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Combustion and Emission Characteristics of Biodiesel with - Methyl Butanoate as Surrogate -

Sibendu Som*, and Douglas E. Longman

Transportation Technology Research and Development Center,
Argonne National Laboratory, Argonne, IL 60439

Combustion and emission characteristics of compression ignition engines depend strongly on inner-nozzle flow and spray behavior. These processes control the fuel-air mixing, which in turn is critical for the combustion process. Previous studies by us have highlighted the differences in the physical and chemical properties of petrodiesel and biodiesel, which significantly altered the inner-nozzle flow and spray structure. The current study is another step in this direction to gain understanding on the influence of fuel properties on the combustion and emission characteristics of the compression ignition engine. N-heptane and methyl butanoate were selected as surrogates for diesel and biodiesel fuel respectively, since the chemical kinetic pathways were well understood. Liquid length and flame lift-off length for diesel and biodiesel fuels were validated against data available in literature. Biodiesel predicted lower soot concentrations. Although prompt NOx was higher for biodiesel, total NOx was lower due to reduced thermal NOx. The ignition delay and NOx emissions predicted by these simulations do not agree with trends reported in literature; hence, this study highlights the need for developing better fuel surrogates for diesel and biodiesel fuels.

1. Introduction

Energy security and environmental concerns have stimulated worldwide interest in biologically derived alternative fuels. Further utilization of biodiesel for CI engine applications can be facilitated by better understanding of its auto-ignition and emissions characteristics. Detailed combustion simulations of biodiesel can be performed with reliable reduced mechanisms for biodiesel surrogates. Although several surrogate fuels for biodiesel have been proposed, the lack of reduced mechanisms inhibits their use for CI engine modeling. Brakora et al. [1] developed a reduced mechanism using methyl butanoate as a surrogate for biodiesel, which consists of 41 species and 150 reactions. While performing CI engine simulations using KIVA, they assumed that the injection characteristics would be similar for diesel and biodiesel fuels, which may not be an accurate assumption. The mechanism successfully predicted ignition timing, pressure, and heat-release-rate characteristics. Using the same biodiesel surrogate, Ra et al. [2] performed parametric studies to investigate the effects of various physical properties on combustion characteristics. They observed that the results were most sensitive to liquid density, vapor pressure, and surface tension. Golovitchev and Yang [3] developed a kinetic model for RME with methyl butanoate as a surrogate fuel. The reduced mechanism consisted of 88 species and 363 reactions and was validated against shock-tube and flame speed data. Compression ignition engine simulations were also performed. Um and Park [4] developed a kinetic model for biodiesel derived from rice oil with a mixture of methyl

butanoate and n-heptane (NHPT) as a surrogate. Simulations captured the CO and HC emissions well for different blends of diesel and biodiesel. However, NOx emissions were not accurately predicted.

The literature search identified relatively few studies dealing with fundamental combustion and emission characteristics of biodiesel fuels. These characteristics of a conventional CI engine are strongly coupled with the flame lift-off behavior, as demonstrated by several previous studies [5,6,7,8]. While the flame lift-off characteristics of diesel fuel and its surrogates (such as NHPT) have been investigated in great detail, only recently, the lift-off characteristics of biodiesel fuel (soy-methyl ester) were investigated by Lee and co-workers [9] and Mueller et al. [10]. Lee and co-workers [9] measured flame lift-off in a constant volume combustion vessel with optical access ports and observed that lift-off length of biodiesel was higher than that of diesel # 2 fuel. They also observed significant reduction of soot for biodiesel fuel. Mueller et al. [10] measured flame lift-off lengths in a single-cylinder engine with optical access and observed that lift-off length of a diesel-like fuel (with a cetane number of 45) was marginally higher than that of biodiesel.

Previous studies by Som et al. [11] have identified the differences in inner-nozzle flow, as well as non-evaporating, and evaporating-spray characteristics of diesel and biodiesel fuels using computational tools. The current work extends previous studies under non-reacting conditions by including detailed kinetic models for the oxidation of these fuels along with emission models for soot and NOx formation. The major objective of the present study is to quantify differences between the combustion and emission characteristics of diesel and biodiesel fuels. Since there are significant differences in the thermo-transport and chemical properties of these fuels, the combustion and emission characteristics of biodiesel can be expected to differ from those of diesel. Detailed two-phase-flow simulations were performed in an engine modeling software, CONVERGE [12,13], to examine the combustion and emission characteristics of diesel and biodiesel fuels under diesel engine conditions. The difference in NOx emission characteristics of diesel and biodiesel is also investigated further.

