

An Experimental Investigation of the Origin of Increased NO_x Emissions When Fueling a Heavy-Duty Compression-Ignition Engine with Soy Biodiesel

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ABSTRACT

It is generally accepted that emissions of nitrogen oxides (NO_x) increase as the volume fraction of biodiesel increases in blends with conventional diesel fuel. While many mechanisms based on biodiesel effects on in-cylinder processes have been proposed to explain this observation, a clear understanding of the relative importance of each has remained elusive.

To gain further insight into the cause(s) of the biodiesel NO_x increase, experiments were conducted in a single-cylinder version of a heavy-duty diesel engine with extensive optical access to the combustion chamber. The engine was operated using two biodiesel fuels and two hydrocarbon reference fuels, over a wide range of loads, and using undiluted air as well as air diluted with simulated exhaust gas recirculation. Measurements were made of cylinder pressure, spatially integrated natural luminosity (a measure of radiative heat transfer), engine-out emissions of NO_x and smoke, flame lift-off length, actual start of injection, ignition delay, and efficiency. Adiabatic flame temperatures for the test fuels and a surrogate #2 diesel fuel also were computed at representative diesel-engine conditions.

Results suggest that the biodiesel NO_x increase is not quantitatively determined by a change in a single fuel property, but rather is the result of a number of coupled mechanisms whose effects may tend to reinforce or cancel one another under different conditions, depending on specific combustion and fuel characteristics. Nevertheless, charge-gas mixtures that are closer to stoichiometric at ignition and in the standing premixed autoignition zone near the flame lift-

off length appear to be key factors in helping to explain the biodiesel NO_x increase under all conditions. These differences are expected to lead to higher local and average in-cylinder temperatures, lower radiative heat losses, and a shorter, more-advanced combustion event, all of which would be expected to increase thermal NO_x emissions. Differences in prompt NO formation and species concentrations resulting from fuel and jet-structure changes also may play important roles.

INTRODUCTION

Biodiesel is defined as a “fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats” [1]. Biodiesel has been demonstrated to be a viable fuel for compression-ignition engines, both when used as a blend with petroleum-derived diesel and when used in its neat form (*i.e.*, 100% esters) [2]. It should be noted that biodiesel is distinct from renewable diesel, which is a non-oxygenated, paraffinic fuel produced by hydrotreating bio-derived oils or fats in a refinery (*e.g.*, [3]).

Biodiesel has many desirable attributes, but it also has some characteristics that, if improved, would enhance its widespread acceptance. Some advantages of biodiesel are that it: can be produced domestically; is renewable; is biodegradable; reduces exhaust levels of regulated emissions including unburned hydrocarbons (HC), carbon monoxide (CO), and particulate matter (PM) [2,4]; is miscible with petroleum diesel; is generally compatible with the existing fuel-distribution infrastructure in the US; has excellent lubricity; and has a high flash point [5]. Some current barriers to biodiesel use include increased emissions of nitrogen oxides

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(NO_x) [2,4], decreased oxidative stability, degraded cold-flow performance relative to petroleum diesel [5], and increased dilution of lubricating oil due to fuel impingement on in-cylinder surfaces when early- or late-injection strategies are employed [6]. Excellent reviews of biodiesel production, processing, and properties are available [2,7].

There are also a number of barriers to biodiesel use that are unrelated to its fuel properties. For example, some have argued that biodiesel is not likely to be available in sufficient volumes to significantly offset petroleum use. Although the production capacity of biodiesel has been increasing rapidly over the past decade, as of 2007 it was only ~1% of domestic diesel-fuel consumption [8,9], due primarily to the limited supply of bio-derived oils and fats [10]. Currently in the USA, the majority of biodiesel is produced from soybeans, and biodiesel production can adversely affect food supply and prices. In fact, many of the oils and fats used for the production of biofuels are suitable for human consumption, and such “food vs. fuel” considerations have generated concerns [10]. Finally, converting and using land to grow biofuel feedstocks may have undesirable impacts on net greenhouse-gas (GHG) emissions. The magnitude of the effects of such “indirect land-use changes” on biodiesel lifecycle GHG emissions likely will be important for determining the long-term feasibility of agriculture-based biodiesel production [11].

Nevertheless, researchers are currently investigating strategies for producing bio-derived lipids (such as the free fatty acids and mono-, di-, and tri-glycerides from which biodiesel is made) that avoid some or all of the above problems. Algae have shown promise for increasing the available volume of biodiesel, since the lipid yield per unit area per unit time for algae can be one to two orders of magnitude greater than that for a typical oilseed crop (e.g., soybeans or rapeseed) [12,13]. Furthermore, algal oils would be a new feedstock stream, and their use to produce fuel would not decrease the supply of oils and fats traditionally used to produce food. The land-use effects of algal biodiesel production on GHG emissions remain to be quantified. Given the likely tremendous negative societal impacts from energy-security and climate-change issues, and the potential benefits of biodiesel in these regards, further study of the full range of issues from biodiesel production to end-use appears warranted.

The elevated NO_x emissions that are generally reported when fueling with biodiesel are a barrier to its widespread use in the US [14], with highly populated states such as Texas and California prohibiting the use of fuels that increase NO_x emissions [15,16]. An improved understanding of the mechanisms responsible for the biodiesel NO_x increase could lead to inexpensive and effective mitigation strategies. As a result, a number of studies have been conducted in this area over more than a decade, and a number of hypotheses have been proposed in the literature to explain the biodiesel NO_x increase. In general, the hypotheses can be grouped into two broad categories: 1) combustion effects (e.g., [17]) and 2) engine-calibration effects (e.g., [18]). This

paper focuses on combustion effects, but it should be noted that engine-calibration effects on NO_x emissions can be of the same order of magnitude as combustion effects [18]. In light of the comparable efficiencies and significantly lower PM, HC, and CO emissions that are typically reported when biodiesel blends are used, this observation indicates that a vehicle powertrain that can properly account for the presence of biodiesel in the fuel has the potential to outperform one optimized for conventional diesel fuel alone. For example, a slightly higher level of exhaust gas recirculation (EGR) could be used to trade off some of the biodiesel PM benefit for lower NO_x emissions. Ultimately, tailpipe-out emissions depend not only on fuel and combustion characteristics and engine calibration, but also on the drive cycle employed and the exhaust aftertreatment system.

