

Oxides of nitrogen emissions from biodiesel-fuelled diesel engines

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ABSTRACT

Biodiesel has received, and continues to receive, considerable attention for its potential use as an augmenting fuel to petroleum diesel. Its advantages include decreased net carbon dioxide, hydrocarbon, carbon monoxide, and particulate matter emissions, and fuel properties similar to petroleum diesel for ease of use in diesel engines. Its disadvantages include poorer cold flow characteristics, lower heating values, and mostly reported higher emissions of oxides of nitrogen ($\text{NO}_x = \text{NO} + \text{NO}_2$, where NO is nitric oxide and NO_2 is nitrogen dioxide). This latter disadvantage (i.e., higher emissions of oxides of nitrogen) is the focus of this review article. NO_x formation mechanisms are complex and affected by several different features (e.g., size, operating points, combustion chamber design, fuel system design, and air system design) of internal combustion engines. The slight differences in properties between biodiesel and petroleum diesel fuels are enough to create several changes to system and combustion behaviors of diesel engines. Combined, these effects lead to several complex and interacting mechanisms that make it difficult to fundamentally identify how biodiesel affects NO_x emissions. Instead, it is perhaps better to say that several parameters seem to most strongly influence observed differences in NO_x emissions with biodiesel, thus introducing several possibilities for inconsistency in the trends. These parameters are injection timing, adiabatic flame temperature, radiation heat transfer, and ignition delay. This article provides a review of the rich literature describing these parameters, and provides additional insight into the system responses that are manifested by the use of biodiesel.

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1. Introduction

1.1. Motivation

Combustion within the transportation sector, such as is in the internal combustion engine, composes a major part of society's energy conversion and CO₂ emission footprint [1,2]. Improvements in the transportation sector's energy conversion efficiency and CO₂ emissions can be realized with diesel engines using biodiesel fuel [3–5]. Diesel engines, partly due to their conventional use of fuel-lean combustion processes, inherently emit relatively lower CO₂ emissions than their gasoline engine counterparts. With the use of biodiesel fuel – which, from a life-cycle perspective, results in substantially decreased atmospheric carbon emissions [5] – diesel engines offer the potential to substantially reduce energy consumption [4] and decelerate the increase in atmospheric carbon concentrations [5].

Mainstream deployment of biodiesel-fuelled engines, however, is facing a formidable challenge: characteristically increased emissions of NO_x [6]. Several published studies exist, as will be summarized next, to explain the potential increases in NO_x emissions with biodiesel fuels; yet, considerable inconsistencies exist in the explanations thus making the fundamental understanding incomplete. The need to better understand the mechanisms causing increased NO_x emissions with biodiesel fuel in diesel engines – the so-called biodiesel NO_x penalty – and thus potentially transform the barriers of mainstream deployment of biodiesel fuel in the transportation sector has motivated this detailed literature review.

1.2. Background

Biodiesel, throughout this text, implies a fuel composed of glyceride-free mono-alkyl esters of long-chain fatty acids converted from triglycerides such as biologically-based fats and oils [7–9]. The alkyl ester generally takes the form of methyl ester, which is often classified as fatty acid methyl ester (FAME). Other alkyl esters, such as ethyl ester, have occasionally been used. A feedstock is the raw material from which oils and fats are derived. Rapeseed¹, soybean, cottonseed, linseed, and peanut are common vegetable-oil feedstocks. Other feedstocks could include sources such as waste cooking grease or beef tallow. In some cases it is possible for these unprocessed feedstocks to be used directly in an engine application. Complications, however, may arise with the direct use of these oils and fats within an engine. They can cause severe injector coking, piston ring sticking, and engine deposits which will render the engine inoperable [7–9]. Several studies (e.g., [10–13]) evaluate unmodified (or unprocessed) oils; their results will not be emphasized in this review. The process of converting the unmodified oil or fat into a suitable fuel – i.e., the conversion of a triglyceride to an alkyl ester – is called transesterification. Transesterification is the process where a triglyceride is stripped of its fatty esters, by reacting it with an alcohol (usually methanol, but others may be used) in the presence of a catalyst (such as sodium or

potassium hydroxide, but others may be used) [14–16]. In addition to the fatty acid esters, glycerol is a by-product. The glyceride-free fatty acid esters are then termed “biodiesel”. A replication of the transesterification process provided in [17] is shown in Fig. 1 for informational purposes. Note that R1 through R3 represent fatty acid chains of either the triglyceride or the methyl ester.

The widespread use of biodiesel is based on the following positive attributes [18,19]:

- Biodiesel is renewable and non-petroleum-based;
- Biodiesel can reduce greenhouse gas emissions;
- Biodiesel is less toxic and is biodegradable;
- Biodiesel can reduce tailpipe emissions of particulate matter (PM), CO, HC, and other air toxics;
- No or minor modifications are needed for the traditional compression ignition engine to use biodiesel;
- Biodiesel compression ignition engines are similar in operation as conventionally-fuelled diesel engines.

Biodiesel also has some negative attributes [18,19]:

- Lower heating value, less favorable cold flow properties, lower volatility, and higher viscosity (data shown later in Table 2);
- Lower storage stability and material compatibility issue;
- Possibly higher NO_x emission;
- High manufacture cost because of transesterification and expensive feedstocks;

Among the above attributes, higher NO_x emissions from biodiesel engines are a major concern and serve as the motivation for this literature review. NO_x emissions from combustion system

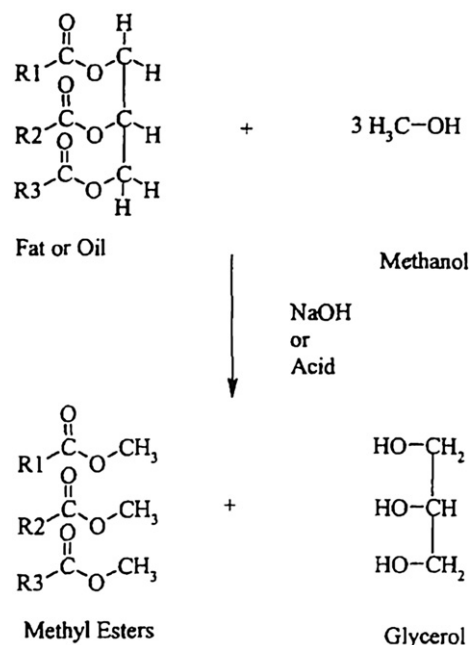


Fig. 1. A diagram representing the transesterification process, replicated from [17]. The general scheme of the process is to modify a triglyceride (a fat or oil which is a glyceride with three fatty acids, represented as R1, R2, and R3) into a fatty acid methyl ester.

¹ At this point, it is worthwhile to identify a somewhat ambiguous use of the word “rapeseed”, which could be used to identify the inedible high erucic acid oil or the edible low erucic acid oil (the latter which is CANadian Oil Low Acid, or canola oil). Throughout this article, “rapeseed” refers to the high erucic acid oil and “canola” refers to the low erucic acid oil.

result from the formation of NO during the combustion process; a portion of NO₂ and other oxides of nitrogen may oxidize from NO downstream of the combustion process. NO formation mechanisms, which depend on the combination of certain molecular species, are generally well-understood (briefly summarized below) and provide the basis for understanding differences in NO_x emissions between biodiesel and petroleum diesel. Slight or dramatic differences in certain properties between the fuels create different environments for NO formation; most research studies relate the effect of fuel properties to the well-known NO formation mechanisms to understand why NO_x emissions differ between the fuels. Outside the context of fuel comparison, NO_x remains a key emission of interest because of its role in atmospheric ozone formation. As such, NO_x is a key constituent under regulation by most governmental agencies. A summary of the fundamental physical and chemical parameters influencing NO formation and the associated NO_x emissions with biodiesel is necessary.

1.3. Objective

The objective of this report is to provide a thorough and complete literature review on the current state of this fundamental understanding and to guide the continuing study of changes in NO_x emissions due to biodiesel combustion in diesel engines. Several literature reviews exist regarding the processing and use of biofuels in a diesel engine (e.g., [9–17,20,21]); this literature review explicitly focuses on the issue of NO_x emissions related to biodiesel. To meet this objective, the authors have reviewed over 300 technical articles discussing NO formation, NO_x emissions characteristics of biodiesel- and diesel-fuelled engines, and diesel combustion. From this, about 120 provide the most necessary information related to this article's objective. The article first summarizes the general properties of biodiesel and indicates how these may affect NO formation mechanisms. The general NO formation mechanisms are summarized to create a fundamental basis for further discussion. A characteristic comparison between biodiesel- and petroleum diesel-fuelled engines and their NO_x emissions are made. The article culminates in a thorough discussion about several potential contributions to differences in NO_x emissions between biodiesel- and petroleum diesel-fuelled engines. Specific topics of discussion in this latter section include injection timing, injection pressure and spray, ignition delay, combustion stages and heat release, heat radiation from soot, combustion temperature, and system response issues. The article concludes with a summary and conclusions.

2. Biodiesel properties

The current specification for biodiesel (B100) in the United States is ASTM D6751-09 [22]; the major requirements of this specification are shown in Table 1. Aside from cetane number and viscosity, other properties having influence on NO_x emissions, i.e. density, bulk modulus, iodine number, oxygen content, aromatics content, and heating value, are not requirements of ASTM D6751. In use more commonly, however, is blended petroleum diesel with up to 20% biodiesel. The current ASTM specification for petroleum diesel (ASTM D975-09B, [23]) allows up to 5% by volume biodiesel. Petroleum diesel fuels that contain between 6% and 20% by volume biodiesel are currently specified by ASTM D7467-09A [24]. All ASTM specifications require the fuels (either 100% biodiesel or blended fuels) to meet the specified standards, regardless of biodiesel feedstock. Both feedstock and transesterification process have an impact on biodiesel fuel properties, as identified by [19] and [25].

Table 2 provides measured properties of diesel, B100, and B20 as reported in several references [9,25–29]. The properties in Table 2 are generally targeted when explaining differences in NO_x

Table 1

Detailed requirements for biodiesel taken from ASTM D6751-09 [22].

Property	Method	Limits ^a	Units
Calcium and Magnesium, combined	EN 14538	5 max	ppm (μg/g)
Flash point	D 93	93 min	°C
Alcohol control (one of the following):			
Methanol content	EN 14110	0.2 max	mass %
Flash point	D 93	130 min	°C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40 °C	D 445	1.9–6.0	mm ² /s
Sulfated ash	D 874	0.020 max	% mass
Sulfur ^a	D 5453	0.0015 max	% mass
Copper strip corrosion	D 130	No. 3 max	—
Cetane number	D 613	47 min	—
Cloud point	D 2500	Report	°C
Carbon residue	D 4530	0.050 max	% mass
Acid number	D 664	0.50 max	mg KOH/gm
Cold soak filterability	Annex A1	360 max	seconds
Free glycerin	D 6584	0.020 max	% mass
Total glycerin	D 6584	0.240 max	% mass
Phosphorus content	D 4951	0.001 max	% mass
Distillation temperature, T90	D 1160	360 max	°C
Sodium and Potassium, combined	EN 14538	5 max	ppm (μg/g)
Oxidation stability	EN 14112	3 minimum	hours

^a The specification also includes a higher sulfur grade of biodiesel, S500, that allows 0.05 wt% sulfur but all other requirements are identical.

emissions from engines using the different fuels. The tabulation of B20 properties is incomplete since the missing properties are not explicitly provided in the reviewed literature. Some of the missing values, however, might be evaluated through interpolation between diesel and B100 values. Throughout this manuscript, Table 2 will be referenced when describing the influence of differences in properties on certain engine features (e.g., bulk modulus effect on injection timing).

Table 3, taken from [30], provides the fatty acid compositional information about different types of biodiesel oils. The structure of the methyl ester, with the relative positioning of the fatty acid chains, is shown in Fig. 1 [17]. The third row of Table 3 lists chain information about the corresponding fatty acid; the chain information has the following format: (number of carbon atoms): (number of double bonds). The data in Table 3 allows for the assessment of the chain length, saturation degree, and C/H ratio of different biodiesel fuels. The significance of Table 3 is the demonstration of widely varying fatty acids that could compose biodiesel. Thus, it becomes important to understand which feedstock is used to make biodiesel, as this will affect the number of carbon atoms per molecule and the bond structure of the molecule. These molecular attributes eventually affect fuel properties.

