Impacts of biodiesel combustion on NO\textsubscript{x} emissions and their reduction approaches

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**A B S T R A C T**

Increasing energy demand and environment concerns have prompted an evolution of alternative fuel sources. As an alternative fuel source, biodiesel is attractive because it reduces engine emissions. However, biodiesel produces higher NO\textsubscript{x} emissions compared to ordinary diesel fuel. Previous researches have established many factors that cause biodiesel to produce elevated NO\textsubscript{x} emissions. This study reviews the impacts of biodiesel combustion on NO\textsubscript{x} emissions and their reduction approaches in diesel engines. The first part of this study recapitulates the NO\textsubscript{x} formation mechanisms for understanding the kinetics behind the NO\textsubscript{x} formation reactions. The second part describes the factors affecting on NO\textsubscript{x} emissions. This paper established that higher NO\textsubscript{x} emissions are produced for biodiesel combustion which is influenced by several factors such as physicochemical properties and molecular structure of biodiesel, adiabatic flame temperature, ignition delay time, injection timing and engine load conditions etc. The final section discusses on the reduction of NO\textsubscript{x} emissions from biodiesel fuelled engines for both pre and post combustion techniques. The results of reduction approaches of the NO\textsubscript{x} emissions implies, exhaust gas recirculation (EGR) and retarded injection timing are effective as well as low cost techniques than others. Between these two techniques, EGR reduces the NO\textsubscript{x} emissions at 5–25% EGR rate adequately in biofuelled engine by controlling oxygen content and combustion peak temperature with slightly decreasing HC and CO emissions. However this technique shows few penalties on smoke and PM emissions as well as brake specific fuel consumption if not perfectly optimized.

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Abbreviations: NO\textsubscript{x}, oxides of nitrogen (NO, NO\textsubscript{2}); HC, Hydrocarbon; CO, carbon monoxide; PM, particulate matter; \(T_{\text{ad}}\), adiabatic flame temperature; NHD, n-hexadecane; HMN, 2,2,4,4,6,8,8-heptamethylnonane; CN45, 35.3 vol% NHD with balance HMN; CN70, 64.7 vol% NHD with balance HMN; CN45, 35.3 vol% NHD with balance HMN; IMEP, indicating mean effective pressure; SOI, start of injection; \(\phi\), stoichiometric air fuel mixture; BSFC, brake specific fuel consumption; BTE, Brake thermal efficiency; FAME, fatty acid methyl ester; JME, jatropha oil methyl ester; JOME, jojoba oil methyl ester; SME, soybean oil methyl ester; SOME, sunflower oil methyl ester; WOME, waste cooking oil methyl ester; CSOME, cottonseed oil methyl ester; COME, corn oil methyl ester; CME, canola oil methyl ester; NOME, neem oil methyl ester; ROME, rapeseed oil methyl ester; TOME, tall oil methyl ester; CNOME, coconut oil methyl ester; TPOME, thevetia peruviana oil methyl ester.

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1. Introduction

Petroleum-based fuels play a very significant role in the fields of industrial growth, transportation, agriculture, etc, due to their availability, combustion properties and high heating value. However, the reserves of these fuels are rapidly depleting due to increased fuel consumption. According to the estimation of the International Energy Agency, by 2030 global energy consumption will be increased about 53\% [12]. The United States Energy Information Administration (EIA) has projected that the world’s liquid fuel consumption will increase from 86.1 million barrels/day, to 110.6 million barrels/day by 2035 [3,4]. The emissions caused by the burning of petroleum-derived fuels have a serious effect on both the environment as well as human health. Fossil fuel depletion, increasing the price of fossil fuel and global environmental concerns have generated more interest in alternative, environmentally friendly sources of fuel. Therefore, it has become a global agenda to develop clean alternative fuels that are domestically available, environmentally acceptable, and technically feasible. Biodiesel is considered as a better choice of alternative fuel due to its environmentally friendly characteristics and similar functional properties of diesel fuel. Biodiesel has an immense potential to be a part of the future energy mix. In developing countries, using biodiesel in internal combustion engines can play an important role in reducing the fossil fuel demand, the environmental impact, and the adverse effects on human health [5]. Biodiesel is renewable and can be produced directly from edible and non-edible vegetable oils, recycled waste vegetable oils, and animal fats through the transesterification process [2]. Generally, biodiesel fuels offer reduction of harmful pollutant emissions such as CO, HC and PM, but it produces higher NO\textsubscript{x} emissions [6–16]. The NO\textsubscript{x} emissions are the most harmful parameters that affect the environment through acid rain, human disease, etc. Furthermore, CO and NO are primary pollutants in the formation of tropospheric ozone, which is an important greenhouse gas [17]. The United States Environmental Protection Agency (EPA) estimated an average 10\% increase in NO\textsubscript{x} emissions for a pure (100\%) biodiesel fuel compared to conventional diesel fuel [4,18]. Wu et al. [19] found that the reduction of exhaust emissions fuelled with five types of biodiesel individually as a range such as PM, dry soot, HC and CO to be about 53–69\%, 79–83\%, 45–67\%, 4–16\%, respectively, but an increase in NO\textsubscript{x} of 10–23\% compared with petroleum diesel. Very few authors have found reduced the NO\textsubscript{x} emissions for biodiesel fuels combustion [20–22]. Sun et al. [10] reported that biodiesel fuel gives higher NO\textsubscript{x} due to: the advancement of injection timing, the higher T\textsubscript{ad}, less radiative heat transfer, increase in ignition delay, higher degree of unsaturation, and high oxygen content, etc. As use of biodiesel in diesel engine has increased tremendously, higher NO\textsubscript{x} emissions could become a significant barrier to its spread in the market. Therefore researchers are persistently looking for a reliable and economically viable solution to this problem. Some of them have already managed to establish some techniques. This will help end users to overcome the problem of biodiesel expansion.

Many researchers have examined the combined analysis of the effect of biodiesel combustion on engine performance and emissions; and reduction of the NO\textsubscript{x} emissions but few of them attempted to review them [23,24]. This paper presents a comprehensive review on the effects biodiesel combustion on NO\textsubscript{x} emissions of biodiesel fuelled engines, in order to provide useful information to engineers, policy makers, industrialists and researchers. Articles from highly rated journals as well as SAE technical papers are reviewed to discuss the notable factors affecting NO\textsubscript{x} emissions of biodiesel fuel. Finally, reduction techniques of the NO\textsubscript{x} emissions (both pre and post combustion) are described for biodiesel fuelled engine.

2. NO\textsubscript{x} formation mechanisms

Nitrogen oxide is the generalized term for NO and NO\textsubscript{2} given with the formulae of NO\textsubscript{x} [25]. Understanding the kinetics behind the NO\textsubscript{x} forming reaction is important for taking attempt to reduce the NO\textsubscript{x} emissions. The thermal (Zeldovich), prompt (Fenimore), N\textsubscript{2}O pathway, fuel-bound nitrogen and the NNH mechanism are the most common mechanisms for NO formation in diesel combustion [26]. Among them thermal and prompt are the dominant mechanisms of NO\textsubscript{x} formation in biodiesel combustion [27]. The atmospheric or molecular nitrogen is the main source of nitrogen for NO\textsubscript{x} formation during conventional combustion of typical petroleum and bio-based fuels. Based on literatures, the general NO\textsubscript{x} formation mechanisms are summarized below [10,23,28–32].

2.1. Zeldovich mechanism

NO\textsubscript{x} formation occurs at temperature above 1700 K by this mechanism [23]. At this temperature nitrogen (N\textsubscript{2}) and oxygen
(O\textsubscript{2}) react through a series of chemical steps known as Zeldovich mechanism. The rate of formation increases rapidly with temperature. This mechanism of thermal NO\textsubscript{x} formation is believed to be the predominant contributor of total NO\textsubscript{x}. The basic kinetic equations for thermal NO\textsubscript{x} formation are described by the following chemical reactions (1)–(3).

\begin{align*}
N\textsubscript{2} + O\rightarrow& NO + N \quad (1) \\
N + O\textsubscript{2} + NO + O \rightarrow& NO + O\textsubscript{2} + N \quad (2) \\
N + OH + NO + H \rightarrow & NO\textsubscript{2} + H\textsubscript{2} \quad (3)
\end{align*}

The first step is rate limiting, and due to its high activation energy (314 kJ/mole), requires high temperatures to proceed. Reaction (3) is only significant under reducing conditions. Residence time and the concentration of nitrogen and oxygen also have an influence on the production of thermal NO [28]. Hu and Huang [33] theoretically proved that NO\textsubscript{x} formation depends directly on two factors: the concentration of reactants, and temperature.