NO_x-FORMATION CHEMISTRY – Before attempting to define an experiment or interpret data related to combustion aspects of the biodiesel NO_x increase, it is helpful to have some understanding of the chemical-kinetic pathways by which NO_x is formed during combustion. The literature contains some excellent references on this topic (e.g., [19-21]), though the focus generally has been on NO_x formation in nonpremixed gaseous-fuel jets at atmospheric pressure rather than under diesel-combustion conditions. The consensus from these references is that the primary NO_x-formation mechanism under most conditions is the thermal (or Zeldovich) mechanism, which consists of the following reactions [19]:



The timescales of these reactions are comparable to typical engine combustion durations, and this has two consequences: 1) equilibrium NO_x concentrations are not typically reached within the combustion chamber of an engine, and 2) longer residence times of in-cylinder gases at high temperature will lead to higher NO_x emissions. Some NO_x also may originate from the prompt (or Fenimore) and N₂O mechanisms [19,20,22], but the importance of these mechanisms under diesel conditions is not well understood, and this paper will mainly consider thermal NO_x production. For thermal NO_x production, assuming a steady-state for N-atoms in the reactions in Eq. 1 above gives a simple rate expression for NO formation when NO concentrations are well below equilibrium [20]:

$$\frac{d[\text{NO}]}{dt} = 2k[\text{O}][\text{N}_2], \quad (2)$$

where [NO], [O], and [N₂] are nitric oxide, atomic oxygen, and molecular nitrogen concentrations, respectively. In general, the reaction-rate coefficient *k* increases very rapidly with temperature and has the form [23]:

$$k = BT^{\alpha} \exp\left(\frac{-E_a}{R_u T}\right), \quad (3)$$



where B , α , E_a , and R_u are constants. Due to this strong temperature dependence, thermal NO formation is generally neglected for temperatures less than approximately 1800 K [20]. Summarizing the above information, thermal NO_x formation has the potential to be increased by any in-cylinder combustion strategy that increases: 1) in-cylinder temperatures, 2) the residence time of the in-cylinder mixture at high temperatures, or 3) O-atom or N₂ concentrations.

DIESEL COMBUSTION EMPLOYING A SINGLE INJECTION NEAR TDC – It is also helpful to have a physical understanding of the diesel combustion process when attempting to understand how fuel changes affect NO_x emissions. Fortunately, a conceptual model of diesel combustion that employs a single injection event near top-dead-center (TDC) at the end of the compression stroke has been developed by Dec [24].

Figure 1 shows a schematic of the quasi-steady period of diesel combustion adapted from the conceptual model of Dec [24] (also see Figs. 17-19 of [24] for more detail about the temporal development of the jet). The following is a summary of the Dec conceptual model (extended through the expansion stroke) with a focus on NO_x formation. Fuel is injected into a high-temperature, high-density charge-gas mixture near TDC. As the fuel jet penetrates into the combustion chamber, it entrains ambient charge-gas, which vaporizes the liquid fuel and creates a premixed mixture with the bulk of the fuel mass in rich regions. After a short (< 1 ms) ignition delay, the premixed fuel/charge-gas mixture autoignites. Some NO_x formation will occur in near-stoichiometric regions around the periphery of the reacting mixture during the ignition event, but NO_x formation is expected to be limited because the bulk of the premixed region at ignition is fuel-rich, where [O]-values and temperatures are expected to be low (see Eq. 2). Hence, this is not expected to be a primary source of NO_x at moderate and higher loads. Nevertheless, the ignition event will cause a rapid temperature increase (due to volume expansion of the reacting mixture further compressing the in-cylinder charge) that could accelerate subsequent NO_x formation.

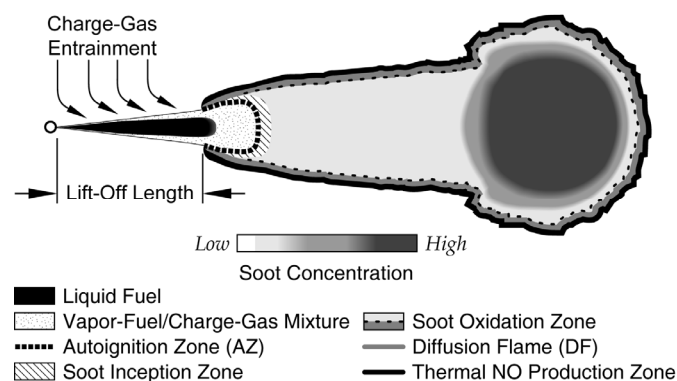


Figure 1. Schematic of a reacting DI diesel jet during the quasi-steady period of combustion (adapted from [24] and slightly modified near the lift-off length based on results from [29]).

Shortly after ignition, a diffusion flame (DF) is established around the periphery of the jet, and a standing premixed autoignition zone (AZ) stabilizes near the lift-off length (LOL), as shown in Fig. 1. The LOL is defined as the distance from the injector orifice exit to the upstream-most extent of the DF. Because the products from the AZ are fuel-rich (equivalence ratio typically greater than 3 [24]), they are expected to have low [O]-values and temperatures below 1800 K, so significant thermal NO_x formation is not expected in the region downstream of the AZ and within the DF. Nevertheless, prompt-NO pathways could be important in these fuel-rich mixtures [19,22,25,26]. Though not explicitly depicted in Fig. 1, the products from the upstream regions of the DF mix with those from the AZ and are convected downstream, where they increasingly dilute the reacting mixtures in the downstream regions of the DF and the jet core. This quasi-steady period continues until injection ends, after which time the last of the liquid fuel vaporizes [27]. Mixing-controlled combustion continues until the majority of the fuel vapor and soot are oxidized or until in-cylinder temperatures drop to sufficiently low values due to gas expansion from piston motion and/or the exhaust valves opening. Based on temperature, mixture stoichiometry, and residence-time considerations, the bulk of NO_x formation is expected to occur on the lean side of the DF during the quasi-steady combustion period and in the bulk gases after the primary heat release has ended [24,28].

