A Review on the Effects of Biodiesel Blends on Compression Ignition Engine NOx Emissions
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ABSTRACT
Biodiesels are produced by the transesterification of corresponding triglyceride feedstocks of vegetable (example: soybean, canola, palm, karanja) or animal fat sources. Currently, the leading feedstocks are soybean oil in the U.S., canola oil and rapeseed oil in Canada and Europe, and palm, karanja, jatropha and other oils in Asia. Due to the cost and production considerations of these biodiesels, blending biodiesels with the petroleum fuels appears to be a prudent option in the near-term. The use of biodiesels in compression ignition engines results generally in a reduction in the emissions of carbon monoxide (CO), hydrocarbons (HC), and particulate matter (PM), but a slight increase in the oxides of nitrogen (NOx) emission. The reported NOx emissions do not exhibit definitive trends and the results are significantly influenced by many factors, including engine type and design, test cycle, start of injection, ignition delay, fuel composition, adiabatic flame temperature, radiative heat transfer, fluid dynamics and combustion phasing. Due to appreciable variations in the physical properties and the highly nonlinear nature of the combustion process, the NOx emission with biodiesel blends does not vary monotonically with the percentage of biodiesel in the blend. Hence, the intricate dependence of NOx on biodiesel and its blending effect cannot be completely explained under all engine type and operating conditions. Although the literature contains several studies on the performance and emissions of compression ignition engines fueled with neat biodiesels, the information on the effects of blends is scattered and has not yet achieved a definitive status to explain the blending effect on NOx. Hence, this work was motivated to review the available data with respect to the NOx emission from engines fueled with the petroleum diesel/biodiesel blends.

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1. Introduction
Biodiesels, considered as alternative fuels to petroleum diesel, are defined as fatty acid methyl or ethyl esters derived from triglycerides of vegetable oils or animal fats. The utilization of biodiesels reduces greenhouse gas emissions, assists in sustainable energy development, and enhances energy independence due to the renewable and biodegradable nature of these fuels. Besides being close to environmentally carbon-neutral, biodiesels have properties similar to those of petroleum fuels and can be blended with petroleum fuels and used in existing engines without major modifications. Furthermore, they contain fuel-bound oxygen while being free of aromatic content; therefore, blends of biodiesels and petroleum fuels present the capability of reducing soot emissions from engines. Extensive studies have been conducted on the potential of biodiesels and the feasibility of commercializing them in the long run, as presented in comprehensive reviews [Van Gerpen, 2005; Meher et al., 2006; Agarwal, 2007]. With the current understanding of combustion characteristics of biodiesels, only blending of biodiesel (usually in volumetric percentage) with petroleum fuels is considered feasible in the near-term due to limited current availability of the commercial biodiesels and the lack of experience on the long-term effects of handling, transportation, storage, and combustion of these biodiesels and blends on the engines and the environment. Currently, there are about 250 biodiesel fueling stations in the United States providing a range of biodiesel blends ranging from B20 to B100 (number indicating the volumetric percent of biodiesel) with B20 being the widely available blend [Alternative Fuels Data Center, 2015]. However, the commercial use of biodiesel has not been widely popular. One reason is a dearth of definitive understanding about the long-term impact of biodiesel and their blends with petroleum fuels on engines, especially on the engine power performance and regulated gaseous emissions. Previous studies have revealed that the use of biodiesels and their blends in a compression-ignition engine resulted in an appreciable reduction in the emissions of particulate matter, HC and CO, but an increase in NOx emissions, compared to the use of diesel fuel. This increase in NOx emission is termed the biodiesel NOx effect, which has remained a prolonged issue over this decade. The US Environmental Protection Agency [2002] has categorized NOx as one of the key pollutants in engine emissions that can affect the human respiratory system. The biodiesel usage in the U.S alone is expected to reach 4000 million gallons (15000 million liters) in 2030. Hence, a comprehensive knowledge of the effects of biodiesels and their blends on NOx is required for the use

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of biodiesels to become prevalent. Therefore, it is crucial to understand the effects of fuel properties and operating characteristics of the engines on biodiesel NOx emission to develop enhanced mitigation and abatement techniques. The objective of this review article is to provide a comprehensive picture of the influence of fuel composition, engine calibration settings, fuel fluid dynamic parameters, and interactions of thermo-fluid-chemical parameters on the compression-ignition engine NOx emission when fueled with biodiesel and their blends with petroleum fuels. Throughout this article, biodiesel blends are referred to as Bxx, where B stands for biodiesel irrespective of the feedstock and xx stands for the volumetric percent of biodiesel in the blend. For example, a B20 blend consists of 20% biodiesel and 80% petroleum diesel (by volume).