2.2. Prompt or Fenimore mechanism

The presence of a second mechanism leading to NO\textsubscript{x} formation was first identified by Fenimore and was termed “prompt NO\textsubscript{x}”. There is a good evidence that prompt NO\textsubscript{x} can be formed in a significant quantity in some combustion environments; such as in low-temperature, fuel rich conditions and where residence time is short [32,34]. Prompt NO\textsubscript{x} is most prevalent in rich flames. The actual formation involves a comply series of reactions and many possible intermediate species. Prompt NO\textsubscript{x} is produced when hydrocarbon fragments react with nitrogen in the combustion chamber to form fixed nitrogen species such as HCN [35]. After that these nitrogen-containing fragments react with atmospheric nitrogen. Prompt NO\textsubscript{x} is more sensitive than thermal NO\textsubscript{x} in fuel chemistry because of the dependence on hydrocarbon fragments. Miller and Bowman [36] studied the mechanism and modeling of nitrogen chemistry in combustion and stated that in order to estimate the total NO\textsubscript{x}, the prompt NO\textsubscript{x} must be considered, which was also verified by the recent study by Ren and Li [37]. The prompt NO\textsubscript{x} is generally formed through the following reactions (4) to (8).

\begin{align*}
CH + N\textsubscript{2} \rightarrow & HCN + N \quad (4) \\
CH\textsubscript{2} + N\textsubscript{2} \rightarrow & HCN + NH \quad (5) \\
N + O\textsubscript{2} \rightarrow & NO + O \quad (6) \\
HCN + OH \rightarrow & CN + H\textsubscript{2}O \quad (7) \\
CN + O\textsubscript{2} \rightarrow & NO + CO \quad (8)
\end{align*}

Here, CH and CH\textsubscript{2} are the significant contributors to form prompt NO\textsubscript{x} (Eqs. (4) and (5)). The formation of prompt NO\textsubscript{x} is proportional to the number of carbon atoms in each unit volume. Prompt NO\textsubscript{x} is independent of the parent hydrocarbon. The amount of HCN increases with increasing the concentration of hydrocarbon radicals which enhances with increasing equivalence ratio. Prompt NO\textsubscript{x} formation increases with an increasing equivalence ratio and then reaches a peak and decreases because of a shortage of oxygen.

2.3. Fuel NO\textsubscript{x} mechanism

Fuel NO\textsubscript{x} is formed when nitrogen that is chemically bound in the fuel combines with excess oxygen during the combustion process. The type of NO\textsubscript{x} is negligible for both diesel and biodiesel because of low nitrogen levels [23]. Biodiesel has an average nitrogen concentration of only 0.02% [35]. Addition of additives containing nitrogen atoms e.g. pyridine, pyrrole etc. may lead to more fuel NO\textsubscript{x} formation. This can be attributed to weaker C–N bond compared to N–N bond. The C–N bond in pyridine and pyrrole are shown in Fig. 1. The main pathway for this type of NO\textsubscript{x} formation involves the creation of intermediate nitrogen containing species such as HCN, NH\textsubscript{x}, NH, or CN. These molecules can then be oxidized to form NO\textsubscript{x} [34].

2.4. N\textsubscript{2}O pathway mechanism

The NO\textsubscript{x} formation due to the N\textsubscript{2}O pathway is another essential mechanism in a combustion process under high pressure and lean air-fuel ratio compared with Fenimore NO\textsubscript{x} and a minor contribution to the formation of NO\textsubscript{x} related to the thermal NO mechanism [38]. In this mechanism, the reaction occurs between N\textsubscript{2} and atomic oxygen to form N\textsubscript{2}O by a three-body reaction.

\begin{equation}
O + N\textsubscript{2} + M \rightarrow N\textsubscript{2}O + M
\end{equation}

Here, the molecule M is required to execute this reaction. The N\textsubscript{2}O formed in reaction (9) can then react to form NO which is shown in Eq. (10).

\begin{equation}
N\textsubscript{2}O + O \rightarrow NO + NO
\end{equation}

2.5. The NNH mechanism

Under the condition of high concentration of atoms in fronts of flame in combustion process the reaction (Eq. (11)) contributes significantly to produce NO.

\begin{equation}
O + NNH \rightarrow NO + NH
\end{equation}

The mechanism requires the participation of H atoms to form NNH (diazanul) from N\textsubscript{2}, as well as O atoms to react with NNH [26].

3. Factors affecting NO\textsubscript{x} emissions

Many researchers have proposed many possible reasons for the increase of NO\textsubscript{x} emissions when biodiesel is used in diesel engine [10,23,28]. Summarizing of the review on factors affecting biodiesel NO\textsubscript{x} as well as other criteria emissions is presented in Table 1. On the other hand few of them also found reduced NO\textsubscript{x} emissions using biodiesel fuels [39,40]. They have also proposed other mechanisms. No single factor is responsible for these NO\textsubscript{x} effects. However the exact cause is still under investigation. The possible causes that have been proposed by the researchers to explain the biodiesel NO\textsubscript{x} increase are presented in this section.

3.1. Physicochemical properties of biodiesel

The physical and chemical properties of biodiesel such as: viscosity, density, bulk modulus of compressibility, sound velocity, cetane number, iodine value, surface tension, thermal conductiv-

![Fig. 1. Organic, fuel bound nitrogen compounds in solid fuels.](image)
### Table 1

Summarizing the review on factors affecting biodiesel NO$_x$ as well as other criteria emissions.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Engine used &amp; condition</th>
<th>Results compared to diesel fuel (%)</th>
<th>Explanation for higher NO$_x$</th>
<th>Source</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>NO$_x$</td>
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<tr>
<td></td>
<td></td>
<td>Others emission</td>
<td></td>
<td></td>
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</tbody>
</table>
| POME25             | ILROSKAR TV-1, IC, DI, NA, WC, DE, Max power output: 5.2 kW, IT 23.51
|                    |                                                                                        | ↑ high                             | Fuel burn during the late phase | [41]   |
|                    |                                                                                        | ↑ less                             | of combustion resulting in      |        |
|                    |                                                                                        | ↑ less                             | higher exhaust temperature      |        |
|                    |                                                                                        | ↑ less                             | because of having higher        |        |
|                    |                                                                                        | ↑ high                             | molecular weights.              |        |
|                    |                                                                                        | ↑ high                             | Higher the number of double     |        |
|                    |                                                                                        | ↑ high                             | bounds in the biodiesel         |        |
|                    |                                                                                        | ↑ high                             | molecular structure.            |        |
|                    |                                                                                        | ↑ high                             |                               |        |
|                    |                                                                                        | ↑ high                             |                               |        |
| POME50             | MP, full load, CS = 1500 rpm                                                           | ↑ high                             |                               |        |
| POME75             | Max engine power of 44 kW at 2132 rpm, 8-mode cycle                                    | ↑ high                             |                               |        |
| POME100            |                                                                                       | ↑ high                             |                               |        |
| POME20             | 3C, 2.5L Perkins AD 3–152 Max engine power                                            | ↑1.24                              |                               |        |
|                    | of 44 kW at 2132 rpm, 8-mode cycle                                                     | ↑(0.32 – 25)                       |                               |        |
| POME50             |                                                                                       | ↑ high                             |                               |        |
| ROME100            |                                                                                       | ↑ high                             |                               |        |
| ROME100            |                                                                                       | ↑ high                             |                               |        |
| ROME80             |                                                                                       | ↑ high                             |                               |        |
| ROME100            |                                                                                       | ↑ high                             |                               |        |
| ROME50             |                                                                                       | ↑ high                             |                               |        |
| WOME5, WOME10, WOME20, WOME30 |                                                                                       | ↑ high                             |                               |        |
|                    |                                                                                       | ↑ high                             |                               |        |
| WOME25, WOME50, WOME75 |                                                                                       | ↑ high                             |                               |        |
|                    |                                                                                       | ↑ high                             |                               |        |
| SWE5               |                                                                                       | ↑ high                             |                               |        |
| SWE20              |                                                                                       | ↑ high                             |                               |        |
| SWE50              |                                                                                       | ↑ high                             |                               |        |
| SWE100             |                                                                                       | ↑ high                             |                               |        |
| JME5, JME10, JME20, JME50 & JME100 |                                                                                       | ↑ high                             | The higher bulk modulus           |        |
|                    |                                                                                       | ↑ high                             | and sound velocity and viscosity,|        |
|                    |                                                                                       | ↑ high                             | lead to an advanced              |        |
|                    |                                                                                       | ↑ high                             | start of injection. This,       |        |
|                    |                                                                                       | ↑ high                             | jointly with any cetane number   |        |
|                    |                                                                                       | ↑ high                             | increase, may slightly advance   |        |
|                    |                                                                                       | ↑ high                             | the start of combustion.         |        |
Fuel viscosity has a significant effect on NOx emissions. Anderson and Olsen [54] analyzed NOx emissions as a function of viscosity and found an increase in NOx with increasing viscosity at low temperatures. Generally, the kinematic viscosity of biodiesel is greater than that of diesel fuel (Table 2), which reduces fuel leakage during injection and leads to increased pressure as well as advanced injection timing [55]. The advance in injection timing facilitates increased fuel mass injection which in turn results in increased NOx emissions. Moreover, Yuan and Hansen [56] observed reduced NOx emissions of about 3.52% with reduced viscosity of soy methyl ester to a level of petroleum diesel fuel. The NOx emissions increase with increasing fuel density as well as decreasing cetane number (CN) [29,57,58]. The start of injection (SOI), the injection pressure, and the fuel spray characteristics are affected by the fuel density, which influences combustion as well as emissions. In modern diesel engines, fuel injection systems measure the fuel by volume. As a result, the changes in the fuel density will greatly affect the mass of fuel injected and corresponding NOx emissions [57]. Moreover, Boehman et al. [59] found the relationships between FAME density and NOx emissions as increased NOx emissions with increasing FAME density.