Physical and chemical processes within a diesel engine — such as injection timing, fuel vaporization, and ignition delay — are altered with the use of biodiesel fuel relative to petroleum diesel fuel. The differences in chemical composition and structure between the fuels manifest such differences in engine processes, which ultimately lead to differences in engine parameters (i.e., performance, efficiency, and emissions). By evaluating the reporting of such differences in the literature e.g., [27,30–35], Table 4 indicates (in the first data column) how biodiesel generally differs on a relative basis from petroleum diesel for several properties. Table 4 also indicates (in the remaining data columns) how the relative difference in the property affects various engine parameters. For example, the first row states that the liquid density of biodiesel is relatively higher than that of petroleum diesel (indicated by the plus sign). As a result of biodiesel having a higher density, it: 1) partially influences the fuel injection timing by advancing it (plus sign), 2) partially influences the fuel injection pressure (for non-common rail fuel systems) by increasing it, 3)

Table 2

Measured properties of diesel, B100 and B20 retrieved from the specified literature [9,25–29].

Property	Unit	Diesel	B100	B20
Carbon content	mass %	86.7 ^a	77.1 ^a	—
Hydrogen content	mass %	12.71 ^a	11.81 ^a	—
Oxygen content	mass %	—	10.97 ^a	—
Nitrogen content	mass %	0.0001–0.003 ^c	0.002–0.007 ^c	—
C/H Ratio (mass basis)	—	6.82 ^a	6.53 ^a	—
Saturates content	vol. %	63 ^a	—	—
Olefins content	vol. %	1.3 ^a	—	—
Aromatics content	vol. %	35.7 ^a	—	—
Sulfur content	mass %	0.041 ^a	<0.005 ^a	0.00205 ^b
Typical formula	—	C _{14.09} H _{24.78} ^a	C _{18.74} H _{34.43} O ₂ ^a	—
Average molecular weight	g/mol	193.89 ^a	291.62 ^a	—
Density, 21 °C	g/mL	0.8537 ^a	0.8814 ^a	0.8577 ^b
Kinematic Viscosity, 40 °C	mm ² /s	2.8271 ^a	4.2691 ^a	2.862 ^b
Cloud point	°C	–20–0 ^d	–5–10 ^d	–12.0 ^b
Cold filter plugging point	°C	–25–0 ^d	–5–10 ^d	—
Pour point	°C	–35–0 ^d	–15–10 ^d	—
Bulk modulus of compressibility (as a function of pressure in MPa)	MPa	12.392 ^a P + 1595.1 ^f	11.316 ^a P + 1747.5 ^f	—
Speed of sound (as a function of pressure in MPa)	m/s	4.5129 ^a P + 1375.8 ^f	3.8555 ^a P + 1410 ^f	—
Cetane number	—	42.6 ^a	51.5 ^a	—
Acid number	mg _{KOH} /g	—	0.38 ^c	0.14 ^b
Flash point	°C	67 ^e	141 ^e	—
Higher heating value	MJ/kg	45.339 ^a	39.871 ^a	—
Lower heating value	MJ/kg	42.64 ^a	37.388 ^a	—

^a Ref. [26].

^b Ref. [25].

^c Ref. [9].

^d Ref. [27].

^e Ref. [28].

^f Ref. [29].

partially influences fuel spray penetration by decreasing it, 4) partially influences fuel spray angle by decreasing it, 5) has no influence on fuel spray atomization, 6) partially influences ignition delay by increasing it, 7) and 8) has no influence on heat release or combustion temperature. It should be noted that Table 4 summarizes explicitly what is reported in the cited literature for

a corresponding property. It could be argued that the table is incomplete in characterizing how a property manifests a change in a certain engine parameter; the authors have avoided altering what the cited literature identifies as the corresponding effect. Another note is that other literature report similar findings and influences; the cited literature is chosen for demonstration purposes.

Some fuel properties in Table 4 are closely related, such as bulk modulus of compressibility and speed of sound, as can be shown by their similar effects on engine parameters. Some engine parameters are also closely related, such as injection timing and ignition delay, as can be shown by their dependence on similar fuel properties. It can also be seen that physical properties are reported to mainly affect physical processes, while chemical properties are reported to mainly affect chemical processes.

Chemical properties of a fuel (e.g., hydrocarbon structure, aromatic content) are suggested to dominate a fuel's effect on combustion and emission formation [33,36]. Physical properties (e.g., viscosity, density) generally affect injection timing, fuel atomization, and fuel evaporation, which eventually have indirect effects on combustion and emission formation; some of these latter effects are called system responses, as will be discussed further below. Through experimental and numerical studies, Ra et al. [31] show significant effects of the fuel physical properties on ignition delay and burning rates at various engine operating conditions. Considering their effects on NO_x emission, the most significant fuel properties include density, viscosity, oxygen content, aromatics content, heating value, while the most significant engine parameters are ignition delay and combustion temperature.

As described by the US Environmental Protection Agency [6], the net difference in NO_x emissions from biodiesel-fuelled engines (relative to petroleum diesel-fuelled engines) is the coupling of multiple effects from various properties. This conclusion is further supported by extensive experimental work by Mueller et al. [37]. A simple systematic issue is the base petroleum fuel either used for comparison or used as the base fuel (if evaluating a blend with biodiesel). Through a statistical analysis of available data in the literature, [6] determined that the base fuel used in a blend appears to have a significant effect on the correlation between biodiesel concentration and resulting emissions. In other words, the properties of the petroleum fuel used as the base in a blend with biodiesel can affect the relationship between changes in emissions and biodiesel concentration in the blend.

To provide more fundamental insight into how the above-described properties affect biodiesel combustion and emissions formation, the ensuing discussion will describe general NO

Table 3

Fatty acid composition (%mass) of 15 types of biodiesel oils [30].

Oil Type	Fatty acid composition (%mass)									
	Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Erucic
	8:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2	18:3	22:1
Beef tallow	0	0.1	0.1	3.3	25.2	19.2	48.9	2.7	0.5	0
Butterfat	5.5	3	3.6	11.6	33.4	11.4	27.8	3.1	0.6	0
Canola	0	0	0	0.1	3.9	3.1	60.2	21.1	11.1	0.5
Coconut	8.3	6	46.7	18.3	9.2	2.9	6.9	1.7	0	0
Corn	0	0	0	0	9.9	3.1	29.1	56.8	1.1	0
Cottonseed	0	0	0	0.8	22.9	3.1	18.5	54.2	0.5	0
Lard	0	0.1	0.1	1.4	25.5	15.8	47.1	8.9	1.1	0
Olive	0	0	0	0	11	3.6	75.3	9.5	0.6	0
Palm	0.1	0.1	0.9	1.3	43.9	4.9	39	9.5	0.3	0
Peanut	0	0	0	0	10.4	8.9	47.1	32.9	0.5	0.2
Rapeseed	0	0	0	0	2.7	2.8	21.9	13.1	8.6	50.9
Safflower	0	0	0	0.1	6.6	3.3	14.4	75.5	0.1	0
Soybean	0	0	0	0.1	10.3	4.7	22.5	54.1	8.3	0
Sunflower	0	0	0	0.1	6	5.9	16	71.4	0.6	0
Sunola	0	0	0	0	3	4.4	88.2	4.3	0.1	0

Table 4

The effects of property differences between biodiesel or its blend and petroleum diesel on engine parameters. A plus sign in the “difference” column indicates biodiesel has a higher value of the listed property relative to petroleum diesel. A plus sign in the remaining data columns indicates the corresponding difference in the property increases or advances the respective engine parameter. A minus sign indicates a decrease or a retarding.

	Difference	Injection timing	Injection pressure	Fuel spray penetration	Fuel spray angle	Fuel spray atomization	Ignition delay	Heat release	Combustion temperature
Physical Properties									
Liquid density ^a	+	+	+	–	–		+		
Bulk modulus of compressibility ^b	+	+	+	+					
Speed of sound ^b	+	+	+	+					
Liquid viscosity ^a	+	+			–	–	+		
Surface tension ^a	+	+		+		–			
Vapor pressure ^a	–	–				–	+		
Volatility ^c	–					–			
Liquid specific heat ^a	–					+	–		
Vapor specific heat ^a	–					+	–		
Heat of vaporization ^a	+						–		
Chemical Properties									
Chain length ^d	+	–					–		
Oxygen content ^c	+	+						+	+
Aromatics content ^e	–	+						+	+
Sulfur content ^f	–							+	
Saturation (iodine value) ^d	–						+		+
Cetane number ^g	+						–		
Heating value ^c	–								–

^a Ref. [31].

^b Ref. [32].

^c Ref. [33].

^d Ref. [30].

^e Ref. [34].

^f Ref. [27].

^g Ref. [35].

formation. Further, the discussion will link the differences in fuel properties to their effects on various portions of the engine cycle. The fuel property effects will be evaluated in the context of fundamental NO formation, to provide information on how a fuel property effect may alter engine NO_x emissions. Additionally, the influence of system response issues will be described.

3. General nitric oxide formation mechanisms

NO formation mechanisms are richly reported in the literature. Based on the reviews of [38–44], general NO formation mechanisms are summarized below.

The common mechanisms for NO formation in diesel combustion are: thermal (Zeldovich), prompt (Fenimore), and fuel-bound nitrogen. The principal source of nitrogen for NO formation during conventional combustion of typical petroleum- and bio-based fuels is atmospheric (molecular) nitrogen.

This article focuses primarily on the potential effects of biodiesel on thermal mechanism. The thermal mechanism is based on the extended Zeldovich mechanism, represented by Reactions (1) through (3), which involves atmospheric nitrogen and occurs during combustion or shortly thereafter in the post-flame gas region [38]:



The forward and reverse reaction rate constants of Reactions (1)–(3) are generally exponentially dependent on temperature, and recent reaction rates are provided by Dean and Bozzelli [43]. As a basic demonstration of this temperature dependency, several simplifying assumptions are applied to Reactions (1)–(3) to result

in Equation (4) [38]. The first assumption applied to the development of Equation (4) is that the nitrogen chemistry is de-coupled from the combustion reactions. Although combustion reactions generally occur much faster than nitrogen chemistry [45], the presence of O and OH radicals in thermal mechanism (which are also important species in combustion reactions) may require the chemistries to be coupled for accurate NO prediction [40]. When decoupling is assumed, concentrations of O, O₂, OH, H, and N₂ can be approximated by their equilibrium concentrations at equilibrium temperature (second assumption applied to the development of Equation (4)). Finally, the third assumption applied to the development of Equation (4) is that nitrogen radical (N) is in steady-state concentration.

$$\frac{d[\text{NO}]}{dt} = \frac{6 \times 10^{16}}{T^{1/2}} \exp\left(\frac{-69,090}{T}\right) [\text{O}_{2,\text{eq}}]^{1/2} [\text{N}_{2,\text{eq}}] \times (\text{moles/cm}^3 - \text{sec}) \quad (4)$$

Via integration of Equation (4), [NO] represents the concentration (moles/cm³) of NO at time *t* (sec), and [O_{2,eq}] and [N_{2,eq}] represent the equilibrium concentrations (moles/cm³) at temperature *T* (K) of oxygen and nitrogen, respectively. Finally, it should be noted that the forward reaction rate constant for Reaction (1) is used from [38] to develop Equation (4). The large activation energy and inverse temperature relationship in the exponential term imposes a strong temperature dependency on NO formation rate.

The contributions of non-thermal mechanisms (prompt-NO and fuel-bound nitrogen) are generally accepted as less important than thermal mechanism (i.e., Reactions (1)–(3)). Numerical simulations conducted by Ban-Weiss et al. [44] reveal the significance of the thermal mechanism as it influences NO formation in a well-mixed “balloon” of methyl butanoate (a methyl ester surrogate for biodiesel). Their results are summarized in Table 5. The shown data reveal the relative (to total predicted NO_x concentration) decrease in NO_x concentration when the listed mechanism is removed. For

Table 5

Numerically calculated influence of various formation mechanisms on biodiesel NO concentrations [44].

Removed mechanism	Predicted nitric oxide concentration (ppm)	Relative decrease when removed (%)
–	747	–
N ₂ O mechanism	742	1
Fenimore HC/N	650	13
Thermal (Zeldovich)	60	92
Thermal and HC/N	59	92

example, consider first that (with all mechanisms participating) the total predicted NO_x concentration is 747 ppm. If the N₂O pathway (a low-temperature mechanism involving molecular nitrogen [43]) is removed (so that only thermal and prompt mechanisms participate), predicted NO_x concentration decreases 1% relative to the total predicted NO_x concentration. If the HC/N mechanism is removed (so that only N₂O and thermal mechanisms participate), predicted NO_x concentration decreases 13% relative to the total predicted NO_x concentration. The significant feature of Table 5 is the dominance of the thermal mechanism in the total predicted NO_x concentrations. This result agrees with other studies [46–48] evaluating the effect of the thermal mechanism on NO formation. Further, studies [28,40,49] that focus on quantifying prompt-NO mechanism suggest its significance in overall NO formation, yet acknowledge the dominance of the thermal mechanism.