Given this foundation, one can begin to systematically consider the main hypotheses that have been proposed to explain the biodiesel NO_x increase. These hypotheses include [4,17]:

- Injection timing:** The higher bulk modulus of biodiesel causes the pressure wave in the fuel line of a pump-line-nozzle injection system to travel faster, which causes an advance in the start of injection. This injection-timing advance leads to an earlier start of combustion, yielding longer residence times and/or higher in-cylinder temperatures, which lead to increased NO_x emissions.
- Combustion phasing:** The somewhat higher cetane number of biodiesel (relative to US #2 diesel) causes ignition to occur earlier in the cycle. This allows the combustion products to have a longer residence time at high temperatures, which increases NO_x emissions.
- Premixed-burn fraction:** Because biodiesel contains oxygen, it premixes more fully during the ignition delay, and a larger fraction of its heat release occurs during the premixed-burn phase of combustion at ignition. Combustion that is more premixed has higher oxygen concentrations and therefore produces more NO_x. The difference in NO_x produced during the premixed burn is responsible for the biodiesel NO_x increase.
- Kinetics:** There are differences in the chemical-kinetic pathways that form NO_x when biodiesel is used, and these are responsible for the biodiesel NO_x increase. Arguments based on differences in prompt NO formation seem to be the most common in this category. Such arguments could be categorized as follows:

increased levels of CH being produced at the AZ (see Fig. 1) during biodiesel combustion (e.g., [25]), which leads to the production of N-atoms in the jet core followed by prompt NO formation once the mixture is convected to the DF where oxygen and OH are present.

- E. Adiabatic flame temperature: Biodiesel has a higher adiabatic flame temperature than conventional diesel, so thermal NO_x production is higher (e.g., [26]).
- F. Radiative heat transfer: Biodiesel produces less soot because it is an oxygenated fuel. Because soot radiation is the primary means of heat loss from an in-cylinder flame, radiative heat losses are lower for biodiesel flames, which produce higher actual flame temperatures and more thermal NO_x (e.g., Fig. 25 in [17] and p. 158 of [2]).

The work described herein will address the effects listed above, except for injection-timing effects, which appear to be well understood (i.e., advancing injection timing increases NO_x emissions). Mechanisms in addition to those presented above have been proposed, and they may be important as well, but they will not be explicitly addressed herein. H.L. Mencken once wrote that the prototype of the scientist is "...not the liberator releasing slaves, the good Samaritan lifting up the fallen, but the dog sniffing tremendously at an infinite series of rat-holes" [30]. This characterization certainly appears to be applicable to the study of the many potential causes of the biodiesel NO_x increase.

The basic concept of the experimental approach employed in this work is simple, as follows. An optical engine was operated using neat biodiesel, biodiesel doped with a compound to increase radiative heat transfer from the flame, and a hydrocarbon reference fuel. A constant start of injection and start of combustion were maintained for all three fuels to minimize premixed-burn fraction and other phasing effects on NO_x emissions for the different fuels. The engine was operated using both undiluted intake air and intake air diluted with simulated EGR. NO_x differences were measured for the different fuels at the different dilution levels, and the radiative heat losses during combustion were rank-ordered for the different fuels. If lower radiative heat loss from the biodiesel flame is the primary reason for the NO_x increase, and if doping the biodiesel raises its radiative heat transfer up to that of the hydrocarbon reference fuel, then there should not be a NO_x increase for the doped biodiesel. Because there was a NO_x increase even with the doped biodiesel, other hypotheses were explored. Ultimately, the experimental results are used to obtain an improved understanding of biodiesel and other fuel effects on NO_x emissions.

EXPERIMENTAL

FUELS – Four fuels were employed in this study: two biodiesel fuels, denoted B_x (where *x* ≡ the volume percentage of soy biodiesel in the blend), and two blends of the cetane-number primary-reference fuels, denoted CN_y (where *y* ≡ the cetane number of the blend). Approximately 3.5 liters of each fuel were

required for the experiments reported herein. This small amount was sufficient because the single-cylinder engine was operated in a skip-fired mode, as described in the "Engine" subsection below. Figure 2 shows the molecular structures of the primary compounds present in the set of four fuels. In the C_X:Y notation for the methyl esters, *X* and *Y* are the number of carbon atoms in the alkyl chain and the number of carbon-carbon double-bonds (i.e., unsaturations) in the alkyl chain, respectively. Table 1 lists some relevant fuel properties.

Neat Soy Biodiesel (B100) – The first fuel was a neat soy-derived biodiesel, Nexsol BD-0100 (Lot #PN00106080) purchased from Peter Cremer North America (Cincinnati, OH, USA). This is a soy biodiesel composed of methyl palmitate (C16:0), methyl stearate (C18:0), methyl oleate (C18:1), methyl linoleate (C18:2), and methyl linolenate (C18:3) in the mole fractions shown in Fig. 3. To limit oxidation of the B100 after receipt but prior to use in these experiments (approx. 5 weeks), the B100 was stored with nitrogen gas in the headspace of the Teflon fuel container, in the dark, at 20 ± 1°C. The B100 met the ASTM D 6751 specification for biodiesel blendstock when it was purchased, and it did not contain antioxidant or other additive(s).

