Turbulent spray combustion simulations based on a new skeletal mechanism for n-dodecane

O. Samimi Abianeh1*, Matthew A. Oehlschlaeger2, Chih-Jen Sung3
1 Department of Mechanical Engineering, Georgia Southern University, Statesboro, GA.
2 Department of Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY.
3 Department of Mechanical Engineering, University of Connecticut, Storrs, CT.

Abstract
A study of turbulent spray combustion of n-dodecane was conducted using computational fluid dynamics simulations. We report a new skeletal mechanism based on the reduction of a detailed kinetic reaction mechanism for high pressure conditions (50-60 bar), temperatures from 750 to 2500 K, and a range of equivalence ratios from 0.5 to 1.5. The skeletal mechanism has 85 species and 266 reactions. The mechanism was implemented in a computational fluid dynamic code to model the combustion of n-dodecane in a high pressure (60 bar) and temperature (900 K) constant volume chamber. A dynamic structure turbulence model with fine mesh size was utilized. Both first-stage low-temperature combustion, or cool-flame, and second-stage high-temperature combustion were observed due to the decrease in the gas temperature surrounding the spray caused by the fuel evaporative cooling. The species mass fraction histories were studied numerically to find a correlation between first-stage and second-stage combustion and species consumption. Species mass fractions, combustion chamber pressure, and combusting n-dodecane vapor penetration histories were studied computationally, and the results were compared with experiments to find a numerical equivalent to the light-based activated OH chemiluminescence ignition delay experiment.

*Corresponding author: oabianeh@georgiasouthern.edu
Introduction

The turbulent spray combustion process is multiphysics, multi-scale, and highly coupled in nature: it involves turbulence, autoignition, two-phase flows, and complex spray physics. Most of the computational fluid dynamics (CFD) sub-models should be revisited and validated separately to solve the complexity of the turbulent spray combustion problem with accuracy and predictability.

Some of the deficiencies in turbulent spray combustion modeling and experimentation are explored in the following. The first inaccuracy and uncertainty comes from the mesh resolution. Different CFD sub-models require different mesh resolutions, and utilizing the minimum mesh resolution of all of the sub-models may violate other sub-model requirements or the physics behind the problem. This deficiency is exemplified by using a mesh resolution of less than nozzle diameter with the Blob droplet breakup model [1]. The injected droplets have the same diameter as the nozzle in the Blob droplets breakup model, and the momentum and energy of these droplets are coupled with the gas momentum and energy for the same mesh. But having a mesh smaller than droplet diameter violates this momentum and energy coupling, as there are several meshes inside of each injected droplet that do not comprise a gas phase.

Another complexity focuses on turbulence modeling. Reynolds Averaged Navier Stokes (RANS) turbulence model provides averaged data and cannot predict the highly transient nature and shape of turbulent spray. Large Eddy Simulation (LES) and Direct Numerical Simulation (DNS) have been utilized in spray modeling, resulting in some valuable information. However, most of the error and uncertainty comes from the droplet breakup model. All of the developed breakup models need coefficient retuning by changing the fuel or injector, which makes these models highly unreliable.

The other source of error stems from the kinetic model. The detailed kinetic model, which already has ignition delay uncertainty in respect to experimental data, should be reduced to a smaller size to make it suitable for utilization in CFD code, which results in more error and uncertainty. Most of the CFD codes do not account for the heat transfer inside of the droplet, and the fully mixed droplet models are used in evaporation modeling. Therefore, the droplet will heat up faster, and its lifetime will be shorter and under-predicted [2].

The collision model of multi-component droplets also needs to be revisited. The droplet collision model was developed for mono-component fuel by using the Weber number, and was extended to include the multi-component droplet. The model extension is primarily the same as the previous model, but utilizes the average property of one or both of the droplets to calculate the Weber number [3]. An issue arises when two droplets with different components collide with each other. There is no reliable model to answer how the mixture will be reorganized between the droplets after the collision, or the outcome of the model.