In relation to biodiesel, however, some studies suggest that observed differences in NO_x emissions (relative to petroleum diesel) could result from a shift in the relative dependencies on thermal and prompt mechanisms. Cheng et al. [49] for example mention that the altered relative contribution of prompt mechanism could be important when diagnosing differences in NO_x emissions of biodiesel fuels. Related, McCormick et al. [28] state that changes in NO_x emissions between biodiesel and petroleum diesel fuels are driven largely by pre-combustion chemistry of hydrocarbon free radicals. Thermal mechanism is largely unaffected by fuel chemistry, whereas prompt mechanism is sensitive to radical concentrations within the reaction zone. Related to this, Garner et al. [50] observe increased acetylene concentrations and carbon–carbon double bonds in the pyrolysis of saturated and unsaturated biodiesel surrogates in a high pressure shock tube, meant to replicate in-cylinder diesel conditions. They [50] suggest the increased acetylene production may contribute to increased prompt NO formation and cause the increased NO formation observed with highly unsaturated biodiesel fuel (e.g., soy biodiesel). It should be noted, however, that in-cylinder engine experiments have not yet observed increases in NO formation due solely to prompt mechanism. In-cylinder engine behavior with biodiesel may be different and cancel any potential increases in hydrocarbon radicals. For example, Mueller et al. [37] observe differences in mixture stoichiometry at ignition between biodiesel and petroleum diesel; such differences could alter the perceived influence of prompt mechanism.

4. Comparison of NO_x from biodiesel and petroleum diesel

Much of the reported literature reveals inconsistent trends in the effect of NO_x emissions with the use of biodiesel. It is possible, for the sake of interest, to determine the distribution of NO_x emission trends between biodiesel and petroleum diesel. This distribution can further be “conditioned” by identifying the associated distribution in engine hardware (i.e., fuel system) and engine displacement. Additionally, there is a distribution of experiment type (i.e., engine test versus vehicle test) and fuel feedstock in the literature. It is possible that much of the variability in the NO_x trend

with biodiesel is partly the result of the variability in the experiments and test apparatuses reported in the literature. Fig. 2, which shows the above-described distributions, is meant to illustrate the point of variability in engine hardware, engine size, experiment type, and fuel feedstock. Although the reported distributions may impact the inconsistent trends in biodiesel NO_x emissions, the article does not purport to connect any one distribution with an associated trend in NO_x behavior (e.g., Fig. 2 does not intend to suggest that increases in NO_x emissions are only associated with pump-line/mechanical injectors).

The observed trends in NO_x emissions based on review of certain literature are categorized into five groups (similar to that done by Lapuerta et al. [27]), as follow:

- Group 1: increase (e.g., [51,52])
- Group 2: increase with certain operating conditions, blends, or compositions; small changes otherwise (e.g., [37,53])
- Group 3: little or no difference (e.g., [54])
- Group 4: decrease (e.g., [55])
- Group 5: uncertain or no comment (e.g., [19]).

The distribution of reviewed literature involving engine experiments versus vehicle experiments is also given. Tat et al. [56] demonstrate that the average engine load conditions are much lower during vehicle testing compared to engine testing. Eckerle et al. [35] describe similar observations. The blends of fuels vary widely, ranging from as little as B5 (5% volume biodiesel with petroleum diesel) upward to B100. The most common comparisons are among pure petroleum diesel, B20, and B100. The primary feedstocks for biodiesel in the United States are soybean oil (soy methyl ester) and waste cooking oil (WCO) in the form of yellow grease methyl ester [25]. A little over half of the reviewed literature use these two feedstocks, as shown in Fig. 2. The remaining reviewed literature includes modified waste cooking oil in forms other than yellow grease methyl ester, rapeseed oil methyl ester, and a collection of several other feedstocks consisting of coconut oil methyl ester, palm oil methyl ester, and rapeseed oil ethyl ester.

The EPA released a database study [6,37] that statistically determines the possible impact that biodiesel blending has on NO emissions from on-highway heavy-duty diesel engines. The results, including emission behavior for other criteria pollutants, are shown as Fig. 3. NO_x emission is shown to increase linearly as biodiesel concentration increases. For soy-based biodiesel, NO_x is reported to increase by 2% with B20 fuel [6]. The EPA stipulates that the studied dataset does not include EGR- or diesel aftertreatment-equipped engines. In the context of that stipulation, Yanowitz and McCormick [57] conducted a survey of more recent engine technology. In a literature assessment of 49 biodiesel-based experiments, their study reveals no statistical evidence that average NO_x emissions between petroleum diesel (B0) and B20 are different when pre-1992 two-cycle engines are removed from the analysis. Related, their [57] study mentions that several researchers are able to demonstrate NO_x neutrality (or NO_x decrease) with biodiesel through engine calibration changes.

Such an issue of engine calibration changes is discussed by Eckerle et al. [35], who consider that both combustion and controls must be taken into account when determining the net NO_x effect between biodiesel and petroleum diesel fuels. In their investigation, the impact of the change of engine control settings to compensate for different heating values of the test fuels is separated from fundamental combustion effects. At higher speeds and loads, the change in engine control settings lead to a NO_x increase on the order of 3–4%. At lower load conditions, the changes in engine control reduce NO_x by 5%. Data that reveal systematic

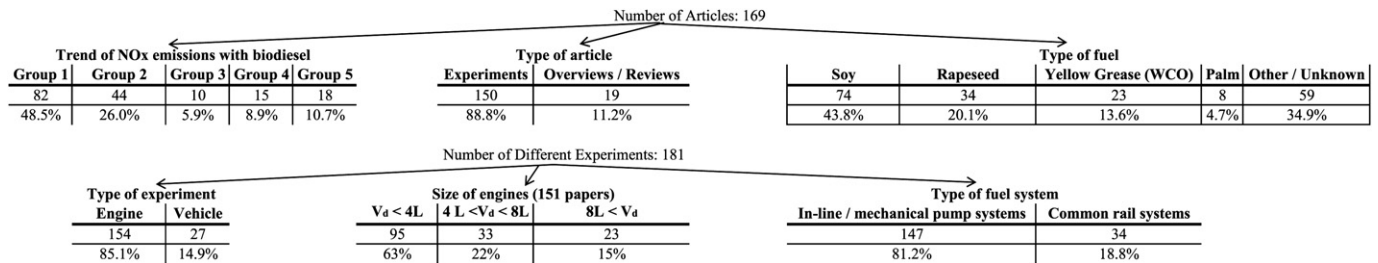


Fig. 2. Distribution of various studies reporting the behavior of NO_x emissions with biodiesel relative to petroleum diesel. Group 1 indicates the study demonstrates an increase in biodiesel NO_x emissions relative to petroleum diesel. Group 2 reports increases or decreases depending on engine operating condition and biodiesel feedstock. Group 3 reports no differences. Group 4 reports decreases. Group 5 does not address or makes no comment about NO_x emissions behaviors between the fuels. While also illustrating the variability in NO_x emissions behavior, the figure also illustrates the variability in the biodiesel feedstocks, types of studies, sizes of engines, and types of fuel systems.

changes (or non changes) in the engine controller, as a result of the use of biodiesel, are shown toward the end of this article.

5. Definitions of fundamental and system response effects

Apparent from this discussion, there are several factors affecting the differences in NO_x emissions between biodiesel and petroleum diesel fuels. This article characterizes two types of general effects that may alter NO_x emissions: 1. Fundamental effects, and 2. System response effects.

- Fundamental effects are those that directly result in a change to combustion or to the NO formation mechanisms. Examples of fundamental effects include a) presence of oxygen in biodiesel, which results in less soot formation, causing less radiation heat transfer and thus higher reaction temperatures, b) different carbon and hydrogen content in biodiesel molecule, yielding different stoichiometric air-fuel ratios and heating values, thus different adiabatic flame temperatures, and c) different viscosity of biodiesel, yielding different spray pattern behavior (i.e., penetration, breakup, and atomization). These specific examples are described in more detail in different sections of this manuscript.
- System-response effects are those that, due to a change in fuel property, alter the operation of system components which thus

alter combustion and NO formation. One example system response effect is the artificial advance in injection timing as a result of biodiesel's higher bulk modulus (described more thoroughly below). This is classified as a system response since a difference in property changes the behavior of the system. Knowledge that this behavior is less prevalent in common-rail engines (i.e., system dependent) confirms that such effects are system response. Another example of a system response issue would be different turbocharging characteristics at similar speeds and loads, manifested by differences in exhaust temperature between biodiesel and petroleum diesel operation. These types of system responses are considered *passive* system responses, to contrast them with the actively controlled system responses described next.

- Active, or controlled, system responses are those that are manifested by some change in a reference parameter for the control algorithm. For example, Eckerle et al. [35], explains that all control parameters of an engine's electronic control system are governed off engine speed and fuel injection pulsewidth (extrapolated to represent engine torque, or load). The injection pulsewidth controls the volume of fuel through the injector. Given biodiesel's relatively lower heating value (in spite of its slightly higher density, see Table 2), a longer injection pulsewidth is necessary to deliver roughly the same amount of energy when matching engine torque between fuels. The longer injection pulsewidth is interpreted by the engine controller as a higher load, potentially causing a change to other control parameters (e.g., injection timing and exhaust gas recirculation level). Further discussion surrounding this topic is provided below in the section titled System Response Issues.

The direction and magnitude that fundamental and system response effects have on biodiesel NO_x emissions seem to be strongly linked to the design characteristics of the engine (i.e., size, operating points, combustion chamber design, fuel system design, and air system design). This statement is supported by the varying trends in NO_x emissions data summarized in Fig. 2 and discussed in the above section. As a result of these connections among fundamental effects, system response effects, and the characteristics of the engine, details of the engines under study will be provided in as far as is available in the cited literature.

6. Potential contributions to differences in NO_x emissions

The ensuing discussion focuses on several engine parameters reportedly affected by the use of biodiesel fuel. Considering the differences in fuel properties and the fundamental mechanisms through which NO is formed, connections are made between affected engine parameters and changes in NO_x emissions.

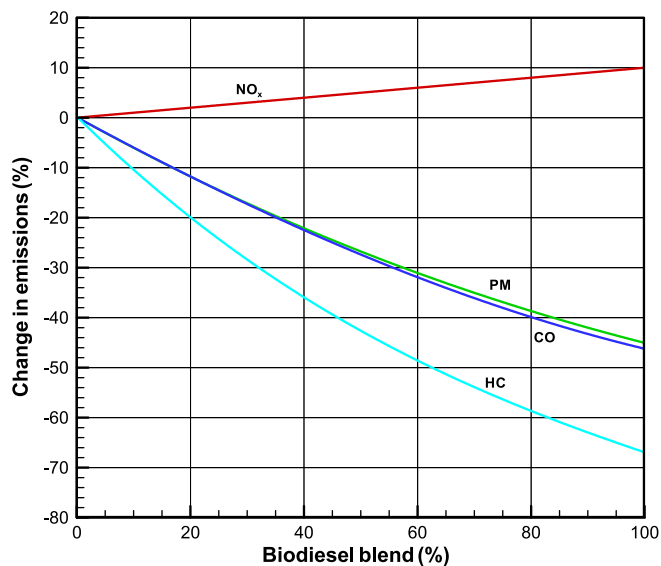


Fig. 3. NO_x, PM, CO, and HC % changes as biodiesel blending percentage increases as determined by the EPA through statistical regression of publicly available data on on-highway heavy-duty truck engines [6,37].

6.1. Injection timing

Most studies report that the start of fuel injection is advanced for biodiesel relative to petroleum diesel in rotary/distributor-style fuel injection systems. For example, in the experiment carried out by Monyem et al. [58] actual injection timings occurred earlier with biodiesel in spite of no changes to the injection timing setting. In their experiment, B100 fuel injects about 2.3° earlier than the studied petroleum diesel fuel. Blending biodiesel with petroleum diesel lessened the effect, where a B20 blend injects 0.25° – 0.75° earlier than the petroleum diesel fuel. The observed artificial advance of injection timing is attributed to differences in the fuels' densities, bulk modulus of compressibility, and speed of sound [59,60]. By using the equations listed in Table 2 for bulk modulus and speed of sound (assuming a fuel injection pressure of 30 MPa), the bulk moduli are 1967 MPa and 2087 MPa and the speeds of sound are 1511 m/s and 1526 m/s for petroleum diesel and biodiesel, respectively. Essentially, these property differences cause a faster pressure rise within the fuel injector; since diesel fuel injector needle valves are hydraulically opened, a faster rise in fuel pressure will cause the needle to open earlier [19,61]. This phenomenon largely affects rotary/distributor-style fuel injection pumps [13,25,29,44,55,59,62,64–67]. The same effect, however, is not present on common-rail fuel injection systems [68]. In connection with the discussion in the above section, this effect on NO_x is considered a system-response effect.

