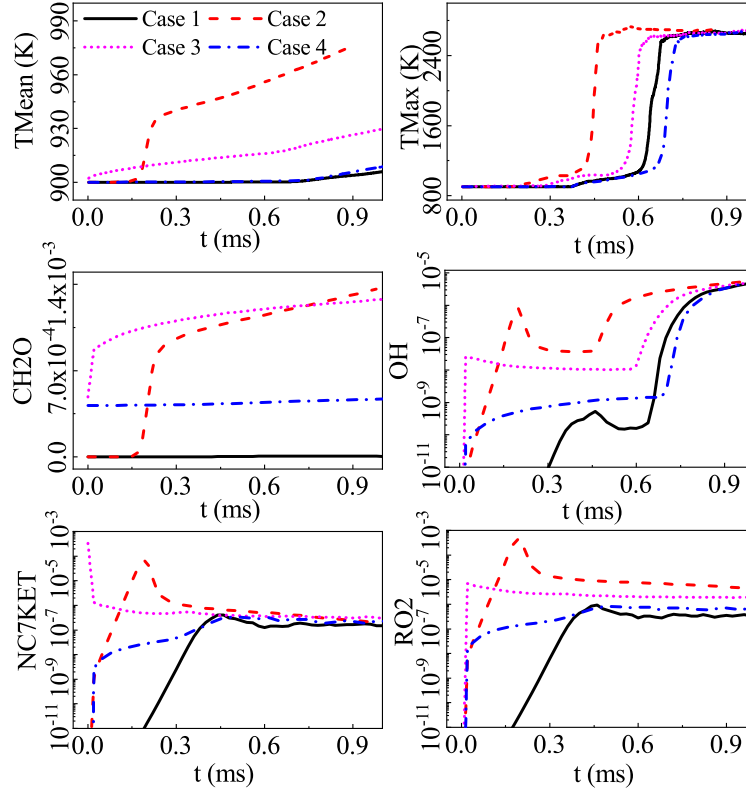


Figure 5: Temporal evolution of mean temperature, maximal temperature, and mean species mass fractions (CH₂O, OH, NC₇KET, RO₂) in the combustor.

261 n-heptane and a FCR of 82%. The LTI products start to react almost immediately,
 262 forming OH radicals (via decomposition of NC₇KET to OH radicals), while also
 263 giving rise to a noticeable heat release in the ambient mixture. Due to the large
 264 amount of mass in the ambient gas, the mean temperature in the combustor shows
 265 an immediate increase, along with an immediate increase of pressure, cf. Figs. 4
 266 and 5. The mixing layer of the ambient gas and the vapor n-heptane from the liquid
 267 jet is, however, not as quickly ignited as in Case 2. The lower level of n-heptane in
 268 the LTR gas is the reason behind the longer IDT in Case 3 as compared with that

269 of Case 2, due to the weaker NTC effect. This also explains the longest IDT of
270 Case 4 among all cases, since the case has the highest LTR temperature, thus, the
271 highest FCR, and the lowest mass fraction of n-heptane in the LTR gas, among all
272 cases. Although the mass fractions of OH, NC₇KET and RO₂ are evident shortly
273 after the start of injection, the cool flame is rather weak, as is evident from the
274 nearly constant mean temperature, and mass fractions of CH₂O and OH, before
275 the onset of HTI. In fact, the IDT of Case 4 is even longer than that of Case 1 (a
276 case without any fuel in the ambient gas). The longer IDT with increasing FCR is
277 consistent with the experiments of Geng *et al.* [3].

278 As the ambient gas Φ increases from 0.3 in Case 4 to 0.5 in Case 5, the
279 inhibiting effect of LTR products on n-heptane ignition is more significant, cf.
280 Fig. 6. Comparing Cases 5 and 4 with Case 1, it is found that the inhibiting effect
281 of LTR products on HTI is more obvious than on LTI. As the LTR products have a
282 lower capability to release heat from low temperature chemistry [35], the maximal
283 temperature increase is rather slow in the transition process from LTI to HTI in
284 Case 5, which delays the HTI [36]. This is consistent with the n-heptane NTC
285 effect. Higher n-heptane level in the mixture leads to stronger NTC effect and
286 higher heat release from low temperature ignition.

287 Fig. 7 shows the temporal evolution of flame liftoff length, LOL. For all cases,
288 the onset of HTI is at a downstream position, and the ignition fronts propagate
289 upstream with time, giving rise to a decreasing LOL. It is evident that the LTR gas
290 has significant effects on the LOL; a higher FCR leads to a longer LOL. The value
291 of LOL is closely correlated with the value of IDT, i.e., a shorter IDT corresponds
292 to a shorter LOL, indicating that the leading front of the lifted flame is assisted by
293 the ignition reactions upstream the lifted flame [20].