Tat et al. [60] reported that, vegetable oils and their methyl esters are less compressible and have greater speed of sound, which means they have a higher bulk modulus of compressibility than diesel fuel. As a result, the fuel injection pressure develops faster and the fuel is injected sooner. Earlier start of injection delivers increased fuel mass delivery in most engines. Combustion of higher quantity mass develops an elevated temperature, which causes more NOx formation. Tat and Van Gerpen [61] studied the effect of fuel property changes on injection timing and finally reported advanced injection timing of about 1° due to the high value of bulk modulus and the speed of sound which may be partially responsible for increasing the NOx emissions. It was also found that 60 vol% blend of biodiesel and a paraffinic solvent (Norpar-13) displays the same bulk modulus of compressibility as a diesel fuel [59]. Hence, one scheme for combating the “biodiesel NOx effect” is to use highly paraffinic diesel fuels, such as F-T diesel as the diesel base stock.

The higher cetane number of biodiesel implies shorter ignition delay which reduces the combustion temperature as well as residence time, consequently less NOx formation [62,63]. In general, higher saturated fatty acids biodiesel such as coconut, palm and tallow shown in Table 3, produce less NOx than mineral diesel and have a higher cetane number [64,65]. Despite of having a high cetane number, it produces higher NOx than diesel fuel usually. Wang et al. [66] gave suggestion of this regard that, high CN of biodiesel tend to increase peak pressure and temperature due to shortened ignition delay which leads to enhanced NOx formation. Mueller et al. [67] also investigated the biodiesel NOx effect and reported that somewhat higher cetane number of biodiesel relative to diesel causes ignition to occur earlier in the cycle. This allows the combustion products to have a longer residence time at high temperatures, which increases NOx emissions.

The Iodine value (IV) of biodiesel directly impacts on NOx emissions. The emissions of NOx increase with an increasing iodine value of biodiesel, which was investigated by McCormick et al. [58]. The measurement of the degree of unsaturation of fatty acid is indicative of the iodine value. Thus, a higher degree of unsaturation indicates a higher iodine value. Wyatt et al. [68] carried out emission tests with the TOME (IV: 53.6), lard methyl ester (IV: 62.5) and chicken fat esters (IV: 77.4) and compared with SOME (IV: 129.1) and found that NOx emissions are linearly correlated
with an IV of fatty acid ester. Moreover, Peterson et al. [69] conducted emission tests with several FAME fuels and reported that with increase in IV from 7.88 to 12.95, the NOx emissions were raised by 29.3%.

The NOx concentration is considered as a strong function of fuel surface tension [71]. It has been found that the increase in surface tension will result in increases in NOx emissions. According to [28], the surface tension of biodiesel is 22% higher compared to diesel. Diesel spray properties, specifically the droplet size distribution and Sauter mean diameter (SMD), are influenced by fuel surface tension and viscosity. The SMD has been found to increase with increasing surface tension and viscosity. The SMD of biodiesel fuels varies from 5 to 40% higher than diesel fuel. Moreover, the increased droplet size can reduce the fraction of fuel burned in the premixed combustion phase and lead to increased duration of diffusion flame combustion [70]. Hence increases the NOx concentration.

Other physical properties of biodiesel such as liquid thermal conductivity, radiative heat loss and vapor heat capacity are slightly lower than diesel fuel which allows to rise its temperature at a faster rate once injected, resulting in evaporated droplets sooner than petroleum diesel. Sun et al. [10] reported that biodiesel combustion inside cylinder has less radiative heat transfer due to less soot formation which can be ascribed as a cause of NOx emissions. So variations of these properties have significant influences on NOx formation rate.

### 3.2. Adiabatic flame temperature

Ban-Weiss et al. [29] reported that unsaturated molecules show higher $T_{ad}$ than their saturated counterparts based on combustion of model compounds. Theoretically it can be said that biodiesel gives higher flame temperature than conventional diesel because of having a higher concentration of unsaturated compounds. The increased thermal NOx formation would be expected due to higher flame temperature. However, there is little experimental evidence to suggest that changes in $T_{ad}$ when using biodiesel is a major contributor to the observed NOx effect [67]. Moreover, Glaude et al.


[72] identified the effect of $T_{ad}$ on NOx for biofuels and fossil fuels. The synopsis of this deduction is that for biodiesel fuel, gas turbine emits slight less NOx compared to diesel due to lower $T_{ad}$ shown in Table 4.

### 3.3. High oxygen content

Biodiesel is an oxygenated fuel and it contains oxygen of about 11% by weight [28,98]. Several scientists [6–14,16,19,99,100] have investigated the effects of biodiesel fuel on exhaust emissions, and found a significant reduction in CO, sulfur, smoke, PM, and noise emissions. They explained these attributing to the high oxygen content leading to complete combustion. The presence of oxygen in biodiesel fuel results in higher heat release during the premixed phase combustion. Rapid breakage of hydrocarbon contributes to a hotter combustion process, which can be regarded as the main contributor to increased NOx emissions [67,101]. Nabi et al. [102] tested a four-stroke diesel engine with KOME biodiesel and observed that NOx increased by about 15% under high load conditions, because of the 12% oxygen content of B100, which resulted in a higher gas temperature in the combustion chamber. Lin et al. [82] observed a comparison of eight kinds of vegetable oil methyl ester (VOME) fuels in diesel engines and showed that every biodiesel fuel emits more NOx compared to diesel fuel, within a range from 5.58% to 25.97%. Rao et al. [94] concluded in their article that due to the 11% oxygen content in KOME fuel, NOx emissions were higher. They reported that the oxidation of nitrogen is improved with the presence of more oxygen in KOME fuel, which raised the combustion bulk temperature during the combustion period. In contrast, Lapuerta et al. [86] inferred that the oxygen content of biodiesel could not be the cause for an increase in NOx because the oxygen/fuel mass ratio of biodiesel (2.81) is less than that of the diesel (3.58). Lapuerta et al. [76] also showed that there was no significant difference between the diesel and biodiesel NOx emissions. They tested different blends of waste cooking oil methyl and ethyl esters in a 2.2 L, CRDI diesel engine and found a very slight difference in NOx emissions between the biodiesel and diesel fuel.

In contrast, some researchers [20–22] reported that the oxygenated biodiesel produced less NOx emissions than diesel fuel. Nabi [21] found from his theoretical investigation that the $T_{ad}$ decreases due to an increase in the oxygen content of the oxygenated fuels, and as a result, NOx emissions decrease linearly, which is shown in Fig. 2. He showed that indicated thermal efficiency mostly depends on the oxygen content of the oxygenated fuels, and is almost constant at oxygen content below 30% w/w, but decreases gradually with the increase in oxygen content above 30% w/w. Furthermore, it was observed that due to the higher oxygen content, viscosity, density, and lower calorific value, the $T_{ad}$ decreases, as reported by Gongping et al. [20]. Sendzikiene et al. [22] tested a single-cylinder direct injection AVL test engine with tri-component (ROME-D-E) fuel and found that the optimum oxygen content in the mixture of this tri fuel is 15–19% considering performance and emissions. Fig. 3 shows that if the oxygen content in the (ROME-D-E) fuel mixture is more than 19%, NOx emissions decrease, but rapidly increases the CO for two given conditions. This is why it is necessary to minimize the oxygen content in the fuel to obtain the optimum results of engine performance and emissions for oxygenated fuel.