The causes of differences in bulk moduli between fuels are believed to result from differences in structure rigidity and inter-molecular forces that dictate the free space between molecules [69–72]. Aromatic compounds are less compressible than their saturated counterparts while long-chain paraffins are the most compressible of hydrocarbons. Petroleum diesel typically consists mostly of long-chain alkanes (high compressibility), with up to about 30% aromatic augmentation (from chemical reforming). The compressibility of hydrocarbon families is ranked as follows:

Aromatics < Cycloalkanes < Olefins ~ Branched Chain Alkanes < Short Chain Alkanes < Long Chain Alkanes

Biodiesel reportedly has lower compressibility (higher bulk modulus), partly due to the presence of oxygen in the fuel structure. Oxygen creates a permanent dipole moment in the molecule; this dipole moment results in stronger hydrogen bonding and increased molecular affinity of oxygenated fuels, compared to pure

hydrocarbon fuels. These factors reduce the free space between molecules in biodiesel, decreasing its compressibility (high bulk modulus) relative to diesel fuel [71].

Differences in fuel viscosities between the fuels may also contribute to artificial advances in fuel injection timing. Low viscosity results in increased fuel leakage, which causes a decreased rate of pressure rise and thus delays start of injection [33]. Shown in Table 2, biodiesel has a higher viscosity which results in less leakage and contributes to a higher rate of pressure rise (and thus an earlier start of injection) [73].

In addition to the above-described passive system responses, biodiesel may also introduce controlled system responses resulting from a controlled change to injection timing [27,57,62,74]. Typically, injection timing is adjusted as load changes to maintain appropriate levels of noise, efficiency, and/or emissions [77]. The direction and magnitude of the change in timing with load, however, varies among engine designs. For example, Fig. 4 shows a retard in injection timing as load increases in a medium-duty diesel engine [68] for both biodiesel and petroleum diesel (reference) fuels (the low-load aberration in Fig. 4 results from the use of pilot at low-load). Other studies [27,56,62] observe advances in injection timing, however, as engine load increases. This becomes a controlled system response for biodiesel because a longer injection pulsewidth is required to match engine torque in a comparison between petroleum diesel and biodiesel (biodiesel's lower heating value requires a longer injection pulsewidth to deliver roughly the same amount of energy).

This perceived increase in engine load manifested by an increased injection pulsewidth is cited for causing slight retard in the injection timing of biodiesel in one of the engines studied by Boehman et al. [74]. Contrarily, other studies (including a different engine observed by Boehman et al. [74]) observe slight advances in biodiesel injection timing [27,56,62] relative to the same torque operation with petroleum diesel. Finally, Fig. 4 [68] reveals for that engine under study there is generally no change in injection timing with the use of biodiesel (the apparent retard in biodiesel main injection timing at the low-load/low speed condition is not outside the bound of uncertainty). Such differing observations suggest that much of the variability in the behavior of NO_x emissions with biodiesel is closely coupled to differing system response issues present among the studies.

An advance in injection timing is considered as a main reason for observed increases in NO_x emissions with biodiesel

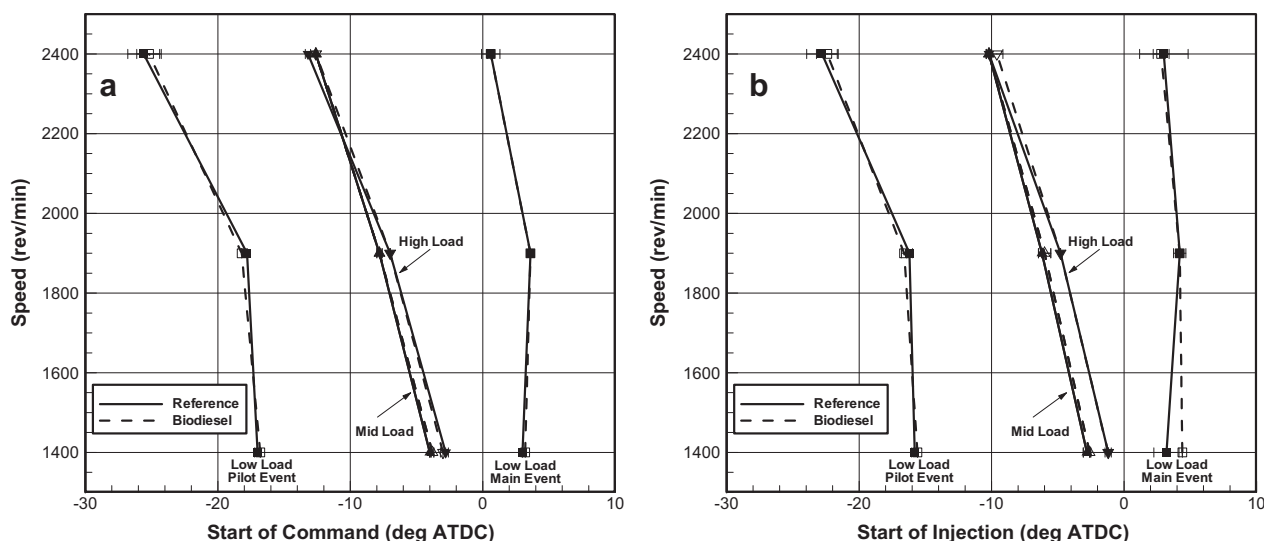


Fig. 4. (a) Start of command and (b) start of injection for nine engine operating conditions in a common-rail medium-duty diesel engine using biodiesel and petroleum diesel (reference) fuels [68].

[27,58,60,76]. Injection timing advance generally lengthens the ignition delay (time period between start of injection and start of combustion, see discussion below); this allows additional time for premixing fuel and air and generally increases the premix portion of diesel combustion [77]. An increase in the premix portion of diesel combustion increases reaction temperatures when diffusion combustion commences, elevating diffusion reaction temperatures and ultimately post-flame gas temperatures. As described earlier with Equation (4), an increase in post-flame gas temperature increases NO formation rate. Injection timing advance also typically advances start of combustion, which can increase reaction time and generally increase overall gas temperatures [71,78,79].

Szybist et al. [71] identify interesting NO_x emissions characteristics with injection timings for several different fuels, including biodiesel, at high- and low-load conditions. Fig. 5 (a) illustrates NO_x emissions as functions of injection timing at high load condition while Fig. 5 (b) illustrates the same at low-load conditions for several different types of fuels (biodiesel fuels are identified as B20, B40, and B100 while the petroleum-based fuel is identified as BP325). Notice that the relationships between NO_x emissions and injection timing at high load are independent of fuel type (Fig. 5 (a)). This could suggest that high load NO_x emission differences (between fuels) are mainly due to artificial shifts in injection timing, manifested by differences in fluid properties (such as bulk modulus). In contrast, the low-load condition demonstrates unique NO_x emission behavior for each fuel (Fig. 5 (b)). This may suggest that, in addition to artificial advances in injection timing, other mechanisms are contributing to differences in NO_x emissions between fuels.

Several studies point to slight controlled injection retard to mitigate observed increases in NO_x emissions [13,37,58,61,80–82]. Introducing a pilot fuel injection may also offer flexibility to do the same [83]. Retarding injection timing tends to increase particulate matter; thus, coupling injection retard with an oxidation catalyst (to remove soluble organic fraction of particulate matter) is considered an option [17].

6.2. Injection pressure, spray, mixing

As discussed earlier, fuel injection pressure is affected by fluid properties such as density, compressibility, and speed of sound [59,60]. In particular, the peak fuel injection pressure is directly proportional to the bulk modulus [64]. In conventional mechanical fuel systems, biodiesel exhibits higher injection pressures due to its higher bulk modulus. Equation (5), taken from [84], provides insight into how differences in bulk modulus and density affect either the injection duration or the mass flow rate:

$$m_f = C_D A_n \sqrt{2\rho_f \Delta P} \frac{\Delta\theta}{360N} \quad (5)$$

in Equation (5), m_f is the mass of fuel delivered per cycle, C_D is the injector tip nozzle discharge coefficient, A_n is the nozzle flow area, ρ_f is the fuel density, ΔP is the pressure drop across the nozzle, $\Delta\theta$ is the injection duration, and N is the engine speed. If mass flow rate were to stay constant, this would result in shorter injection duration (and coincidentally a lower volumetric flow rate) for biodiesel since its density and injection pressure are higher [79]. For a fixed rack position (or pulsewidth) where injection duration remains constant, however, an increase in injection pressure and density results in increased mass delivery [53,85]. Injection durations between petroleum diesel and biodiesel fuels usually do not match closely for constant load conditions, since biodiesel has a substantially lower heating value (per Table 2, which shows biodiesel's heating value about 12% lower than petroleum diesel).

Fuel spray atomization and penetration affect air mixing and evaporation rate, and are affected by a fuel's composition, viscosity, density, surface tension, bulk modulus, and boiling point [65,86,87]. The Sauter mean diameter can be used to describe the quality of atomization of the injected fuel, and its variation between fuels is reported in several studies [51,83,88–90]. Allen and Watts [30] state that the Sauter mean diameter of methyl ester biodiesel varies from 5 to 40% higher than petroleum diesel fuel. An increase in the Sauter mean diameter reduces the premix phase of combustion, causing an increase in the diffusion phase of combustion [17].

Differences in spray penetration between biodiesel and petroleum diesel fuels seem to have inconsistent trends. Choi and Reitz [91] report that biodiesel has longer fuel penetration due to higher injection pressure and increased viscosity. Yuan et al. [51], however, observe different relative behaviors in spray penetration depending on the biodiesel feedstock; soy methyl ester biodiesel has a longer penetration length while yellow grease methyl ester has a shorter penetration length than diesel fuel.

Fuel injection profiles with consideration to pilot injection have been investigated by Suh et al. [83] on a common-rail engine. Their study reveals similar patterns between fuels when no pilot injection is used (i.e., single injections). Cases that utilize pilot injection, however, reveal differences in profiles. The authors attribute these differences to the spray development of biodiesel during the pilot injection period.

6.3. Ignition delay

Ignition delay, conventionally defined as the time between start of injection and start of combustion (which also has varying

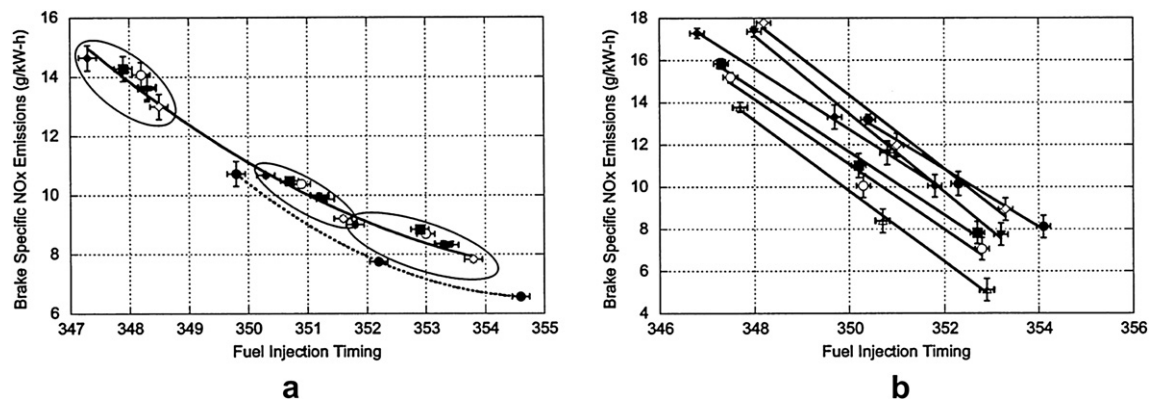


Fig. 5. Brake specific NO_x emissions versus controlled fuel injection timing (in crankangle degrees) at (a) 3600 rev/min, 75% load and (b) 3600 rev/min, 25% load. Data from several fuels are shown, based on the following key: (Δ) BP325, (○) B20, (■) B40, (◆) B100, (▼) FT20, (◇) FT40, and (●) FT100. Data plots from [71].

definitions), for biodiesel is generally shorter than that for petroleum diesel [8,36,61,64,92–96]. For example, Nagaraju et al. [94] show no statistical change in start of injection between bio- and petroleum-based fuels, yet show a 29% shorter ignition delay (about 2 crank angle degrees) for B20. The lack of change in injection timing may be attributed to their use of a common-rail fuel system, which is consistent with data shown in Fig. 4 [68]. Fig. 6 illustrates the decreased ignition delay typically observed with biodiesel. Fig. 6 (a) shows the normalized mass fraction burned curves (calculated from measurements of in-cylinder pressure [97]) as functions of engine crankangle (in degrees after top dead center, or deg ATDC) for petroleum diesel (reference) and biodiesel at 1400 rev/min, high-load condition [68]. The injection timings associated with this condition are shown in Fig. 4. Notice that, in spite of having the same injection timing, biodiesel ignites (i.e., shows positive mass fraction burned) sooner than petroleum diesel fuel. This is true at all studied high-load conditions, as shown in Fig. 6 (b), where ignition delays are shown as functions of engine speed. In fact, this is true at all nine operating points reported in Bittle et al. [68].