1.1. Statistics and significance of literature review

The United States Environmental Protection Agency, EPA [2002] has published a technical evaluation of the impact of biodiesel on exhaust emissions from compression ignition engines. EPA [2002] reported the averaged results of all these studies in which the use of biodiesel and its blends has a conspicuous and persistent favorable impact on the emissions of carbon monoxide (CO), hydrocarbons (HC), particulate matter (PM) and a relatively small negative influence on NOx emission. The averaged results show a monotonic increase of up to 10% NOx with neat biodiesel and a reduction of up to 50% and 68% of CO and HC respectively. Although the report provided an approximate trend of biodiesel effect on emissions of regulated pollutants, it does not contain sufficient experimental results for the blends having greater than 20% of biodiesel. The statistical data employed for this study predominantly constitute emission results from B20 and B100. Moreover, these correlations have been developed based on a maximum likelihood curve-fitting approach instead of least-square regression. Hence, to provide a visual assessment of the goodness of fit, the report also compared the actual percent change in NOx emissions of biodiesel and its blends from the corresponding emissions of the base fuel, which typically is the No. 2 diesel in most of the studies. The average effect of biodiesel on NOx emission was seen to be small, but with a high variance, which resulted in difficulty in discerning a clear pattern. In the current review article, the engine NOx literature has been updated with more recent works and findings along with the assessment compiled by Hoekman et al. [2011]; the total number of studies considered for this review with a breakdown of different volumetric proportion of blends and resultant change in NOx emissions are presented in Table 1. This table contains the emission data from the engine tests reported and is grouped together as biodiesel (irrespective of the fuel feedstock), yet most of these studies employed biodiesel from soybean oil. Similar to the study by EPA, B20 constitutes the major data points with a scarce representation of higher biodiesel blend levels. We have plotted Figure 1 based on the data from Table 1 and Figure 2, an average value of the percentage variation of NOx emission index (g/kW-hr) with biodiesel content in the blends. The wide scatter in the results from these studies reveals the indefinite trend of NOx emission with the biodiesel content. This assessment again shows that the NOx emission and its dependence on the fuel chemistry and content of biodiesel are difficult to ascertain since the effects are highly variable.

<table>
<thead>
<tr>
<th>Biodiesel blend level (vol. %)</th>
<th>Average reduction of thermal input (MJ/kg) from base (diesel) fuel with biodiesel blending (%)</th>
<th>No of studies that show an increase</th>
<th>No of studies that show decrease</th>
<th>No of studies that show no change</th>
<th>Total number of studies considered</th>
<th>Average percentage variation of NOx from base (diesel) fuel</th>
<th>Standard deviation of percentage variation of NOx from base (diesel) fuel</th>
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<tr>
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<td>0</td>
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<td>5</td>
<td>0</td>
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<td>92</td>
<td>27</td>
<td>3</td>
<td>122</td>
<td>7</td>
<td>14</td>
</tr>
<tr>
<td>Total</td>
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<td>147</td>
<td>27</td>
<td>542</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

* Considering heating value of diesel as 44MJ/kg and average value of biodiesel as 39.6 MJ/kg (from Table 3); * Includes data collected from [Hoekman et al., 2011]

Table 1: Statistics of the effect of biodiesel content in the blend on NOx emission from studies considered in this review

In summary, a potential drawback in compiling these results from a wide range of experimental studies would be an inconsistent comparison of emission data in terms of engine type, load settings, engine speed settings, and fuel-air ratio during combustion which are not the characteristics of fuels alone. These presentations pose a risk of observing trends that may not correspond only to the parameters under study. Based on these developed correlations, it is difficult to confidently predict the amount of NOx emitted from any biodiesel-fueled engine and to conclude the biodiesel blending effect on NOx emissions.

2. NOx formation mechanisms with biodiesels

Nitrogen oxides present in atmosphere induce photochemical smog formation. The nitrogen oxides of environmental interest are NO, N2O and NO2 among which the NO and NO2 are collectively referred to as NOx [Lissianski et al., 2000; Fattah et al., 2013]. The more stable NO always predominates over the other oxides of nitrogen in the combustion flue gas. The coupled concentrations of NO and NO2 are decided by the fast radical reactions: NO2 reacts with O, H and OH to form NO and NO2.
Figure 1 Percentage variations of NO$_x$ emission from studies considered in this review

Figure 2 Average values of percentage variations of NO$_x$ emission with standard deviation from tests considered in this review
reacts with HO₂ to form NO, [Lissianski et al., 2000]. In several high-
temperature combustion processes, the predominant form of NO is 
produced as nitric oxide (NO), while the concentrations of NO₂ are 
typically less than 5% of total NO levels. NO₂ abatement techniques 
require a basic understanding of the kinetics behind the NO₂-forming 
reactions. Although the NOₓ reaction mechanisms have been detailed in 
the literature, the following section outlines some recent literature 
pertaining to the various mechanisms contributing to the formation of 
NO, and the general reactions involved in the formation of NO₂ and 
N₂O.

2.1 Nitric oxide (NO) emission
The atmospheric nitrogen is the prevalent source of nitrogen for NO 
production during the combustion of petroleum and FAME (Fatty Acid 
Methyl Ester)-derived fuels with air as the oxidizer. The thermal 
(Zeldovich), prompt (Fenimore), N₂O pathway, fuel-bound nitrogen 
and the NNH mechanism are the identified mechanisms for NO formation in 
diesel combustion which are summarized below.

2.1.1. Thermal mechanism
Thermal mechanism is the primary route by which NO formation 
occur at temperatures typically above 1800K [Hoekman and Robbins, 
2012]. At this high temperature, nitrogen (N₄) and oxygen (O₂) react 
through a set of chemical reactions in which the NO formation rate 
increases exponentially with temperature. The fundamental kinetic 
equations for thermal NO formation (R1-R3) along with their reaction 
kinetic parameters are presented in Table 2. The NO reaction rate is 
influenced by temperature, residence time and concentrations of nitrogen 
and oxygen in the combustion environment [Varatharajan and 
Cheralathan, 2012]. A correlation for the thermal NO emission index 
in automobile engines was developed by Saravanan et al. [2012]:

\[
\text{NEI} = 20956.69 \times (1 + C [1 - 9.91 \times 10^{-3} T^2 - 1.608L - 18.431]) 
\times \exp(2.9 \times 1D - 19.627) \times \exp\left(4626.4/\tau_f\right)
\]