Doped Biodiesel (B94) – The second fuel was B100 doped with a compound to increase soot formation, and thereby radiative heat loss, from the flame. The dopant was phenanthrene (denoted A3), a 3-ring aromatic species, and it was added such that B94 contained 6 wt% of A3. The A3 was purchased at 98% purity from Sigma-Aldrich (Milwaukee, WI, USA). Because the A3 was not readily soluble in B100, it was mixed into B100 by immersing a beaker of B100 plus powdered A3 in an ultrasonic bath until A3 was no longer visible (approx. 30

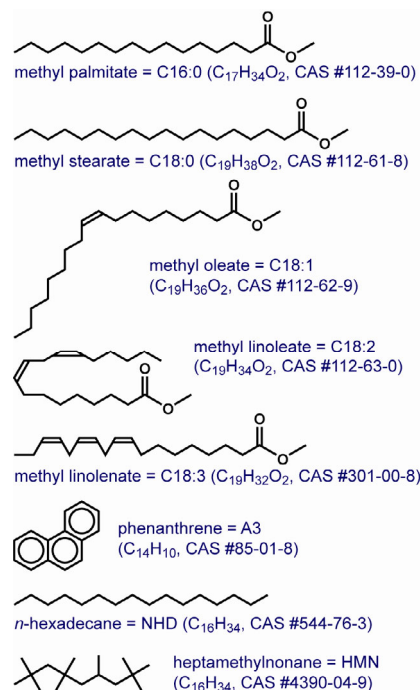


Figure 2. Molecular structures, names, abbreviations, chemical formulas, and Chemical Abstracts Service (CAS) numbers of compounds comprising the fuels used in this work. Molecular structures are from [31].

Table 1. Selected Fuel Properties

FUEL	q_{LHV}^a [MJ/kg]	$\rho @ 20^\circ\text{C}^b$ [kg/m ³]	CN ^c [-]	MW ^d [g/mol]	$\phi_{\lambda,F}^e$ [-]	$(A/F)_{st}^f @$ 20.9% O ₂ [-]	$(A/F)_{st}^f @$ 16.5% O ₂ [-]	C/H ^g [-]	(C/H) _{eff} ^h [-]
B100	37.4	877 ⁱ	49.9 ^j	292.3	27.41	12.49	16.13	0.544	0.522
B94	37.5	905 ^j	49.9 ^k	281.5	29.13	12.51	16.15	0.569	0.548
CN45	43.9	786	45.0 ^m	226.4	∞	14.96	19.32	0.471	0.471
CN70	43.9	780	70.0 ^m	226.4	∞	14.96	19.32	0.471	0.471
D2	42.9 ⁿ	842 ⁿ	~45 ⁿ	—	∞	14.52	18.75	0.552	0.552

^aLower heating value; ^bdensity; ^ccetane number; ^dmolecular weight; ^eoxygen equivalence ratio of the fuel, see Eq. 13; ^fstoichiometric ambient-gas/fuel mass ratio; ^gmolar carbon-to-hydrogen ratio; ^heffective molar carbon-to-hydrogen ratio, see Eq. 18; ⁱfrom product literature; ^jestimate obtained by averaging densities calculated assuming: 1) no volume change from B100, and 2) no density change from B100; ^kassumed same value as for B100; ^mby definition of diesel primary reference fuel blends; ⁿfrom 2007 #2 ULSD product literature [32]

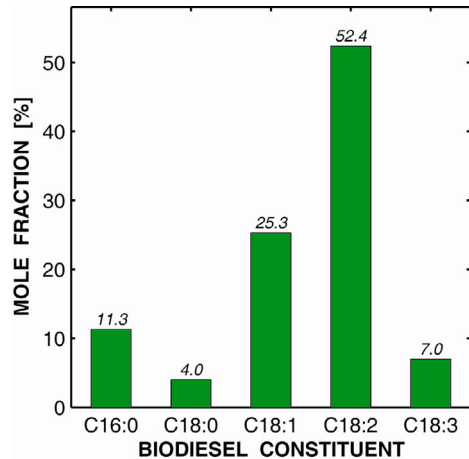


Figure 3. Neat soy biodiesel (B100) composition from fatty acid methyl ester (FAME) analysis results provided by the vendor.

minutes). Following this sonication process, the B94 was passed through a 5.0- μm Teflon filter purchased from Millipore (Bedford, MA, USA) that had been pre-saturated with B100. The mass increase of the filter resulting from B94 passage was found to be 0.02% of the mass of A3 added, indicating that the A3 was thoroughly mixed with the B100 and was not removed by filtration.

Cetane-Reference-Fuel Blends (CN45 and CN70) – Two well-characterized hydrocarbon fuels were created to provide a basis for comparison to results with B100 and B94 fueling. The two cetane-number primary-reference fuels, *n*-hexadecane (denoted NHD) and 2,2,4,4,6,8,8-heptamethylnonane (denoted HMN), both purchased from Sigma-Aldrich in 98% or higher purity, were blended to create two paraffinic fuels with known cetane numbers. The first was a 45-cetane fuel, denoted CN45, containing 35.3 vol% NHD with balance HMN. The second was a 70-cetane fuel, denoted CN70, containing 64.7 vol% NHD with balance HMN. CN45 was formulated to have the same ignition delay as B100 and B94 at the selected operating conditions. CN70 was blended to have a shorter ignition delay, to provide insight into first-order effects of increasing the cetane number of the hydrocarbon reference fuel.

ENGINE – The Sandia Compression-ignition Optical Research Engine (SCORE) is a single-cylinder version of a Caterpillar® heavy-duty engine that has been modified by Sandia to provide extensive optical access to the combustion chamber. A schematic of the SCORE is shown in Figure 4 and its principal specifications are provided in Table 2.

