**Advancement of Biodiesel Fuel Quality and NOx Emission Control Techniques**

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# Abstract

Sustainable waste derived biodiesel can substitute significant amount of fossil-based fuels currently used for marine propulsion, agricultural processes, small scale power generation, and in heavy goods vehicles. However, biodiesel fuel quality varies depending on the feedstock type, production method and storage conditions. Meeting biodiesel standards and reduction of NOx emissions are two main challenges when biodiesels are being used in the internal combustion engines. This study aims to address these two challenges by using biodiesel-biodiesel blending and various NOx reduction techniques. Biodiesels produced from waste resources and inedible plant seed oils are investigated. Fuel properties, biodiesels standards, and engine test results are reviewed. It was found that that blends of animal fat biodiesels and vegetable oil biodiesels are likely to improve fuel properties and combustion characteristics. The biodiesel-biodiesel blends also help to reduce exhaust pollutants. The saturation level of the biodiesel fuel is increased through this technique. Animal fat biodiesels are composed of saturated fatty acid methyl esters, and vegetable oil biodiesels are composed of unsaturated fatty acids. The NOx gas emission reduction techniques are investigated and categorised under three sub-groups, fuel treatment, engine adjustment and exhaust after-treatment. Based on the state of art review, scopes for future R&D topics are presented for researchers and relevant industries.

# Highlights

* Blends of animal fat and WCO biodiesels can improve the fuel properties
* Biodiesel emulsification by 30% water can reduce the NOx emission by up to 60%
* Antioxidant additives can reduce biodiesels NOx emission by up to 9%
* Water injection through inlet manifold can reduce biodiesels NOx emission by 50%
* SCR is the leading NOx mitigation technique with efficiency of up to 85%

**Keywords:** Additives, Advanced combustion, Biodiesel, Climate, Control techniques, Diesel engine, Emulsification, Ester’s content, Fuel quality, NOx emission, Saturation level, Sustainability, Waste to fuel

**Word count:** 9825

# Abbreviations

|  |  |  |  |
| --- | --- | --- | --- |
| ASTM | American Society for Testing and Materials  | HLB | Hydrophilic-lipophilic balance |
| BSFC | Brake specific fuel consumption | HRR | Heat release rate  |
| BTE | Brake thermal efficiency  | ID | Ignition delay  |
| CI | Compression ignition | IDI | Indirect injection |
| CN | Cetane number | LHV | Lower heating value  |
| DI | Direct injection | LTC | Low temperature combustion |
| DOC | Diesel oxidation catalysts | m | Mass |
| DPF | Diesel particulate filter | Mf | Mass flow rate of fuel  |
| DU | Degree of unsaturation  | Mh | Molecular weight of hydrophilic |
| EGR | Exhaust gas recirculation | Mi | Molecular weight of lipophilic |
| FAME | Fatty acid methyl ester | PM | Particulate matter |
| FFA | Free fatty acid | RCCI | Reactivity controlled compression ignition |
| FTIR | Fourier transform infrared spectroscopy | SCR | Selective catalytic reduction |
| GHG | Greenhouse gas | SOI | Start of injection  |
| HCCI | Homogeneous charge compression ignition | WCO | Waste cooking oil |
| HHV | Higher heating value  |  |  |

# 1.0 Introduction

The gradual increase in earth surface temperature is causing serious problems such as melting polar ice, rising sea levels, drought and climate change [1]. It is well known fact that the global warming is accelerating by the excess emissions of greenhouse gases (GHG). Combustion of fossil fuels is one of the main sources of GHG emission [2]. The World Bank reported that 80.7% of the world’s energy was met by fossil fuels in 2017 [3]. Biodiesels are a promising source of alternative energy for replacing fossil-based fuels. The main advantages of using biodiesels are, they are (i) biodegradable (ii) sustainable (iii) can be produced from any organic substances including wastes and (iv) can reduce exhaust gases such as HC, CO and smoke when used in the internal combustion engines. Biodiesels can be produced from waste resources, so using biodiesels can help in the management of the waste resources. Biodiesels can be used in variety of applications such as in marine engines, agriculture machineries, small scale power generation, aircraft engines, mobile engines, and for process heating. Fuel properties of biodiesels are very important, use of low-quality biodiesels can harm engine components and lead to unstable operation of the plant. On the other hand, compared to fossil diesel, high quality biodiesels produce higher NOx emissions when used in diesel engines (known as the NOx penalty [4]) [5]. Biodiesel’s fuel quality and higher NOx gas emissions are two important challenges to address when biodiesels are used in the internal combustion engines.

Food vs. fuel have fostered a growing interest in waste-derived biofuels such as biodiesels from animal fats, waste cooking oils and inedible vegetable oils [6]. Animal fats and used cooking oil (WCO) are considered as wastes and disposal of them is subject to certain procedures in the EU and UK [7]. According to the quality protocol, which is a joint initiative between the Environment Agency and Waste and Resources Action Programme (applies to England, Wales, and Northern Ireland), animal waste and WCO feedstock can be regarded as fully recovered if they are converted into biodiesel in a feasible way [7].

This initiative makes the waste feedstock interesting for biodiesel production. Oil and fat feedstock (triglycerides) can be converted into biodiesel (fatty acid methyl ester) by transesterification technique [8]. Other techniques such as pyrolysis (thermal cracking) and emulsification can be used to convert wastes into biofuels [9]. The advanced biofuels types are regulated by the renewable energy directive [10]. They are generally produced from invaluable resources such as crude glycerol, algae, sewage sludge etc., some of which can be used for biodiesel production. Biodiesel production and is considered the most promising technique in terms of energy efficiency and overall enhancement of fuel properties [11]. It is expected that the use of biodiesels in the engines will provide better performance [12] and fewer emissions [13]. Biodiesel occupies the bigger portion of the renewable energy supply. In 2018, share of biodiesel on UK’s renewable fuel supply was 47% [14]. Biodegradability, carbon neutrality, environmental attributes and applicability to diesel engines (without any major modifications) make waste derived biodiesels viable alternative fuels [15]. Waste derived biodiesels can be viable sustainable alternatives to diesel, and can play an important role in mitigating the GHG emissions [16]. The other alternative energy sources that can be produced from waste resources are biohydrogen [17] and biogas [18]. They are not included in this work.

Biodiesel has promising fuel properties, the chemical structures of biodiesel and petroleum diesel are different. Biodiesel is composed of various fatty acid methyl esters (FAME) which are long carbon chains, whereas fossil diesel has aromatics compounds. This difference in chemical structure creates variations on fuel properties, which ultimately affects engine operation i.e., engine performance, combustion characteristics and exhaust gas emissions. Thus, any biodiesel to be used in the diesel engine has to fulfil the British and European standard BS EN 14214. However, it is not easy to produce biodiesel which satisfies this norm. Biodiesel fuel properties depend on the feedstock. Hence, matching the biodiesel standard could be harder for a specific feedstock. For example, biodiesels derived from WCO have high unsaturation compound which reduces resistance to oxidation and causes early degradation [19]. Another general drawback of biodiesel use is increased NOx gas emissions, which is known as the NOx penalty of biodiesels [4]. Literature reported that the PM, HC, CO and CO2 emissions can be significantly reduced by using biodiesel instead of fossil diesel [20]. Studies addressed increased NOx emission issues when neat biodiesel was used in diesel engines [21]. There are various techniques to tackle this challenge including use of fuel additives such as alcohols and antioxidants [22]; engine parameters and components modifications such as injection timing [23], advanced combustion techniques HCCI and RCCI engines [24]; and exhaust gas after-treatment systems. Among these techniques, the cutting-edge technology is the exhaust after-treatment systems which are installed on exhaust systems of the engines. Selective catalytic reduction (SCR) and lean NOx trap are the most used after-treatment technologies. The SCR is done by injecting urea in the exhaust gas, which reacts with the NOx emission [25]. The lean NOx trap technique uses expensive catalysts with rich metals such as Palladium, Platinum and Rhodium to mitigate NOx gases [26].

The existing literature covers mostly use of single biodiesel in diesel engines and specific challenges and issues related to that biodiesel. To the best of authors knowledge, no study was found investigating both challenges together i.e., enhancement of biodiesel quality for meeting biodiesel standards and viable NOx mitigation methods. This study will significantly contribute as the fuel property enhancement would improve biodiesels engine performance and reduce engine out emissions. The investigation of NOx mitigation technologies would address the increased NOx gas emission issue when biodiesel is used instead of diesel. Biodiesels produced form waste feedstock such as animal fats, waste cooking oils, inedible vegetable oil and other advanced biofuels are reviewed in terms of their fuel characteristics and engine test results. The NOx emission mitigation techniques are reviewed and summarised. By this means, sustainable way of biodiesel property enhancement will be addressed, and available cutting-edge technologies will be highlighted for addressing the NOx penalty of biodiesels. The biofuels other than the different variation of biodiesels are out of scope of this study. The impacts of this study are (i) to improve fuel combustion and reduce exhaust gas emissions by means of biodiesel-biodiesel blending, (ii) to avoid use of fossil diesel or other unsustainable additives, (iii) to promote 100% biodiesel use in diesel engines or maximise the biodiesel fraction in fossil diesel blends, (iv) to have an understanding of source of feedstock be blended with each other to improve the fuel properties, (v) to review and propose viable NOx emission mitigation techniques for biodiesel operation. Finally, areas for future R & D topics will be presented in the conclusions section to help the industries involved and academic researchers.