predicted using this correlation agreed with experimental measurements 
within 20%.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>A (\text{cm}^3/(\text{gmol-s}))</th>
<th>n</th>
<th>(E_a/R_\text{(T_f)})</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>R1</td>
<td>O + N₂ ↔ NO + N</td>
<td>1.95E+14</td>
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<td>38367</td>
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<tr>
<td>R2</td>
<td>N + O₂ ↔ NO + O</td>
<td>6.40E+09</td>
<td>1</td>
<td>3160</td>
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<tr>
<td>R3</td>
<td>N + OH ↔ NO + H</td>
<td>3.80E+13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R4</td>
<td>CH + N₂ ↔ HCN + N</td>
<td>4.40E+12</td>
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<td>11060</td>
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<tr>
<td>R5</td>
<td>CH₂ + N₂ ↔ HCN + NH</td>
<td>1.00E+13</td>
<td>0</td>
<td>37240</td>
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<tr>
<td>R6</td>
<td>HCN + OH ↔ CN + H₂O</td>
<td>3.90E+06</td>
<td>1.83</td>
<td>5180</td>
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<tr>
<td>R7</td>
<td>CN + O₂ ↔ NCO + O</td>
<td>1.00E+13</td>
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<td>0</td>
</tr>
<tr>
<td>R8</td>
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<td>4.13E+10</td>
<td>0</td>
<td>7890</td>
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<tr>
<td>R9</td>
<td>N₂O + O ↔ NO + NO</td>
<td>6.60E+13</td>
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<tr>
<td>R10</td>
<td>O + NH₂ ↔ NO + NH</td>
<td>5.00E+13</td>
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<td>0</td>
</tr>
<tr>
<td>R11</td>
<td>HO₂ + NO ↔ NO₂ + OH</td>
<td>2.20E+12</td>
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<td>240</td>
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<tr>
<td>R12</td>
<td>O + NO₂ ↔ NO + O₂</td>
<td>3.90E+12</td>
<td>0</td>
<td>120</td>
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<tr>
<td>R13</td>
<td>H + NO₂ ↔ NO + OH</td>
<td>1.30E+14</td>
<td>0</td>
<td>180</td>
</tr>
<tr>
<td>R14</td>
<td>NH + NO ↔ N₂O + H</td>
<td>3.00E+18</td>
<td>-1.65</td>
<td>720</td>
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<tr>
<td>R15</td>
<td>NCO + NO ↔ N₂O + CO</td>
<td>1.40E+18</td>
<td>-1.73</td>
<td>384</td>
</tr>
</tbody>
</table>

*Rate constants are given by, \(k = A \times \exp\left(-E_a/R\_\text{\(T_f\)}\right)\)

2.1.2. Prompt mechanism
Fenimore identified another important pathway resulting in NO 
formation which is termed as prompt NO mechanism. It is significant in 
some combustion environments where low-temperature fuel-rich 
conditions prevail, while the residence time is short [Fenimore, 1971]. 
Prompt NO is produced when hydrocarbon radicals react with nitrogen 
to form highly reactive cyano radicals such as HCN in the combustion 
chamber [Fernando et al., 2006]. Prompt NO is also more sensitive to 
the fuel chemistry than thermal NO because of the dependence on 
hydrocarbon radicals. Miller and Bowman [1989] studied the mechanism 
and modeling of nitrogen chemistry in combustion and concluded that 
the prompt NO mechanism was important in the NO formation and 
could not be neglected while estimating the total NO₂ production, 
particularly in a fuel-rich combustion environment. The prompt NO 
mechanism involves a set of chemical reactions as shown by reactions R4 
to R7 in Table 2. Prompt NO formation increases with equivalence ratio 
due to the availability of CH, CH₂ and HCN radicals that are prevalent in 
fuel-rich hydrocarbon flames, reach a peak, and decreases because of 
lack of oxygen. These hydrocarbon and cyano radicals are considered to 
be the significant contributors of prompt NO.

2.1.3. Fuel NO mechanism
Fuel NO is formed when the fuel-bound nitrogen reacts with excess 
oxxygen during combustion and is negligible for both diesel and biodiesel 
combustion because of low nitrogen levels in the fuel; biodiesel has a 
mean nitrogen concentration of only 0.02%. The presence of nitrogen-
containing compounds such as pyridine, pyrrole etc. may also tend to 
form more fuel NO. This is due to the weaker C-N bond present in these 
chemical compounds compared to the N-N bond in molecular nitrogen. 
The fuel NO pathway involves the formation of nitro-radicals such as 
HCN, NH₂, NH, or CN, which then be oxidized to form NO [Fernando 
et al., 2006].

2.1.4. N₂O Intermediate mechanism
The intermediate mechanism (N₂O pathway) is another essential 
mechanism that becomes significant in high-pressure combustion processes 
[Dean and Bozzelli, 2000]. In this mechanism, the reaction occurs 
between N₂ and atomic oxygen to form intermediate N₂O by a three-
body recombination reaction (R8) where the collision partner M 
collectively represents all the molecules present in the combustion medium 
and plays a key role in the execution of this reaction. The N₂O formed in 
reaction (R9) can then react to form NO.

2.1.5. The NNH mechanism
Under certain combustion regions like flame fronts where atomic 
concentrations are high, (R10) contributes to NO production. This 
mechanism requires interaction between hydrogen atoms and molecular 
nitrogen to form highly reactive NNH radicals which further react with 
atomic oxygen to form nitric oxide [Dean and Bozzelli, 2000].
2.2 Nitrogen dioxide (NO$_2$) emission

In the previous section, several reactions that lead to the formation of NO were discussed. Under certain conditions, a significant amount of NO can be converted to NO$_2$. The fastest flame reaction forming NO$_2$ is R11 (Table 2), which is important whenever the concentration of NO is significant, typically in the temperature range of 600 to 1000 K under fuel-lean conditions. However, at higher temperatures NO dissociates quickly into H atoms and O$_2$ and the higher prevailing concentrations of H, O and OH lead to more rapid NO$_2$ loss through the reactions (R12 and R13). This rapid loss of NO$_2$ is significant and is reflected as a lower NO$_x$ concentration in the combustion flue gas.