The experimental data of turbulent spray combustion also needs to be utilized carefully. The jet (vapor) penetration boundary is not yet quantified [4], and the ignition delay timing is a light-based measurement, which cannot be easily used for spray modeling validation purposes [4]. The Engine Combustion Network (ECN) of Sandia [4] is dedicated to conducting experiments for turbulent spray evaporation, combusting, and non-combusting. ENC has conducted several comprehensive series of spray measurements of n-dodecane and other mono-component fuel. These experiments are mainly conducted by Sandia National Laboratory and IFP, and are available on the Sandia website [4]. For example, Spray A experiments, which will be discussed in more detail later, were conducted at low and high temperature conditions relevant to compression ignition engines. Additionally, boundary conditions necessary for CFD simulations were determined accurately and the uncertainties were addressed.

This paper is organized in the following way: computational methodologies and CFD sub-models are explained briefly, followed by results and discussion sections. The n-dodecane mechanism development is described and the ignition delays of several mechanisms are compared with shock tube experimental data. The evaporating non-combusting spray is modeled initially, and is used for tuning the spray breakup model coefficients. The spray and jet penetrations and fuel vapor mass fraction are compared with the experiments. Finally, the turbulent spray combustion is modeled and compared with experimental data by using two mechanisms to study the effect of mechanism reduction error on final spray autoignition results. The uncertainties and embedded errors of each step are discussed. Nevertheless, the most important objective of this paper is to find a technique to compare the ignition delay of light-based experiments with CFD simulations.

Computational Methodology

CONVERGE CFD software package [5], Chemkin-Pro [6], and Workbench [7] are used as the computational framework for modeling the spray, simulating the combustion, and mechanism reductions, respectively. This section presents an overview of the mesh manipulation, numerical algorithms, and physical sub-models used in the current work.

*Corresponding author: oabianeh@georgiasouthern.edu
Computational Algorithm

In the present study, the conservation equations are solved using the finite volume method, and a second order accurate spatial discretization scheme is used for the governing conservation equations. In order to maintain stability, time accuracy is set to first order by running fully implicit. The transport equations are solved using the Pressure Implicit with Splitting of Operators (PISO) method of Issa [8]. Variable time-stepping is used in the current study. The time-step is automatically calculated for each computational cycle based on the maximum allowed CFL numbers (based on velocity 1, based on viscosity 2.5, based on speed of sound 50), as well as spray, evaporation, and combustion time-step control methods. The simulations in this study are run parallel on distributed memory machines using the Message Passing Interface (MPI).

Mesh Characteristics

A coarse mesh was used in this work to minimize the mesh number and solution time. Mesh embedding and adaptive mesh refinement were also utilized to fulfill the sub-models mesh requirements, such as spray model and an increase in the accuracy of the solution. Senecal et al. [9] studied the grid dependency of the solution by using a large eddy simulation turbulent model. The grid independent solution for mesh resolution of less than 0.125 mm was achieved and the modeling predictions of spray and vapor penetrations were closer to the experimental data after reducing the mesh size to less than 0.125 mm, as discussed by Senecal et al [9]. The spray and vapor penetration locations overpredicted using the mesh size of 0.125 mm as shown in Figure 1. The minimum mesh size of 0.0625 mm is used in current experiments for both non-reacting and reacting evaporating sprays, and the predicted results of spray and vapor penetration converged to the experiments by using this resolution, as shown in Figure 1. The finer mesh resolution of 0.03125 mm is also studied for non-combusting evaporating spray and the results are shown in Figure 1. The predicted vapor penetration by using mesh size of 0.03125 mm is closer to experimental data but it is computationally extremely expensive for modeling the spray autoignition, and was not studied further in the current work. To achieve the mesh resolution of 0.0625 mm, a coarse mesh of 2 mm was used over the whole domain, and the mesh was refined in certain areas to reach 0.0625 mm. The conical embedded mesh refinement with a resolution of 0.0625 mm was used at nozzle exit as shown in Figure 2 to resolve the complex flow behavior at the nozzle exit. Adaptive mesh refinement (AMR) was also used in the whole domain except in the conical embedded mesh. AMR automatically refines the grid based on fluctuating and moving conditions, such as temperature and velocity, up to the certain predefined mesh resolution of 0.0625 mm in the current work. The velocity of 1 m/s and temperature of 2.5 °K were used as sub-grid criteria for activation of AMR. See Reference [5] for more details. The initial number of cells without AMR (e.g., at time zero) were around 163,000 cells, and the maximum number of generated cells in the entire domain was limited to 1 million during the solution. For simulations of non-combusting spray and vapor penetration were similar for 1 million mesh cells and 2 million mesh cells as shown in Figure 1.