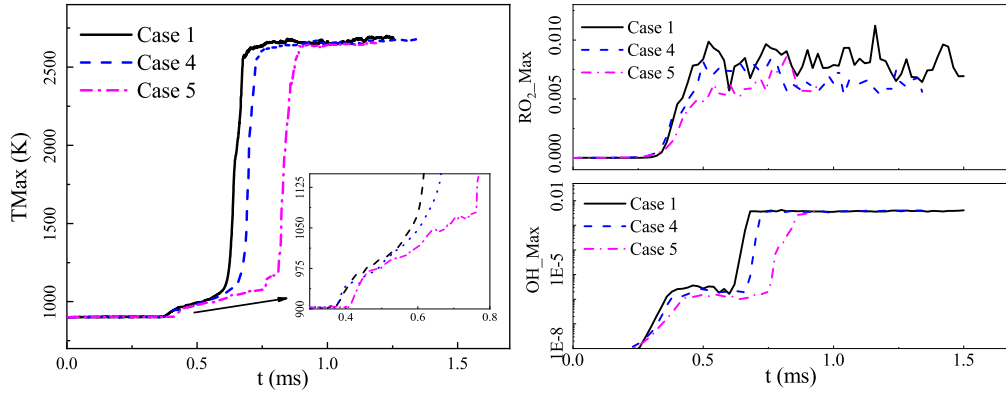


Figure 6: Temporal evolution of maximal temperature and species mass fractions (OH and RO_2) in the combustor for Cases 1, 4 and 5.

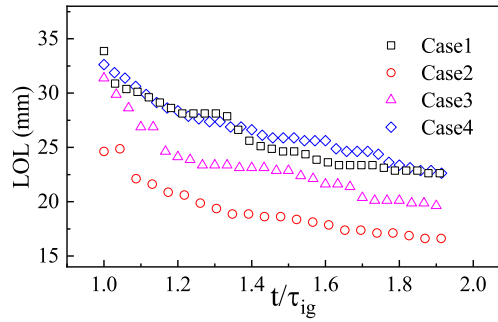


Figure 7: Temporal evolution of LOL. Time is normalized by the value of IDT.

294 4.3. Flame Structure

295 Fig. 8 shows a 2D distribution of the instantaneous heat release rate, HRR,
 296 after the onset of HTI. Considering that Cases 1 and 4 have a similar IDT and LOL,
 297 they are selected and compared here to investigate the effects of ambient LTR gas
 298 on the structure of the spray flame. Following the definition of local equivalence
 299 ratio (Φ) in Ref. [37], the Φ iso-contour lines shown in Fig. 8 consider the fuels
 300 from both the ambient gas and the injected fuel. For both Cases 1 and 4, the onset
 301 of HTI (indicated by the high HRR region) occurs in the fuel-rich region at the

spray tip, and a low HRR region from LTI (cool flame) is shown in the upstream region. The HTI fronts propagate upstream towards the LTI region and the HTI and LTI regions merge together at about $1.4\tau_{ig}$.

Downstream of the HTI fronts, a diffusion flame (DF) is formed around the stoichiometric iso-contour line ($\Phi = 1$) with a thin heat release layer, and a lean premixed flame (LPF) is formed in the proximity of the DF in the fuel-lean region. As evident in the time interval from $1.12\tau_{ig}$ to $1.42\tau_{ig}$, the double-layer flame structure propagates downstream, due to continuous injection of the liquid fuel and the penetration of the vapor fuel. As the process is evolving in time, for the single-fuel case, Case 1, the LPF and DF separate each other in space and the LPF is gradually weakened and quenched eventually, once the mass fraction of the fuel vapor in the mixture downstream of the flame is too low to sustain the LPF. In the LTR gas RCCI case, Case 4, the LPF and DF separate in the periphery of the spray but they stay close to each other at the spray tip. The LPF releases considerable heat at $\Phi \sim 0.5$ as it propagates outwards into the ambient gas. The LPF flame is sustained due to the presence of LTR fuels in the ambient mixture.