2.3 Nitrous oxide (N$_2$O) emission

At low combustion temperatures and high pressures, nitrous oxide formation by the ter-molecular reaction (R8) is significant. The N$_2$O formed in this reaction reacts with oxygen atoms exothermally to form NO (as discussed in section 2.1.4). Various nitrogen-containing radicals contribute to the formation of N$_2$O as in R14 and R15. However, the N$_2$O formed in these reactions undergoes further reactions forming NO which is more stable than N$_2$O.

In a compression ignition engine, the combustion reactions are characterized by high temperature, varying residence time depending on the injection timing, localized fuel rich conditions (though overall fuel lean) and high pressure. These reactions favor NO formation predominantly, in different pathways described above, out of which the thermal and prompt mechanisms are considered to be significant in the biodiesel engine combustion.

3. Experimental evidences of biodiesel impact on NO$_x$ emission from compression-ignition engine exhaust

This section reviews the experimental studies on various aspects of engine operation, fuel properties and combustion processes and their influence on the emission of NO$_x$ measured in the engine exhaust.

3.1. Effects of fuel composition

The fuel composition is a broad factor which comprises of influential parameters such as fuel feedstock, level of unsaturation, biodiesel blend level, oxygen content and cetane number. The following section discusses the effect of these parameters on the NO$_x$ emission from the compression ignition engines.

3.1.1. Biodiesel feedstock / Level of unsaturation

Several studies reported differences in NO$_x$ emission of biodiesels from different feedstocks [Graboski et al., 2003; Saravanan et al., 2009; Saravanan et al., 2010; Hoekman and Robbins, 2012; Varatharajan and Cheralathan, 2012]. Graboski et al. [2003] conducted experiments with neat methyl esters and ethyl esters in a 6-cylinder, 4-stroke, direct injection diesel engine to understand the effect of hydrocarbon chain length on the NO$_x$ formation with saturated methyl esters based on their composition - lauric (C12), palmitic (C16) and stearic (C18) acids and found that esters with shorter carbon chain produced higher NO$_x$ emissions. For example, the specific NO$_x$ emission index of methyl stearate (C18) was about 8% lower than that of methyl laurate (C12). The authors also found a strong linear relationship between increasing NO$_x$ with level of saturation (number of double bonds) in the fuel. For example, the specific NO$_x$ emission index of C18 ester with three double bonds was 16% higher than that of C18 ester with one double bond. Possibly, the double bonds resulted in some pre-combustion chemistry that increased NO$_x$ formation. Finally, the authors concluded that the NO$_x$ emissions increased due to the decrease in average carbon chain length and increase in level of unsaturation; therefore, the most intrinsic way to revamp the emission performance was to alter the fuel chemistry, since molecular structure was the basis of fuel properties such as cetane number, density, boiling point and ignition delay. It is now widely acknowledged that increasing unsaturation and decreasing carbon chain length both lead to an increase in NO$_x$ emission. This information has been developed from the experimental and numerical demonstration in several works [Graboski et al., 2003; Sun et al., 2010; Xue et al., 2011; Hoekman and Robbins, 2012; Varatharajan and Cheralathan, 2012; Palash et al., 2013] involving pure FAME components as well as practical biodiesel fuels employing a wide variety of engines and test cycles. Lin et al. [2009] found that palm oil methyl ester (POME) and palm kernel oil methyl ester (PKOME) resulted in a lower increase (15% and 5% respectively) in NO$_x$ concentration (ppm) and a significant reduction (59% and 73% respectively) in smoke emissions than petroleum diesel and vegetable oil methyl ester (VOME) fuels (soy methyl ester, peanut oil methyl ester, corn oil methyl ester, sunflower oil methyl ester, rapeseed methyl ester and waste fried oil methyl ester). The authors attributed this behavior to the more saturated carbon bonds of POME (about 50%) and PKOME (about 80%), when compared to other VOME fuels, and suggested that a fuel with more saturated carbon bonds would result in reduced NO$_x$ emissions. The exact pathways by which the fuel composition effects influence NO$_x$ are still ambiguous, but these parameters are recognized to critically influence the observed NO$_x$ emissions.

3.1.2 Biodiesel content

Many publications in the literature suggest that NO$_x$ emission increased with the biodiesel content in the blend. Lertsathapornsuak et al. [2008] noted that the NO$_x$ emission index (g/kWh) increased about 12% and 5% for neat palm biodiesel (B100) and B50 than diesel at 25% load condition; and an increase of about 26% and 9% in NO$_x$ emission index for B100 and B50 while maintained the engine speed at 1500 rpm. A study by Luján et al. [2009] on high speed direct injection, 4-cylinder, diesel engine with high pressure common-rail injection system during the standardized MVEG-A cycle (European Motor Vehicle Emission Group A) simulated the road load conditions. It was fueled by biodiesel (from vegetable oil) and its blends B30, B50 and B100. The authors observed that the increase in NO$_x$ concentration (ppm) for B30, B50 and B100, compared to the base diesel fuel, was 21%, 26% and 45%, respectively. Similar trend was observed by Buyukkaya [2010] with rapeseed methyl ester/diesel blends. Gumus and Kasifoglu [2010] tested three blends of apricot seed kernel oil methyl ester (B5, B20 and B50) with diesel fuel in a compression ignition engine and found a monotonic increase in NO$_x$ concentration with the biodiesel content. They attributed this behavior to the fuel-bound oxygen of the biodiesel.