The engine was operated in a skip-fired mode to reduce the required frequency of window cleaning and the risk of window failure due to thermal and mechanical stresses. Skip-firing reduces the amount of heat rejected to the coolant, so an electrical heater under closed-loop control was employed to maintain the coolant temperature at 95°C. Skip-firing also reduces the concentration of residuals trapped within the cylinder from the previous fired cycle (*i.e.*, scavenging is enhanced because there are a number of motored cycles between two consecutive fired cycles), but this is not expected to have a significant effect on the results presented herein. The fuel injector was fired once every

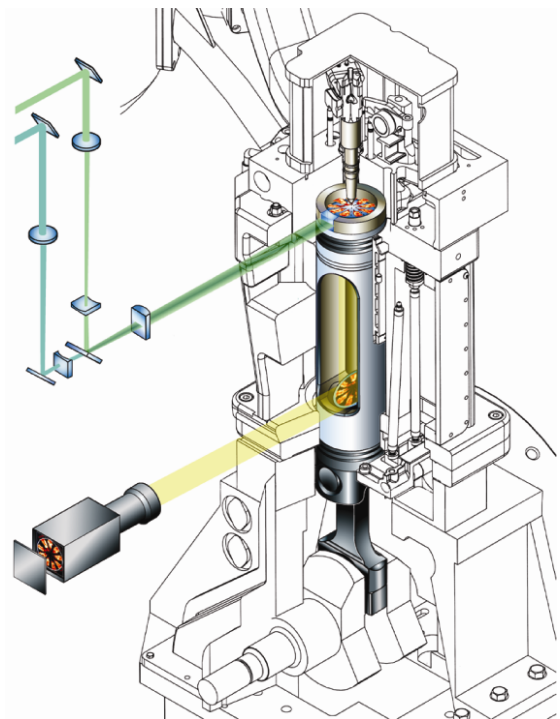


Figure 4. Schematic of Sandia Compression-ignition Optical Research Engine (SCORE).

8th engine cycle for all operating conditions in this study. The fuel injector used in the engine was a Caterpillar Hydraulically actuated, Electronically controlled Unit Injector (HEUI[®]) capable of producing injection pressures as high as 142 MPa. Specifications of the fuel-injection system are provided in Table 3.

Table 2. SCORE Specifications

Engine type	Single-cylinder
Cycle	4-stroke CIDI
Valves per cylinder	4
Bore	125 mm
Stroke	140 mm
Intake valve open ^a	32° BTDC exhaust
Intake valve close ^a	153° BTDC compression
Exhaust valve open ^a	116° ATDC compression
Exhaust valve close ^a	11° ATDC exhaust
Connecting rod length	225 mm
Connecting rod offset	None
Piston bowl diameter	90 mm
Piston bowl depth	16.4 mm
Squish height	1.5 mm
Swirl ratio ^b	0.59
Displacement per cyl.	1.72 liters
Compression ratio	11.8:1
Simulated compr. ratio ^c	16.0:1

^aAll valve timings are for 0.03 mm lift

^bMeasured at the Caterpillar Technical Center using an AVL swirl meter

^cMotored-TDC temperature, pressure, and density in a 16.0:1 compression-ratio engine are matched in the optical engine by preheating and boosting the pressure of the intake-gas mixture supplied to the optical engine (see Table 4)

Table 3. Fuel-Injection System Specifications

Injector type	Caterpillar HEUI A
Injector model	HIA-450
Nozzle style	Single-guided VCO
Number of orifices	6
Orifice diameter (nom.)	0.163 mm
Hydro-erosion	13%
Orifice L/D	8.0
Included spray angle	140°
Oil rail pressure	20.8 MPa (3000 psig)
Max. fuel-injection pressure	142 MPa (20600 psig)
Pressure intensification ratio	6.85:1
Valve opening pressure	31 MPa (4500 psig)

The SCORE differs from a production engine in that the bottom of the piston bowl (top of the piston-crown window) is flat rather than contoured. In addition, the compression rings are positioned lower on the optical piston to allow for the placement of windows in the piston bowl-rim and to prevent the rings from riding over windows in the cylinder wall. These modifications result in an increased clearance volume and hence a decreased compression ratio in the SCORE relative to the 16.0:1 compression-ratio engine simulated in this work. To help compensate for these differences, the temperature and pressure of the SCORE intake mixture are increased so that in-cylinder conditions are

representative of those in a 16.0:1 compression-ratio engine over a given crank-angle range of interest. Motored top-dead-center (TDC) conditions in the 16.0:1 compression-ratio engine were matched in the present study. Further details of the SCORE can be found in [33] and [34].

OPERATING CONDITIONS – All data in this study were acquired under steady-state operating conditions at a speed of 800 rpm, using a single fuel-injection event near TDC. The relatively slow engine speed was chosen because others have observed the largest NO_x increases with biodiesel fuels at lower engine speeds [35]. As discussed below, the crank angle at which fuel began to enter the combustion chamber, *i.e.*, the actual start of injection (SOI_a), was determined via optical imaging. SOI_a values for this work fell within the range from -2.2 to -1.0° after TDC (ATDC). The start of combustion (SOC) is defined as the crank angle after SOI_a at which the apparent heat-release rate first becomes positive. SOC values for this work fell within the range from -0.1 to 0.5° ATDC.

Loads of 4.0, 8.0, 12.0, and 15.0 bar gross indicated mean effective pressure (IMEP) were investigated. IMEP is calculated from the work done during the compression and expansion strokes only. This metric is preferable to brake mean effective pressure (BMEP) for this study because pumping and frictional work in our externally boosted, single-cylinder engine are not representative of those in a production, multi-cylinder engine. Each load point was achieved within a window of ± 0.05 bar IMEP, load points were randomized over each run day, and data were acquired for at least 3 repeats of each load point.

Two sets of in-cylinder conditions were employed: one without EGR to represent early-1990s engines that remain in use today, and one with a moderate level of simulated cooled EGR (discussed below) to represent newer-technology engines. The intake-mixture and in-cylinder parameters are summarized in Table 4.