### 3.4. Molecular structure of biodiesel fuel

Many researchers [25,81,103] observed that, the biodiesel molecular structure has a substantial impact on combustion and hence emissions. The structural formula and fatty acid composition of some biodiesel fuels are presented in Table 3. Shahabuddin et al. [97] reported that the cetane number, heat of combustion, melting point, and viscosity of neat fatty compounds increase with increasing chain length and decrease with increasing unsaturation of the FAME molecule. Furthermore, the heating value, melting point, cetane number, viscosity and oxidation stability decrease whereas density, bulk modulus, fuel lubricity and iodine value increase as the degree of unsaturation increases. McCormick et al. [58] investigated the impact of biodiesel chemical structure on NOx emissions; specifically fatty acid chain length and number of double bonds, and found that NOx increases with an increasing number of double bonds of the fuel, which can be quantified as the iodine value. McCormick et al. [104] studied various biodiesel with different degrees of unsaturation and reported that progressively increasing NOx emissions due to the use of biodiesel fuels with higher degrees of unsaturation, which correlates with higher $T_{ad}$. Ban-Weiss et al. [29] investigated numerically to show the biodiesel NOx effect and found enhanced the NOx emissions of about 21% due to higher peak flame temperature of the double bonded methyl trans-2-butanoate about 14 °K than the single-bonded methyl butanoate. Pattamaprom et al. [105] analyzed the performance and emissions using palm olein and palm stearin (co-products of palm oil refining processes) biodiesel fuels and reported that palm olein has a slightly higher degree of unsaturation than palm stearin, which leads to a lower cetane number and
thus, a higher combustion temperature, which implies greater NO\textsubscript{x} formation.

In contrast point of view, Mueller et al. [67] presented an argument about the dependability of NO\textsubscript{x} increasing of biodiesel on T\textsubscript{ad}. From Fig. 4, the authors reported that T\textsubscript{ad} for biodiesel is lower than that for diesel surrogate fuels, as well as higher than CN70 and CN45. If differences of T\textsubscript{ad} were the NO\textsubscript{x} controlling factor, then it could be surmised from Fig. 4 that biodiesel fuels would have lower NO\textsubscript{x} than diesel; B94 would always have significantly higher NO\textsubscript{x} than B100; and CN70 would have higher NO\textsubscript{x} than CN45, but this was contradictory to other work in the literature. Zhang and Boehman [85] argued that having double bonds in biodiesel leads to the formation of free radicals that advances prompt NO\textsubscript{x}. The linear chain of the unsaturated fatty acid decreases due to the presence of double bonds in the molecules, leaving less space for the molecules to compress together and hence, reduces compressibility [28,60].

### 3.5. Premixed-burn fraction

Because of having oxygen into biodiesel, it premixes more fully during the ignition delay, and a larger fraction of its heat release occurs during the premixed-burn phase of combustion at ignition. The combustion that is more premixes has higher oxygen concentrations and therefore produces more NO\textsubscript{x}. The difference in NO\textsubscript{x} produced during the premixed burn is responsible for the biodiesel NO\textsubscript{x} increase.

### 3.6. Chemical kinetics effect

There are differences in the chemical-kinetic pathways that form NO\textsubscript{x} when fuel is used as biodiesel, and these are responsible for the biodiesel NO\textsubscript{x} increase. Arguments based on differences in prompt NO formation seem to be the most common in this category. Such arguments typically depend on increased levels of CH being produced at the AZ shown in Fig. 5 during biodiesel combustion [106]. These level leads to the production of N-atoms in the jet core followed by prompt NO formation once the mixture is convected to the DF where oxygen and OH are present.

### 3.7. Hydrogen addition into the combustion chamber

Tsolakis et al. [107] carried out an experiment to observe the effects of addition small amount of hydrogen to the engine intake with or without EGR in diesel engine fuelled with 20% ROME. They concluded that addition of H\textsubscript{2} into the combustion chamber through the engine intake reduces both NO\textsubscript{x} and smoke simultaneously. This is attributed to the hydrocarbon fuel replacement by hydrogen resulting from the addition of hydrogen and the subsequent reduction hydrocarbon fuel flow into the engine. The use of a small amount of hydrogen gave longer ignition delay (retard) by 2° CA, but the combustion duration was faster by about 5% when compared to ULSD and B20 operation without hydrogen. At the same time, the engine efficiency and the combustion quality were not affected adversely.

### 3.8. Ignition delay time

The time between the injection start and onset of combustion is called the ignition delay time. Ban-Weiss et al. [29] reported that in a combustion chamber, the reactants are rapidly preheated due to a longer ignition delay time, which results in an increase of the flame temperature and corresponding NO\textsubscript{x} emissions. Benjumea et al. [93] reported that biodiesel fuels, having higher degree of unsaturation have longer ignition delay time which results in higher T\textsubscript{ad}. Therefore, NO\textsubscript{x} emissions increase according to the thermal NO\textsubscript{x} mechanism. But in general case, the ignition delay of...
In combustion systems, injection timing is also an important parameter that affects combustion temperature and hence NOx emissions. The start of fuel injection is advanced for biodiesel compared with petroleum diesel in rotary/distributor-style fuel injection systems, which has been reported by several authors [29,60,109–113]. Monyem et al. [113] carried out an experiment with a diesel engine fuelled by biodiesel without changing injection systems, which has been reported by several authors [10,96,97,108–116] to show that even with biodiesel, such as; the high cetane number, high ignition quality, increased chain length and degree of unsaturation etc., advances the combustion timing lead to shorter ignition delay and consequently, higher NOx formation. Schönborn et al. [96] investigated the effect of molecular structure of natural biodiesel (NB) and single molecule fatty acid esters (SMFAE) on the combustion behavior under diesel engine conditions. They reported that for a shorter ignition delay time, the relationship between NOx emissions and the Tad becomes gradually steeper. This means that the influence of Tad on total NOx emissions is stronger, which is shown in Fig. 6. The Tad plays an important role in forming NOx because of the higher ignition quality of biodiesel fuel.

### 3.9 Injection timing (IT)

In combustion systems, injection timing is also an important parameter that affects combustion temperature and hence NOx emissions. The start of fuel injection is advanced for biodiesel compared with petroleum diesel in rotary/distributor-style fuel injection systems, which has been reported by several authors [29,60,109–113]. Monyem et al. [113] carried out an experiment with a diesel engine fuelled by biodiesel without changing the setting of the injection timing and observed that B100 and B20 fuel injects about 2.3° and 0.25°–0.75° earlier, respectively, than the studied petroleum diesel fuel. This injection timing advance can be attributed due to several properties of biodiesel e.g. high density, higher bulk modulus of compressibility, and greater speed of sound [96,117]. The higher bulk density and viscosity move the pressure wave inside the fuel pipe lines more quickly and an earlier needle lift results in advanced injection. Szybist et al. [118] studied injection and combustion processes of soy-derived biodiesel blends and Fischer–Tropsch (FT) diesel fuel. Their results showed that soy-derived biodiesel blends produced advance SOI timing of about 1.1° crank angle relative to diesel fuel because of the lower compressibility (higher bulk modulus). From the information in Table 5, it can be seen that increasing NOx emissions with biodiesel is mainly caused by the advancement of injection timing, which has also been described by other researchers [117,119,120]. Injection timing advance generally lengthens the ignition delay; this permits additional time for premixing the fuel and air, which normally increases the premix portion of diesel combustion that increases the reaction temperature. Finally, it reaches an elevated diffusion reaction temperature to post-flame gas temperature. An increase in post-flame gas temperature enhances the NOx formation rate. An advance of injection timing also typically progresses the onset of combustion, which can increase the reaction time and generally increase the overall gas temperatures [10,115,118].