On the other hand, Kalligeros et al. [2003] found a monotonic decreasing trend of NO$_x$ concentration in the biodiesel blends containing 10%, 20%, and 50% of two types of methyl esters from sunflower oil and olive oil, in a single-cylinder diesel engine. At 3.80 kW load, B10, B20 and B50 of sunflower oil methyl ester with marine diesel produced about 3%, 5% and 6% lower NO$_x$ concentration, while B10, B20 and B50 of olive oil methyl ester produced about 8%, 14% and 14.5% lower NO$_x$ concentration than marine diesel. The variation in the NO$_x$ reduction potential between the different biodiesel feedstock was attributed to the difference in cetane number of biodiesels; it was hypothesized that the higher cetane number of olive oil methyl ester (CN: 61) than that of sunflower oil methyl ester (CN: 58) resulted in increased reduction of NO$_x$ concentration; the cetane index of marine diesel was reported as 46.

Interestingly, some other publications in the literature showed that the NO$_x$ emissions varied non-monotonically with the biodiesel content in the blend [Labbecks and Slanec, 2006; Lin et al., 2007; Pereira et al., 2007; Fountaras et al., 2009; Aydin and Bayindir, 2010]. The authors attributed these variations to the differences in the degree of evaporation and the combustion processes in the engine, since the calibration settings of the conventional diesel engine could have been not ideal for all proportion of biodiesel blends at all operating regimes. A non-monotonic NO$_x$ variation was observed with a water-cooled, single- cylinder compression ignition engine fueled with polanga methyl ester and its blends (20, 40, 60, and 80%) with diesel [Sahoo et al., 2007]. The NO$_x$ concentration from B20 was found to be 2% higher than diesel while neat biodiesel produced 4% lower NO$_x$. The authors attributed the variations to the differences in compression ratio, residence time and temperature distribution among the tested fuels. Biodiesels derived from jatropha, karanja and polanga oil and their blends (B20, B50 and B100) were tested in a 3 cylinder, compression ignition engine [Sahoo et al., 2009]. It was observed that the increase in NO$_x$ emission (with peak NO$_x$ occurred with biodiesel blends at all operating regimes. A non-monotonic NO$_x$ content, with diesel fuel in a compression ignition engine and found a monotonic increase in NO$_x$ concentration with the biodiesel content. They attributed this behavior to the fuel-bound oxygen of the biodiesel.

3.1.3 Oxygen content

The fuel-bound oxygen content of the blend is proportional to the volumetric concentration of biodiesel in the blend. Generally, the increased NO$_x$ emissions in biodiesel and their blends are attributed to the higher
oxygen content in the biodiesel [Godiganur et al., 2010; Gumus and Kasifoglu, 2010] due to a linear increasing trend of NOx with the increase in mass percentage of fuel oxygen. However, there are studies that do not agree with this linear increase; a linear decrease [Kalligeros et al., 2003] in NOx emission or a non-monotonic increase or decrease with the oxygen content in the fuel [Sahoo et al., 2007; Fontaras et al., 2009; Aydin and Bayindir, 2010] have been documented.

Canakci [2005] studied No. 2 diesel fuel (no fuel bound oxygen), No. 1 diesel fuel (no fuel-bound oxygen), SME (11% oxygen by mass / 3.6% oxygen by volume) and B20 (20% SDE and 80% No.2 diesel) (2.2 % oxygen by mass / 0.7 % by volume) in a turbocharged diesel engine and observed the brake specific NOx index (g/kWh) of the SME and B20 blend were increased by 11% and 1%, respectively compared to the No. 2 diesel. Similarly, the NOx emissions of SME fuel was about 6% lower than that of No. 2 diesel fuel, while there was no appreciable difference of oxygen concentration in the exhaust between the fuels tested. Therefore, in addition to the fuel-bound oxygen effect of biodiesel, more research is required to identify the properties that impact the combustion reactions favoring NOx emission. Puhan et al. [2005] questioned the availability of fuel-bound oxygen for NOx formation and argued that the esters might decarboxylate and form CO2 early during the combustion. It is evident that additional studies are essential to understand the significance of fuel-bound oxygen effect, especially their impact in the formation of NOx during combustion in engines.

3.1.4 Effects of cetane and iodine numbers

Auto-ignition of the injected fuel is a critical factor in the performance and operation of compression ignition engines. Cetane number is a property of the fuel that quantifies the self-ignition characteristics and ignition delay time of a fuel in an engine cycle; the higher the cetane number, the shorter the ignition delay [Pulkrabek, 2004]. Cetane numbers for various esters of the saturated fatty acids ranging from C8 to C18 have been determined according to ASTM D613. For methyl esters, the cetane number would be found to increase nonlinearly with the fatty acid chain length [Klopfenstein, 1985]. The higher cetane number of biodiesel reduces the ignition delay and also leads to the advancement in combustion. Consequently, with the availability of oxygen, higher temperature together with longer residence time, may lead to the increase of NOx emissions. Several researchers, e.g., Lim et al. [2014] used this reasoning to describe the increased NOx emissions with biodiesel content. However, this reasoning is debatable. Higher cetane number results in not only an early onset of combustion, but also leads to lower amount of fuel burning in the premixed-combustion mode, which result in lower temperature and residence time in the combustion chamber, causing a lower NOx formation. Wu et al. [2009] observed that the brake specific NOx emission index (g/kWh) of palm methyl ester (PME) was 7% lower than that of waste oil methyl ester (WME), even though both had almost the same oxygen content of about 11.2% by mass. This was credited to the higher cetane number of PME (64 for PME compared to 56 for WME) which could reduce ignition delay and amount of fuel consumed in the premixed phase, resulting in a reduction of in-cylinder temperature and subsequently reducing NOx emission. Many authors [Gaboroski et al., 2003; Kalligeros et al., 2003; Puhan et al., 2005; Knothe et al., 2006; Karavalakis et al., 2009] concluded that NOx emissions decreased with an increase in cetane number.