Simulated EGR – The EGR rate is defined as the mass fraction of recirculated exhaust in the intake-gas mixture [36]. Due to the skip-fired operation of the optical engine, the intake mixture obtained by recirculating its exhaust would have lower CO₂ and H₂O concentrations, and a higher O₂ concentration, than the intake mixture in a comparable continuously fired engine operated at the same EGR level. For this reason, EGR was simulated in the optical engine by diluting dry intake air with N₂ and CO₂. The intake mixture for simulating EGR effects in the optical engine was formulated so that it had the same O₂ mole fraction and specific heat capacity at TDC as the mixture when real EGR is used. The computations that estimate the real EGR composition and properties assume complete combustion and no condensation of water from the recirculated exhaust gases. The 4.0-, 8.0-, 12.0-, and 15.0-bar IMEP load conditions at 16.5% O₂ mole fraction correspond to conditions with 54, 40, 31, and 26% EGR, respectively, in a continuously fired engine with a 16.0:1 compression ratio and motored-TDC conditions as shown in Table 4.

Changing the test fuel changes the EGR rate at each load by < 1% for the fuels used in this work. The EGR rate required to reach 16.5% O₂ drops as the engine load increases because the exhaust-gas mixture contains less O₂ as the load increases.

Table 4. Intake and In-Cylinder Parameters

EGR level	None	Moderate
Intake-mixture composition		
O ₂ mole fraction [%]	20.9	16.5
N ₂ mole fraction [%]	78.1	78.9
CO ₂ mole fraction [%]	0.0	3.9
Ar mole fraction [%]	0.9	0.7
Molecular weight [g/mol]	28.96	29.39
Coolant temperature [°C]	95	95
Actual intake-manifold conditions (CR = 11.8:1)		
Temperature [°C]	116	95.0
Density [kg/m ³]	2.07	2.74
Pressure [bar]	2.31	2.85
Polytropic compression coefficient	1.343	1.339
Simulated intake-man. conditions ^a (CR = 16.0:1)		
Temperature [°C]	77	58
Density [kg/m ³]	1.5	2.0
Pressure [bar]	1.5	1.9
Motored TDC conditions ^a		
Temperature [K]	910	850
Density [kg/m ³]	24	32
Pressure [bar]	63	77

^aAssumes polytropic compression process with given coefficient.

DIAGNOSTICS

Cylinder Pressure – Cylinder-pressure data were acquired to enable the calculation of apparent heat-release rate (AHRR), gross IMEP, combustion-phasing parameters, and in-cylinder temperatures. Cylinder-pressure data were recorded with 0.5-CAD resolution throughout each fired cycle using a high-speed (>100 kHz bandwidth) water-cooled quartz piezoelectric transducer mounted in the cylinder head. The transducer was manufactured by AVL List GmbH (Graz, Austria), Model QC32C. The absolute value of the cylinder pressure was determined by referencing it to the pressure measured ~10 mm upstream of the plane where the intake charge enters the cylinder head. This measurement was made using a high-speed piezoresistive strain gauge pressure transducer from Kulite Semiconductor Products (Leonia, NJ, USA), Model HEM-375. Other details of the cylinder-pressure data acquisition system for the SCORE can be found elsewhere [34,37].

A Fourier-transform-based algorithm was used to lowpass-filter the pressure data in software before the AHRR was calculated. The filter passes frequencies up to 1000 Hz without attenuation; the amplitudes of signal components with frequencies above 1000 Hz are reduced by a Gaussian roll-off function that falls to 1.0% transmission at 4200 Hz. Each cylinder-pressure or AHRR curve shown in this work is an average of data

acquired from approximately 60 fired cycles at the given test condition.

Spatially Integrated Natural Luminosity (SINL) – Estimating the amount of radiative heat transfer from the reacting in-cylinder mixture is important because one hypothesis under consideration in this work relies on differences in radiative heat transfer between biodiesel and the hydrocarbon reference fuels to explain the differences in their engine-out NO_x emissions. SINL is used to estimate the amount of radiative heat transfer from the reacting in-cylinder mixtures in this work.

It is perhaps easier to define natural luminosity before attempting to define SINL. Natural luminosity is defined as the broadband light emitted from the combustion chamber during a fired cycle. Natural luminosity arises from both soot incandescence and chemiluminescence, but the contribution from soot incandescence has been shown to be 4 to 5 orders of magnitude higher than that from chemiluminescence during the mixing-controlled combustion phase when conventional diesel fuels and operating strategies are used [34,38].

SINL is defined as the instantaneous flux of natural luminosity integrated over the entire field of view. In the present work, the field of view is the area of the combustion chamber visible through the piston window (see Fig. 6 below). An SINL measurement was recorded every 0.5 CAD using a high-speed (1-MHz bandwidth), large-area photo-receiver with 400-1070 nm spectral sensitivity from New Focus (San Jose, CA, USA), Model 2031. Natural luminosity passing through the piston window was collected and focused onto the surface of the detector using a Nikkor (from Nikon Corp., Tokyo, Japan) 50-mm, f/1.4 lens.

Soot was deposited on the piston window at a finite rate at each fuel, load, and EGR condition. This soot absorbed and/or scattered some fraction of the SINL signal, such that SINL curves acquired later within a 60-cycle run appear to have been attenuated by a multiplicative factor between 1.0 (no attenuation) and 0.4 (60% attenuation) relative to curves acquired earlier in the run. To account for this, the peak SINL levels for the first 15 cycles were fit with a quadratic to determine the peak SINL for a theoretical “Cycle #0” that would not include the effects of signal attenuation by soot. Next, each of the SINL curves from the first 15 cycles was normalized by its respective peak value, and then these curves were averaged together. Finally, the normalized average curve was multiplied by the Cycle #0 peak value to yield the SINL curve for the given run. Figure 5 shows examples of SINL and AHRR data for B100, B94, and CN45 at the 8.0-bar IMEP, 16.5%-O₂ mole-fraction operating condition.