2. Computational-Physical Model

The simulations in simplified combustion systems such as 0-D and 1-D reactors are performed in CHEMKIN software [14]. Diffusion flame simulations are performed using the OPPDIF application [15]. Fuel spray and combustion simulations were performed using the Eulerian-Lagrangian approach in the computational fluid dynamics (CFD) software CONVERGE [12,13]. It incorporates state-of-the-art models for spray injection, atomization and breakup, turbulence, droplet collision, and coalescence. The gas-phase flow field is described using the Favre-Averaged Navier-Stokes equations in conjunction with the RNG k-ε turbulence model, which includes source terms for the effects of dispersed phase on gas-phase turbulence. These equations are solved using a finite volume solver. The details of these models can be found in previous publications [16,17,18]. Detailed kinetic modeling is performed using the SAGE chemical kinetic solver [12,13] and is directly coupled with the gas-phase calculations using a well-stirred reactor model. N-heptane is used as a surrogate for diesel fuel while methyl butanoate (MB) is used as a surrogate for soy-biodiesel fuel. The NHPT mechanism was developed at Chalmers University [19] and consists of 42 species and 168 reactions. The reduced mechanism for biodiesel combustion [1] is comprised of 33% MB and 67% NHPT and consists of 41 species and 150 reactions. In order to examine the NOx emission characteristics, a reduced NOx model [20] from GRI-3.0 mechanism [21] was incorporated into the NHPT and biodiesel mechanisms. This NOx chemistry model has been previously validated against flame measurements at different conditions [22]. A few hundred elementary-gas-phase reactions are involved in the formation of NOx, which can be formed or destroyed by at least five separate reaction processes [23]. They are classified as: thermal, prompt, N_2O, NNH, and reburn routes. Under CI engine conditions, the NOx formation mainly occurs through thermal, prompt, and N_2O route [24], which are investigated further.

3. Results and Discussion

3.1 Ignition and Flame Stabilization Characteristics -

Parameter	Quantity
Injection System	Common Rail
Orifice Diameter	145 μm
Injection Pressure [bar]	1340
Injection Quantity [mm^3]	20 per orifice
Chamber Density [kg/m^3]	15
Chamber Temperature [K]	1000 to 1200 Base case: T = 1000 K
Ambient O_2 concentration [%]	21
Injection Duration [ms]	3.5

Table 1: Range of conditions for combusting spray experiments performed by Wu et al. [9].

Figure 1a presents liquid and lift-off lengths for diesel and biodiesel versus time from SOI for the simulated cases described in Table 1, at an ambient temperature of 1000 K. Liquid penetration is seen to increase to a certain value and then stabilize at about 0.5 ms from SOI. Liquid length is established at a location where the fuel-injection rate balances the fuel-evaporation rate. The fluctuations in the liquid length of both fuels are turbulence induced. The liquid length for biodiesel is about 8-9 mm higher than that of diesel under the conditions investigated which is consistent with results reported earlier [25]. The flame is established upstream of liquid length and then is seen to move downstream towards the injector for both the fuels and stabilizes at about 1.75 ms from SOI. It is interesting to note that for diesel fuel (under the conditions investigated) lift-off length is always higher than liquid length. However, for biodiesel fuel, lift-off length is lower than liquid length after 0.75 ms from SOI. The corresponding computed flame images (including liquid and lift-off locations) at representative times are shown in Figure 1b. The field of view is 110 mm x 65 mm in the axial and radial directions respectively. The direction and POI are also marked. Due to the axisymmetric nature of the spray and combustion processes, images are presented on a cut-plane through the center of the fuel jet. Liquid fuel is shown with green color droplets at 0.1 ms from SOI for both fuels. While the penetration is similar for both the fuels, clearly, the spray is broader for biodiesel, mainly due to its higher heat of vaporization. The occurrence of ignition is indicated by the appearance of two flame kernels downstream of the liquid fuel at 0.5 ms after SOI. The flame is asymmetrical about the spray axis and is more developed for diesel fuel. The asymmetry is attributed to insufficient number of spray parcels residing in the domain, especially at 0.5 ms after SOI. This is mainly due to enhanced breakup owing to higher amount of inner nozzle cavitation and turbulence (cf. Table 1) for diesel fuel. The difference in ignition delay of both fuels is further investigated in detail in the following text. As the flame front develops and propagates downstream, the ignition location (base of the flame) seemingly moves upstream, as indicated in t = 1.0 ms and t = 2.0 ms plots. The flame base is stabilized at about 1.5 ms after SOI at the lift-off length, which is marked by the white solid line. The established liquid length for both the fuels are also shown at 1 ms, marked by white dashed lines. After 3 ms from SOI, the flame front is seen to reach the end-wall of the combustion chamber. More importantly, the spray flame interaction shown by the liquid fuel droplets entering the high temperature combustion regions i.e., lift-off length being shorter than liquid length, is clearly seen. This aspect is also further analyzed at higher ambient temperature conditions in the next section.