# 2.0 Biodiesel from waste feedstock

Based on the type of feedstock, biodiesels can be categorised as first generation (1G), second generation (2G) and third generation (3G). The first generation biodiesels are produced from edible vegetable oils [16] such as sunflower oil [27], rapeseed oil [28], rice bran oil [29], soybean oil [30] etc. Biodiesels produced from non-edible oils are categorised as 2G biodiesels [16]. The 3G biodiesels are mainly produced from algal biomass. There are some waste feedstock such as waste animal fats, waste cooking oil and sewage sludge [31] which can be used for biodiesel production. Waste cooking oils can be categorised into two different subgroups. The first subgroup is the remaining oils after cooking purpose, known as yellow grease [32]. Being a waste product along with high availability [33], makes yellow grease waste cooking oil (WCO) a cost-effective feedstock for biodiesel production [34]. The second subgroup, which is also known as brown grease, is the food grease which is collected via grease traps [32]. Grease traps are placed on the sewer system i.e., after the sink. Design of the grease trap separates the grease/oil and water. Brown grease feedstock have 15% higher free fatty acid (FFA) value than yellow grease [32]. The relatively high FFA content of brown grease make the biodiesel production process more difficult compared to yellow grease feedstock. Waste cooking oil is the single largest share (about 42%) of total biofuel supply to the UK [14]. The conditions for a feedstock to produce advanced fuels are explicitly defined in EU directive EN 2018/2001 (RED II) [10]. The most common feedstock to produce advanced biodiesel are algae, that are produced and collected on land such as in photobioreactors or ponds. The other feedstocks that can be used for advanced biofuel production includes but not limited to straw, animal manure, sewage sludge, tall oil pitch, crude glycerine, bagasse, grape marc, wine lees, nut shells, husks, corn cob [10]. Transesterification is a well-known method to produce biodiesel from organic feedstock. The process started in early 1940 for simplyfting the glycerol extraction during soap production [35], later this process was used for biodiesel production. Methanol is widely used alcohol for the transesterification process [36]. Other alcohol such as ethanol is used in transesterification process [37], but this is mainly on research and demonstration scale. At the end of the transesterification process, phase separation occurs, and two liquids are obtained which are biodiesel at the top and glycerine at the bottom [38]. Figure 1 shows various stages involved in the transesterification process.

 

**Fig. 1.** Biodiesel production flow chart - pretreatment and transesterification.

# 3.0 Biodiesel fuel properties

The physical and chemical properties of the biodiesel depend on the feedstock type. Thee feedstock affects triglycerides carbon chains length, and number of double bonds exists in each chain [39]. Table 1 shows fuel properties of the commonly found FAMEs in biodiesel composition. The GC-MS analysis can be done to determine the types of FAME composition. The FAME composition can be used to predict various properties such as calorific value and density. However, estimation of flash point and oxidation stability of a biodiesel might not be accurate enough when FAME composition is used as basis [40], and needs to measure according to EN 14214 standard [41].

**Table 1** Properties of some fatty acid methyl esters.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  | [42] |  | [43] | [41] |  |  |
| **FAME** | **Name of** | **Formula** |  | **Cetane** | **Viscosity** | **density** | **HHV** |  | **LHV** | **Carbon** | **Hydrogen** | **Oxygen** |  | **Iodine** |  | **Molecular** |
|  | **FAME** |  |  | **Number** | **at 40 °C** | **at 20 °C** |  |  |  | **Content** | **Content** | **Content** |  | **Value** |  | **structure** |
|  |  |  |  |  | **(mm2/s)** | **(g/cm3)** | **(MJ/kg)** |  | **(MJ/kg)** | **(%)** | **(%)** | **(%)** |  | **(g/100g)** |  |  |
| C12:0 | Lauric acid | C13H26O2 |  | 62[43] | 2.45 | 0.8692 | 37.91[43] |  | 35.30 | 73.02 | 12.23 | 14.76 |  | 0 |  |  |
| C14:0 | Myristic acid | C15H30O2 |  | 65.4 | 3.33 | 0.8665 | 38.79 |  | 36.20 | 74.35 | 12.44 | 13.21 |  | 0 |  |  |
| C16:0 | Palmitic acid | C17H34O2 |  | 73.9 | 4.37 | 0.8644 | 39.56 |  | 36.44 | 76[44] | 12.56 | 11.85[44] |  | 0 |  |  |
| C16:1 | Palmitoleic acid | C17H32O2 |  | 53.3 | 3.59 | 0.8764 | 39.3 |  | 36.55\* | 76[44] | 12[44] | 11.94[44] |  | 95 |  |
| C18:0 | Stearic acid | C19H38O2 |  | 82.3 | 5.59 | 0.8627 | 40.18 |  | 37.50 | 77[44] | 12.73 | 10.74[44] |  | 0 |  |  |
| C18:1 | Oleic acid | C19H36O2 |  | 61.7 | 4.6 | 0.8746 | 39.93 |  | 37.44 | 76.99 | 12.2 | 10.8 |  | 86 |  |
| C18:2 | Linoleic acid | C19H34O2 |  | 41.1 | 3.79 | 0.8865 | 39.68 |  | 37.15 | 77.43 | 11.58 | 10.99 |  | 173.2 |  |  |
| C18:3 | Linolenic acid | C19H32O2 |  | 20.5 | 3.11 | 0.8985 | 39.43 |  | 36.67\* | 78[44] | 11[44] | 10.96[44] |  | 261.6 |  |  |
| C20:0 | Arachidic acid | C21H42O2 |   | 90.8 | 7 | 0.8613 | 40.7 |   | 37.85\* | 77[44] | 13[44] | 9.82[44] |  | 0 |   |  |
| C22:0 | Behenic acid | C23H46O2 |  | 100[44] | 8.6 | 0.8627 | 41.63[43] |  | 38.87 | 77.9 | 13.08 | 9.02 |  | 3[43] |  |  |

\*Considering the relation between the reported HHV and LHV values, missing LHV values are estimated as 93% of the reported HHV values.

Table 1 shows that longer carbon chain lengths generally have higher cetane number, viscosity, HHV, LHV, carbon content, hydrogen content, melting point, and iodine number of FAMEs. The number of double bonds in FAMEs is another important factor as it directly affects the degree of unsaturation. Almost all fuel properties are affected with the presence of double bonds. Cetane number and viscosity of C18:0 was reduced from 82.3 to 61.7 and 5.59 mm2/s to 4.6 mm2/s respectively, when there was a double bond existed in its structure, C18:1 (Table 1). However, higher degree of unsaturation increases oxidation susceptibility of biodiesel [45].

The FAME composition of waste and vegetable oil derived biodiesels are investigated and shown in Table 2. It was found that the FAME compositions of the same feedstock may vary due to reasons such as species/origin of the feedstock, pre-treatment, biodiesel production procedure, biodiesel storage and measurement techniques.

**Table 2**

FAME compositions of some animal waste and vegetable oil biodiesels.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|   | **Feedstock** | **C14:0** | **C16:0** | **C16:1** | **C18:0** | **C18:1** | **C18:2** | **C18:3** | **Others** | **Reference** |
| Animal Waste | Chicken fat | 0.7 | 20.9 | 5.4 | 5.6 | 40.9 | 20.5 | 0.0 | 6.0 | [46]  |
| Chicken fat | 1.3 | 23.0 | 5.4 | 7.0 | 38.0 | 27.6 | 1.7 | 0.0 | [47] |
| Duck fat | 0.8 | 24.2 | 0.3 | n/a | 72.5 | 2.2 | n/a | 0.0 | [48]  |
| Duck fat | 0.5 | 23.4 | n/a | 5.0 | 29.4 | 34.0 | 3.2 | 4.5 | [49] |
| Goose | 0.3 | 20.5 | 2.6 | 5.6 | 46.4 | 13.6 | 0.7 | 10.3 | [6] |
| Sheep fat | 3.0 | 27.0 | 2.0 | 24.1 | 40.7 | 2.0 | n/a | 1.2 | [50] |
| Sheep fat | 0.8 | 28.1 | 0.4 | 27.2 | 31.3 | 1.6 | 0.6 | 10.0 | [51] |
| Pork lard | n/a | 28.1 | n/a | 11.6 | 38.1 | 18.8 | 3.4 | 0.0 | [52] |
| Pork lard | 1.1 | 19.8 | 2.0 | 11.8 | 44.7 | 10.9 | 1.0 | 8.7 | [6] |
| Sardine Fish oil | 7.4 | 18.7 | 7.7 | 2.5 | 11.5 | 0.0 | 3.1 | 49.1 | [53] |
| Sardine Fish oil | 6.8 | 20.3 | 6.5 | 4.3 | 19.8 | 2.6 | 1.6 | 38.1 | [54] |
| Beef tallow | 2.7 | 25.3 | 2.0 | 34.7 | 29.9 | 0.8 | n/a | 4.6 | [55] |
| Beef tallow | 6.3 | 28.0 | 4.7 | 18.0 | 41.0 | 3.3 | 0.8 | 0.0 | [47] |
| Veal tallow | 5.8 | 23.2 | 3.2 | 13.0 | 37.8 | 6.3 | 0.6 | 10.2 | [6] |
| Turkey fat | 0.5 | 17.9 | n/a | 6.1 | 30.1 | 41.1 | 3.2 | 1.1 | [56]  |
| Vegetable oil | Cottonseed oil | 0.8 | 22.9 | 0.0 | 3.1 | 18.5 | 54.2 | 0.5 | 0.0 | [42]  |
| Cottonseed oil | 23.4 | n/a | n/a | n/a | 22.6 | n/a | 52.4 | 1.6 | [57] |
| Sunflower | 0.1 | 6.0 | 0.0 | 5.9 | 16.0 | 71.4 | 0.6 | 0.0 | [42]  |
| Sunflower | n/a | 6.3 | n/a | 4.3 | 80.4 | 7.7 | 0.3 | 1.0 | [58] |
| Waste cooking oil | n/a | 10.9 | 0.6 | 4.0 | 38.1 | 40.5 | 4.7 | 1.2 | [58] |
| Waste cooking oil | 1.1 | 11.5 | 0.6 | 4.2 | 35.2 | 39.7 | 6.2 | 1.4 | [59] |
| Waste cooking oil | 0.3 | 7.7 | 0.5 | 3.5 | 32.3 | 53.3 | 0.3 | 2.1 | [60] |