The relationship between the true radiative heat transfer from a combusting mixture and its SINL signal magnitude depends on three factors: 1) the temperature distribution throughout the radiating soot volume, 2) the optical thickness distribution across the soot volume (because SINL is a line-of-sight measurement), and 3) the area of the radiating soot volume from which signal

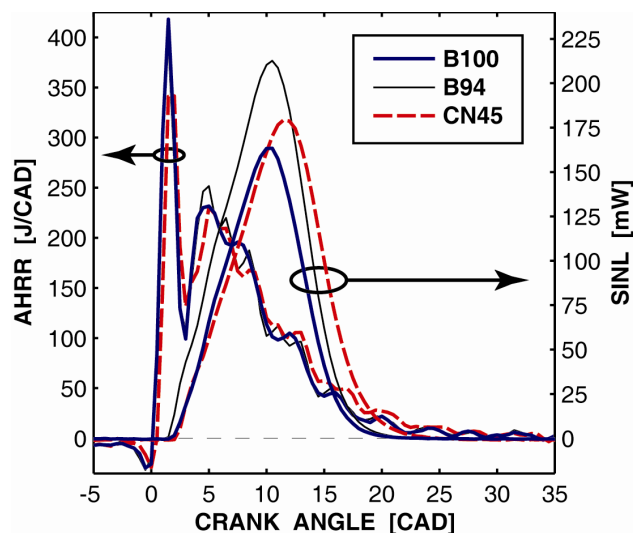


Figure 5. SINL and AHRR data for B100, B94, and CN45 at the 8.0-bar IMEP, 16.5% O₂ mole-fraction condition. The SINL for B94 is larger in magnitude than that for B100, indicating that doping B100 with the 3-ring aromatic species causes the SINL to increase at the given conditions, as desired. Also, the SINL signal is zero until well into the premixed burn, supporting the claim that the signal is dominated by soot incandescence, which is the primary mode of heat loss from a diesel flame. The AHRR curves are similar for all of the fuels.

is collected. Because the temperature, optical-thickness, and area variations over the soot volume and over time were not independently measured, the true radiative heat-transfer rate cannot be uniquely determined from the SINL signal. Nevertheless, it can be shown that SINL should be sufficient to rank-order trends in radiative heat transfer between fuels in the present work. More details about the use of SINL as a measure of radiative heat transfer are provided in Appendix A.

Engine-Out Emissions – Exhaust-gas samples were drawn to emissions analyzers through a heated Teflon sampling line installed downstream of an exhaust surge tank. The surge tank has a volume of 125 liters and serves to dampen pressure oscillations in the exhaust system as well as to mix the gases leaving the engine from both fired and motored cycles. NO_x was measured using a California Analytical Instruments (Orange, CA, USA) Model 600 heated chemiluminescence detector (HCLD), and smoke emissions were measured using an AVL Model 415S smoke meter.

The procedure for acquiring the emissions data was as follows. First, the engine was motored at 800 rpm for 45 s to allow the conditions in the intake manifold to stabilize, at which time a data-logging computer began measuring emissions levels from the HCLD at a rate of approximately 20 Hz. One minute after the start of motoring, the smoke meter began acquiring its sample and the injector began firing. (The first smoke from firing is captured by the smoke meter due to the finite transit time of the sample through the line.) Each engine run consisted of 60 skip-fired cycles, *i.e.*, a total skip-firing period of 72 s. Engine motoring continued well after the

end of firing to allow the exhaust surge tank to purge and to allow measured emissions levels to return to their baseline values. The HCLD and the smoke meter ended their sample collection 150 s and 120 s after the start of engine firing, respectively, while the engine was still motoring with the desired simulated-EGR mixture supplied at the intake.

Because the SCORE is skip-fired for relatively short durations, pollutant concentrations in its exhaust do not match those that would be measured if the engine were continuously fired until emissions reached steady-state levels. The differences are due to: 1) the large volume of the exhaust surge tank introducing a transient in the measured emissions such that steady-state concentrations are not reached during the 72-s duration of engine firing, and 2) dilution of the exhaust gas from the fired cycles by that from the interspersed motored cycles.

To address differences in gaseous emissions levels due to the first issue noted above (*i.e.*, to determine concentrations that appropriately represent those that would be measured during steady-state skip-fired operation), the entire transient history of each gaseous species is integrated (to provide a ppm-s result), and the result is divided by the duration of engine firing. This yields the measured average mole fraction of the given species in the skip-fired exhaust.

To address the difference in gaseous emissions due to skip-firing (*i.e.*, the second issue noted above), the measured average mole fraction of each species in the skip-fired exhaust can be multiplied by the total number of engine cycles per fired cycle, which is 8 for the current conditions. Another way to remove the dilution effect of skip-firing is to use the measured average skip-fired mole fraction to compute an indicated specific emission level (*e.g.*, in g/hp-hr) by dividing by the indicated power output during the fired cycles only. The indicated specific NO_x emissions reported below were calculated using the latter approach and assuming that the molar mass of NO_x is equal to that of NO₂ (*i.e.*, 46 g/mol), as per conventional practice [39]. Finally, filter smoke numbers (FSN) were corrected for dilution due to skip-firing by assuming the sample volume is that which would pass through the smoke meter over the duration of the fired cycles only. In other words,

$$\text{corrected sample volume} = \frac{\text{duration of fired cycles}}{\text{sample duration}} \times \text{actual sample volume} \quad (4)$$

For the sample duration of 120 seconds, and 60 fired cycles at 800 rpm, the correction factor becomes 0.075.

Flame Lift-Off Length – The flame lift-off length is the distance from the fuel-injector orifice exit at which the lifted diesel flame stabilizes during mixing-controlled combustion. Flame lift-off lengths were measured using spectrally filtered OH chemiluminescence images obtained during the fuel-injection period following the

end of the premixed burn (EOPMB) [40]. OH chemiluminescence at 310 nm is a reliable marker of the flame lift-off location because the predominant light emission from the stabilization region of a diesel spray is from this band of OH chemiluminescence. The EOPMB is defined as the crank angle corresponding to the first local minimum in the apparent heat-release rate (AHRR) curve after the peak associated with the premixed burn.