### 3.10 Engine load condition

The variation of engine load has the greatest effect on combustion temperature and exhaust emission. Sze et al. [122] reported that the change in NOx emissions increases linearly with the average cycle load. Zang and Boehman [85] investigated both low and high load conditions in order to detect the effect of the three fuels, named ultra-low sulfur diesel fuel (BP15), B20 (20% biodiesel into BP15), and B40 (40% biodiesel into BP15) on NOx,

---

### Table 5

<table>
<thead>
<tr>
<th>Engine specification</th>
<th>Fuel</th>
<th>Advance SOI timing</th>
<th>NOx emission compared to diesel combustion</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A John Deere diesel engine</td>
<td>Vegetable derived B100, B20</td>
<td>B100 (2.3 CA)</td>
<td>↑</td>
<td>[113]</td>
</tr>
<tr>
<td>A John Deere 4276T, Cyl: 4, 4S, TC, DI, diesel engine</td>
<td>Soybean biodiesel B100, B20</td>
<td>B100 (2.28 CA)</td>
<td>↑ 6–9%</td>
<td>[118]</td>
</tr>
<tr>
<td>Yanmar L70 EE, AC, 4S, Cyl: 1, DI diesel engine, maximum power output: 5.8 hp with high load (75%) and low load (25%), at 3600 rpm</td>
<td>Soy-derived biodiesel (COME (diesel) 5° CA</td>
<td>B5 13.03%, B20 18.6%, B50 9.14, B100 12.92</td>
<td>↓</td>
<td>[121]</td>
</tr>
</tbody>
</table>

**Note:** AC= Air Cooled, NS= Number of stroke, Cyl= number of cylinder, CA= crank angle, TC= turbocharged.
emissions. Their results indicated slightly less NO\textsubscript{x} emissions under low loads and obviously more NO\textsubscript{x} emissions under high load conditions for biodiesel compared to baseline diesel fuel which is shown in Fig. 7. Fig. 8 shows that using pilot double injection at low load condition reduced the NO\textsubscript{x} emissions greatly compared to high load condition by reducing the combustion peak temperature. Yoon and Lee [123] also agreed with this finding. However, they also found that significantly lower NO\textsubscript{x} emissions emitted under dual-fuel (biogas–diesel and biogas–biodiesel) operation for both cases of pilot fuels compared to single-fuel mode at all engine load conditions. Another finding from their experiment was that the combination of ULSD and biogas produces less NO\textsubscript{x} than biodiesel and biogas combination at any load condition. The main reason for this is that biodiesel has faster injection and early ignition characteristics that contribute to reaching a higher combustion pressure and temperature, promoting thermal NO\textsubscript{x} emissions. Eckerle et al. [124] also reported after making combination with experimental and modeling work that the NO\textsubscript{x} effect of biodiesel varied significantly with load. Under high load conditions, where diffusion flame combustion process dominates, it was shown that engine control parameters had a more significant influence on biodiesel's NO\textsubscript{x} increase. On the other hand under low load conditions with more premixed combustion, others factors were more influential.

4. Reduction of the NO\textsubscript{x} emissions

NO\textsubscript{x} reduction techniques can broadly be classified into two groups as: pre combustion treatment techniques and post combustion treatment techniques. To meet the stringent vehicular exhaust emission norms worldwide, several pre and post combustion treatment techniques have been employed in modern engines. Both NO\textsubscript{x} reduction techniques are discussed in this section.

4.1. Pre combustion treatment techniques

Use of different additives into fuel, exhaust gas recirculation (EGR), water injection, water fuel emulsion and retardation of injection timing are the common pre combustion treatment techniques to reduce NO\textsubscript{x} emissions.

4.1.1. Use of different additives

Different types of additives such as metal-based, oxygenated fuel (dimethyl ether, ethanol, and methanol), diesel–vegetable oil blends, antioxidant, cetane number improver etc. are generally used to reduce the NO\textsubscript{x} emissions form biodiesel combustion. By using ethanol into biodiesel as an additives reduces the NO\textsubscript{x} emissions because of its having lower heating value [125]. The cetane number improver is used to reduce the biodiesel NO\textsubscript{x} emissions by decreasing engine ignition delay and premixed combustion phase which implies to burn less fuel during the premixed combustion phase [62]. The maximum combustion temperature would be decreased, which suppresses the NO\textsubscript{x} formation. However some effective cetane improvers such as 2-ethylhexyl nitrate (EHN), di-t-butyl peroxide (DTBP) are mostly used in biodiesel to reduce the NO\textsubscript{x} emissions [23,30]. On other hand McCormick et al. [104] found addition of EHN as a cetane improver into 20% soy based biodiesel did not show any measurable effect to reduce the NO\textsubscript{x} emissions. Antioxidant additives can be reduced the formation of free radical by four methods; chelating the transition metal catalysts, chain breaking reactions, reducing the concentration of reactive radicals and scavenging the initiating radicals and corresponding reduction of prompt NO\textsubscript{x} [126]. Many researchers [127,128] reported on the effects of additives and catalysts on combustion, performance, and emission characteristics for biodiesel; the conclusions were that additives can improve the combustion characteristics. Table 6 presents a summary of NO\textsubscript{x} reduction results by using different additives with various biodiesel fuels. From this table it can be observed that, additives e.g. 1% of ODA antioxidant, Mn, Ni, Mg, Co, (DGMME + DGMBE), 20% ethanol, 5% diethyl ether etc. can reduce NO\textsubscript{x} emissions with a decrease in the CO and smoke range 13–64.28% and 16.67–30.91%, respectively compared to fuel without additives. Antioxidant p-phenylenediamine in biodiesel can reduce NO\textsubscript{x} emissions by 43.55% compared to pure JME, but it increases the CO and HC emissions. On the other hand, 12 μ/mole Mg in 10% chicken fat biodiesel increases NO\textsubscript{x} emissions by about 5%; but it decreases CO and HC emissions.

4.1.2. Exhaust gas recirculation (EGR) method

Exhaust gas recirculation (EGR) is a pre-treatment technique, which is being used widely to reduce the NO\textsubscript{x} emissions from diesel engines by controlling oxygen density and combustion peak temperature [136,137]. The EGR mechanism decreases the combustion gas temperature, which is normally acceptable without any dilution effect and an inert gas effect with a higher specific

<table>
<thead>
<tr>
<th>Test fuel</th>
<th>Additives</th>
<th>Engine condition</th>
<th>Results</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>POME20</td>
<td>1% of ODA</td>
<td>IDI,4C, 50 N/m load, @2250 rpm</td>
<td>NO\textsubscript{x}↓22.69%, CO\textsubscript{j}, HC↓</td>
<td>[129]</td>
</tr>
<tr>
<td>TOME60</td>
<td>Mn and Ni</td>
<td>Unmodified DI DE at full load</td>
<td>NO\textsubscript{x} reduction rate for (TOME60Ni , TOME60Mn), CO\textsubscript{j} (64.28%), Smoke↓ (30.91%), CO\textsubscript{j} (56.42%) and Smoke↓ (30.43%). Low NO\textsubscript{x} emissions measured at (B60-8Mg and B60-12Mg) fuel.</td>
<td></td>
</tr>
<tr>
<td>TOME60</td>
<td>Mg and Mo</td>
<td>1C, DI, DE at full load and speed vary</td>
<td>Reduced the NO\textsubscript{x} emissions.</td>
<td>[132]</td>
</tr>
<tr>
<td>POME</td>
<td>DGMME and DGMBE</td>
<td>1C, Kirloskar AV-1 engine</td>
<td>CO\textsubscript{j} (53.37%) and Smoke↓ (29.47%). Measured low NO\textsubscript{x} emissions at T60-BCo</td>
<td></td>
</tr>
<tr>
<td>TOME60</td>
<td>Cobalt (Co)</td>
<td>1C, DI DE at full load and speed vary</td>
<td>CO\textsubscript{j}↑13%, smoke↑9%, SFC↑5.2%, NO\textsubscript{x}↑5%</td>
<td>[133]</td>
</tr>
<tr>
<td>10% chicken fat biodiesel</td>
<td>12 μ/mole Mg</td>
<td>45,1C,AC,DI,Diesel engine</td>
<td>NO\textsubscript{x}↓12%, CO\textsubscript{j}16.67, CO\textsubscript{j}↓ 18.75%, SFC↓152</td>
<td>[134]</td>
</tr>
<tr>
<td>SOME80</td>
<td>20% ethanol</td>
<td>1C, 4S, DI DE</td>
<td>NO\textsubscript{x} emissions↓43.55% but (CO &amp; HC) compare to pure Biodiesel.</td>
<td>[27]</td>
</tr>
<tr>
<td>JME</td>
<td>Antioxidant p-phenylenediamin</td>
<td>1C, 4S, WC, DE, 4.4 kW power</td>
<td>The serial of NO\textsubscript{x} reduction rate higher to lower (BE-1- B30- BE-2).</td>
<td>[135]</td>
</tr>
</tbody>
</table>