According to Table 2, C18:1 and C16:0 are two main FAMEs found in animal fat derived biodiesels with average percentage content of 37 and 23 respectively. On the other hand, C18:2 and C18:1 are found to be two main FAMEs in waste cooking oil biodiesels with average content of 45% and 35% respectively. Vegetable oil biodiesels are mainly composed of unsaturated FAMEs; thus, their iodine values are higher than that of animal fat biodiesels. Fuel properties of some popular biodiesels derived from animal fats, cottonseed oil and WCO are presented in Table 3. Literature reported that HHV of the animal fat-based biodiesels are higher than vegetable oil and WCO derived biodiesels (Table 3). This is because of the higher saturation level of the animal fat-based biodiesels, with relatively lower amount of polyunsaturated FAMEs. Due to the same reason, viscosities and cetane numbers of animal fat-based biodiesels were observed to be higher than that of vegetable oils and WCO based biodiesels.

**Table 3**

Fuel properties of biodiesels obtained from waste animal fats and vegetable oils including waste cooking oil.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Feedstock** | **HHV** | **Viscosity** | **Density** | **Cetane** | **Iodine** | **Flash** | **Pour** | **Acid** | **Ref.** |
|  |  | **at 40 °C** | **at 15 °C** | **Number** | **Value** | **Point** | **Point** | **Value** |  |
|  | **(MJ/kg)** | **(mm2/s)** | **(g/cm3)** | **(-)** | **(g/100g)** | **(°C)** | **(°C)** | **(mg/g)** |  |
| Beef tallow | 41 | 5.29 | 0.859 | 58.2 | 44 | 161 | 14 | 0.2 | [47] |
| Chicken | 41.5 | 5.56 | 0.887 | 57.4 | 38 | 176 | 12 | 0.8 | [47] |
| Duck fat | n/a | 4.363 | 0.8785 | n/a | n/a | n/a | n/a | n/a | [49] |
| Fish oil | 40.1 | 4.741 | 0.885 | 52.6 | n/a | 114 | n/a | n/a | [54] |
| Sheep fat | n/a | 5.98 | 0.856 | 59 | 126 | n/a | -5 | 0.65 | [51] |
| Turkey fat | n/a | 4.49 | 0.886 | 52.4 | 91.67 | 178 | 4 | 0.49 | [56]  |
| Cottonseed | 37.5 | 3.75 | 0.885 | 52.8 | n/a | 128 | n/a | n/a | [61]  |
| Waste cooking oil | n/a | 4.6 | 0.871 at 20°C | 51 | n/a | n/a | n/a | n/a | [59] |
| Waste cooking oil | 42.7 | 5.3 | 0.897 | 54 | n/a | 196 | -11 | 0.2 | [62] |

##

About 21 research studies have been reviewed in this section. The review shows that there is a solid consensus about the FAME breakdown of the biodiesels originated from animal fats and vegetable oils (including WCO) biodiesels. Table 2 shows unsaturated FAME dominated (higher FAME fraction) biodiesels and saturated FAME dominated biodiesels. This reveals that the biodiesels which are dominated by the unsaturated FAMEs such as C18:1, C18:2 and C18:3 are produced from vegetable oils, whereas the saturated FAME such as C16:0 and C18:0 dominated biodiesels are originated from animal fats. The only disagreement among the researchers is about the fuel properties of the waste cooking oil biodiesel. Various sources of waste cooking oils used by the researchers (i.e., the usage conditions, type of the cooked food etc) caused the variations in the fuel properties of the WCO derived biodiesels. These findings highlight a gap in the literature about the potential blending of saturated FAME dominated biodiesels with unsaturated FAME dominated biodiesels as their blends could optimise the fuel properties. To better understand this gap and future R & D progress, engine testing of these biodiesels should be investigated.

# 4.0 Engine operation using biodiesels and other advanced biofuels

**4.1. Animal fat biodiesels**

Li and Li [63] stated that the exhaust gas temperature of fish oil biodiesel (F100) was 18℃ (4.7%) lower than diesel operation at maximum speed. Similarly, Behcet et al., stated that exhaust gas temperatures of C20 and F20 were 10oC higher than diesel [64]. Godiganur et al., reported increased exhaust gas temperatures for F100 and F20 by 125oC and 32oC, respectively [65]. Table 4 and Figure 2 summarised the engine performance and exhaust emission characteristics of the reviewed animal fat-based biodiesels and/or blends.

**Table 4**

Engine performance and exhaust emissions characteristics of animal fat biodiesels compared to diesel.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|   |   |   | **Brake**  | **Brake**  |  | **Exhaust gas emissions** | **Exhaust gas** |
| **Reference** | **Test fuel** | **BTE** | **Torque** | **Power** | **BSFC** | **CO2** | **CO** | **HC** | **NOx** | **Smoke** | **Temperature** |
|  |  | **(%)** | **(%)** | **(%)** | **(%)** | **(%)** | **(%)** | **(%)** | **(%)** | **(%)** | **(⁰C)** |
| [64] | F20 |  | -3.2 | -4.33 | 8.3 | -7.87 | -24.4 | -53.5 | 13.77 | -16 | 10 |
| [64] | C20 |  | -1.9 | -2.4 | 5.2 | -7.87 | -19.8 | -20 | 13.77 | -10 | 10 |
| [13] | T5 | -3 |  | -2.3 | 6 |  | -14 |  | -20 | -16 | 12 |
| [13] | T20 | -4 |  | -2.3 | 12 |  | -16 |  | -40 | -27 | 30 |
| [13] | T50 | -5 |  | -4.33 | 18 |  | -5 |  | -12 | -45 | -10 |
| [13] | T100 | -7 |  | -9 | 25 |  | -15 |  | -39 | -57 | 5 |
| [63] | F100 | -3 |  |  | 13 |  | -9 |  | 14.3 | -10 | -18 |
| [65]  | F100 | -5 |  |  | 20.7 |  | -59 | -40 | 14.3 |  | 125 |
| [65]  | F20 | 1 |  |  | 0 |  | -22 | -13.3 | 4.4 |  | 32 |
| [66]  | C20 | 1.3 | 1.4 |  | -3.8 | -1 | -55 | -24 | 2.7 | -8.9 |  |
| [66] | C50 | 0.8 | 1.5 |  | 1.9 | -3.9 | -50 | -12 | 3.3 | -6.7 |  |
| [67] | S30 | 0 |  |  | 5 |  | -25 |  | 12 |  |  |
| [54] | F100 | -12 |  |  |  | 13 | -33.7 | -26.2 | -5.2 |  |  |
| [68] | SS20 | -6.7 |   | 4 | 8.3 | 33 | -30 |   | 12.5 | -71.4 |   |

F100: fish oil methyl ester, C20: Chicken biodiesel 20% + diesel 80%, T100: Tallow biodiesel, S30: Sheep biodiesel 30% + diesel 70%,
SS20: Sheep skin biodiesel 20% + diesel 80%

|  |  |
| --- | --- |
| (a) | (b) |

**Fig. 2.** Changes in (a) engine performance and (b) exhaust emissions characteristics of animal fat biodiesels compared to fossil diesel.

Lin and Li’s study reported that the brake specific fuel consumption (BSFC) of fish biodiesel (F100) was recorded 12.9% higher than diesel and 3% lower than W100 (not shown in Table 4) [63]. Likewise, Godiganur et al., stated that BSFC for F100 operation was 20.7% higher than that of diesel when operated at full load [65]. Behcet et al., observed 8.3% increase in BSFC when the engine was operated with F20 fuel instead of diesel fuel [64]. The increase in BSFC can be related to the energy content of the fish biodiesel, which requires higher fuel to be burned to produce the same power output [56]. This fact also negatively influences the brake thermal efficiency (BTE). Literature tabulated in Table 4 reported biodiesel operation gave rreduced BTE in the range of 3- 12%. In contrast, Godiganur reported that the BTE was increased when B20 blend was used [65]. However, the author reported that BTE values were decreased when higher proportion of biodiesel was used in the blend. This increasing BTE can be attributed to higher diesel content in the blend. Likely, Sen et al., reported slightly improved BTE by 1.3% and 0.8% for C20 and C50 biodiesels [66]. However, these results were also contradicting with their BSFC values for C50 as reported 1.9% higher than diesel. This may be due to the operating condition of the experiments.