Spray Modeling

Accurate predictions of spray droplet dynamics and breakup are essential for modeling the subsequent vaporization, ignition, and combustion phenomena. The present simulations employ the “Blob” injection method of Reitz and Diwakar [1] in which “ parcels” of liquid with a characteristic size equal to the effective nozzle diameter are injected into the computational domain. The atomization of the liquid blobs and subsequent droplets are simulated with models based on the Kelvin-Helmholtz (KH) and Rayleigh-Taylor (RT) instability mechanisms [5, 10]. The model coefficient was tuned for the conditions of the current study based on the spray and jet penetrations shown in Table 1.

The No Time Counter (NTC) collision model of Schmidt and Rutland [11] was used in the present work. The outcome of a collision was predicted to be bouncing, stretching separation, reflexive separation, or coalescence [12].

A single-component evaporation model [e.g., 13] was used in the present calculations. The basis of this model is the Frossling correlation, which calculates the time rate of change of drop radius based on the laminar mass diffusivity of the fuel vapor, mass transfer number, and Sherwood number. The droplets are assumed to be fully mixed and there is no gradient of temperature and component mass fraction inside of the droplet. Raoult’s law is utilized in modeling to correlate between the vapor mass-fraction of the component over the surface and its mole fraction in the condensed phase.

Turbulence Modeling

The Large Eddy Simulation (LES) turbulent model is used in spray combustion simulation. One equation dynamic structure of Pomraning [14] is utilized for LES turbulent modeling.
Combustion Chemistry Modeling

The SAGE detailed chemistry solver [15] was used for the reacting cases in the current study.

Reaction Mechanism Overview

A n-dodecane skeletal mechanism was developed based on Westbrook et al. [16] detailed n-octane to n-hexadecane mechanism. The updated detailed mechanism, with a release date of Feb 9th, 2008 was utilized for mechanism reduction. The Chemkin-Pro [6] and Workbench [7] were utilized for mechanism reduction. Different reduction methodologies such as DRGEP and DRG with sensitivity analysis were coupled together to reduce the size of the mechanism.

The final skeletal mechanism has 85 species and 266 reactions by accepting a maximum 10% error margin in total ignition delay difference between detailed and skeletal mechanisms at two temperature points, 750 and 2000 K. The comparisons of several different mechanisms with experiments are shown in Figure 3. None of the mechanism satisfy the experimental data. All of the mechanisms over-predict the ignition delay for low temperature, or temperatures lower than 850 K. Simulated ignition delays using the detailed mechanism of Narayanaswamy et al. [17] are closer to the experiments than those using the other mechanism at high temperature condition. In this paper, two mechanisms, currently developed mechanism and Luo et al. [18] mechanism, are implemented in computational fluid dynamics for spray modeling.

Results and Discussions

The Sandia constant volume vessel and Spray A were modeled by using the computational fluid dynamics code at the experimental conditions of Table 2. The spray (or liquid) and jet (or vapor) penetrations are shown in Figure 4. The simulated spray penetration is very close to the experiment, but the jet penetration is slightly over-predicted with respect to the experimental data. The jet penetration over prediction could be due to uncertainties in the experiments, as the experimental data came from capturing images of the developing spray and finding the boundaries of spray and jet. Differences could emanate from the interpretation of simulation results. In the experiments, the fuel vapor mass fraction at the boundary of the jet is unknown. In the simulations it is arbitrarily set to 0.001 for determination of spray boundary.