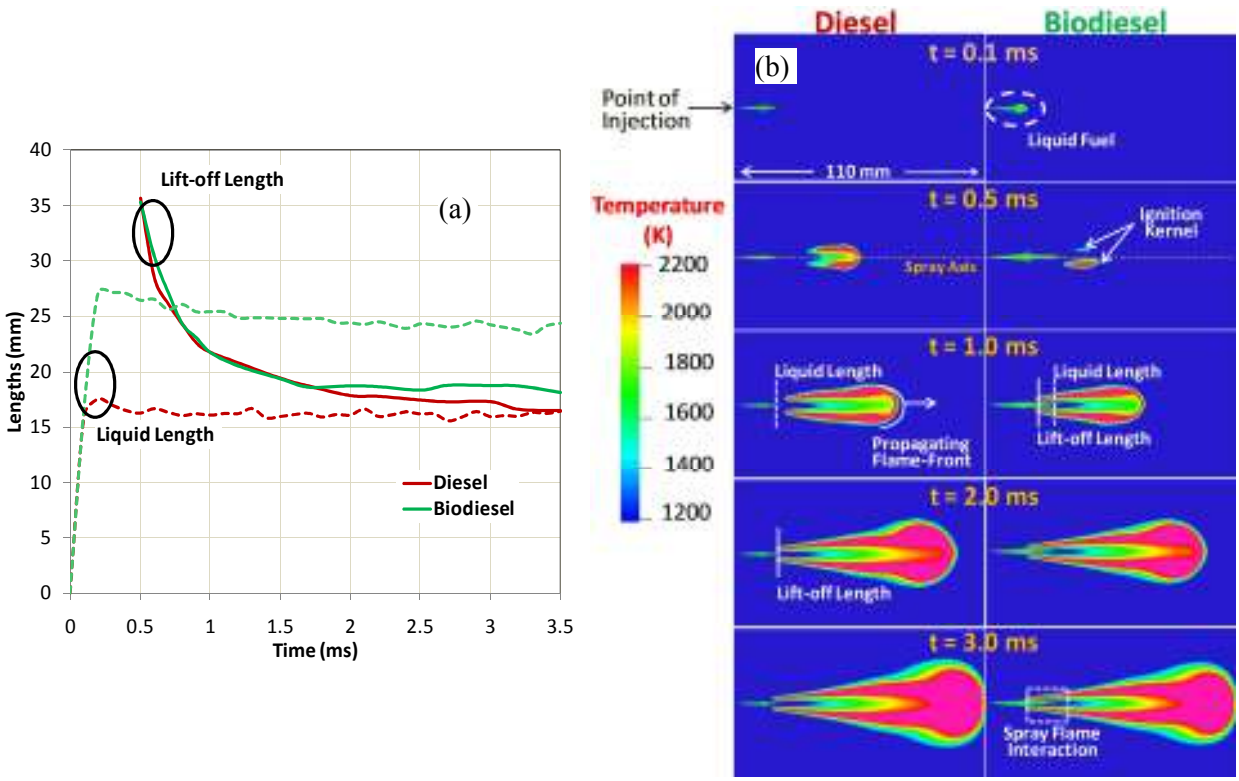

Figure 1: (a) Liquid length and flame lift-off length vs. time from SOI, (b) Computed liquid fuel penetration and temperature contours, for diesel and biodiesel fuels corresponding to the base case.

3.2 Emission Characteristics

Figure 2a presents volume-averaged NOx and soot concentrations versus time for the two fuels. The values are first normalized by the total amount of fuel injected for each fuel. These values were further normalized using the maximum soot and NOx values (which were observed for diesel fuel). Results do not indicate the classical tradeoff between NOx and soot concentrations, since biodiesel predicts both lower NOx and soot emissions. In general, it is agreed upon that the lower soot for biodiesel is due to the fuel bound oxygen which oxidizes the soot produced. Another reason for lower soot concentrations could be due to lower equivalence ratios at flame lift-off length. It has been shown previously that soot production decreases if the equivalence ratio at lift-off position is closer to stoichiometric [7], which is the case for biodiesel. While the lower soot production with biodiesel is consistent with published results in the literature, the lower NOx emission warrants further investigation. Since the NOx is produced at the diffusion flame, lower flame temperatures for biodiesel during the diffusion-burn period may be the main reason for NOx reduction.