Images through the piston window showing all six fuel jets were conveyed to a CCD camera by a four-mirror arrangement, as shown in Fig. 6. The interline-transfer CCD camera (from Princeton Instruments, Trenton, NJ, USA) had 1300 x 1030 pixel spatial resolution, 300-1000 nm spectral sensitivity, and was used with a UV Nikkor 105-mm f/4.5 lens to acquire the lift-off length images. The CCD array was read at 5 MHz using a Princeton Instruments MicroMax controller that also carried out 5 x 5-pixel on-chip binning to enhance image signal-to-noise ratio. The CCD was electronically gated to provide an exposure period of 417 μ s, corresponding to a crankshaft rotation of approximately 2 CAD. Spectral filtering was accomplished using a combination of three UV laser mirrors and a 310-nm-bandpass filter, all from CVI (Albuquerque, NM, USA). The high-reflectance wavelength region of the UV laser mirrors was centered near the peak of OH chemiluminescence at 310 nm, and was approximately 40 nm wide. The transmission curve of the bandpass filter peaked at 22% and had a full width at half maximum of approximately 10 nm.

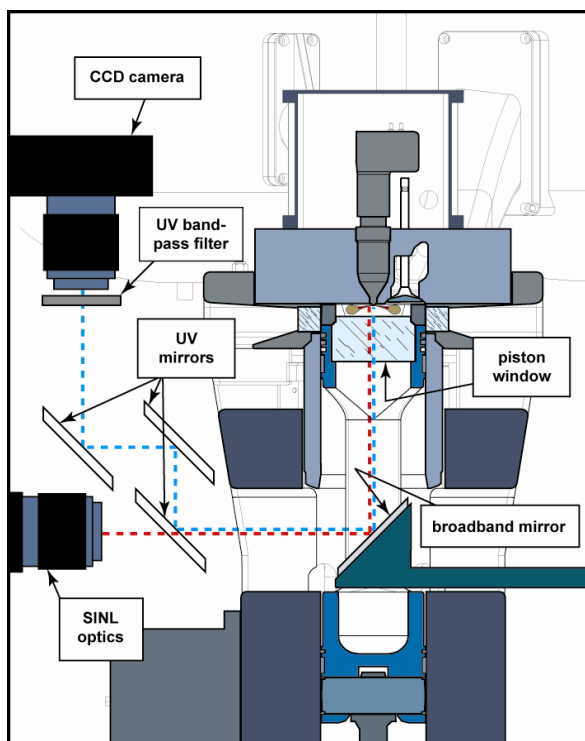


Figure 6. Cutaway view of SCORE showing optical-imaging setup. The CCD camera configuration shown is that used for lift-off length (OH chemiluminescence) measurements. When imaging the fuel spray for actual start of injection measurements, a broadband mirror and 532-nm bandpass filter are used in place of the UV mirrors and UV bandpass filter, respectively.

A flame lift-off length was determined for each jet in each single-cycle OH-chemiluminescence image using an automated image-processing routine. The routine identified the lift-off length as the position along the axis of each jet flame with the greatest axial intensity gradient. This strategy was relatively insensitive to interferences encountered in the engine environment, such as light scattered from the liquid jet or the firedeck.

Figure 7 shows examples of single-cycle, raw, OH-chemiluminescence images and the corresponding indicated lift-off lengths (LOL_i) determined using the automated image-processing routine. LOL_i is the distance from the injector-tip axis (shown by crosshair) to the base of the lifted flame on each jet. Note that liquid fuel upstream of LOL_i is visible in Fig. 7 because chemiluminescence from the flame is elastically scattered to the camera by liquid-fuel droplets. Nevertheless, the strong intensity gradient at the lift-off length makes identification of LOL_i straightforward and robust for the conditions studied in this work.

OH-chemiluminescence images were acquired at 2.5° and 3.0° ATDC for the 20.9% and 16.5%-O₂ mole-fraction conditions, respectively, and images were acquired for all fuels except CN70. The image timings fall within less than 0.5° after EOPMB for each fuel. By EOPMB, the diffusion flame has been established around the periphery of the jet and the lift-off length can be used to estimate the equivalence ratio in the standing premixed autoignition zone at the base of the flame [24]. All images were acquired at a load of 8.0-bar IMEP. The lift-off length at EOPMB is not expected to be significantly different at the other engine loads since the cumulative heat release at EOPMB should be constant when SOI_a , SOC, and injection parameters are held constant, as they were in this work.

LOL_i values were determined for each of the 6 jets in each of 12 single-cycle OH-chemiluminescence images. The LOL_i values for each individual jet were averaged over all images, and any measurements more than 2 standard deviations from the mean value were discarded.

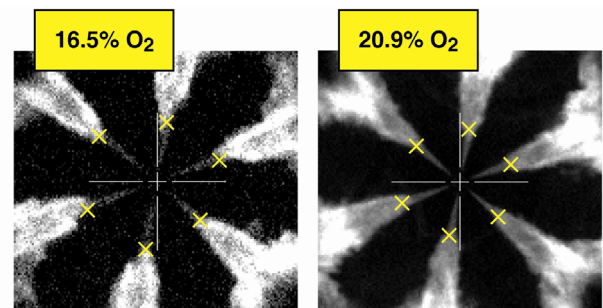


Figure 7. Raw, single-cycle, OH-chemiluminescence images from which lift-off lengths are calculated. Lift-off length for each jet is indicated with an X; crosshair denotes injector-tip axis. Both images were acquired using B100 fuel (images acquired using other fuels are nearly identical). Left and right images are for 16.5% and 20.9% O₂ mole fractions, respectively. Both images have same magnification and spatial extent. Lift-off lengths are longer for conditions with lower O₂ mole fractions.