The other source of uncertainty is the turbulent Schmidt number. By adjusting the turbulent Schmidt number, which is 0.78 in this simulation, the jet penetration can be adjusted. The error between modeling and experiments will be smaller by reducing the mesh size to 0.03125 mm as shown in Figure 1, but with added computational expense. As mentioned before, the jet penetration is computed based on a n-dodecane vapor mass fraction (0.001) for evaporating and combusting spray. As shown in Figure 4, the n-dodecane jet will not penetrate after 0.38 or 4 ms, since it starts combusting and the mass fraction of n-dodecane vapor drops below the 0.001 threshold. The ignition delays of 0.39 and 0.41 ms were reported based on high-temperature chemiluminescence and chamber pressure rise, respectively, for the corresponding conditions [4]. The ignition delay is defined as the time when luminosity reaches 50% of steady high-temperature chemiluminescence (not soot luminosity) in the experiments.

The improved technique to validate the jet penetration is to compare the fuel vapor mass fraction at different axial and radial locations with the experiments as shown in Figure 4. Three different turbulent realizations were simulated and the fuel vapor mass fractions at two directions normal to injector axial direction were plotted for evaporating non-combusting spray. The data of these three realizations at two planes are also averaged and shown in Figure 4. The averaged data shows slightly under-prediction for axial location of 25 mm, but the prediction is close to the experiments at 45 mm from the injector. The under-predictions of mass fraction could be caused by several factors, such as more realizations are needed to find accurate averages, the data should be averaged in more planes normal to the axial direction, and higher mesh resolution (more than 1 million cells) may be needed, which would make the simulations not possible with available computation resources.

The simulated chamber pressure is compared with the experiment to determine and compare the ignition delay, since there is no simulation equivalent to the 50% of steady high-temperature chemiluminescence determined in experiment. Pressure measurements were acquired using a piezoelectric pressure transducer located in a lower corner of the vessel and opposite the injector. The time offset of the pressure measurement was adjusted to account for the delay in the pressure measurement caused by the speed of sound and the distance between the ignition site and the pressure transducer [19]. The chamber pressure is also computed at the same location, and the time offset of the pressure computation was corrected the same manner as in the experiment. The vessel pressure measurement shows that pressure slowly decreases in the chamber during the cool-down period prior to fuel injection [20]. A curve fit of the pressure record prior to injection is made to estimate how this cooling trend affects interpretation of the pressure behavior during injection, ignition, and combustion. The difference between the measured pressure and the cool-down curve fit is the pressure rise caused by fuel combustion, which is
shown in Figure 6. The simulation was carried out twice, first by modeling the combustion, and second by deactivating the combustion and spray models to simulate the pressure drop due to the cool-down. The difference between the two computed pressure rises is also shown in Figure 6. None of the simulations carried out with different mechanisms capture the small pressure rise between 0.2 to 0.3 ms, which could be due to cool-flame chemistry or first-stage ignition. The pressure starts rising in simulations carried out with the current mechanism after 0.3 ms, and the maximum local gas temperature starts increasing at the same time, as shown in Figure 7. With the Luo et al. [18] mechanism, pressure and temperature rise occur later than experiment, around 0.35 ms.

The total species mass fraction history in the combustion vessel is shown in Figure 8. Westbrook et al. [16] described the reaction paths in low- and high-temperature combustion at rapid compression machine conditions, which could be extended to the current work. The cooling effect of fuel evaporation reduces the gas temperature around the spray reach to as low as 500 K, as shown in Figure 9. Therefore, there is a gradient of gas temperature starting from this low temperature and to the combustion vessel temperature (900 K) or higher. Due to flow, these layers are mixed as time passes, and more fuel droplets evaporate. The fuel vapor experiences a range of temperatures and a wide range of low- to high-temperature reaction paths initiated fuel decomposition. A considerable amount of decomposition becomes clear at 0.25 ms as shown in Figure 8. The low temperature combustion can be described by the following steps [21]:

H atom abstraction from the fuel

$$RH + X = R + HX$$  \(1\)

Addition of molecular oxygen to alkyl

$$R + O_2 = RO_2$$  \(2\)

Isomerization to form hydroperoxyalkyl

$$RO_2 = QOOH$$  \(3\)

Addition of additional molecular O

$$QOOH + O = O_2 QOOH$$  \(4\)

Decomposition to OH and ketohydroperoxide

$$O_2 QOOH = OH + KOOH$$  \(5\)

Decomposition to OH and carbonyl radical

$$KOOH = OH + KO$$  \(6\)

At low temperatures, below 750 to 800 K, alkyl radicals will be formed by hydrogen atom abstraction from the hydrocarbon fuel by a radical X as shown by reaction 1. A peak of alkyl formation is observed around 0.33 ms, and the high temperature combustion starts. The rate of alkyl formation will decrease due to the decomposition of RO₂ as shown in Figure 8. RO₂ and hydroperoxyalkyl species mass history also peaks around 0.325 ms, reactions 2 and 3. The mass of RO₂ is 100 times higher than the other radicals at 0.33 ms, which shows reaction 2 as the main chain branching reaction.