The NOx gases are very harmful both for the environment and human health. In human body, lungs are affected by the NOx gas. The NOx gas combines with the water vapour and form nitric acids in the human lungs , which cause respiratory disease [64]. Literature showed that fish and chicken biodiesels increased the NOx emission in the range of 4% to 14.3% (Table 4 and Figure 2) [64]. Most studies reported increased NOx gas emission for biodiesels (Table 4). Few studies reported opposite findings. Tallow biodiesel and blends gave reduced NOx emissions by 20%, 40%, 12% and 39% for T5, T20, T50 and T100, respectively. Similarly, Sakthivel et al., reported a 5.2% decrease in the NOx emission of F100 (not shown in Table 4) [54]. The reasons behind this could be due to varying operating conditions such as feedstock property, additive usage, engine modifications or after-treatment conditions. Masera and Hossain stated that different parameters influences NOx formation and cause contradictory results [69]. Residence time of the fuel-air mixture, spray characteristics, ambient conditions, exhaust gas recirculation (EGR) or other after-treatment applications, physical condition of the experimental equipment, oxygen content and measurement fluctuations were all linked to NOx gas emissions [70]. Particulate matter (PM) is another parameter in exhaust gas which is highly pollutant and harmful for human health. This parameter corresponds to the smoke opacity of the exhaust gas [54]. Lin and Li stated a 4% reduction in smoke opacity for F100 fuel as compared to diesel [63]. In general, smoke opacity followed a decreasing trend as the engine speed decreased. Oner and Altun observed a significant reduction in smoke opacity by 57% when the engine operated with T100 instead of diesel [13]. Biodiesels produced from animal fats gave lower smoke emissions (up to 71% lower than diesel) (Table 4). The main reason for reduced smoke emission is presence of oxygen in biodiesels [5]. The oxygen molecules fill sudden local oxygen vacancies and prevent smoke formation [71]. Another reason for the smoke reduction with biodiesel is the chemical structures of FAMEs, which are free of aromatic compounds [72].

According to Sakthivel et al., CO2 emission in the diesel engine is highly related C molecule stored in the fuel, as it releases during the combustion process and reacts with the oxygen to form CO2 [54]. All carbon atoms in the fuel content convert into CO2 in the case of complete combustion. Behcet et al., reported 7.87% reduction in CO2 emission when biodiesel was used in the engine [64]. In contrast, Sakthivel et al., observed F100 operation gave 6.7% increase in CO2 gas emission than diesel [54]. Jayaprabakar et al., reported 33% increase in CO2 gas emission when SS20 biodiesel blend was used. It was believed that higher oxygen content in biodiesel and higher BSFC caused this characteristics [68]. The higher oxygen content accelerated the combustion, hence higher CO2 emissions was observed. Efficient combustion lead to conversion of more carbon into carbon dioxide rather than carbon monoxide [54]. In the absence of sufficient oxygen, CO gas may be released as a combustion product. Guru et al., stated that the presence of CO emission represents incomplete combustion [73]. Results shown in Table 4 reported CO emissions were lower for animal fat derived biodiesels compared to diesel. Behcet et al., stated that F20 and C20 emitted 24.4% and 19.8% lower CO emissions than diesel [64]. Lin and Li observed 9% reduced CO emission for F100 compared to diesel [63]. Furthermore, the authors reported that the CO gas emission for fish oil biodiesel was reduced by almost 2% than waste cooking oil biodiesel. Godiganur et al., reported that compared to fossil diesel operation, about 59% reduction in CO gas emission was observed when fish biodiesel was used [65]. Sakthivel observed 33.7% decrease in CO emissions for B100 [54]. Oner and Altun reported 14%, 16%, 5%, and 15% reduced CO emissions for T5, T20, T50 and T100 compared to diesel [13]. Current review study demonstrates that biodiesels operation would reduce CO emission compared to diesel. This can be attributed to improved combustion of biodiesel fuel. Unburned hydro carbons (HC) are the result of incomplete combustion [74]. Literature reported decreased HC emissions for biodiesel (Table 4). This demonstrates that biodiesel operation presents improved combustion characteristics compared to diesel fuel. This conclusion agrees with the reduced CO emission results discussed before.

**4.2. Waste cooking oil and inedible vegetable oil biodiesels**

Vegetable oils have attracted the interest of many researchers as they provide a significant energy source. The WCO can be used as an alternative fuel in their ‘second life’. Many studies are available in the literature on the use of vegetable oils and WCO biodiesels as alternative to fossil diesel fuels [75,76]. Table 5 and Figure 3 summarizes the findings from various literature on the use of biodiesels derived from inedible vegetable oils or WCO. More specifically, biodiesels obtained from various waste cooking oils, waste cooking olive oil, cottonseed, Karanja, and Jatropha are reviewed.

**Table 5**

Changes in engine performance and exhaust emissions of the WCO and inedible vegetable oil biodiesels (compared with diesel).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|   |   |   |   | **Exhaust gas emissions** | **Exhaust gas** |
| **Reference** | **Test Fuel** | **BTE** | **BSFC** | **CO2** | **CO** | **HC** | **NOx** | **Smoke** | **Temperature** |
|  |  | **(%)** | **(%)** | **(%)** | **(%)** | **(%)** | **(%)** | **(%)** | **(⁰C)** |
| [78] | W100 | 5 | 2.5 | 3 | -90 | n/a | -4 | -18 | -25 |
| [79] | W100 | 3 | 13 | -20 | -70 | -40 | -10 | n/a | -70 |
| [63] | W100 | -5 | 16 | n/a | -7.3 | n/a | 13 | -21 | n/a |
| [80] | WO100 | n/a | 8.5 | -8.6 | -59 | n/a | -40 | n/a | n/a |
| [81] | CO100 | n/a | 30 | n/a | -52 | n/a | -38 | n/a | -3 |
| [82]  | CO100 | 4 | n/a | n/a | -38 | n/a | -22 | n/a | n/a |
| [83] | CO100 | n/a | 10 | -33 | -20 | n/a | -23 | n/a | -70 |
| [84] | K100 | -20 | 30 | n/a | -92 | n/a | -38 | -50 | 0 |
| [85]  | J100 | -7 | 15 | n/a | -40 | -33 | 10 | -36 | n/a |
| [86] | J100 | -8 | 13 | 40 | -33 | -60 | 52 | -37 | -100 |

W100= waste cooking oil biodiesel, CO= Cottonseed biodiesel, WO100= waste olive cooking oil biodiesel, K100= Karanja biodiesel, J100=Jatropha biodiesel, SO= Soybean biodiesel

|  |  |
| --- | --- |
| (a) | (b) |

**Fig. 3.** Changes in engine characteristics - (a) performance and (b) exhaust emissions.

According to Hossain and Davies, WCO biodiesel gave 5% and 2.5% higher BTE and BSFC than fossil diesel [78]. In-cylinder peak pressure of W100 was 9.7% and 6.7% lower than that of diesel at low and mid-range engine loads, and W100 produced 16% shorter combustion duration [78]. The main drawback was WCO biodiesel produced 3% higher CO2 gas emission than diesel [78]. On the other hand, they reported that WCO biodiesel released 4% and 90% lower NOx and CO emissions than diesel. Similarly, An et al., reported 2% shorter combustion duration for W100 than diesel at all engine loads; this was attributed to the lower calorific value of the biodiesel [79]. In another study, W100 had almost 13% higher BSFC than the other fuels under full load condition [79]. They reported that W100 gave 3% improvement in BTE over diesel at full load [79]. W100 released 70% lower CO than diesel at maximum engine speed (Table 5) [79]. The CO2 and HC emissions were decreased by 20% and 40% respectively when W100 was used in the diesel engine. Interestingly, the authors reported that the NOx emissions at almost all loads were comparable [79]. Very similar results were also observed in another study for W100 except for BTE and NOx [63]. Dorado et al., studied waste cooking olive oil biodiesel in a three-cylinder CI engine [80]. They reported compared to fossil diesel operation, emission of CO, CO2, NO and SO2 gases were decreased by up to 58.9%, 8.6%, 37.5% and 57.7% respectively (Table 5, Figure 3). However, NO2 emission was increased by about 81% [80]. Compared to fossil diesel, Aydin and Bayindir reported that at full load, CO100 fuel gave 20% reduction in engine power, 17% decrease in engine torque and 30% increase in BSFC [81]. However, 52% and 38% reductions in the CO and NOx gas emissions were observed [81]. In another similar study, Dorado et al., reported a significant reduction in SO2 emission by up to 58% with waste cooking olive oil biodiesel operation in a direct-injection diesel engine [80]. Aydin and Bayindir [81] and Karabektas et al., [82], Yucesu and Ilkilic [83] also reported reduction in NOx gas emission around 23% for cottonseed biodiesel CO100 operation. The other emissions like CO and CO2 were reported to be lower than diesel by up to 38% and 33% respectively (Table 5). Furthermore, the BTE of the CO100 was reported to be 4% higher than diesel [82]. The BSFC was reported to be 10% higher than diesel in the study carried out by Yucesu and Ilkilic [83]. Raheman and Phadatare tested Karanja biodiesel K100 and compared the results against fossil diesel operation [84]. They reported a 20% reduction in BTE and 30% increase in BSFC [84]. Engine torque was observed to be 19% lower for K100 than diesel operation [84]. Compared to diesel, exhaust gas emissions of K100 operation were found to be decreased by 92%, 38% and 50% respectively for CO, NOx and smoke emissions [84]. Ganapathy et al., [85] and Chauhan et al., [86] both studied jatropha biodiesel (J100) and reported very similar results in terms of engine performance and exhaust emissions (Table 5). Both studies were conducted on single cylinder diesel engines (Table 5). These studies reported that J100 gave around 8% reduction in BTE, and 15% increase in BSFC (Table 5). Reductions in CO, HC and smoke emissions were observed by up to 40%, 60% and 37% respectively (Table 5). However, CO2 and NOx emissions of J100 were reported to be 40% and 52% higher than diesel at the full load (Table 5). Ganapathy et al., reported 10% increase in NOx emission for J100 at full load and high engine speed conditions [85].