Two interesting points in Case 4 are worthy of discussion. One is that the LPF layer is at $\Phi \sim 0.5$, instead of the ambient LTR gas/air mixture of $\Phi = 0.3$, indicating that the LPF is maintained both by the injected fuel and the ambient fuel. Another point is that the mixing between the injected fuel and the ambient gas in the RCCI case, Case 4, is slower than that in single-fuel case, Case 1, in the spray tip region. This results in a larger fuel-rich region (enclosed by $\Phi > 1.5$) in the RCCI case. Fig. 9 shows a 2D distribution of mixture fraction at the instance of time of 1.2 ms for both Case 1 and 4. The stoichiometric mixture fraction (Z_{st}) iso-line in Case 4 is at a similar streamwise location to that in Case 1 at the spray

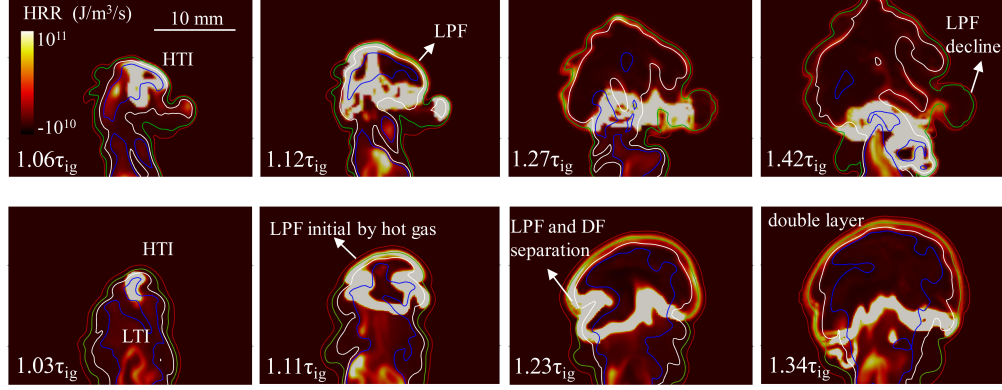


Figure 8: Temporal evolution of heat release rate distribution after high temperature ignition of the spray in Cases 1 (top) and 4 (bottom). Solid blue, white, green and red lines denote the local equivalence ratio 1.5, 1.0, 0.5 and 0.3, respectively.

327 tip, while the iso-line of $0.5Z_{st}$ at the spray tip in Case 4 is much closer to the
 328 iso-line of Z_{st} , than in Case 1. This indicates that the mixing field is influenced by
 329 the LPF in the RCCI case, which has a significant impact on the soot emission to
 330 be discussed below.

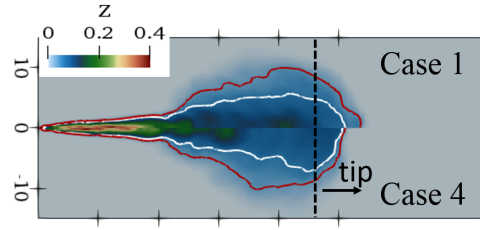


Figure 9: Circumferential averaged mixture fraction distributions at 1.2 ms. Solid white line represents stoichiometric mixture fraction, and solid red line denotes half of stoichiometric mixture fraction.

331 To explain the poor mixing in the RCCI case, Fig. 10 presents the distribution
 332 of Z , HRR and axial velocity, U , along the central axis of the jet. In Case 1, the

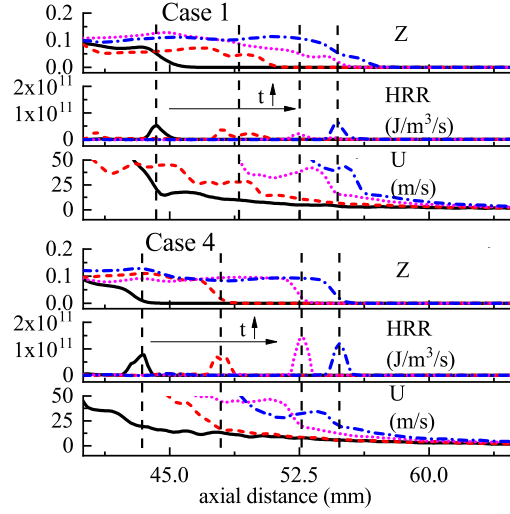


Figure 10: The mixture fraction (Z), heat release rate (HRR) and axis velocity (U) profiles along the central axis line with time evolving. Solid black line: $\tau_{ig} + 0.16$ ms ; red dash line: $\tau_{ig} + 0.36$ ms; magenta dot line: $\tau_{ig} + 0.56$ ms; blue dash dot line: $\tau_{ig} + 0.64$ ms.

333 HRR peak is around Z_{st} , and the value of HRR is lower than that in the RCCI case,
 334 Case 4. The value of U across the HRR layer varies only slightly, which allows
 335 the convective transport of the hot products from the flame to the ambient gas
 336 downstream, therefore, enhancing the mixing of the hot products with the ambient
 337 gas downstream. On the contrary, in the RCCI case, Case 4, the value of HRR is
 338 higher, due to the double-layer DF/LPF structure shown in Fig. 8. The peak HRR
 339 is at a much lower value of Z , i.e., $Z < Z_{st}$. The value of U across the HRR layer
 340 decreases rapidly. This slows down the convective transport of the hot gas from the
 341 flame to the ambient mixture downstream, resulting in a high gradient of mixture
 342 fraction in Case 4, cf. Fig. 9. The rapid decrease of U across the LPF is a result of
 343 pressure loss across the LPF, from the ambient mixture side towards the DF side.
 344 This results in a strong negative pressure gradient along the axial direction, which

345 decreases the axial velocity along the downstream across the LPF.