Similar results are predicted through KIVA-based models, as reported by Yuan et al. [51]. In their study, a detailed numerical spray atomization, ignition, and combustion model is used in KIVA-3 V in predicting combustion behavior of a medium-duty direct-injection engine fueled (individually) by soy methyl ester, yellow grease methyl ester, and conventional petroleum diesel. Both bio-based fuels (soy- and yellow grease-methyl esters) show shorter ignition delays. The variation in ignition delay advance seems to vary with feedstock [36,98]. Kinoshita et al. [98] show the following trend in ignition delay (from shorter to longer) for palm oil ethyl ester, palm oil methyl ester, coconut oil methyl ester, rapeseed methyl ester, and conventional petroleum diesel:

Palm oil ethyl ester < Palm oil methyl ester < Coconut oil methyl ester < Rapeseed methyl ester < Petroleum diesel

Decreases in biodiesel ignition delay reported by others include 1.06° by Canakci [26] and 1.1° by Tat et al. [56], both reporting differences between soy methyl ester and petroleum diesel. If injection timing is also advanced with biodiesel, the net effect on start of combustion can be dramatic. Canakci and Van Gerpen [59] report a 3.41° combustion advance for SME and a 4.16° combustion advance for yellow grease methyl ester, both relative to petroleum diesel.

The relative shortening of ignition delay is reported to vary with engine load and speed. Lu et al. [60] report that biodiesel ignition delay is 10%–42.9% shorter (relative to petroleum diesel) from a low engine load to a high engine load, respectively, at 1300 rev/min. Similarly, biodiesel ignition delay is 17.2%–35.3% shorter from a low engine speed to a high engine speed, respectively, at 75% engine load. These trends may depend on the type of injection system (or other parameters), however, as Fig. 6 reveals varying relative changes to ignition delay between petroleum diesel and biodiesel. Bittle et al. [68] further show this inconsistent behavior at other speeds and loads between the fuels.

Several studies consider the physical and chemical properties affecting biodiesel ignition delay [31,36,44,96]. Through numerical simulation, Ra et al. [31] show that certain physical properties – namely, vapor pressure, surface tension, and heat capacity – have a significant influence on differences in ignition delay between biodiesel and petroleum diesel fuels. Their study, which involves the use of diesel and biodiesel surrogates, identifies that biodiesel vapor pressure is relatively lower than petroleum diesel. The lower vapor pressure results in slower evaporation rate, which tends to increase ignition delay. Biodiesel's higher surface tension contributes to an advance in injection timing; its influence on ignition delay is complex due to competing interactions with atomization, penetration, droplet size, and evaporation [78]. Biodiesel's lower heat capacity allows its temperature to rise at a faster rate once injected, resulting in evaporated droplets sooner than petroleum diesel. This effect presumably contributes to a shorter ignition delay. Related to chemical properties, most studies tend to identify the increased chain length of biodiesel as the primary contributor to shorter ignition delays [36,44,96]. Double-bond structuring of fatty acid chains (i.e., increased unsaturation of the fatty acid ester) tends to lengthen ignition delay. Finally, increases in the chain length of the alcohol moiety will shorten ignition delay [36]. The balance between the chemical and physical mechanisms, based on the empirical evidence, presumably results in a net decrease in ignition delay.

Like differences in injection timing, differences in ignition delay between biodiesel and petroleum diesel fuels are rationalized as contributing to (or offsetting) differences in NO_x emissions [17,26,29,36,37,44,56,58,60,71,96,99–102]. Cetane number (CN), which identifies the ignition delay of a test fuel relative to n-cetane ($\text{C}_{16}\text{H}_{34}$), is generally used to characterize the ignition delay of a fuel.

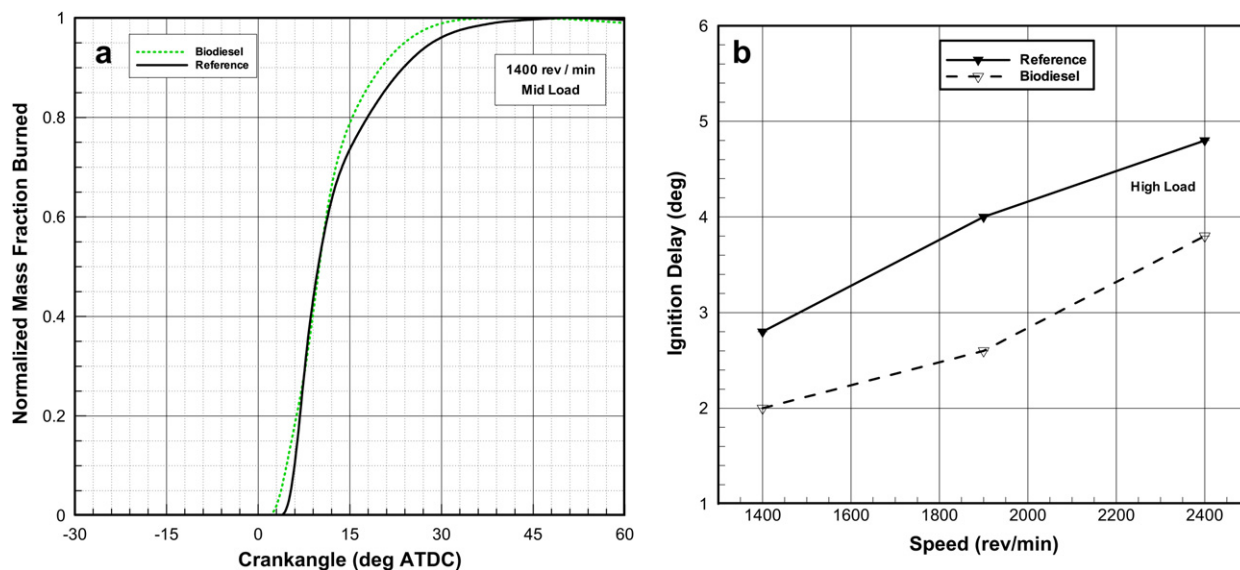


Fig. 6. (a) Normalized mass fraction burned as function of engine crank angle at 1400 rev/min, mid-load condition and (b) ignition delay for high-load conditions as function of engine speed in a common-rail medium-duty diesel engine using biodiesel and petroleum diesel (reference) fuels [68].

A CN = 100 represents an equal ignition delay between the test fuel and n-cetane. A high CN suggests a short ignition delay. Although biodiesel typically has higher CN relative to petroleum diesel, its ignition delay seems to be shorter than that predicted by its CN, thus perhaps making it an imperfect measure for comparing ignition delays between fuels [49]. With petroleum fuel, a decrease in ignition delay conventionally results in an increase in particulate matter (PM) and a decrease in NO_x emissions [103]. Thus, biodiesel's shorter ignition delay could be an offsetting effect to its reportedly higher NO_x emissions. Evidence of this is supported by McCormick et al. [27,104] where they observe cetane enhancers, such as 2-EHN and DTBN, to decrease NO_x emissions with biodiesel fuel.

6.4. Combustion stages and heat release

From a macroscopic perspective, the overall combustion characteristics of low concentration blended biodiesel with petroleum diesel are quite similar to those of pure petroleum diesel. For example, Suh et al. [83] found that combustion pressure and rate of heat release between petroleum diesel and B5 (5% biodiesel volumetrically mixed with petroleum diesel) are similar. Comparisons between pure biodiesel and pure petroleum diesel, however, reveal interesting dissimilarities, as shown in Fig. 7. Fig. 7 shows the rate of heat release for petroleum diesel and biodiesel in a medium-duty diesel engine at (a) high-, (b) mid-, and (c) low-load conditions (all at 1400 rev/min) [68]. By focusing on just the petroleum diesel heat release profiles, notice that the usual characteristics of conventional diesel combustion [77] are present. Specifically, the common “two-stage” heat release with premixed burn followed by diffusion burn is present at the high load condition, shown in Fig. 7 (a). The relative fractions of premixed and diffusion burn are functions of several things, including ignition delay. A short ignition delay generally results in a smaller fraction of premixed burn and a correspondingly higher fraction of diffusion burn [77]. This is apparent in the comparison between petroleum diesel and biodiesel heat release rates. At the high load condition (Fig. 7 (a)), biodiesel exhibits a shorter ignition delay, and thus very little premix burn. Correspondingly, its fraction of diffusion burn is relatively higher than that of petroleum diesel. This is also clear at the mid-load condition (Fig. 7 (b)), where biodiesel exhibits a smaller fraction of premix burn than petroleum diesel. Petroleum diesel at the mid-load condition exhibits mostly premixed burn; diffusion burn becomes dominant late in the heat release (around 15° ATDC). Biodiesel, on the other hand, exhibits diffusion burn much earlier (around 6° ATDC). The low-load case is unique to the high- and mid-load cases, in that it utilizes pilot injection; thus, the second injection for both fuels injects into a relatively higher temperature environment, establishing diffusion burn for both fuels much sooner after start of the second injection.

Other studies [8,10,53,60,65,98,105] similarly report reductions in the fraction of premixed burn with biodiesel fuel, although injection timings may be changing (either through controlled or artificial changes imposed by biodiesel) in some of the cited studies. In addition to the shorter ignition delay of biodiesel (e.g., higher cetane number), its lower volatility is cited as also contributing to decreased fractions of premixed burn. The lower volatility results in fewer evaporated droplets during the ignition delay period (which is already shortened due to biodiesel's naturally shorter ignition delay), further compounding a reduction in premixed burning (relative to petroleum diesel). These effects may contribute to observations made by Mueller et al. [37], who conclude that biodiesel fuel-air mixtures ignite and react closer to stoichiometric than petroleum diesel fuel-air mixtures; the effects of which are discussed more thoroughly below.

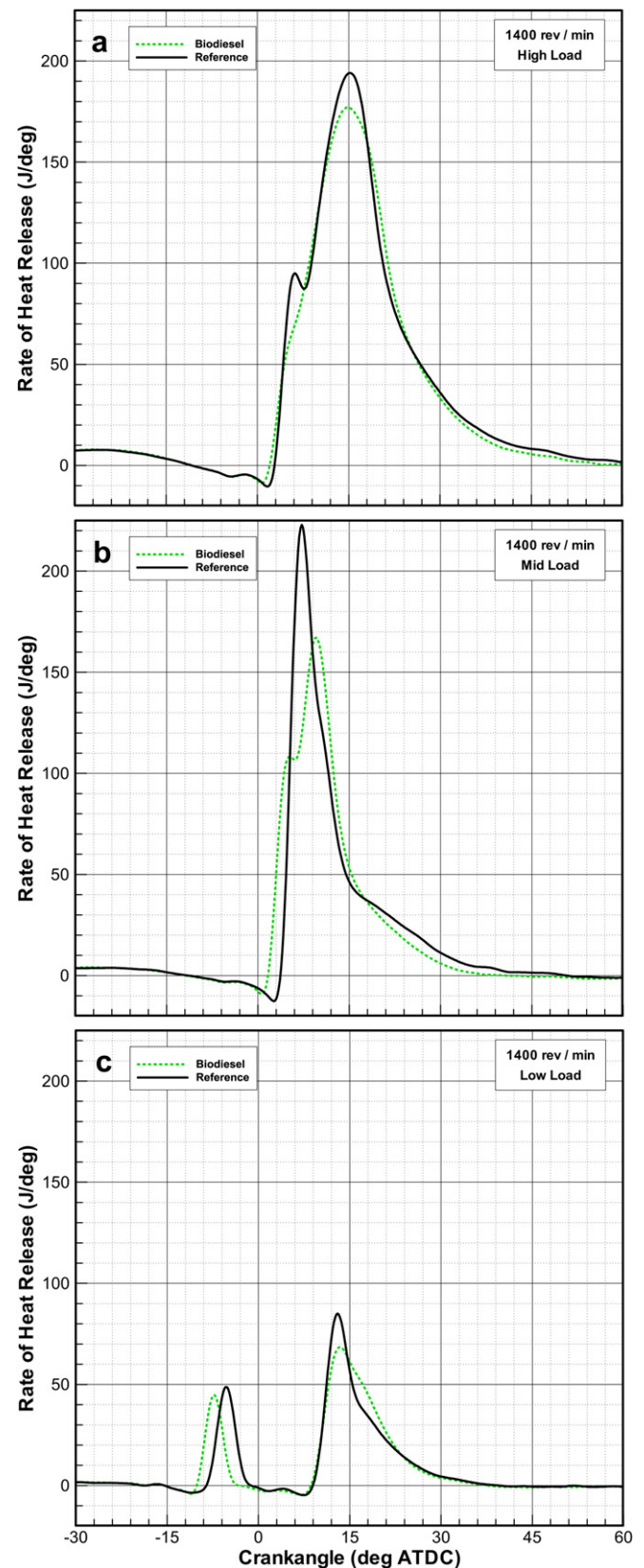


Fig. 7. Rates of heat release as function of engine crank angle at 1400 rev/min, (a) high-, (b) mid-, and (c) low-load conditions for petroleum diesel (reference) and biodiesel [68].