Note: DE=diesel engine, DI=direct injection, DGMME=diethylene glycol mono methyl ether, DGMBE=diethylene glycol mono butyl ether, ODA=octylated diphenylamine antioxidant.
heat ratio, such as carbon dioxide and H$_2$O [138,139]. Both these molecules have higher heat capacity than air [140]. The availability of the amount of oxygen in the intake mixture is low due to air displacement by recirculated exhaust gas. The effective air-fuel ratio is lower because of the reduction of oxygen for combustion, which affects exhaust emissions. The specific heat of intake mixture increases after a mix up between the recirculated exhaust gas and intake air, which results in the reduction of the flame temperature because more energy is needed to preheat the incoming mixture [137]. As a result, the combined effect of lower amounts of oxygen in the intake air and the reduction of the flame temperature reduces the NO\textsubscript{x} formation rate [137,141]. Some researchers [142–145] investigated the effect of EGR on an engine fueled with diesel, biodiesel and gasoline, which proved the effectiveness of the EGR method as a part of NO\textsubscript{x} reduction technology. Tsolakis et al. [146] investigated the effect of EGR on engine performance and emission for a diesel engine operated with ROME and ULSD blended fuels. The authors observed that the use of 20% EGR was more effective and achieved a reduction of about 10% and 30% at 4.5 bar IMEP for B50 and B100, respectively, with 3° CA retardation in IT. However, at 6.1 bar IMEP NO\textsubscript{x} reduction was about 20% for both B50 and B100 without significant effect on fuel consumption and engine efficiency. Entering more H$_2$O vapor and CO$_2$ into the combustion chamber due to the increase in SFC of biodiesel fuel, lowers the air/fuel ratio ($\lambda$) for biodiesel compared with the operation of ULSD fuel, which are vital for greater NO\textsubscript{x} reduction using EGR. Table 7 presents the NO\textsubscript{x} emissions reduction results by using the EGR method for petroleum and various biodiesel blended fuels. It is observed that for diesel fuel, a drastic NO\textsubscript{x} reduction of about 41.4–65.2% at 12–20% EGR rate was obtained with decreasing HC, smoke and CO$_2$, but increasing BSFC compared with neat diesel combustion without EGR. On the other hand for various pure and blends of biodiesel fuels by using EGR rate (5–25%), the reduction of NO\textsubscript{x} was about 25–75% with slight decreasing HC and CO emissions, but increasing BSFC and smoke emission. For 20% JME biodiesel at 10% EGR rate, both NO\textsubscript{x} and smoke emission reduced by about 36% and 31%, respectively, which was positive at a time reduction of NO\textsubscript{x} and smoke emissions.

### 4.1.3. Water injection method

Water injection (WI) into the combustion chamber is another important method for controlling NO\textsubscript{x} emissions from internal combustion engines. There are two ways to inject water into a combustion chamber as: inlet water injection and water injection to combustion chamber directly [151]. Samec et al. [152] showed that an inlet water injection system, both multipoint WI in the intake pipes and single point WI upstream or downstream of the compressor produced in turbocharged engine the same reduction of NO\textsubscript{x} emissions. Hountalas et al. [153] investigated the effect of both water-fuel emulsion (see next section) and water injection...
into the intake manifold on reduction of NO\textsubscript{x} emissions, through testing in direct injection heavy-duty diesel engines by varying the percentages of injected water. The outcome from their analysis of NO\textsubscript{x} reduction technologies was that the water–fuel emulsion was better than water injection, but both were more efficient than conventional diesel engine operation. However, direct water injection has an advantage over the water–diesel emulsion system, which is, it offers the possibility to change the water-to-fuel ratio during changes of the parameters of the engine [151]. Tesfa et al. [154] experimented with the effect of water injection on engine performance and emission characteristics for a direct injection (DI) turbocharged diesel engine fuelled with ROME. They concluded that water injection in the intake manifold did not show any important variation of the peak cylinder pressure and heat release rate of the bio-fueled engine, but that it does affect the premixed combustion temperature, which is the main factor for NO\textsubscript{x} emissions. From the data in Table 8, it is found that the water injection method reduces NO\textsubscript{x} emissions by up to 50% for both diesel and biodiesel fuelled engines with a slight increase in CO and BSFC, as well as a decrease in BTE. Recently, Adnan et al. [155] studied the influence of variable water injection timing on the performance and emission analysis fueled with hydrogen in a compression ignition engine. In their experimental setup, water was injected from 20 BTDC to 20 ATDC for the injection duration of 20 CA and 40 CA. They concluded that the lowest NO\textsubscript{x} emissions were observed in the water injection timing of 0 CA and duration of 40 CA, but that this produced the highest O\textsubscript{2} and SO\textsubscript{2} emissions.

4.1.4. Water–fuel emulsion method

The use of the emulsification method is motivated by both cost reduction and the potentially effective techniques for reducing exhaust emissions from diesel engines. Water/diesel (W/D) emulsified formulations are mainly used to reduce the emissions of NO\textsubscript{x}, SO\textsubscript{2}, CO, and particulate matter (PM) without decreasing the engine’s performance. The water–diesel emulsion method is used to reduce the local T\textsubscript{ad} by vaporizing the water, taking heat from the combustion chamber, which results in a reduction of NO\textsubscript{x} emissions [157]. Tran and Ghojel [158] also reported that water diesel emulsion (WDE) and direct water injection (DWI) are two effective methods effective for introducing water into diesel engine combustion chambers to reduce NO\textsubscript{x} emissions by lowering the flame temperature. Introduced water particles convert into steam due to the high pressure and temperature inside the combustion chamber at compression stroke, removes some heat from the engine cylinder to fulfill the latent heat requirement. Table 9 shows the effect of water emulsion with fuel on exhaust emission and the T\textsubscript{ad} and it is found that the water–diesel emulsion process decreases the NO\textsubscript{x} about 9–60% compared to neat diesel under low speed conditions. However, most authors [156,159–162] found this process increases the HC and CO emissions, except some researchers [79,162] who experimented under low and partial load conditions. It is also observed that by water–diesel emulsion, the fuel decreases the T\textsubscript{ad} by about 15–26 K compared with the base fuel [78,79]. Water biodiesel emulsion fuels also give a slight decrease in NO\textsubscript{x} relative to biodiesel and diesel fuels without emulsion. Subramanian [156] also investigated experimentally a comparative analysis between water-fuel emulsion and timed injection of water into the intake manifold of a diesel engine, to establish the best solution for the reduction of NO\textsubscript{x} and smoke emissions. The experimental results indicated that both NO\textsubscript{x} reduction technologies reduced NO\textsubscript{x} emissions by about 37% compared to baseline diesel, but the controlling capacity of smoke emission for water-fuel emulsion was more than water injection. After a huge comparative study, the author suggested

![Fig. 9. Results of NO\textsubscript{x} emissions for different injection timing and pressure at 25% load for SME40 fuel [171].](image)

Table 9

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>Engine and test condition</th>
<th>NO\textsubscript{x}</th>
<th>Other emissions</th>
<th>T\textsubscript{ad}/BSFC/BTE</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water emulsified diesel</td>
<td>4 cycle, WC, 6C, 121 kW; LS: 1000 rpm, HS: 1400 rpm</td>
<td>[9.5% at LS &amp; 29% at HS with (W/O)]</td>
<td>(HC, CO, smoke) with emulsion ratio (W/O)</td>
<td>Minor BSFC% at LS but BSFC% at HS &amp; BSFC% BTE not change</td>
<td>[159]</td>
</tr>
<tr>
<td>Water–diesel emulsion: 20%+EGR, 16.7%</td>
<td>4C, DI, Ford diesel engine.</td>
<td>↓ up to 60%</td>
<td>HC%, smoke%, CO%</td>
<td>T\textsubscript{ad}↓ about 26 K, BTE↑ slightly.</td>
<td>[160]</td>
</tr>
<tr>
<td>Water–oil emulsified</td>
<td>IID, TC, DE, speed: 2087–3175 rpm</td>
<td>↓</td>
<td>THC%</td>
<td>T\textsubscript{ad}↑ about 15–25 K, BSFC% BTE↑ at LL &amp; at FL</td>
<td>[78]</td>
</tr>
<tr>
<td>Diesel + GS/CS=5–15% water</td>
<td>XLD418 type DE of Ford,4S, 4C; WC: speed: 1000–5000 rpm</td>
<td>↓ (high) at GS (15% W)</td>
<td>CO% compared to neat diesel, PM% (68–72%)</td>
<td>T\textsubscript{ad}↑ about 15–25 K, BSFC% BTE↑ at LL &amp; at FL</td>
<td>[79]</td>
</tr>
<tr>
<td>Water–diesel emulsion (0.4:1)</td>
<td>4S, AC, 1C, CI engine; CS: 1500 rpm</td>
<td>↓ (37.6%)</td>
<td>HC%, CO%</td>
<td>T\textsubscript{ad}↑ about 15–25 K, BSFC% BTE↑ at LL &amp; at FL</td>
<td>[156]</td>
</tr>
<tr>
<td>9413D + 53H\textsubscript{2}O + 0.5% tween 20 + 0.5% span 20</td>
<td>Comet DE, 2C, Vertical WC, 7.5 kW, 1500 speed</td>
<td>↓(30–50%)</td>
<td>HC% at LL but at HL, CO% with H\textsubscript{2}O emulsion</td>
<td>–</td>
<td>[161]</td>
</tr>
<tr>
<td>D78.5% + 10H\textsubscript{2}O + additives 11.5%</td>
<td>Toyota, 4C, 4S, DE; speed: 1000–4000 rpm</td>
<td>↓30.6%</td>
<td>(HC%, CO%) at partial load, but (HC%, CO%) at FL</td>
<td>BTE↑ 14.2%</td>
<td>[162]</td>
</tr>
<tr>
<td>10% CH\textsubscript{3}OH + cooling biodiesel</td>
<td>4C, DI, DE; speed:1800 rpm</td>
<td>↓6.2%</td>
<td>–</td>
<td>BTE↑ at LL but at HL</td>
<td>[163]</td>
</tr>
<tr>
<td>Biodiesel, diesel, BD7010E20M micro emulsion fuel</td>
<td>1C, WC, DI, diesel engine; CS: 1500 rpm</td>
<td>Emission of NO\textsubscript{x} less than (diesel, BD)</td>
<td>BD–Micro emulsion fuel–Diesel for HC &amp; smoke; (BD–BD7010E20M–Diesel) for CO</td>
<td>BSFC% but BTE not vary compare to diesel fuel.</td>
<td>[164]</td>
</tr>
<tr>
<td>H\textsubscript{2}O-BD-diesel Nano emulsion</td>
<td>Diesel engine</td>
<td>↓</td>
<td>CO%</td>
<td>–</td>
<td>[165]</td>
</tr>
</tbody>
</table>