**4.3. Biodiesel-biodiesel blends and other advanced biofuels**

Use of biodiesel-diesel blends in diesel engines are common practice. Very few studies were found on biodiesel-biodiesel blends. Studies found on biodiesel-biodiesel blending are reviewed in this section. Benjumea et al., conducted an experimental study to observe the effects of degree of unsaturation (DU) of palm oil and linseed oil biodiesels [87]. According to them, peak heat release rate (HRR) of the linseed oil biodiesel was 40% higher than palm oil biodiesel [87]. In the case of exhaust gas emission, the authors found out that biodiesel containing higher iodine value released approximately 40% higher NOx gases, and slightly higher smoke opacity compared to biodiesel with lower iodine value content [87]. Rajkumar and Thangaraja tested karanja and coconut biodiesels in a four-cylinder turbocharged diesel engine [88]. They observed an increasing trend in the peak in-cylinder pressure and NOx gas emissions when the proportion of karanja biodiesel was increased in the blends [88]. Sanjid et al., blended kapok and moringa biodiesels with diesel and found comparable engine performance with neat biodiesels and diesel. Biodiesels-diesel blends gave 13-17% higher NO gas emissions than diesel [89]. However, HC and CO emissions were reported to be reduced by 38% and 31% respectively for KB10MB10 blend [89]. Dos Santos et al., studied the traceability of biodiesel-biodiesel mixtures collected from different regions of Brazil [90]. Usta et al., highlighted the importance of using soap stock feedstock, which is a by-product of edible oil extraction process [91]. This feedstock is sustainable, and economically feasible. However, free fatty acid values of soap stock is generally high, which complicates the biodiesel production from soap stock when compared to other feedstock such as vegetable oils [91]. Hence, the authors mixed hazelnut soap stock with waste sunflower oil in 50/50 ratio to reduce the overall free fatty acid content and viscosity value of the feedstock [91]. The WCO collected from fast food shops with high free fatty acid content (about 10%) was blended with the WCO obtained from catering industries [92]. Sharma and Ganesh investigated two different biodiesel blends prepared from linseed, karanja, palm and sunflower biodiesels [93]. The first blend was composed of 25% of all biodiesels; whereas, the second blend contained 37.5% of palm and karanja biodiesels, and 12.5% of linseed and sunflower biodiesels [93]. They reported that the first blend decreased the NOx emission by 20%, but increased the smoke intensity by 30% [93]. In addition, they observed that the CO2 emission was 35% lower when compared to diesel operation [93]. Mehta and Jeyaseelan reported 14% reduction in NO emission with the 80% palm biodiesel - 20% karanja biodiesel blend when used in a 4-cylinder turbocharged direct-injection CI engine [94]. Summarising the biodiesel-biodiesel blending studies, it is clear that this technique is promising for future research. One of the main advantageous of biodiesel-biodiesel blending could be enhancing the utilisation of cheap, highly available, but low fuel quality feedstock such as soap stocks and high free acid content waste cooking oils.

Lapuerta et al., produced advanced biofuel from crude glycerol and used this fuel as blends with fossil diesel by varying the biofuel content from 20 to 80% (vol.) [23]. They reported that the BTE was slightly improved, and the test fuel produced significantly lower HC, CO and smoke emissions [23]. The authors found out that in urban conditions, the NOx emission was slightly higher than diesel. Blends of iso-butanol, n-pentanol, dimethyl carbonate, and fossil diesel was used in a single cylinder DI engine at high loads [95]. The authors reported higher heat release rate and higher in-cylinder pressure due to significant amount of premixed combustion. A reduction in NOx emission was achieved by retarding the fuel injection timings and decreasing EGR content [95]. Frigo et al., tested Levulinate and Dibutyl ether fuels in an air cooled single cylinder direct injection engine; the fuels were produced from cellulose and n-Butanol etherification [96]. The engine performances and NOx gas emissions of the advanced fuels were found to be comparable with the fossil diesel operation [96]. The particulate matter emissions were decreased when they used these advanced fuels. Biodiesels produced from algae are being used in the engines. A review study investigating 16 different types of algae biodiesels showed up to 39% reduction of NOx gas emissions was recorded when neat Azollapinnata algae biodiesel was used in the diesel engine [97]. Algae biodiesels showed promising engine test results in terms of engine performance, combustion characteristics and exhaust gas emissions [97].

**4.4. Summary and R & D gaps**

A detailed study is performed by investing more than 35 research studies on biodiesels produced from different feedstock. Relationship between the biodiesel saturation levels and their effects on the engine performance and emissions are discussed. The results are grouped according to biodiesels saturation levels - animal fat biodiesels which are dominated by saturated FAMEs, waste cooking oil biodiesels which are dominated by unsaturated FAMEs, biodiesel-biodiesel blends and advanced biodiesel (which are generally produced from algae oils) for optimum saturation levels. Enhanced engine performance i.e., higher BTE and lower BSFC was reported for animal fats biodiesel [65] [66]. Use of lower fraction of biodiesel (B20) in diesel might have helped to improve the engine performance. Almost all studies reported lower CO2, CO, HC, and smoke emissions. However, majority of the studies reported increased NOx gas emissions. Biodiesel-biodiesel blends of animal fat, WCO and algae biodiesels could optimise the engine test results due to the enhanced fuel properties. There are limited biodiesel-biodiesel blend studies in the literature which are mainly focused on easing the transesterification process by blending high FAA content vegetable with another vegetable oil with lower FAA content. By this means, easier oil to biodiesel conversion is achieved as the esterification process can be skipped before the transesterification. The research gap highlighted in this study aims to enhance biodiesel fuel properties and the engine test results. The increase in NOx problem (NOx penalty of biodiesels) may not be solved by the biodiesel-biodiesel blend alone. Therefore, the use of NOx emission control strategies is vital for biodiesel applications. This part has been investigated in the following section.

# 5.0 NOx emission mitigation technologies

The NOx gas emission can be reduced through various other ways, some of them are: by adding water (water injection) inside the cylinder, emulsification of biodiesel, use of EGR and by using external accessories in the exhaust systems (after treatment) [99]. Figure 4 shows modern NOx reduction techniques, categorised under three sections: fuel treatment, engine parameters adjustment and after-treatment. Fuel treatment refers to modification of fuel chemistry such as emulsifying, blending, and doping additives. The main aim for fuel treatment and engine parameter modification is to reduce the combustion temperature inside the chamber, and hence lower NOx emission is achieved. The after-treatment systems are connected on the exhaust pipe. Various after-treatment techniques exist such as selective catalytic reduction (SCR), and lean NOx trap.



**Fig. 4.** NOx mitigation techniques - (i) fuel treatment (ii) engine modifications (iii) after-treatment technologies [100].

**5.1. Fuel treatment - emulsification**

This section covers the physical or chemical changes made to the biodiesel fuel in order to achieve lower NOx gas emissions. Figure 5 shows three most popular fuel treatment techniques are: emulsification, diesel blending, and use of additives. Emulsification methods and few case studies related to all three techniques are presented here. Emulsification refers to mixing multiple fluids which are immiscible under normal condition, like biodiesel and water. By using this technique, non-polar and polar fluids can be mixed together and produce stable mixture [101]. The aim in the emulsification of biofuels with water is to improve combustion and reduce harmful gases such as NOx. Emulsification increases the total surface area. In other words, increased contact between the oxygen and fuel yields will lead to more rapid and upgraded combustion in the engine [102]. Water, having a lower boiling temperature, vaporises in the oil which in turn disintegrates the biodiesel cell and results in smaller fuel droplets which is known as micro explosions [103] [104]. Furthermore, additional pressure which occurs due to the spontaneous water explosion contributes to the total force acting on the piston crown and positively affects the engine torque [105]. Figure 5 presents microexplosion process.



**Fig. 5.** Schematic of micro explosion process [100].

In the emulsification process, surfactants are used to blend biodiesel and water. The surfactants help to combine both polar and nonpolar group of molecules and produce stable single phase mixture. Surfactants make water suspend in the fuel, so the water molecules do not undergo direct contact with the metallic surfaces of the engine [106]. Surfactants can be divided into two types in terms of their affinity namely, hydrophilic and lipophilic surfactants [107]. The former has more affinity towards polar liquids like water; and the latter has more affinity towards non-polar liquids. Lipophilic surfactants have more affinity to oil type liquids i.e., biodiesel (methyl esters). Table 6 examines some emulsification studies and NOx reduction potentials. Qi et al., studied the ethanol-soybean biodiesel-water micro emulsion in a single cylinder DI engine [108]. One (1) ml of water was emulsified with 80 ml biodiesel, 20 ml ethanol and 4 grams of Span 80 surfactant. They reported that emulsified fuel had 12.5% lower NOx emission than neat biodiesel. However, this significant reduction was not solely from emulsification, but the contribution of ethanol should not be ignored. In another study, Basha and Anand emulsified 83% jatropha biodiesel with 15% water, they added 2% Span 80 and Tween 80 as surfactants [104]. They reported that up to 23% reduction on NOx gas emission was observed with emulsified biodiesel as compared to neat biodiesel. Their study showed that increasing the water fraction in emulsified fuel gave considerable reduction in NOx gas emission. Similar results was also reported by Annamalai et al., [102]. In their study, the neat waste cooking oil was emulsified with diesel and with various percentages of water i.e., 10%, 20% and 30%. They reported 35%, 50% and 53% reductions of NOx gas emissions when compared to diesel-WCO blend (without water). According to their study, reductions of NOx did not decrease linearly; hence an optimum water fraction must be determined.