3.2. Influence of type of engine and test cycle

Engine type and its test cycles could strongly influence the NOx emission of biodiesels. Tat [2003] demonstrated that the NOx emission from compression ignition engines was significantly influenced by the variation in injection timing and advance due to the impact of fluid properties such as density, isentropic bulk modulus (compressibility) and viscosity. Karavalakis et al. [2009] studied the exhaust emission characteristics of ultra-low sulphur diesel and soy biodiesel blends at proportions of 10% and 30% by volume in a Euro 4 common rail injection diesel engine over various engine test cycles namely New European Driving Cycle (NEDC) and non-legislated Artemis driving cycles which simulate urban, rural and highway driving conditions in Europe. It is interesting to note that driving test cycles significantly influence the amount of NOx emitted during the operation. Among the three Artemis driving cycle conditions, B10 and B30 produced higher NOx (g/km) than the base line diesel. During urban driving conditions, B10 and B30 produced the highest increase in NOx as 14% and 18% respectively. However, in NEDC test cycle, NOx emissions were slightly reduced for both B10 and B30 by 3% and 4% respectively. The authors attributed this observed reduction in NOx to the smooth acceleration profile of NEDC, which dominated the NOx emission mechanism than the physicochemical characteristics of biodiesel. Moreover, the Artemis driving cycles were more aggressive and transient, which would inherently favor the increase of NOx emissions. Hence, although the physicochemical properties and fuel chemistry properties such as saturation level and cetane number play certain roles in the NOx emissions, their relative importance when compared to the engine parameters and the nature of test cycle in certain conditions are inconclusive. Several researchers, e.g., Lim et al. [2014] studied rapeseed methyl ester and its blends B10, B20 and B50 with diesel in three different vehicles (equipped with different exhaust after treatment technologies) over test cycles namely NEDC which is a standard test cycle in Europe and real world testing cycles such as Artemis Urban and Artemis Road. In general, among all the tested conditions, NOx (g/kWh) increased up to 20% with B50 in some cases while most showed an increase in the range of 1 to 10% depending on the blend and the vehicle. Serrano et al. [2015] tested diesel and 20% biodiesel blend (from soy and palm feedstock) in three different test cycles, namely NEDC, URBAN and EXTRA URBAN test cycle. In all three cycles, B20 had lower NOx emission index (g/kWh) than diesel, but the reduction percentage varied with cycles as 10%, 20% and 5% respectively. In summary, all these studies reported different trends with different combination of engine test cycles, biodiesel feedstock and content. Hence the biodiesel and its blending effect on NOx are inconclusive in terms of engine test cycle since several engine and combustion parameters influence the emission characteristics of a particular test cycle which can overshadow the actual emission potential of a particular fuel or fuel blend.

3.3. Effect of injection timing

The fuel injection is an important process in the engine operation and the timing of fuel injection into the combustion chamber is critical and affects the mixture formation and the pre-mixed combustion. Cetane number of biodiesel is greatly influenced by the fluid dynamic properties of the fuel and NOx formation appeared to be dependent on the start of injection timing in compression ignition engines. [Tat et al., 2000; Tat and Van Gerpen, 2003; Boehman et al., 2004; Agarwal et al., 2013]. Carraretto et al. [2004] studied the effect of advance in injection timing (at three crank angle degrees) on NOx emissions from neat methyl oleate. Many authors [Karabalakis et al., 2003; Fossantos et al., 2011] tested soy biodiesel, diesel and their blends (B2, B10, B20) in a locomotive operated in different two cycles namely line haul and switch cycle. The changes in cycle weighted average of NOx (g/kWh) for B2, B10 and B20 were comparable between two cycles, while B100 in switch cycle increased NOx by about 15% over the line haul cycle. Fontaras et al. [2014] studied rapeseed methyl ester and its blends B10, B20 and B50 with diesel in three different vehicles (equipped with different exhaust after treatment technologies) over test cycles namely NEDC which is a standard test cycle in Europe and real world testing cycles such as Artemis Urban and Artemis Road. In general, among all the tested conditions, NOx (g/km) increased up to 20% with B50 in some cases while most showed an increase in the range of 1 to 10% depending on the blend and the vehicle. Serrano et al. [2015] tested diesel and 20% biodiesel blend (from soy and palm feedstock) in three different test cycles, namely NEDC, URBAN and EXTRA URBAN test cycle. In all three cycles, B20 had lower NOx emission index (g/kWh) than diesel, but the reduction percentage varied with cycles as 10%, 20% and 5% respectively. In summary, all these studies reported different trends with different combination of engine test cycles, biodiesel feedstock and content. Hence the biodiesel and its blending effect on NOx are inconclusive in terms of engine test cycle since several engine and combustion parameters influence the emission characteristics of a particular test cycle which can overshadow the actual emission potential of a particular fuel or fuel blend.