Another interesting feature to evaluate between biodiesel and petroleum diesel fuels is the combustion duration. Several studies [8,26,61,65,98,105,106] report a general increase in the combustion duration with biodiesel. Bittle et al. [68], however, report different observations, where biodiesel combustion duration is generally shorter than petroleum diesel combustion duration. This behavior can be observed in Fig. 8, which shows normalized mass fraction burned curves for biodiesel and petroleum diesel at (a) high-, (b) mid-, and (c) low-load conditions (all at 1400 rev/min) in a medium-duty diesel engine [68]. Notice that, in spite of biodiesel igniting sooner in all cases, the mass fraction burned profiles between fuels generally overlap or cross during the 10%–50% burn region. In all cases, biodiesel seems to terminate combustion sooner. If combustion duration is defined as the 10%–90% burn angle, then biodiesel has shorter combustion durations across several speeds and loads, as shown in Fig. 9 [68]. The observed shorter durations may result from biodiesel exhibiting a faster diffusion burn rate than petroleum diesel. This is evidenced in Fig. 8, where initially biodiesel and petroleum diesel may have similar burn rates, but eventually petroleum diesel's burn rate slows as its combustion becomes predominantly diffusive. Similar behavior is also observed by Mueller et al. [37].

The type of feedstock used for the biodiesel may partly explain the inconsistency in combustion duration among studies. For example, Kinoshita et al. [98] tested coconut oil methyl ester, palm oil methyl ester, rapeseed oil methyl ester, palm oil ethyl ester, rapeseed oil ethyl ester and diesel. Similar to what is described in the above sections, they [98] observe earlier injection timings and shorter ignition delays of methyl and ethyl esters than those of diesel. The combustion end timings of all the test fuels, however, are almost the same.

In addition to the inconsistency in the literature regarding the relative combustion durations between biodiesel and petroleum diesel, there also seems to be some inconsistency in the magnitudes of heat release between the two fuels. For example, Kawano et al. [107] report higher maximum heat release of rapeseed oil methyl ester than petroleum diesel. Yu et al. report marginally higher heat release rate during late combustion of waste cooking oil compared to petroleum diesel [10]. Suryawanshi and Deshpande [95] report slightly higher heat release rates of various blends of pongamia oil methyl ester at standard injection timings compared to diesel fuel. Nagaraju et al. [94] report, on average, 8% higher peak rate of heat release of B20 during premixed combustion than petroleum diesel. Similarly, they [94] report higher rates of diffusion combustion with B20, which they also observe as resulting in higher exhaust gas temperatures. They attribute these changes in combustion characteristics to the presence of oxygen in the fuel and late burning of heavy compounds found in biodiesel. Bittle et al. [68], however, reveal lower rates of heat release for biodiesel fuel, as shown in Fig. 7. In a related study [108], similar trends (lower heat release of biodiesel relative to petroleum diesel) are observed at other speed and load conditions.

A portion of these observed differences are dissected by Szybist et al. [71], who report an experimental study that evaluates heat release rates at two different load conditions (high and low-load conditions) for several different fuels. Their results are shown in Fig. 10, where column (A) plots corresponds to the high-load conditions and column (B) plots correspond to the low-load conditions. Each plot within a column corresponds to a nominal injection timing: (a) early injection timing (nominally 12° BTDC), (b) mid injection timing (nominally 9° BTDC), and (c) late injection timing (nominally 7° BTDC). It should be noted that the engine apparatus in this study uses a line-pump injection system, thus injection timings varied about 1.5° for specific fuels around the nominal injection timing setpoints. An interesting observation

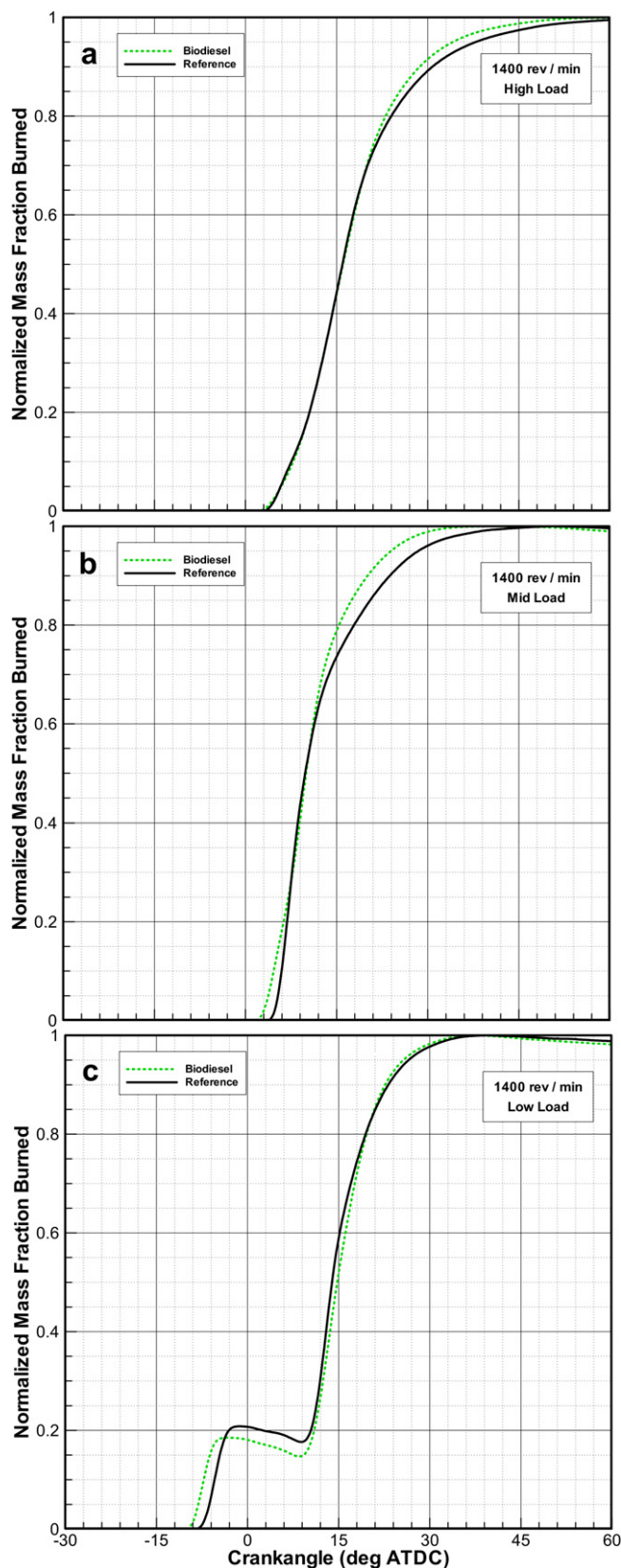


Fig. 8. Normalized mass fraction burned as function of engine crank angle at 1400 rev/min, (a) high-, (b) mid-, and (c) low-load conditions for petroleum diesel (reference) and biodiesel [68].

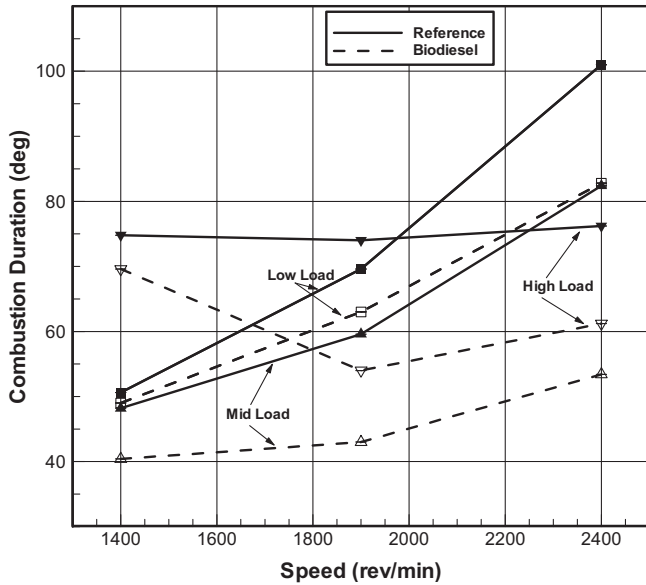


Fig. 9. Combustion duration as function of engine speed at three load conditions in a common-rail medium-duty diesel engine using biodiesel and petroleum diesel (reference) fuels [68].

from Fig. 10 relates to the change in peak rate of heat release as blend ratio decreases from B100 to BP325 (pure petroleum diesel). By evaluating only the biodiesel and petroleum diesel curves in Fig. 10 (B100, B40, B20, and BP325) notice that the peak rate of heat release increases as blend ratio decreases at the high-load

condition. On the contrary, the peak rate of heat release decreases as blend ratio decreases at the low-load condition. Such observations suggest the presence of potentially changing roles of certain fundamental differences between the fuels. They further emphasize the inconsistency reported in the literature about certain trends between the fuels. This is highlighted by the notion that Monyem et al. [58] observe similar behavior as Szybist et al. [71], yet Nagaraju et al. [94] observe differing behavior.

Much of the above discussion is unified by Mueller et al. [37], which relate the changes of biodiesel combustion to their potential effect on NO formation. In this [37] study, it is shown that biodiesel reacting mixtures are closer to stoichiometric during ignition (i.e., premixed combustion phase) and in the standing premixed auto-ignition zone of the diffusion flame (the standing premixed auto-ignition zone is a component of Dec's conceptual model of diesel combustion [110]). Such a phenomenon (i.e., more stoichiometric burning) could lead to higher local and average temperatures, lower radiative heat losses (discussed in more detail below), and more advanced combustion event (due to shorter combustion durations).

6.5. Heat radiation from soot

Almost unanimously, studies report significant reductions in PM (or soot) emission when substituting biodiesel into petroleum diesel. An example of PM decreasing with increased biodiesel content, taken from [6] is shown in Fig. 11. In Fig. 11, PM and PM_D represent the amount of PM emissions from the blend and pure diesel, respectively. The volumetric concentration of biodiesel in the blend is represented as %B (v/v).