**Table 6**

Biodiesel emulsification and NOx reductions.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Reference** | **Biodiesel** | **Diesel** | **Additive** | **Water** | **Surfactant** | **Engine type** | **Max NOx reduction** | **Compared to** |
| [108] | Soybean biodiesel(80 ml) | None | Ethanol(20 ml) | (1 ml) | Span 80(4 g) | 1CY, DI | 12.5% | Neat biodiesel |
| [104] | Jatropha biodiesel(83%) | None | None | (15%) | Span 80 and Tween 80 (2%) | 1CY, DI | 23% | Neat biodiesel |
| [104] | Jatropha biodiesel(83%) | None | Alumina nanoparticle(100 ppm) | (15%) | Span 80 and Tween 80 (2%) | 1CY, DI | 27.7% | Neat biodiesel |
| [102] | WCO(not given) | Diesel(not given) | None | (10%) | Type and amount not given | DI | 45% | Diesel |
| (20%) | 57.7% | Diesel |
| (30%) | 60.6% | Diesel |
| [109] | Annona biodiesel(20%) | Diesel(80%) | None | (5%) | Span 80 and Tween 80 (2%) | Not given | 2.6% | Diesel |
| (7.5%) | 5.2% | Diesel |
| [110] | Jatropha biodiesel(88%) | None | None | (10%) | Span 80 and Tween 80 (2%) | 1CY, DI | 30.3% | Neat biodiesel |
| [110] | Pongamia biodiesel(88%) | None | None | (10%) | Span 80 and Tween 80 (2%) | 1CY, DI | 35.4% | Neat biodiesel |

1CY: Single cylinder, DI: Direct injection, WCO: Waste cooking oil

### 5.2. Fuel treatment - additives

Use of antioxidants for NOx reductions are being investigated. Rizwanul Fattah et al., studied 2(3)-tert-butyl-4-methoxyphenol (BHA) and 2,6-ditert-butyl-4-methylphenol (BHT) synthetic antioxidants as biodiesel additives to reduce NOx gas emission [22]. The authors reported that the NOx emission of biodiesel - diesel (B20) blend was decreased by 7.78% and 3.84% respectively when 2000 ppm BHA and BHT additives were used. However, some negative aspects of the antioxidant doped fuels were also reported. For example, 8-9% increase in CO, 17% and 27% increase in HC, and 16% and 19% increase in smoke emissions were reported for BHA and BHT doped biofuels. Another study stated that the effect of BHT is stronger on non-polar hydrocarbons compared to fatty oils and esters; but its antioxidant efficiency is significantly low at early reaction stages because of the high volatility characteristics [111]. Adam et al., compared the performances of four various antioxidants in terms of NOx reduction potential, they are: N,N′-diphenyl-1,4-phenylenediamine (DPPD), N-phenyl-1,4-phenylenediamine (NPPD), 2(3)-tert-Butyl-4-methoxyphenol, and 2-tert-butylbenzene-1,4-diol (TBHQ) [112]. The four antioxidants were added into diesel-palm oil biodiesel blends (50/50% by volume) at different fractions (Table 7) [112]. They observed a reduction in NOx emission by 9% compared to the base biofuel without additives [112]. However, like previous studies, they also reported approximately 25% increase in CO, 42% increase in HC and 32% increase in smoke opacity [112]. The reason for CO increase can be attributed to antioxidants inherent property of hindering the CO to CO2 conversion [113]. The increase in HC is due to the reduced hydroxyl radicals (OH) which helps to form H2O by breaking down the HC molecules [114]. Reduced oxygen content and increased aromatic compounds explains the reasons for increased in smoke opacity [115].

**Table 7**

Influence of biodiesel fuel additives on NOx and other emissions.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Reference** | **Biodiesel** | **Diesel** | **Additive** | **Engine type** | **Reduction in NOx** | **Increase in** |
| [22] | Coconut biodiesel(20%) | (80%) | 2(3)-tert-butyl-4-methoxyphenol (BHA)(2000 ppm) | 4Cylinder, IDI | 7.78% | 8% CO17% HC16% smoke |
| [22] | Coconut biodiesel(20%) | (80%) | 2,6-ditert-butyl-4-methylphenol (BHT)(2000 ppm) | 4Cylinder, IDI | 3.84% | 9% CO27% HC19% smoke |
| [112] | Palm oil biodiesel(50%) | (50%) | N,N′-diphenyl-1,4-phenylenediamine (DPPD)(2000 ppm) | 4Cylinder, IDI | 9% | 25% CO33% HC20% smoke |
| [112]  | Palm oil biodiesel(50%) | (50%) | N-phenyl-1,4-phenylenediamine (NPPD)(2000 ppm) | 4Cylinder, IDI | 9% | 8% CO42% HC24% smoke |
| [112] | Palm oil biodiesel(50%) | (50%) | 2(3)-tert-Butyl-4-methoxyphenol (BHA)(2000 ppm) | 4Cylinder, IDI | 9% | 25% CO50% HC33% smoke |
| [112] | Palm oil biodiesel(50%) | (50%) | 2-tert-butylbenzene-1,4-diol (TBHQ)(2000 ppm) | 4Cylinder, IDI | 7.5% | 33% CO42% HC38% smoke |

**5.3. Engine parameters and components modifications**

Engine modifications to achieve lower NOx emissions are discussed in this sub section. There are two different types of changes in the engine – components levels and parameter level. The changes on the fuel injection parameters such as (i) injection pressure and timing, (ii) advanced combustion techniques like LTC, HCCI, (iii) dual fuel injection strategies like RCCI, and (iv) water injection methods are investigated. The maximum possible NOx reduction potentials for each of the different changes are being reviewed. In addition, the effects on other gases are also investigated, ie. what happens to other gases when NOx gas is reduced. Biodiesels’ engine performance, combustion and exhaust gas emissions characteristics can be upgraded by injection timing and injection pressure adjustment. To illustrate, injection timing can be reset with respect to cetane number, and injection pressure can be changed with respect to viscosity and density values of biodiesel. Agarwal et al., studied the influence of injection pressures by setting the pressure at 300, 500, 750 and 1000 bar on a common rail direct injection CI engine fuelled with karanja biodiesel-diesel (50/50 by volume) blend [116]. They also varied injection timings between -24° and 4°CA. The authors reported that the NOx emission was decreased when injection pressure was increased. They found out that NOx emissions were reduced at 300 and 500 bar injection pressures, and at -9° and -3°CA injection timings [116]. Similarly, Gnanasekaran et al., studied the effects of injection timing on NOx emission of fish oil biodiesel [117]. They reported that NOx emission was reduced by approximately 2.1% by advancing the injection timing from 24°bTDC to 27°bTDC [117]. However, they found out that the CO emission was increased by about 20% whilst smoke and HC emissions remains unchanged [117]. Deep et al., investigated the influence of injection pressure and injection timing on a single-cylinder diesel engine fuelled with castor biodiesel-diesel blend (20/80 by vol.) [118]. They reported around 16% and 32% reductions in NOx emission by retarding the injection timing from 25° to 23°bTDC and 23° to 21°bTDC, respectively [118]. Similar to other studies, reducing injection pressure by 50 bar resulted in up to 16% reductions in NOx emission [118].

### 5.3.1. Advanced combustion strategies

Various advanced combustion studies were investigated for low NOx emission by applying low-temperature combustion (LCT) strategies [24]. Homogeneous Charge Compression Ignition (HCCI) is an example of advanced combustion techniques which reduces NOx gas emissions [119], and provides high engine performance [120]. The main principle on this technique is to avoid high combustion temperature, which happens due to flame propagation in the cases of SI and CI engines [119]. In HCCI combustion technique, fuel and air is mixed homogenously in the combustion chamber, and local burning of fuel droplets is achieved simultaneously to avoid flame propagation (Figure 6). On the other hand, about 9% increase in HC emission was observed with HCCI combustion [74], this could be a negative side of this technique. The difficulty of low combustion control and high mechanical stress on the combustion chamber were also reported as disadvantages of HCCI technique [121]. To solve these problems, Bessonette et al., conducted a test on a caterpillar 3401E single-cylinder test engine under HCCI conditions [122]. They reported that some drawbacks of HCCI technique can be solved by arranging engine operating conditions i.e., using higher CN fuels at low engine loads, and low CN fuels at higher loads. Variable valve timing [123], optimisation of valve lift [124], and residual gas trapping [125] are other options to improve HCCI combustion operation. Although those research could help to address the disadvantages of the HCCI combustion, the operating range of HCCI is yet to be developed [121].



**Fig. 6.** Schematic of combustion initiation on spark ignition, compression ignition and homogeneous charge compression ignition engines [100].

The dual fuel injection process also known as Reactivity Controlled Compression Ignition (RCCI) is another popular advanced combustion technique [126]. In this type, high reactivity (high cetane number) fuel like biodiesel is injected into combustion chamber [127], and a low reactivity fuel with high octane number (natural gas, alcohols, gasoline) is injected typically in the intake manifold [128] (Figure 7). The combustion starts with the fuel having high reactivity at the top of the combustion chamber, after that it expands towards the bottom of the combustion chamber. By this method, overall combustion duration increases due to the high reactivity differences of two fuels; thus cylinder temperature reduces and produces less NOx gas [129].



**Fig. 7.** RCCI engine operation. Low reactivity fuel is injected at the inlet manifold and high reactivity fuel is injected into combustion chamber [100].