3.4. Effect of engine speed

Engine speed also plays a critical role in the formation of NOx in
compression ignition engines. Several studies proposed that NOx emissions decreased with engine speed [Lin and Li, 2009; Imtanean et al., 2014]. The NOx concentration (ppm) decreased by about 23% between engine speeds of 800 rpm and 2000 rpm for petroleum diesel and biodiesels from cooking oil and marine fish oil in a 4-stroke direct injection, naturally aspirated diesel engine [Lin and Li, 2009]. The authors concluded that, although the increased engine speed caused an increase in the temperature and pressure of burning gas, the reduction of ignition delay resulted in the reduction of residence time available for NOx formation. Interestingly, different trends of NOx emission were reported at two different engine speeds (2000 and 4000 rpm) at the full load condition when diesel, biodiesel from waste cooking oil and their blends of 10%, 20%, 40% and 60% (by volume) were studied in a common rail Euro 3 diesel engine [Zhang et al., 2009]. At 2000 rpm, higher NOx concentration (ppm) was observed with the biodiesel content in the blend, especially with blends higher than 40% of biodiesel content. B100 had about 13% higher NOx concentration than the diesel. However, at 4000 rpm, the NOx concentration did not show any variation with biodiesel content. The authors attributed the observed trends to the common rail injection system where the impact of advanced injection of biodiesel due to higher bulk modulus, density and mechanical pump is no longer a significant factor.

Moreover, a non-monotonic variation of NOx was observed with engine speeds in some studies. Usta [2005] observed different effects of engine speed on NOx concentration (ppm) at different conditions, that is, as engine speed was increased (between 1500 rpm and 3000 rpm), the NOx concentration increased by about 74% at full load, and increased by about 33% at three fourth of rated load, but gradually decreased by 28% at half load for both diesel and its blend (D82.5/TSONE17.5, by volume) with tobacco seed oil methyl ester. Non-monotonic variation of NOx was also reported in several other studies which employed biodiesels different feedstocks ranging from waste frying oil [Usito and Kocak, 2008], tall oil [Keskin et al., 2008], vegetable oil [Chokri et al., 2012], cooking oil [Arslan, 2011], calophyllum inophyllum linn oil which consists of mostly unsaturated fatty acids [Fattah et al., 2014]. A limited source of explanation has been reported in the literature on the engine speed effect on NOx formation. Several studies attributed various parameters such as availability of oxygen, in-cylinder combustion temperature and residence time to the variation of NOx between fuels; but no explanation was given to the non-monotonic effect of engine speed on NOx emissions.

3.5 Effect of engine load

The biodiesel NOx effect was significantly influenced by engine load when tested with biodiesel and its blends with diesel in diesel engines. Several studies reported a monotonic increase in NOx with engine load due to higher temperature generation with increase in load. Usta [2005] reported a monotonic increase of NOx concentration (ppm) at full load for both diesel and its blend (D82.5/TSONE17.5, by volume) with tobacco seed oil methyl ester. Moreover, a non-monotonic variation of NOx was observed with different loads at a given compression ratio. Hence, the engine parameters and the associated phasing of combustion complicate the understanding of already entangled biodiesel and its blending effect on NOx formation in compression ignition engines.

3.6 Fluid dynamics effects

Fluid dynamics of the fuel spray is an important and highly complex phenomenon that significantly influences the phasing of combustion [Sirignano, 1993]. The fuel spray characteristics such as injector penetration length, atomization and mean droplet size along with flow field and heat transfer interactions between droplets are critically influenced by various physical properties of the fuel. Especially, the differences in properties such as density, viscosity, surface tension, etc., between biodiesel and petroleum fuels influence the combustion process and can affect NOx emission [Allen and Watts, 2000; Lee et al., 2005; Ejim et al., 2007; Suh et al., 2007]. Avinash et al. [2007] found a surprising decrease in NOx emissions with load in a single-cylinder, naturally aspirated direct injection diesel engine. A substantial reduction of about 60% in the specific NOx emission (g/kWh) between 25% load and full load when tested with B100 was observed. The authors attributed this trend to the increase in turbulence inside the cylinder, which contributed to a quicker combustion and resulted in lower residence time of the species in the high temperature zones. Agarwal and Rajamohanvar [2009] tested karanja biodiesel and blends (B10, B20, B50 and B75) with diesel in a single cylinder agricultural engine. The authors observed that the neat biodiesel and all the tested blends had comparable NOx emission index (g/kWh), while they were about 45% lower than that of diesel at 20% load.