As the temperature further increases, as shown in Figure 7 with the maximum local gas temperature, the decomposition of RO₂ increases rapidly. Therefore, the chain branching rate and overall rate of reaction will be lowered. Over this range of temperature, HO₂ and H₂O₂ will be produced. By increasing the temperature further, reaction and mixing will cause the rate of hydrogen peroxide (H₂O₂) decomposition to accelerate until it begins to provide significant chain branching, producing two OH radicals for each H₂O₂ species consumed [23]. The hydrogen peroxide decomposition is clearly observed in Figure 8, as around time of 0.4 ms, H₂O₂ mass starts decreasing and OH starts increasing significantly, which shows high temperature combustion. The first peak of OH near 0.315 ms is due to low-temperature first-stage ignition. In this temperature range, the reactions 1-6 result in the formation of two OH radicals for every radical X. In summary, the OH mass fraction history can be utilized to find the ignition delay. The ignition timing based on the mass history of o (start increasing at around 0.37 ms), h (start increasing at around 0.4 ms), alkyl and hydroperoxyalkyl (reach steady state value at around 0.4 ms) are also used to define the ignition delay in comparison with activated OH chemiluminescence or pressure rise.

The temperature contours of the turbulent spray combustion are compared with natural luminosity imaging of Sandia and IFP [22], as shown in Figure 9. The current mechanism was used for this simulation and temperature contours are plotted at 0.45, 0.5 and 0.55 ms. The three high luminosity locations in the experiments at 0.450 ms are predicted in the simulation. The temperature contour shapes at two other times, 0.5 and 0.55 ms, are also similar to the experiments. However, the locations of autoignition, or lift off length, are over-predicted at all times by approximately 5 mm. The lift off length over-prediction could be caused by the mixture preparation, since the n-dodecane mixture is leaner, as shown in Figure 4.

**Conclusion and Summary**

This study focuses on simulation of turbulent spray combustion of n-dodecane at high temperature and pressure in a constant combustion vessel. The Large Eddy Simulation turbulent model, adaptive mesh refinement, and a new skeletal mechanism were utilized for spray evaporation and combustion modeling. A skeletal mechanism for dodecane with 85 species and 266 reactions was developed by reducing a detailed mechanism from Westbrook et al. [16]. The ignition delay predictions of the new skeletal mechanism were compared with experimental data. The current mechanism and previously developed mechanisms were used to study the first-stage and total ignition delays of n-dodecane spray. The evaporating non-combusting n-
dodecane spray was studied initially, and validated using experimental data. The spray and jet penetration, and fuel vapor mass fraction, are in agreement with experiment. The evaporating combusting spray was modeled and time of autoignition was determined using the n-dodecane vapor mass fraction, combustion chamber pressure history, local peak temperature, and species mass history. Comparisons were made between these metrics and ignition delay measurements made using activated OH chemiluminescence. n-Dodecane vapor penetration can be studied computationally, and used for determining the ignition delay timing accurately, since at the time of autoignition, n-dodecane will decompose to other species. The total autoignition timing can hardly be detected using combustion chamber pressure, since the pressure waves propagate from the location of ignition to the walls of the combustion vessel and reflect back. This wave motion makes determination of the time of ignition difficult. The species mass history in the combustion vessel shows first-stage ignition occurs due to spray evaporative cooling during the temperature at the spray-vapor interface by several hundred degrees Kelvin. The modeled species mass history can be used to find the exact location of the first-stage and total ignition delay timings. The ignition timing based on the mass history of o, h, alkyl and hydroperoxyalkyl are also could be used to define the ignition delay as comparison with activated OH chemiluminescence or pressure rise. The temperature history was also studied and compared with light-based experiments, providing a fair agreement regarding the ignition timing. However, the flame lift-off length was over-predicted.