Salahi et al., studied RCCI combustion in an IDI diesel engine using natural gas and diesel low reactivity and high reactivity fuels [126]. They stated that the fraction of highly reactive fuel should be kept relatively low due to the presence of pre-chamber in IDI engine [126]. Mahla et al., studied the duel fuel injection in a single cylinder DI engine using compressed natural gas (CNG) and 20% jatropha biodiesel blended with diesel [130]. They reported a 13% increase in NOx emission with the CNG-biodiesel blend dual injection relative to simple diesel injection. However, the authors found out that with the addition of EGR system at 15% valve opening, the NOx emission was dropped by 25% relative to neat diesel operation at the full load. Gharehghani et al., tested biodiesel-natural gas fuels on a single-cylinder variable compression ratio engine [128]. Up to about 85% and 87% reduction in NOx gas emissions were observed by the authors with RCCI mode relative to neat diesel and neat biodiesel operation. They mentioned approximately 50% higher CO emission and 8 times increased HC emissions when compared to neat biodiesel operation. The chemistry of natural gas might be the reason behind for increased CO and HC emissions. This issue can be addressed by using biofuels as a low reactivity fuel such as bioethanol, butanol, or syngas. It is clear from the literature that that even though the RCCI method can reduce the NOx emission, other emissions may be increased. Development of smart fuel supply system along with a operational algorithm should be developed for RCCI combustion.

**5.3.2. Water injection strategies**

There is a good number of studies available in literature on the effect of water injection into combustion chamber both on spark ignition and compression ignition engines [131]. The main advantage of this technique over the catalytic converter and EGR is the capability of NOx reduction at any engine load without increasing the PM emissions [132]. Similar to emulsification, the injected water reduces the combustion temperature by absorbing the heat during the combustion [133]. Consequently, NOx emission reduces with diminished peak flame temperature. The water can be injected in many different ways. Stanglmaier et al., developed a multi-functional injection system which can inject both fuel and water through the same injector [134]. They injected diesel (70%) + water (30%), reported a reduction in NOx emission by approximately 15% relative to neat diesel operation. However, around 50% and 65% higher CO and HC gases were observed. The injection of water in the intake manifold is relatively easier option than combustion chamber. Subramanian injected 40% (by mass) diesel through the intake manifold and tested in a single -cylinder diesel engine [103]. They reported approximately 41% NOx reduction. However, they found out that the CO, HC and smoke emissions were increased by 6.7%, 33% and 26% respectively. Another study conducted by Tesfa et al., reported that the NOx gas emission of neat rapeseed biodiesel was reduced by up to 50% when water was injected in intake manifold at the flow rate of 3 kg/h [133]. They found out that the CO emission was increased by 40%. Adnan et al., also used water injection through the intake manifold [135]. They reported significant improvement in NOx emission when the water was injected at 2 bar pressure. However, they reported that SO2 emission was 17% higher than without water application. Another study observed 37% reduction in NOx emission by using 270 g/kWh water injection [136]. However, the drawbacks of this technique are higher CO, HC and smoke emissions, increased by up to 100%, 54% and 55%, respectively (Table 8). Table 8 summarises the case studies according to their operation conditions, maximum NOx reductions and drawbacks on other emissions. To sum up, direct water injection found to be a good way of reducing NOx gas emission. However, it was noticed that other exhaust gases like CO, HC, SO2 and smoke emissions were negatively affected by this technique. The reasons behind this is due to the reduced combustion temperature. Another disadvantage of this technique is the direct contact between the water and the metallic surfaces, such as contact of water molecules with intake manifold and combustion chamber surfaces. In the long run this may lead to corrosion and erosion of metals. Long duration engine study is needed to establish the negative effects of water on metallic surfaces,

**Table 8**

Summary of direct water injection studies - maximum NOx reduction at full load and negative aspects of other exhaust gases.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Reference** | **Fuel** | **Water injection** | **Engine type** | **Reduction in NOx** | **Increase in** |
| [103] | Diesel | 40% of diesel by mass | 1CY, water injected through intake manifold | 41% | 6.7% CO33% HC26% smoke |
| [133] | Rapeseed biodiesel (100%) | 3 kg/h | 4CY, DI, turbocharged, water injected through intake manifold | 50% | 40 % CO |
| [135] | Diesel and Hydrogen (5 l/m) | 2 bar | DI, naturally aspired, dual fuel, water injected through intake manifold | 100% | 17% SO2 |
| [136] | Pilot fuel: Diesel (80%) + Biodiesel (20%)Main fuel: Hydrogen (100%) | 270 g/kWh | 1CY, naturally aspired, water injected through intake manifold | 37% | 100% CO54% HC55% smoke |
|  [134] | Diesel (70% by volume) | (30%) | Volvo D-12, DI, water injected directly into the combustion chamber | 15% | 50% CO65% HC |

**5.4. Exhaust gas after-treatment technologies**

Selective Catalytic Reduction (SCR) is considered to be most efficient after-treatment technology for mitigating the NOx emission [137,138]. It was first commercialised for heavy duty CI engines in 2005 [139]. In this technique, water-urea solution is injected into exhaust gases. When the solution reacts with the flowing hot exhaust gases, the solution decomposes to ammonia and reacts with the NOx gases to form N­2 in the presence of catalyst [138]. The honeycomb monolith catalyst made of V2O5-WO3/TiO2 is generally used. After year 2010, the catalyst is shifted to Fe-promoted zeolite due to better durability, reliability and improved activation with NO2 [139]. Equation 1 shows the decomposition of urea [CO(NH2)2] into ammonia [NH3], equation 2 shows how ammonia [NH3] converts nitrogen oxide [NO] and oxygen [O2] into nitrogen [N2] and water [H2O], and equation 3 shows the same conversion for both nitrogen oxide [NO] and nitrogen dioxide [NO2] [140]. Cheruiyot et al., stated that the SCR system operates more efficiently at higher engine loads [141]. NOx formation at high engine loads is higher due to high in-cylinder temperature.

|  |  |
| --- | --- |
| $$(NH\_{2})\_{2}CO+ H\_{2}O \rightarrow 2NH\_{3}+ CO\_{2}$$ | (1) |
| $$4NH\_{3}+4NO+ O\_{2} \rightarrow 4N\_{2}+6H\_{2}O$$ | (2) |
| $$4NH\_{3}+ 2NO + 2NO\_{2} \rightarrow 4N\_{2}+6H\_{2}O$$ | (3)  |

Researchers investigated the efficiency of the SCR method under various conditions. For example, Tadano et al., reported 68% reduced NOx emission for biodiesel with the application of SCR [142]. Sachuthananthan et al., studied the effects of Butylated hydroxytoluene antioxidant and SCR system on a single cylinder diesel engine fuelled with neat neem biodiesel [143]. They reported that neem biodiesel gave about 11% higher NOx emission than diesel without antioxidant and SCR applications. When 100 mg of antioxidant added into 1 kg of neem biodiesel, the NOx emission dropped by 12.5% and 22.2% compared to diesel and neat biodiesel. The NOx emission was further reduced by 82% with the application of SCR after treatment technique [143]. Resitoglu reported that biodiesel promotes the activity of DOC by up to 14.66% compared to fossil diesel, no significant changes in NOx mitigation at the SCR was observed [25]. In another study, Zhang et al., [138] investigated the durability of a 6-cylinder turbocharged diesel engine fuelled with B20 (produced from WCO) with common rail fuel injection system and after-treatment components of DOC and SCR. They reported 25% increase in NOx emission after 500 hours operation of the engine. The main disadvantage of the SCR system is the N2O generation. N2O is a harmful greenhouse gas which is not a typical product of the fuel combustion [139]. Its global warming potential was reported as 298 times greater than CO2 [139]. Moreover, it is a very stable gas in the atmosphere with approximately 114 years of lifetime [144]. Grossale et al., explained the N2O formation from NO2 emission (equation 4, 5 and 6) [145]. Nitrogen dioxide (NO2) and ammonia (NH3) react, and form ammonium nitrate (NH4NO3), shown in equation 4, which then decomposes to nitrous oxide (N2O) and water (H2O) (equation 5). Equation 7 and 8 gives equation 6 which describes the N2O formation from NO2.

|  |  |
| --- | --- |
| $$2NH\_{3}+ 2NO\_{2} \rightarrow NH\_{4}NO\_{3}+ N\_{2}+H\_{2}O$$ | (4) |
| $$NH\_{4}NO\_{3} \rightarrow N\_{2}O+ 2H\_{2}O$$ | (5) |
| $$2NH\_{3}+ 2NO\_{2} \rightarrow N\_{2}O+ N\_{2}+ 3H\_{2}O$$ | (6) |

Cho et al., agreed with the equation 9 [139]. Moreover, Djerad et al., addressed other possible N2O formation reactions for NO emission when reacts with O2 (equations 7 and 8) [146].

|  |  |
| --- | --- |
| $$4NH\_{3}+4NO+ 3O\_{2} \rightarrow 4N\_{2}O + 6H\_{2}O$$ | (7) |
| $$2NH\_{3}+2O\_{2} \rightarrow N\_{2}O + 3H\_{2}O$$ | (8) |

It should be noted thar the SCR systems can reduce the NOx emission very effectively (by up to 82%); however, SCR treatment produces another harmful greenhouse gas, N2O, which is not normally produced through fuel combustion [139]. This fact can be considered as the main drawback of the SCR application.