On the other hand, a non-monotonic response of NOx for the use of biodiesels and their blends with diesel has been widely reported in the literature [Raheman and Phadate, 2004; Suresh Kumar et al., 2008; Dhar et al., 2012; Agarwal and Dhar, 2013; Chavan et al. 2015]. A non-monotonic variation of NOx with the biodiesel content over a wide range of loads was observed by Raheman and Phadate [2004] while testing karanja methyl ester and its blends (B20, B40, B60, B80, by volume) with diesel in a single cylinder, 4-stroke, water-cooled direct injection diesel engine. At full load condition, B20 and B80 produced about 23% lower NOx concentration (ppm) than diesel; while B60 and B100 produced about 38% lower NOx than diesel and B40 recorded about 15% lower NOx than diesel. Hence, it is clear that NOx is sensitive to load where changes in the loading conditions could possibly reverse the NOx formation trends. Suresh Kumar et al. [2008] also observed a non-monotonic variation in NOx concentration with biodiesel content for a wide range of loading conditions while testing pongamia pinnata methyl ester and its blends (B20, B40, B60, B80, by volume) in a similar engine. At 75% load condition, B20 and B100 produced 8% and 25% lower NOx concentration (ppm) than diesel; while B40, B60 and B80 produced about 38% lower NOx than diesel. Though the NOx concentration was decreased with the biodiesel content in the blend, the extent of reduction in NOx was not proportional with the biodiesel content. Agarwal and Dhar [2013] tested karanja biodiesel and blends (B10, B50) with mineral diesel in a direct injection diesel engine. It was observed that B50 and B20 produced 2000 and 6000 rpm, on an engine, B100 had a minimal effect on the spray development. Lower injection velocity of biodiesel due to higher viscosity, and the associated increase in friction between biodiesel spray and nozzle surface causes shorter spray tip penetration; while higher SMD of the biodiesel spray causes a longer tip penetration. These two compensating effects resulted in a similar spray tip
penetration between diesel, biodiesel and their blends. Ejim et al. [2007] reasserted the findings by Allen and Watts [2000] and reported comparable SMDs among neat palm, soybean, cotton seed, peanut and canola biodiesel and their corresponding B5 and B20 blends with No.2 diesel. In a computational study by Yuan and group [2007], for a given engine speed and load, the maximum spray cone angle of diesel and soy biodiesel was found to be 47.5° and 30° and soy biodiesel produced about 8% higher brake-specific NOx than diesel. When the spray cone angle of soy biodiesel was matched with diesel (47.5°), the brake-specific NOx was reduced by 15% between cone angles of 30° and 47.5° of soy biodiesel spray. The authors concluded that a narrow spray angle could significantly emit higher NOx since the narrow sprays induce strong stratification of fuel vapor which brings about local rich or stoichiometric regions that contribute to higher NOx. Yuan and Hansen [2009] predicted that NOx (g/kWh) decreased up to 3.5% when the viscosity of SME was decreased to match with petroleum diesel fuel. They also suggested that smaller spray cone angles and advanced start of injection were the main reasons for increased NOx emission of biodiesel. They concluded that the decreased spray cone angle and increased spray penetration might increase NOx emission. Agarwal and Chaudhury [2012] investigated the spray characteristics in a constant volume spray chamber with diesel, karanja biodiesel and their blends, B5 and B20, and concluded that B100 had highest spray tip penetration, cone angle and spray area followed by B20, B5 and diesel.

In addition to density, surface tension and viscosity, the boiling point of biodiesel could also significantly alter the spray characteristics; higher boiling point of biodiesel increases the combustion duration and cylinder gas temperature both of which could favor NOx formation [Ozezen et al., 2008]. In a recent study, the spray, combustion and exhaust emission characteristics of soy biodiesel in a direct injection common-rail diesel engine were investigated by Yoon et al. [2009] who observed that biodiesel produced larger droplet size (about 12%), similar spray structure, and longer spray tip penetration (about 8% higher) into the cylinder than conventional diesel, which resulted in an increased indicated specific NOx emissions of soy biodiesel by about 19% higher than that of diesel. Ye and Boehmnan [2010] studied the effect of engine injection strategies on the biodiesel NOx effect with a direct injection diesel engine fueled with ultra-low sulphur diesel and its blend with soy biodiesel (B40). For a given speed and load, a higher volume of biodiesel has to be supplied because of its lower heating value compared to petroleum diesel. The increase of fuel consumption could be accomplished by either higher injection pressure or injection duration, which would result in increased NOx emission. Injection characteristics such as mean injection rate, mean injection pressure, injection delay and injection duration increase with the biodiesel content, which could favor NOx formation at certain conditions. Hence, the relative discussed physical properties and their effects on the fluid dynamics of the fuel spray and atomization have critical impact on the combustion and emission characteristics of a fuel at any particular operating condition.

4. Conclusions

In this article, the key parameters that influence NOx emissions in diesel engines fueled with biodiesel blends were identified and broadly classified as fuel chemistry effects, engine control effects and fluid dynamics effects. In most engine studies, with a few exceptions, biodiesel or biodiesel blends resulted in increased NOx emission compared to baseline diesel; however, the change in NOx emission for blends varied non-monotonically with the biodiesel content due to a complex dependence of NOx formation on various factors at various conditions. The relative significance and extent of influence of various physico-chemical factors reviewed in this article differ with engine type, cycle and operating conditions. Hence, a holistic approach is needed to investigate the biodiesel blending effect on NOx emission by discerning the influential factors and then integrating the appropriate individual findings along with the corresponding coupled effects of thermo-fluid-chemical interactions for the particular combustion environment.

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References


| Table 3: Physical and Chemical properties of various methyl esters of fatty acids* |
|------------------|------------------|------------------|------------------|
| Biodeiesel Type  | Density kg/m³    | Kinematic viscosity at 40°C mm²/s | Cetane number |
| Coimbatore       | 918              | 2.7                   | 77.6             |
| Cotton           | 919              | 2.7                   | 75.0             |
| Fish oil         | 920              | 2.8                   | 72.8             |
| Jatropha         | 921              | 2.9                   | 69.4             |
| Linseed          | 922              | 2.9                   | 69.0             |
| Mahua            | 923              | 2.9                   | 65.0             |
| Neem             | 924              | 2.9                   | 62.0             |
| Peanut           | 925              | 2.9                   | 66.0             |
| Palm             | 926              | 2.9                   | 67.0             |
| Pea              | 927              | 3.0                   | 69.0             |
| Rice bran        | 928              | 3.0                   | 70.0             |
| Sunflower        | 929              | 3.0                   | 71.0             |
| Yellow grease    | 930              | 3.0                   | 72.0             |

Ozsezen et al., 2009; Sahoo et al., 2009; Sarin et al., 2009; Wu et al., 2009; Yuan and Hansen, 2009; Karmakar et al., 2010; Pugazhvadivu and Sankarnarayanan, 2010; Varatharajan and Cheralathan, 2012; Chhetri and Watts, 2013; Foroughi et al., 2014; Philipp et al., 2015; Moti et al., 2016.