In order to further investigate the NOx emission characteristics of both these fuels devoid of spray, mixing, and engine effects, counterflow 1-D flame simulations (OPPDIF) were performed using CHEMKIN package. The flame configuration consists of two opposing jets issuing from two coaxial nozzles that are placed one above the other. Fuel (diesel or biodiesel surrogate) flows from the lower nozzle and air from the upper nozzle. The diffusion flame is established under atmospheric conditions and temperatures of the fuel and oxidizer jets are set as 300 K. Since NOx is mainly produced in the diffusion flame region, this simplified flame configuration can provide further insights into the NOx emission characteristics of these fuels. Figure 2b plots the NOx mole fractions under conditions mentioned in the previous paragraph with diesel and biodiesel surrogates. In order to identify the relative importance of different NOx formation routes, the reactions responsible for NOx formation by the other routes were suppressed. Hence, the thermal NOx values were calculated by suppressing the prompt and N_2O

mechanism reactions. The NOx produced with the N_2O route were observed to be negligible under all conditions investigated; hence, they were not reported. The single peak in NOx values locates the diffusion flame region for both the fuels. Thermal NOx production is significantly higher for both the fuels compared to prompt NOx. Higher thermal NOx (and hence total NOx) for diesel surrogate fuel is due to the fact that the flame temperatures (not shown here) were also higher compared to the biodiesel surrogate. However, prompt NOx is observed to be higher for biodiesel surrogate due to higher concentrations of CH and HCN (not shown here) compared to diesel surrogate. Clearly, there are chemical kinetic reasons for higher NOx production for diesel fuel in the current study. Although the biodiesel surrogate predicts higher prompt NOx values, the total NOx (thermal + prompt) does not agree with the trends reported in literature.

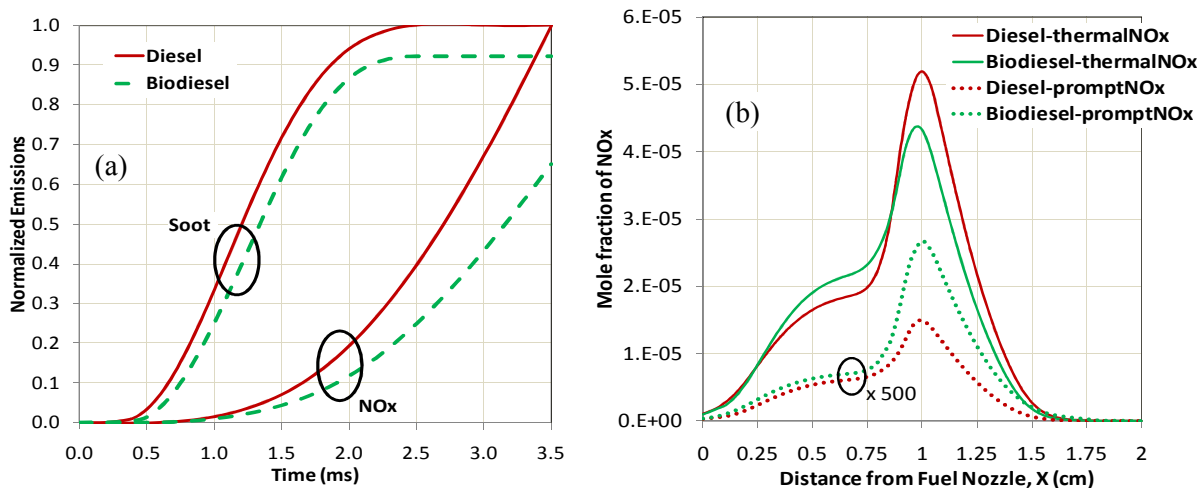

Figure 9: (a) Normalized NOx and soot emissions, for diesel and biodiesel fuels reported in the context of Figs. 1 and tabulated in Table 1, (b) Mole fraction of thermal and prompt NOx vs. distance from fuel nozzle for diesel and biodiesel in 1-D configuration.

Hence, our future work will focus on development of improved chemical kinetic models for diesel and biodiesel fuels. A chemical kinetic model for a mixture of methyl decanoate, methyl decenoate, and NHPT has already been developed by our group [26], and it is able to capture the ignition and flame characteristics at high temperatures very well. Low temperature chemical kinetic pathways will be added to this mechanism for CI engine applications.

4. Conclusions

A computational study was performed to investigate the combustion and emission behavior of biodiesel and diesel fuels. NHPT was used as a surrogate for diesel fuel whereas NHPT+MB were used as a biodiesel surrogate. Three-dimensional turbulent combustion simulations in a constant volume combustion chamber were performed to validate liquid length and flame lift-off characteristics of diesel and biodiesel against data available in literature. Ignition was seen to occur in rich mixtures for both diesel and biodiesel. It was concluded that both NHPT and MB may not be good fuel surrogates, especially at lower temperatures since they are not able to reproduce the cetane number characteristics reported in literature. The emission characteristics of diesel and biodiesel fuels were also compared. The classical NOx and soot trade-off was not observed since both NOx and soot concentrations were lower for biodiesel. While the reduced soot emissions with biodiesel are consistent with other studies in literature, the reduced NOx emissions are not.

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