Note: AC=air cooled, WC=water cooled, HS=high speed, LS=low speed, IID=intercooler indirect injection, CS=Gamma surfactants, CS=conventional surfactants, BSFC=brake specific fuel consumption, BTE=brake thermal efficiency.
that the emulsion method is more efficient than the injection method in reducing both NO\textsubscript{x} and smoke emissions at all loads.

4.1.5. Retardation of injection timing

A slight control on the injection timing by retarding it can reduce the NO\textsubscript{x} emissions significantly [67,104,110,113,166–170]. Graboski and McCormick [70] reported in their review paper which published in 1998 that using biodiesel in both 2-stroke and 4-stroke diesel engines increased NO\textsubscript{x} emissions, but that these increases could be effectively controlled by retarding the fuel injection timing by 1–4\(^\circ\). Later on, Choi and Reitz [171] indicated that for both retarded and split injection techniques reduced the amount of premixed burning, thereby reducing in-cylinder temperatures and found beneficial effect on NO\textsubscript{x} reduction. Kegl [172] demonstrated that biodiesel could produce lower NO\textsubscript{x} emissions compared to diesel, if the injection timing was retarded. Sayin et al. [121] investigated the effect of both advancing and retarding the SOI on exhaust emissions from diesel engines fuelled with CME blends. The authors concluded that advancing the SOI gave the best results for smoke and CO emissions for B100, whereas retardation of the SOI presented the minimum results for NO\textsubscript{x} and CO\textsubscript{2} emissions for both B0 and B100 fuels. Wang et al. [169] investigated NO\textsubscript{x} formation for diesel and biodiesel in a light-duty compression ignition engine by using computational fluid dynamics (CFD) and finally concluded that retarded fuel injection timing is an effective method for reducing NO\textsubscript{x} emissions because of the retarded combustion phasing (lower temperature). The retardation of SOI timing decreases NO\textsubscript{x} emissions because late combustion implies a reduction of effective pressure. Recently Ye et al. [173] observed that NO\textsubscript{x} emissions for SME40 fuelled engine reduced by retarding the IT whereas increased with increasing injection pressure (IP) which is shown in Fig. 9. By applying this method, it reduces the reaction time by the late onset of combustion, which can decrease the overall gas temperature. However, retarded injection timing also reduces the brake thermal efficiency and increases the smoke emission, which is summarized by Rajasekar et al. [24]. Some experimental results are shown in Table 10 about the effect of retarding the SOI timing, where each result represents a reduction of NO\textsubscript{x} by 8.2–40.95\% compared with the original SOI timing, but an increase in HC and CO emissions, except for the experiments of Mani and Nagarajan [174] and Kegl

**Table 10**

<table>
<thead>
<tr>
<th>Engine specification</th>
<th>Retard the SOI timing</th>
<th>Fuel types</th>
<th>Emissions result</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ricardo E6-MS/128/76, 1C</td>
<td>4 CA from ORG 38 CA BTDC</td>
<td>Diesel</td>
<td>↓40%</td>
<td>–</td>
</tr>
<tr>
<td>Super star 7710, 1C,4S, DI</td>
<td>6 CA from ORG 27 CA BTDC</td>
<td>E5 + D95</td>
<td>↓37.3</td>
<td>†</td>
</tr>
<tr>
<td>Ford 6.0 lt. T/C LHR, TC, 6C, DI,</td>
<td>(2–4) CA from ORG 20 CA BTDC</td>
<td>Diesel</td>
<td>↓11%</td>
<td>–</td>
</tr>
<tr>
<td>A John Deere diesel engine</td>
<td>3 CA retarded injection timing</td>
<td>Vegetable derived</td>
<td>↓35–43%</td>
<td>–</td>
</tr>
<tr>
<td>Diesel engine</td>
<td>Retard SOI timing from ORG</td>
<td>Pongamia oil methyl ester (PME)</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>MAN D 2566 MUM, 4S, 6C, WC</td>
<td>4 CA from ORG 23 CA BTDC</td>
<td>ROME100 compared to diesel fuel</td>
<td>↓25%</td>
<td>↓25%</td>
</tr>
<tr>
<td>Kirloskar TAF1 1C, 4S, DI, AC</td>
<td>9, 6, 3 CA from ORG 23 CA BTDC</td>
<td>Waste plastic oil</td>
<td>↓</td>
<td>↓25%</td>
</tr>
<tr>
<td>Small power DE</td>
<td>Retarded SOI</td>
<td>KOME (CME + Diesel), Fuel blends: B0, B5, B20, and B50 &amp; B100.</td>
<td>↓8.2%</td>
<td>B0:40.95, B5:30.28, B20:21.08, B50:31.25 &amp; B100:9.77</td>
</tr>
<tr>
<td>Lombardini 6 LD 400, Cyl:1, IOP: 20 MPa, SOI timing: 20 (deg CA BTDC), CR: 18:1, maximum torque: 21 N/m at 2200 rpm, maximum power: 8 kW at 3600 rpm</td>
<td>5 CA from ORG 20 CA BTDC</td>
<td>KOME</td>
<td>↓38.3%</td>
<td>B0:13.31, B5:11.33, B20:33.3, B50:27.03 &amp; B100:4.68</td>
</tr>
</tbody>
</table>

**Note:** LHR = low heat rejection, TC = turbocharged, DI = direct injection, AC = air cooled.

![Fig. 10. Schematic view of SCR system [181].](image-url)
4.2. Post combustion treatment techniques

A few research groups have performed experiments based on controlling the biodiesel NO\textsubscript{x} emissions in modern engines using advanced after-treatment systems. There are some commonly used after-treatment approaches to reduce the NO\textsubscript{x} emissions from diesel engines such as NO\textsubscript{x} adsorber catalyst (NAC), selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR) and DeNO\textsubscript{x} (Lean NO\textsubscript{x}) catalysts. All of these approaches are considered to have good potential of meeting the US EPA emissions standard.