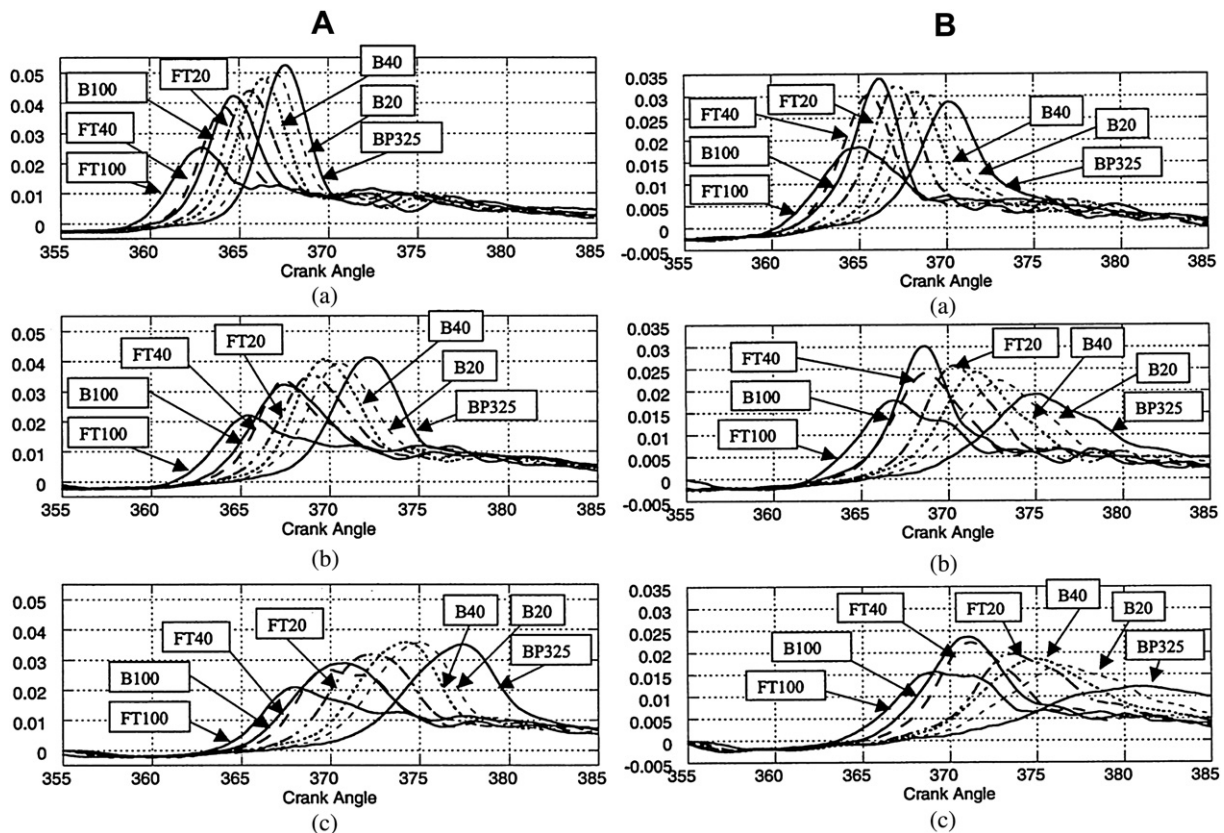


Fig. 10. Rate of heat release (in kJ/deg) at (A) high- and (B) low-load conditions at varying engine crank angle degrees and at (a) early, (b), mid, and (c) late fuel injection timings for several different fuels. Data figures taken from [71].

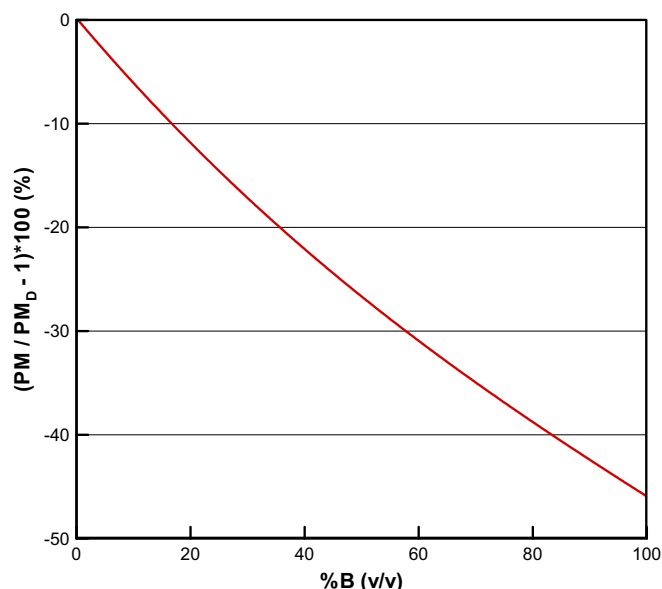


Fig. 11. Reduction in PM (PM represents biodiesel PM and PMD represents petroleum diesel PM) with increase in biodiesel concentration (%B on a volumetric basis) [6].

Some studies [44,49] report the reduction of in-cylinder soot as a possible cause for the differences in NO_x emissions between biodiesel and diesel combustion. Carbonaceous soot, which mostly forms through premixed reactions in the core of a diesel spray jet, acts as an effective heat radiator as it oxidizes through the diffusion flame [105]. This radiative heat transfer, which is an energy transfer mode, results in a reduction in flame temperature (relative to the case of no radiation heat transfer). Thus, the presence of soot during combustion may be a cause of lower NO formation as a result of the radiation heat transfer effect on flame temperature. Biodiesel, which reportedly has less in-cylinder soot, presumably has less radiation heat transfer. Thus, part of the difference in NO_x emissions between biodiesel and petroleum diesel could be explained by the reduction in radiation heat transfer.

Several mechanisms are reported to contribute to lower soot formation in biodiesel: increased fuel-bound oxygen, lower stoichiometric air-fuel ratio (decreased equivalence ratio for same actual air-fuel ratio), decreased concentration of aromatics, advanced start of combustion (due to artificial advance and shorter ignition delay), changed soot particle structure, reduction of fuel-bound sulfur, decreased boiling point, and different sooting tendencies of various biodiesel esters [27,33,35–37,110,111,113–115]. Ullman et al. [111] indicate that increased oxygen content and decreased sulfur content of biodiesel fuel are the most influential parameters manifesting decreased particulate matter formation (relative to petroleum diesel). The general mechanism affected by increased oxygen is summarized by Nylund et al. [33]: the presence of fuel-bound oxygen suppresses soot nucleation early in the formation on the fuel side of the mixing-controlled flame. This nucleation suppression inhibits peak soot production, leads to more complete burning, and reduces the formation of soot precursors (cracked hydrocarbons such as acetylene and ethylene).

The influence of decreased aromatic concentration in biodiesel, in addition to fuel-bound oxygen, may also be important. Aromatics are well known for their strong sooting tendencies [34,112]. The following discussion uses “dilution effect” terminology to indicate the dilution of aromatic concentration in petroleum diesel with the addition (blending) of biodiesel fuel (increased long-chain molecules). A comparison of the decreased sooting tendency between the oxygen and dilution mechanisms is reported by Pepiot-Desjardins

et al. [113]. Oxygenates are mostly linear or slightly branched paraffins containing oxygen moieties, whereas conventional diesel is a mixture of several hundred hydrocarbon molecules containing a significant aromatic fraction (e.g., Table 2 indicates around 35% aromatic concentration). Structural group analysis distinguishes between chemical effects caused by the presence of oxygenated groups in the fuel mixture and mere dilution of the original fuel by the additive. Threshold soot index (TSI) indicates sooting tendency and correlates well with actual PM emissions. The several esters reported in [113] range from C3 to C6 including methyl acetate ($\text{C}_3\text{H}_6\text{O}_2$) and ethyl butanoate ($\text{C}_6\text{H}_{12}\text{O}_2$). As expected, TSI decreases as oxygen concentration increases for oxygenate/diesel mixtures. On the other hand, with a fixed oxygen concentration of 4%, dilution effect is at least twice the oxygen effect for all studied esters.

The seemingly secondary influence of increased oxygen concentration with biodiesel on soot reduction is supported by other literature [35,114,115] as well. For example, Curran et al. [114] demonstrate a relatively small influence of the oxygen effect on sooting tendency. Using kinetic modeling of oxygenated fuel, the study reports that overall oxygen content should be about 30–40% to reduce soot precursors to close to zero. Considering that the oxygen content in biodiesel is around 10% the oxygen-induced soot reduction is noticeable but not extreme. Furthermore, blends of biodiesel with conventional diesel assumedly would have proportionally smaller effects on in-cylinder soot reduction. Also, a study by Mueller et al. [115] suggests that the biodiesel-bound oxygen may be underutilized for reducing soot precursors. In experiments of tri-propylene glycol methyl ether and di-butyl maleate (an ester) – both which have four oxygen atoms per molecule – the former demonstrates decreased sooting tendency. This effect is explained by the high concentration of CO_2 formed directly through two decomposition reactions of the ester. Because the ester directly produces high levels of CO_2 , as opposed to just CO as is done with the ether, it is reported that about 32% of the oxygen in the ester is wasted [115]. Further, the ester forms acetylene (a soot precursor) in its first decomposition reaction. Finally, it is noted that different esters having different sooting tendencies. For example, Graboski et al. [110] report that methyl laurate produces 30% less soot than methyl palmitate; correspondingly, the methyl laurate produces 10% more NO_x .

Although aromatics increase in-cylinder soot formation, and thus presumably increase radiation heat transfer (which would tend to decrease flame temperature), their presence in diesel fuel tend to overall increase flame temperature [34,112]. Correspondingly, aromatics are shown to not only increase exhaust smoke concentrations, but exhaust NO concentrations as well [116]. This NO_x -increasing attribute of aromatics is significant, and contributes to the complication of assessing NO_x differences between petroleum diesel and biodiesel. For example, Eckerle et al. [35] report that normal variations of aromatic concentrations in commercially available diesel fuel can cause more dramatic changes in NO_x emissions than those observed in comparisons with biodiesel. Related, the usual presence of aromatics in petroleum diesel has been targeted as a means to create “ NO_x -neutral” blends with biodiesel [117]. Analyses of various blended fuels suggest that, if other factors are equal, 25.8% aromatics in the base fuel (petroleum diesel) will provide a NO_x -neutral B20 [28,104]. This concentration compares to typical aromatic concentration specifications of 31.9%. Lowering the base fuel aromatic content from 31.9% to 7.5% (nominally 10% aromatic fuel) is very successful at substantially lowering NO_x of B20 [28,104].

6.6. Combustion temperature

Biodiesel combustion is reported to have higher reaction temperatures than petroleum diesel combustion [8,51,61] and this

is the most-commonly cited reason for differences in NO_x emissions between the two fuels [54,118]. Diffusion flame temperature is likely to have a strong influence on NO_x emissions, owing to the dominance of thermal NO formation and the close proximity of the diffusion flame to the NO formation zone [49,109]. Conceptually, increased NO_x could result with biodiesel if the stoichiometric adiabatic flame temperature of biodiesel is higher than that of diesel fuel [49]. In spite of its lower heating value, biodiesel also has a lower stoichiometric air-fuel ratio. Thus, when computing the stoichiometric adiabatic flame temperatures for petroleum diesel and biodiesel, they may closely match. For example, using the standard chemical formulas and lower heating values of the fuels listed in Table 2, the adiabatic flame temperatures are 2281 and 2280 K for petroleum diesel and biodiesel, respectively (assumes stoichiometric mixture with air and equilibrium products of combustion). This simple analysis, however, provides insufficient information and can be misleading depending on the type of biodiesel being studied. For example, Monyem et al. [58] calculate the adiabatic flame temperature of constant-volume and constant-pressure biodiesel and diesel combustion for stoichiometric and lean ($\phi = 0.6$) cases. In all cases, biodiesel has a lower adiabatic flame temperature than petroleum diesel. Under realistic conditions, temperature distribution (flame volume) may also play a role. For example, both soy methyl ester and yellow grease methyl ester have more widespread high-temperature distribution areas than diesel fuel [51].

From macroscopic points of view, advanced injection timing and earlier combustion produce higher temperatures during diffusion combustion [92]. Due to improved diffusion combustion, presumably through the presence of oxygen on the fuel-side of the reaction, reaction temperatures may be higher as the reaction proceeds more quickly [8,10,52,61,78,95]. Reduced radiation heat transfer, as discussed above, may also play a significant role in maintaining relatively higher combustion temperature of biodiesel.

From microscopic points of view, characteristics of biodiesel such as degree of saturation have significant influence on the flame temperature. The number of carbon single bonds in the molecule reflects degree of saturation. Increased single bonds mean increased saturation. The iodine number is a measure of saturation, where low iodine number indicates high saturation (increased single bonds). Several studies correlate the degree of saturation to NO_x emissions; highly saturated fuel molecules produce lower amounts of NO_x emissions [19,28,92,98,110,119]. Biodiesel typically contains more double-bonded molecules than petroleum diesel. Multiple bonds tend to increase flame temperature [44]. This connection between degree of saturation and flame temperature/NO_x emissions is supported by the tendencies of different biodiesels with different degrees of saturation to produce different amounts of NO_x [63]. Chang and Van Gerpen [92] state that blends with saturated esters show the smallest increase in NO_x emissions. Ziejewski and Goettler [119] report that differences in combustion temperature between vegetable and palm oils result from different levels of saturation between the fuels.

6.7. System response issues

The final component to discuss in the comparison between biodiesel and petroleum diesel NO emissions is that of “system response issues”. As discussed above, system responses are those that are manifested by either differences in certain properties between fuels or changes to the operating point on the calibration map as a result of extending the injector pulsewidth to match engine torque. The former manifestation (i.e., differences in certain properties causing a system response) is referred to as “passive” system response in this article. The latter manifestation (i.e.,

changes to the operating point on the calibration map as a result of extending injection pulsewidth to match engine torque) is referred to as “active” system response.