References

Figure 1. Spray and jet penetration for different mesh size. A total spray mass of 97% and minimum fuel vapor mass fraction of 0.001 were employed as thresholds for computational determination of the spray tip location and jet boundary location respectively.

Figure 2. Grid generated at 0.08 ms after start of injection for non-reacting dodecane spray. The domain has a cubic shape with size of 108 mm in each direction. Part of the domain is shown in this picture. The red cloud illustrates injected droplets and green counter is n-dodecane vapor mass fraction.

Table 1. Droplet breakup model coefficients

<table>
<thead>
<tr>
<th>Model</th>
<th>KHRT model (Hybrid of Kelvin-Helmholtz model and Rayleigh-Taylor model)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH model Coefficient</td>
<td></td>
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<tr>
<td>Fraction of injected mass/parcel to create new droplet</td>
<td>0.05</td>
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<tr>
<td>Shed mass constant</td>
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<tr>
<td>Model size constant</td>
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<td>Model velocity constant</td>
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<tr>
<td>Model breakup time constant</td>
<td>4.0</td>
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<tr>
<td>RT model Coefficient</td>
<td></td>
</tr>
<tr>
<td>Model breakup time constant</td>
<td>1.0</td>
</tr>
<tr>
<td>Model size constant</td>
<td>0.1</td>
</tr>
<tr>
<td>Model breakup length constant</td>
<td>10</td>
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</table>
Figure 3. Comparison between simulation (lines) of total ignition delay at 40 bar: simulations carried out with four mechanisms and experimental data (symbols) is from Shen et al [24] (using $P^1$ scaling law adopted in their study) and Vasu et al. [23] (using $P^1$ scaling at $T > 1000$ K, and $P^{1.64}$ scaling at $T < 1000$ K adopted in [17]). Mechanisms are from Narayanaswamy et al. [17], Luo et al. [18], Westbrook et al. [21], and current skeletal mechanism.

Table 2. n-Dodecane spray A operating conditions at Sandia National Laboratories [4]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Quantity</th>
</tr>
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<tbody>
<tr>
<td>Fuel</td>
<td>n-dodecane</td>
</tr>
<tr>
<td>Nozzle orifice diameter</td>
<td>84 µm</td>
</tr>
<tr>
<td>Fuel injection pressure (steady state)</td>
<td>150 MPa</td>
</tr>
<tr>
<td>Injected fuel mass</td>
<td>14 mg</td>
</tr>
<tr>
<td>Fuel injected temperature</td>
<td>373 K</td>
</tr>
<tr>
<td>Injection duration</td>
<td>6.1 ms</td>
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<tr>
<td>Ambient gas temperature</td>
<td>903 K</td>
</tr>
<tr>
<td>Ambient gas density</td>
<td>22.8 kg/m$^3$</td>
</tr>
<tr>
<td>Ambient composition (mole fraction)</td>
<td>$O_2=15.00$, $N_2=75.15$,</td>
</tr>
<tr>
<td></td>
<td>$CO_2=6.22$, $H_2O=3.63$</td>
</tr>
</tbody>
</table>

Figure 4. Spray/Jet penetration for evaporating and combusting n-dodecane spray by using current skeletal mechanism. The vapor penetration is computed based on n-dodecane vapor mixture fraction. The minimum mesh size is 0.0625 mm.
Figure 5. Comparison of n-dodecane vapor mass fraction with experiments at two different locations, 25 and 45 mm from injector. Three different turbulence realizations are shown. The simulated data is averaged in two different directions (planes) for three realizations.

Figure 6. Measured and simulated pressure rise in combustion chamber. The time is corrected for speed of sound. The pressure is measured and computed at the lower corner of combustion chamber opposite to the injector.

Figure 7. Simulated temperature history in combustion chamber.
Figure 8. Total species mass fraction history in combustion chamber.

Figure 9. Measured and predicted results for fuel spray distribution and ignition location and time. The experiments are from IFP and Sandia [22].