4.2.1. NO\textsubscript{x} adsorber catalyst (NAC)

NO\textsubscript{x} adsorber catalyst (NAC) is one of the significant NO\textsubscript{x} reduction techniques which is also called as lean-NO\textsubscript{x} trap system. It can be used in lean-burn gasoline and diesel engines to reduce NO\textsubscript{x} emissions by a number of manufacturers. The working principle of the NO\textsubscript{x} adsorber system is to store NO\textsubscript{x} in a catalyst during periods of lean operation and then release the NO\textsubscript{x} during rich condition of engine [178]. The excess unburned hydrocarbons react to reduce the NO\textsubscript{x} emissions. In a NAC system utilizes an oxidation catalyst to exchange all NO to NO\textsubscript{2}, which is then trapped in an inorganic substance such as barium oxide (BaO). During rich condition of engine, nitrate becomes unstable and decomposes which causes releasing of the stored NO\textsubscript{2}. NAC systems are very sensitive to sulfur contamination because of forming of sulphur compounds to stable sulphates along with NO\textsubscript{x} absorbing materials which reduces the performance of catalyst gradually. Ultra-low sulfur diesel (ULSD) or SO\textsubscript{x} trap is now required to improve the effectiveness and durability of modern diesel emissions control systems. Tatur et al. [179] performed an experiment about biodiesel effects on US light-duty tier 2 engine and emission control using a NAC system. They found that the engine-out NO\textsubscript{x} was somewhat higher for soy-based biodiesel (B20) compared to diesel combustion (by up to 10%), while tailpipe-out NO\textsubscript{x} was slightly lower. The higher exhaust temperature of diesel combustion was the main contributor of higher tailpipe-out NO\textsubscript{x} compared to B20. As a result, the NAC was more effective for biodiesel (B20) combustion to trap NO\textsubscript{x} emissions than diesel combustion.

4.2.2. Selective catalytic reduction (SCR)

At stationary combustion installations, the selective catalytic reduction (SCR) has been used to reduce NO\textsubscript{x} emissions for many years by ammonia (NH\textsubscript{3}). With SCR, a different catalyst bed is used to convert the NO\textsubscript{x} into water and nitrogen (N\textsubscript{2}) directly [180]. However, separate injection system is required to inject the chemical reducing agent into the exhaust stream, ahead of the SCR catalyst. For vehicle applications, the reducing agent is not NH\textsubscript{3} but an aqueous solution of urea (NH\textsubscript{2}CONH\textsubscript{2}) [181]. The conversion mechanism of NO into N\textsubscript{2} is presented with the schematic view of the SCR system in Fig. 10. A greater issue concerning about an ammonia based SCR system is that using a slight excess of ammonia which produces “ammonia slip” emissions. But introducing slight excess of NH\textsubscript{3} is helpful to get the maximum reduction of NO\textsubscript{x} emissions. McWilliam and Zimmermann [182] investigated the effect of biodiesel usage in a HD Caterpillar engine equipped with a vanadium-based SCR system. Author found that the NO\textsubscript{x} conversion efficiency of the SCR system was reduced by 6% when operating on B100 because of reducing the NO\textsubscript{2}/NO\textsubscript{x} ratio substantially. This adversely affected the ammonia-driven reduction reactions within the SCR, and caused an increase in ammonia slip emissions. An additional oxidation catalyst may be used to overcome the ammonia slip emissions problem.

4.2.3. Selective non-catalytic reduction (SNCR)

Selective non-catalytic reduction is another method used to reduce NO\textsubscript{x} emissions. This involves the injection of a NO\textsubscript{x}-reducing agent, such as ammonia or urea, into the boiler exhaust gases at a temperature of approximately 760–870 °C in the absence of any catalyst. The ammonia or urea breaks down the NO\textsubscript{x} in the exhaust gases into water and atmospheric nitrogen. The mechanism of NO\textsubscript{x} reduction after treatment system as SNCR is shown in Fig. 11. It can be reduced NO\textsubscript{x} emissions up to 70% [35]. Kralh et al. [183] reported on addition of amine compounds at relatively high concentrations (2−4%) to both conventional diesel and biodiesel fuels. Authors presented a strong argument that SNCR could reduce the NO\textsubscript{x} emissions from diesel engine in an efficient way when proper compounds are chosen to do the work. However, the NO\textsubscript{x} reduction approaches as SNCR has some restrictions to apply commercially due to amine solubility’s and high cost.

4.2.4. DeNO\textsubscript{x} (Lean NO\textsubscript{x}) catalysts

Application of DeNO\textsubscript{x} or “Lean NO\textsubscript{x}” catalysts is another important NO\textsubscript{x} reduction after-treatment system. These use the same operating principle as SCR but use hydrocarbons as the NO\textsubscript{x} reductant instead of an ammonia solution [178]. The converting reaction of NO\textsubscript{x} into N\textsubscript{2} by using DeNO\textsubscript{x} catalysts is presented in Eq. (12).

\[
\text{HC} + \text{NOx} \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O}
\]

These catalysts can be divided into two groups: passive and active DeNO\textsubscript{x}. Though the passive systems are simple, reliable and low cost, but their capacity is limited due to selective nature of the reaction and low concentration of HC in exhaust. On the other hand, enrichment of the exhaust gases with additional HC material has been perceived as a solution to this problem. In general, such enrichment could be realized by two methods: injection of HC preferably diesel fuel and later in-cylinder injection in a common rail fuel system. Catalysts with HC enrichment can overcome the problem of passive DeNO\textsubscript{x} system. DeNO\textsubscript{x} or “Lean NO\textsubscript{x}” catalysts...
convert to a significant fraction of NOx to N2O which is a potent greenhouse gas.

5. Summary and conclusion

Biodiesel, produced from renewable and often domestic sources, is a more sustainable source of energy and will therefore play an increasingly significant role in meeting energy demands. Therefore, research on the different feedstock and their influence on performance and emissions are increasing progressively. However NOx emissions from biodiesel fuelled engine is the major concern of the researchers. The effects of different notable factors on NOx emissions in biodiesel fuelled engine and its reduction approaches (both pre and post combustion) have been investigated in this work. The effective NOx reduction approaches are retarded injection timing and EGR system which are able to overcome the problems of biodiesel NOx effect. However, the following conclusions could be drawn from the analysis of the related literatures in this article:

1. In general, thermal NOx is a dominant mechanism in the combustion processes; however, prompt NOx also contributes significantly in biodiesel combustion.
2. The presence of oxygen in biodiesel fuel results in higher heat release during the premixed phase combustion which can be regarded as the main contributor to increased NOx emissions. However less NOx emissions for oxygenated fuels were also observed by few researchers.
3. Biodiesel has a high cetane number that implies shorter ignition delay and reduction of NOx emissions is expected. However elevated combustion temperatures reached during the combustion process due to advanced combustion timing and longer residence period, increase NOx emissions.
4. Physicochemical properties of biodiesel such as: Viscosities, density, bulk modulus of compressibility, iodine value, surface tension are higher than diesel that influences biodiesel NOx effect.
5. Higher adiabatic flame temperature may be one of the reasons for biodiesel NOx emissions; however, it could not be the exact reason. Degree of unsaturation of biodiesel fuel is the main responsible for the higher Tad.
6. Biodiesel produces higher NOx emissions with increasing engine load and vice versa. Addition of small amount H2 into combustion chamber through engine intake can reduce the NOx and smoke emissions simultaneously.
7. Addition of additives into biodiesel reduces the NOx emissions effectively by improving fuel properties such as viscosity, density etc. However this poses engine operating cost and durability of engine.
8. The injection timing of biodiesel is advanced compared to neat diesel fuel due to higher density, high bulk modulus of compressibility, etc., which results in more NOx emissions. By applying the retarded injection timing method, NOx can be reduced by 8.2–40% relative to the original injection timing, but in most cases, this technology increases CO and HC emissions, as well as BSFC.
9. EGR is the method with the greatest potential for reducing NOx emissions. It reduces NOx emissions with biodiesel by about 25–75% at 5–25% EGR rate. It also decreases HC and CO emissions slightly, but raises the BSFC and smoke emission.
10. The water injection method reduces NOx emissions by up to 50% for diesel and biodiesel fuelled engines. However it increased CO and BSFC slightly, as well as decreased BTE by reducing the premixed combustion temperature.
11. Water-fuel emulsions are more efficient for reducing NOx emissions than the water injection method because of low cost, greater reduction of smoke, and reduction the local adiabatic flame temperature, etc. However they are inherently unstable and prone to phase separation, which may damage engine.
12. Applying exhaust after-treatment systems in biodiesel engine may be required to meet the progressively stringent diesel engine emissions standards. However increased GHG, higher engine operating cost, ammonia slip emissions etc. makes them unviable as long term solution.

Further studies are required to determine the effect of biodiesel combustion on NOx formation by changing different engine parameters e.g. fuel injector, ignition timing and engine calibration (air/fuel ratios, injection pressure, injection timing, injection phasing). Furthermore, research on several new combustion technologies such as low temperature combustion (LTC), homogeneous charge compression ignition (HCCI), and premixed controlled compression ignition (PCCI) are also needed to control biodiesel NOx emissions. Moreover, studies undertaking exhaust after-treatment systems for biodiesel fuelled engine is necessary for long term commercial use.

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