The Lean NOx trap is another exhaust gas after-treatment technology that involves precious metals in its content such as Palladium, Platinum and Rhodium [26]. It is frequently used together with the other exhaust gas after-treatment technologies including SCR. This system traps NOx emission at the lean conditions, then converts into nontoxic gases such as N2 and H2O during the rich conditions with the help of reductants such as HC and CO [147]. The simplified reaction mechanism is given under three stages which are (i) storage of the NOx in the form of NO2 as the BaCO3 converts into BaNO3 (equations 9 and 10); (ii) release of NOx as BaNO3 converts back into BaCO3 (equations 11 and 12); and (iii) conversion of NO2 into N2, H2O and NH3 with the help of available HC and CO (equations 13, 14, 14 and 16) [147].

|  |  |
| --- | --- |
| $$NO+\frac{1}{2}O\_{2}\rightarrow NO\_{2}$$ | (9) |
| $$2NO\_{2}+BaCO\_{3}+\frac{1}{2}O\_{2}\rightarrow Ba\left(NO\_{3}\right)\_{2}+CO\_{2}$$ | (10) |
| $$Ba\left(NO\_{3}\right)\_{2}\rightarrow BaO+2NO\_{2}+\frac{1}{2}O\_{2}$$ | (11) |
| $$BaO+CO\_{2}\rightarrow BaCO\_{3}$$ | (12) |
| $$NO\_{2}\rightarrow NO+\frac{1}{2}O\_{2}$$ | (13) |
| $$NO+CO\rightarrow CO\_{2}+\frac{1}{2}N\_{2}$$ | (14) |
| $$\left(2m+\frac{n}{2}\right)NO+CmHn\rightarrow mCO\_{2}+\left(m+\frac{n}{4}\right)N\_{2}+\frac{n}{2}H\_{2}O$$ | (15) |
| $$NO+\frac{5}{2}H\_{2}\rightarrow NH\_{3}+H\_{2}O$$ | (16) |

DiGiulio et al., tested the cycle durations for lean and rich conditions for a lean NOx trap consisting of Pd, Pt, Rh, CeO2 and BaO at 250 ℃ and 500 ℃ [148]. The maximum NOx conversion and NH3 yield were found to be 87% and 46% for lean and rich conditions respectively, and with 60s and 15s at 250 ℃ [148]. The NH3 in the lean NOx trap is used in the downstream SCR system. However, similar to SCR technology, lean NOx trap also have N2O slip especially below 250 ℃ [148].

In this section, the NOx reduction strategies are covered under 3 subcategories (Figure 4) which are fuel treatment, engine modification and exhaust gas after-treatment. Among the biodiesel emulsification studies, Span 80 and Tween 80 are the commonly used surfactants used to embed the water droplets in biodiesel fuel. Emulsification technologies reported NOx reduction between 3% and 60% (Table 6). Most used antioxidant fuel additive is BHA with the highest reported NOx reduction of 9% (Table 7). The other effective method is the water injection through intake manifold with the maximum NOx reduction of 50% (Table 8). However, the side effects of this method gave up to 100% increase in CO emissions and considerable increases in other harmful gas emissions (Table 8). It can be noted that there is not enough knowledge in the literature about the long-term side effects of the water injection into combustion chamber. The water molecules are in the direct contact with the metal walls of the combustion chamber which may cause corrosion and/or erosion problems. The exhaust after-treatment technology which is one of the widely used NOx control strategy in the market can provide NOx reduction more than 80% due to its cutting-edge design and ammonia injection. The outcome of NOx mitigation technology reviews carried out in the current work are in-line with the other studies found in the literature [149] investigating water injection, engine modification and biodiesel emulsification techniques [99]. However, this study covers additional techniques such as antioxidant fuel additives and exhaust gas after-treatment systems.

Biodiesel-biodiesel blending together with the NOx mitigation technique is suggested as feasible solution to meet both biodiesel fuel quality and NOx mitigation. Figure 8 shows that biodiesels produced from animal fats has high fraction of saturated FAMEs, hence their blends with WCO or algae biodiesels can improve the fuel properties. The improved fuel properties are likely to increase the NOx emission due to higher combustion temperatures. Therefore, use of NOx emission control techniques like SCR after-treatment system is strongly recommended.



**Fig. 8.** Biodiesel-biodiesel blending, and use of the SCR after=treatment

# 6.0 Economic aspects

An overview of the economic aspects of biodiesels’ fuel property enhancement trough biodiesel-biodiesel blending and NOx mitigation technologies is discussed in this section. According to life cycle cost analysis, the economic value of WCO is about 31% higher as compared to fossil diesel [150]. The major factors were reported as the cost of WCO collection from various locations with a factor of 83%, and the cost of methanol used in the transesterification process [150]. Biodiesel-biodiesel blending technique proposed in this study to improve fuel properties would not impact the costs as the mixing between the two different biodiesels would not require any special equipment or chemicals. The economic aspects of the NOx reduction technologies were analysed in detail for a marine engine [151]. Table 9 shows equipment cost and cost per kW power produced by the marine engine at different engine speed and load conditions [151]. The NOx reduction technologies show cheaper with the increasing engine power. This can be explained by making more out of the fixed instalment cost at higher operating conditions. The fuel switching method is given as the cheapest method in Table 9 which may allow the fuel switch between fossil to biofuels as well as biodiesel-biodiesel mixtures. The SCR technology which is one of the most effective NOx mitigation technologies, is found to be around 43 $/ kW for a 12 cylinder 1400 litre engine operating at 100 rpm.

**Table 9**

Economic aspects of the NOx mitigation technologies, adapted from [151].

|  |  |
| --- | --- |
|  | **Test engines and conditions** |
| Engine speed (rpm) | 650 | 550 | 500 | 130 | 110 | 100 |
| Engine power (kW) | 4500 | 9500 | 18000 | 8500 | 15000 | 48000 |
| Number of Cylinders | 9 | 12 | 16 | 6 | 8 | 12 |
| Cylinder volume (litre) | 35 | 65 | 95 | 380 | 650 | 1400 |
| **NOx reduction technology** | **Economic cost per produced power ($ / kW)** |
| Emulsified fuel | 19.2 | 12.5 | 8.4 | 13.9 | 10.1 | 4.4 |
| Direct water injection | 41.2 | 30.9 | 25.2 | 33.4 | 34.5 | 23.1 |
| Selective Catalytic Reduction (SCR) | 86.7 | 56.7 | 38.9 | 73.9 | 63 | 43.4 |
| Exhaust Gas Recirculation (EGR) | 19 | 12 | 8.6 | 13.1 | 10.5 | 5.2 |
| Seawater scrubber | 93.7 | 65.7 | 49.9 | 72.2 | 57.5 | 35.8 |
| Fuel switching | 7.8 | 4.6 | 3.2 | 5 | 3.7 | 1.6 |

# 7.0 Conclusions and scope for future R&D

In this study, two challenges of biodiesels combustion are investigated. Options for biodiesel fuel property enhancement and NOx emission reduction techniques are critically reviewed, In addition, an in-depth review is carried out un this study on biodiesel feedstock, transesterification details, biodiesel quality, engine tests, and engine modifications technologies. After understanding the published studies and careful analysis of the literature, the following findings and knowledge gaps are found:

* Fuel properties of biodiesels produced from waste cooking oils (including inedible vegetable oils) and animal fats are very different. fuel properties of waste cooking oil and inedible vegetable oil biodiesels are superior to animal fat biodiesels mainly in terms of viscosity and acid value. On the other hand, animal fat biodiesels are better than waste cooking oil and inedible vegetable oil biodiesels in terms of higher heating value, cetane number and iodine value. From the literature review it is discovered that fuel properties could be optimised by blending these opposite groups of biodiesels. Hence, it is suggested to investigate the biodiesel-biodiesel blends for improved fuel properties and better combustion in the internal combustion engines.
* Literature review showed that biodiesels derived from vegetable oils are blended with each other for various purposes like cheap production, enhance fuel properties and ease transesterification. However, biodiesels derived from waste cooking oil and vegetable oils are likely to have similar fuel properties as they are mainly composed of unsaturated FAMEs. On the other hand, animal fats, which are composed of saturated FAMEs, are also important feedstock used for biodiesel production. Blends with unsaturated biodiesels could provide promising fuel properties and engine results. Thus, it is recommended to investigate on blending waste cooking oil biodiesel or inedible vegetable oil biodiesels with animal fat biodiesel to test fuel properties, diesel engine performance, combustion, and emissions characteristics.
* The effect of degree of unsaturation of biodiesel is investigated [43,87,150]. The previous studies tested biodiesels produced from soy, canola, rapeseed, palm, linseed, and tallow to understand the effect of degree of unsaturation. However, effect of other fuel properties such as viscosity, density, heating value, volatility, carbon, hydrogen, and oxygen contents etc. influences the results. It is believed that this parameter can be analysed in more detail when the effects of fuel properties other than degree of unsaturation are minimised. In this regard, it is recommended to investigate the effect of degree of unsaturation in more detail such as by blending two biodiesels having different degree of unsaturation values each other at different volume fractions.
* This review shows that biodiesels have comparable and even higher NOx emissions compared to diesel. Researchers have investigated various techniques to reduce the NOx emission i.e., fuel treatment, engine modifications and after-treatment. Among these options, fuel additives such as alcohols and antioxidants are found effective way of NOx reduction, but their side effects are also observed as increase on other emissions like CO, HC, and smoke opacity. Considering the effectiveness of the additives, it is recommended to investigate new additives which would reduce the NOx emission by minimising or eliminating the increase on the other harmful exhaust gases.
* Exhaust after-treatment system such as SCR is a promising technology to reduce up to 82% NOx gas emission coming out from the engine. However, the use of catalytic converter may cause problems like high back pressure, erosion, clogging, expensive cost and limited life time [151]. It is suggested to investigate non-catalytic after-treatment technologies with commercially available injection agent to reduce NOx emission. Although such a technology is likely to give lower NOx reduction efficiency, it would be suitable for the low power density diesel engines which cannot handle high back pressure of the existing SCR system. The after-treatment system could compensate (to some extend) the absence of the catalytic by upgrading the turbulence and residence time of injected fluid and exhaust gases. This is a topic for after treatment industries for further development.
* Use of biodiesels are increasing as a promising diesel alternative. Their uses in marine and aviation sectors are getting much attraction in recent years. It is important to carry out long term engine durability study combining biodiesel-biodiesel blending and NOx after treatment techniques. This is an important R&D topic for the industry and researchers involved in this topic.

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