An example of a system response is the artificial advance of injection timing with the use of biodiesel, as described above. The advance in injection timing may be manifested by a difference in property (i.e., bulk modulus) between biodiesel and petroleum diesel – a passive system response. A change in injection timing may also be manifested by a change to the operating map from which control parameters are specified – an active system response. In other words, because the injection pulsewidth is typically longer with biodiesel (due to its lower heating value) and most engine control systems use pulsewidth as an input to the calibration map (which controls parameters such as injection timing), the changed injection pulsewidth may change other controlled parameters (in spite of the same engine speed and torque). The elimination of a passive system response would require a substantial design change to the system component being affected. In the example of bulk modulus manifesting an earlier injection timing of biodiesel, this response could be designed out of the system by employing common-rail fuel system. Fig. 4 identifies the insensitivity of a common-rail fuel system to differences in the fuels’ fluid properties. The manifestation of an active system response, however, is rather arbitrary. Tat et al. [56], for example, observe an advance in injection timing as injector pulsewidth increases. Typically, diesel injection timing is retarded as injector pulsewidth increases (i.e., engine load increases), to subdue increases in noise with substantially high amounts of premixed burning [75]. Bittle et al. [68], however, observe no changes to the calibrated, or commanded, start of injection as pulsewidth increases for biodiesel as shown in Fig. 4.

There are other system response issues, outside of injection timing, that may also influence NO emissions. These system responses include exhaust gas recirculation, injection pressure, intake manifold pressure (i.e., boost pressure), and any other parameter that is dynamically linked among fuel, in-cylinder processes, and out-of-cylinder components. Such system responses make it difficult to quantify specific reasons that may cause differences in NO emissions between biodiesel- and diesel-fuelled engines and likely contribute to the variations in NO emissions that are reported in the literature. The continuing presence of advanced technology on diesel engines, however, renders it possible to *a priori* detect and mitigate any changes to emissions [120], thus potentially enabling the use of biodiesel fuel.

6.8. Summary

While this article is not able to identify a specific cause for changes in NO emissions between biodiesel and petroleum diesel fuel, it is able to collect all the major factors that seem to contribute to such changes and qualitatively provide them in a summary fashion. Fig. 12 is an attempt at such a qualitative summary. This qualitative summary figure is similar to one provided by Khan [121], as that figure related to smoke in diesel engine exhaust. In Fig. 12, the various pathways of NO formation are shown. As the figure reads from left to right, higher to lower order parameters are connected in various pathways. In other words, a lower order parameter (listed on the right of the figure) is suggested to affect higher order parameters in the connected pathways. A bold line connecting two parameters suggests that an increase (or advance) in the lower order parameter increases (or advances) the higher order parameter. For example, a non-bolded line connects radiation heat transfer to post-flame gas temperature; that is, an increase in radiation heat transfer decreases post-flame gas temperature.

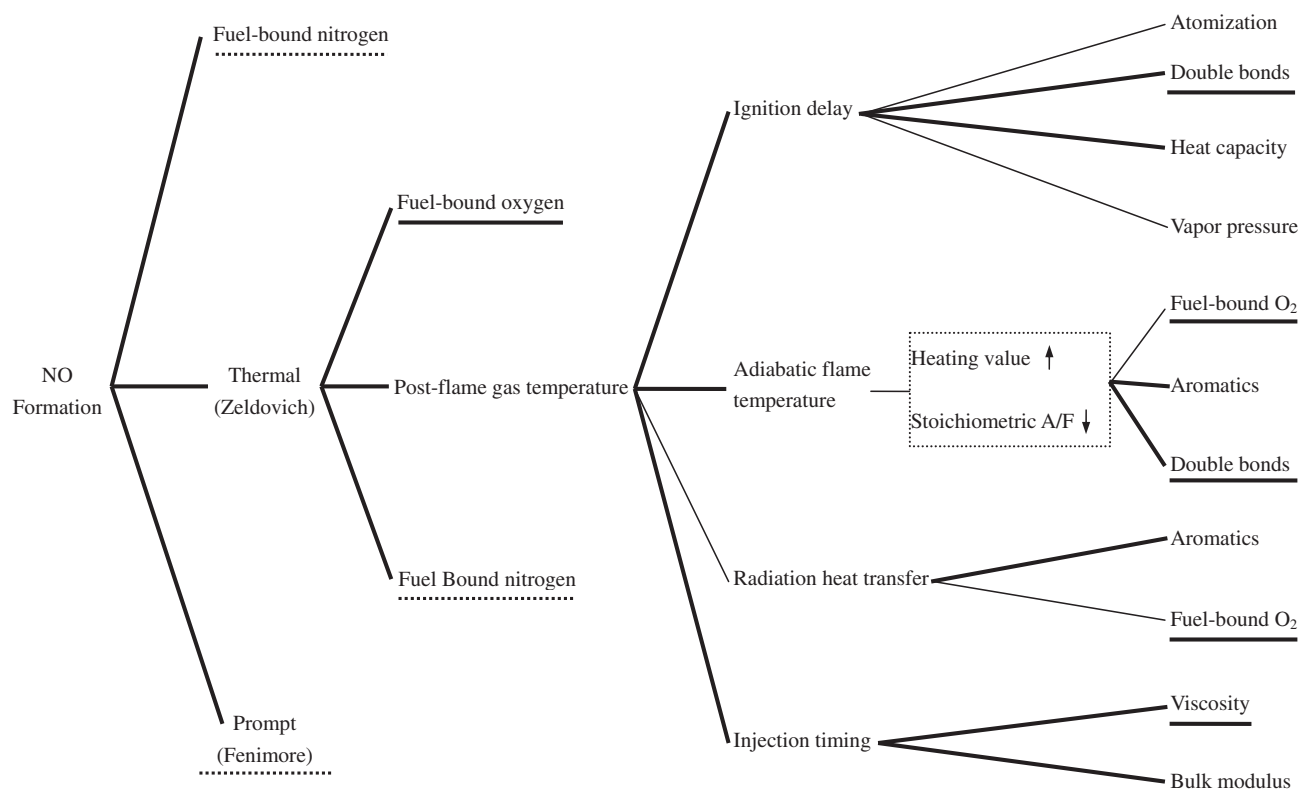


Fig. 12. Qualitative summary figure of major factors affecting nitric oxide emissions from a diesel engine. A bold underline of a parameter indicates the parameter is higher with biodiesel. A dashed underline of a parameter indicates uncertainty as to how the parameter changes with biodiesel. A bold line connecting parameters indicates that an increase (or advance) in the lower order parameter (right hand side) will increase (or advance) the higher order parameter.

The comparison between biodiesel and petroleum diesel adds an additional level of detail to the figure. A lower order parameter that is underlined indicates that such a parameter is higher with biodiesel than with petroleum diesel. For example, fuel-bound oxygen is underlined; indicating that biodiesel has higher fuel-bound oxygen than does petroleum diesel. For some lower order parameters, either through reported uncertainty in the literature or no found literature discussing the topic, the relative differences between biodiesel and petroleum diesel are not known. In these cases, the lower order parameters are underlined with a dashed line.

It is worth mentioning the presentation of adiabatic flame temperature in Fig. 12. Thermodynamically, adiabatic flame temperature is a function of heating value and stoichiometric air/fuel ratio. Lower-order parameters, however, influence both heating value and stoichiometric air/fuel ratio. Thus, fuel-bound oxygen, aromatics, and double bonds are listed as the lower-order parameters affecting adiabatic flame temperature (with heating value and stoichiometric air/fuel ratio being “intermediate” parameters). The arrows alongside heating value and stoichiometric air/fuel ratio indicate their relative influence on adiabatic flame temperature.

Thus, the figure attempts to qualitatively summarize the many observations made regarding the differences between biodiesel and petroleum diesel as related to the impact on NO emissions. The pathways shown in Fig. 12 certainly do not account for all mechanisms participating in the formation of NO, or the ways they differ between fuels. For example, spray formation and penetration effects on the relative fractions of premixed and diffusion burning are left out due to their complicated and inter-changing behavior. Attempts to include all these mechanisms will have the tendency to over-simplify the interactions. Instead, Fig. 12 identifies the

complexities associated with attempting to singly determine how NO emissions differ between biodiesel and petroleum diesel fuels, and illustrates how discrepancies about NO emissions with biodiesel come to exist in literature.

7. Conclusions

In general, it is not consistent that NO_x emissions from biodiesel-fuelled (pure or blended) engines are higher than those from petroleum diesel-fuelled engines. Inconsistencies appear among studies as engine type, engine technology, and fuel feedstock differ. Inconsistencies even appear within studies at different operating points (for example, low load versus high load). Although a non-trivial number of studies reveal inconsistencies in relative differences in NO_x emissions between biodiesel and petroleum diesel fuels, much of the literature reports higher NO_x emissions with biodiesel. The major reported reasons for observed differences in NO_x emissions between biodiesel and petroleum diesel fuels are as follows:

- System response issues, either passive (such as artificial advances in injection timing due to high bulk modulus of fuel) or active (such as controlled changes to injection timing with increased fuel injection pulsewidth to match engine torque), will have differing effects on NO_x emissions. Artificial advances in injection timing, which tend to increase NO emissions with biodiesel, are most-commonly cited as a system response issue that influences NO_x emissions. System responses develop when differences in fuel properties cause a component of the system to respond differently than with petroleum diesel. An example of a passive system response is the increase in bulk

modulus of biodiesel causing higher rates of pressure rise in a mechanical injector pump, thus resulting in an earlier start of injection. Active, or controlled, system responses develop when increases in injector pulsewidth (a parameter by which other controlled parameters are referenced) with biodiesel (due to biodiesel's lower heating value) cause a change to other control parameters, such as injection timing. Other system responses (i.e., fuel injection pressure, boost pressure, exhaust gas recirculation level) may also be manifested in the use of biodiesel and could have favorable or unfavorable effects on NO_x emissions. Both types of system responses (passive and controlled) depend strongly on the design of components or the developed calibration of the engine.

- Advances in start of combustion, manifested either by biodiesel's inherently shorter ignition delay or the combination of biodiesel's inherently shorter ignition delay and artificial advances in injection timing. The esters composing biodiesel possess long-chain species which tend to exhibit shorter ignition delays (in spite of increased unsaturation, which tends to lengthen the ignition delay of biodiesel). Further, biodiesel has differences in heat capacity, vapor pressure, and atomization which affect physical ignition delay. The advance to start of combustion may result in higher post-flame gas temperatures, thus increasing NO formation. Further, and in spite of shorter ignition delays, biodiesel also tends to exhibit shorter combustion durations. In addition to elevating combustion temperatures, a shorter combustion duration coupled with shorter ignition delays creates longer residence time for post-flame nitrogen chemistry to occur.
- Adiabatic flame temperature, affected by the fuels' heating values and stoichiometric air/fuel ratios, may vary for biodiesel relative to petroleum diesel. Biodiesel fuels consistently have lower heating values than petroleum-based fuels. They correspondingly also have lower stoichiometric air/fuel ratios, which in the balance may yield stoichiometric adiabatic flame temperatures that are similar between the fuels. Several fuel parameters participate in affecting adiabatic flame temperature, including the amount of fuel-bound oxygen, the level of aromatics in petroleum diesel, and the number of double-bonded species in biodiesel.
- Decreased radiation heat transfer with biodiesel, manifested by the decreased concentrations of aromatic species and increased concentrations of fuel-bound oxygen, tends to increase post-flame gas temperature (and thus increase NO emissions). This effect may be small, however, given the relatively small contribution by radiation heat transfer (even in diesel combustion systems). Further, the aromatic species tend to have higher adiabatic flame temperatures. Thus, although the decreased radiation heat transfer from decreased aromatic species may raise post-flame gas temperature in biodiesel, the higher aromatic species concentrations in petroleum diesel may correspondingly raise flame temperatures in petroleum diesel.
- Finally, as indicated at the start of the Conclusions and related to system response issues, inconsistencies in reported NO_x emissions behavior between biodiesel and petroleum diesel fuels among studies may largely be linked to differences in engine design and technology. Study comparisons using different sized engines (based on displacement), different fuel systems (i.e., common rail versus in-line/mechanical pump systems), different air systems (e.g., naturally aspirated versus turbocharged), and different control systems (mechanical versus electronic) will likely report variability in NO_x emissions behavior between fuels, indicating the significance that these engine parameters have on overall emissions behavior.

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