346 4.4. Emission Formation

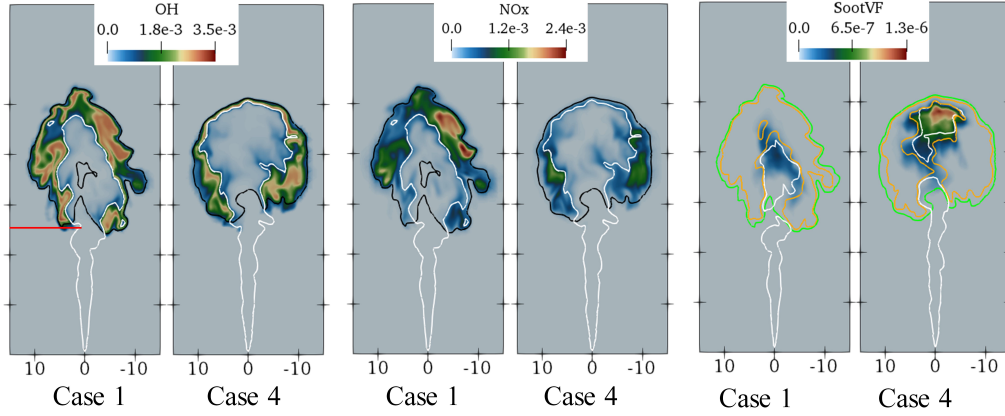


Figure 11: Instantaneous distributions of the mass fractions of OH radicals and NOx, and soot volume fraction (SootVF) at time of $\tau_{ig} + 0.5$ ms. OH: white line: $\Phi = 1.3$; black line: temperature of 1800 K; red line: lift-off length from experiment [30]. NOx: white line: $\Phi = 1.3$; black line: temperature of 1800 K. Soot volume fraction: white line: temperature of 1600 K; green line: temperature of 2200 K; yellow line: $\Phi = 2$.

347 Fig. 11 shows the instantaneous fields of mass fractions of OH and NOx, and
 348 the soot volume fraction, SootVF. OH is found in the mixture of $\Phi < 1.5$. The
 349 region of high NOx overlaps with the high OH region. In Case 4, due to the
 350 presence of LPF, the OH and NOx regions at the spray tip are rather thin; thus, the
 351 production of NOx in the RCCI case is lower than that in the single fuel case, Case
 352 1. Soot is shown to be generated in the region of $\Phi > 2$ and temperature between
 353 1600 K and 2200 K, consistent with Ref. [38]. A larger soot zone is shown at
 354 the central fuel-rich region close to the spray tip in the RCCI case, whereas the
 355 single-fuel case, Case 1, exhibits a significantly smaller soot region and a lower

soot volume fraction. This is well consistent with the mixing field shown in Fig. 9.

5. Conclusions

The combustion characteristics and NO_x/soot formation in n-heptane spray flames in a constant volume combustion vessel, under conditions relevant to the low temperature reform (LTR) gas reactivity controlled compression ignition (RCCI) combustion, is studied using large eddy simulations with a transported probability density function (PDF) sub-grid scale model. The spray model and LES-PDF combustion model are validated against ECN Spray-H experimental results. Very good agreement between the LES results and experiments is obtained for the spray liquid length, vapor fuel penetration length, mixture fraction profile, pressure rise profile, ignition delay time (IDT), and liftoff length (LOL). The LES results are used to analyze the combustion and emission process. The following conclusions are drawn.

The IDT of the spray and the LOL of the spray flame are sensitive to the LTR gas composition, thus, to the LTR temperature (reform temperature). Both the IDT and LOL increase with increasing LTR temperature, due to the decreasing effect of cool flame in the n-heptane ignition process. The reaction zone structure in the RCCI case is significantly different from that of the n-heptane spray flame case. The RCCI case exhibits a double-layer flame structure at the spray tip and in the periphery of spray flame, consisting of a mixing-controlled diffusion flame (DF) layer and a lean premixed flame (LPF) layer on the lean side of DF. The presence of LPF affects the mixing process around the spray tip, resulting in a much lower NO_x production at the flame tip. However, the fuel-rich region upstream of the flame

tip is larger in the RCCI case, which results in a higher level of soot formation.

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