



A comprehensive review on the application of bioethanol/biodiesel in direct injection engines and consequential environmental impact



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ABSTRACT

Bioethanol/biodiesel are deemed a highly suitable alternative to conventional fuels in the near future due to their versatility in production techniques and operability. This paper examines the engine performance and possible scope of improvement in direct injection engines powered by biofuel blends. The obtained outcomes from this review are mainly focused on three distinguished fuel properties: fuel feasibility, emissions, and engine performance. Critical analysis of these factors is followed by the highlighting of the possible scope of improvement. This review indicates that biofuels perform best with additives or as an additive when used with traditional petroleum fuels. Research analysis indicates that biodiesels show significant improvement in ignition delay due to higher oxygen content compared with traditional petroleum fuels and produce lower emission of pollutant gas. However, engines have shown a decrease in performance regarding power output, torque, and fuel efficiency. The suggested improvement to counter these issues include the addition of nanoparticles, exhaust gas recirculation, ethanol/methanol fumigation, and introduction of various methyl esters into the mixture.

1. Introduction

Internal combustion engines that run on fossil fuels are widely used as main instrument for power generation in almost all sectors involved in development ie, transportation, construction, industry, electricity generation etc. due to their efficiency factors. Modern technologies and researches are focusing on reducing fossil fuel-dependency to ease the environmental burden. Although, large engines and power generators are not ready just yet to run on batteries due to their requirement of large batteries/power storages. Besides, as the transformation of combustion engine to electric engine is still taking shape and developing, any premature transformation to electric vehicle will have severe consequences to the sustainability foundation, ie, social, economic, environment (Kalghatgi, 2018).

Nonetheless, currently there are tremendous effort has been given to develop petroleum-based conventional fuels driven internal combustion engines that produces less emission without compromising the desired

outcome. As such, researches on production of biodiesel from reusable or waste organic products have been ratcheted up and biodiesel-biofuel-additives based fuels were tested extensively for the past decades. All these efforts from the researchers around the globe strongly suggest that all sectors involved in development will be predominantly powered by mostly fossil fuels and combustion engines, therefore, to achieve sustainability the engines along with fuels and their blends must be sorted which perform best yet cause least emission (Leach et al., 2020).

In order to fully understand the performance benefits of biofuels on a direct injection (DI) diesel engine, a variety of performance aspects of the engine need to be considered. This work will explore the various engine performance aspects to determine the feasibility and possible benefits of biofuels. There is always a demand for fuel and additives for better performance of the existing engines without any changes or modification to it. Therefore, many researchers have investigated the biodiesel and its blends with antioxidants or nano or oxidative additives. Review articles with in-depth analysis of specific and limited additives are available; although there is limited literature on inclusiveness to most of the effects

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Abbreviations

CO	Carbon monoxide
CO ₂	Carbon dioxide
NO _x	Nitrogen oxides
HC	Hydrocarbon
SO ₂	Sulphur dioxide
DI	Direct Injection
O ₂	Oxygen
g/kWh	gram per Kilowatt-hour
rpm	Revolutions per minute
BMEP	Brake Mean Effective Pressure
BP	Brake Power
BSFC	Brake Specific Fuel Consumption
BTE	Brake Thermal Efficiency
COME	Canola Oil Methyl Ester

CI engine	Compression Ignition Engine
DE	Diesel-Ethanol
EGR	Exhaust Gas Recirculation
FOBAS	Fuel Oil Bunkering Analysis and Advisory Service
HO	Hydroxyl gas
HPSS	High Pressure Supply System
ICE	Internal combustion engine
LPSS	Low Pressure Supply System
LTC	low-temperature combustion
NO _x	Nitrogen Oxides
PBDF	Petroleum-Based Diesel Fuel
PFR	Premixed Fuel Ratio
SFC	Specific Fuel Consumption
S100	100% Soy Bio-diesel
ULSD	Ultra Low Sulphur Diesel
WPOME	Waste Palm Oil Methyl Ester

of additives and their usage.

This report gathers information from multiple sources of literature related to the topic. The fuels that will be discussed in this report shall comprise pure diesel, diesel-biodiesel blends, diesel-bioethanol blends, and diesel-biodiesel-bioethanol blends. Moreover, biodiesel nanoparticles, biodiesel antioxidant, and biodiesel oxidative additives will be discussed. Comparison will be made between the different fuels and their effect on compression ignition DI diesel engine, where a conclusion will be drawn through a detailed discussion. For this purpose, a wide range of nanoparticles and their oxides are reviewed. Data from different types of fuels and the blends of their variable concentrations and proportions were analysed in this comparative study to understand the niche of these renewable fuels in the future market for powerful engines. In doing so, much focus was given to the fuel quality and its combustion behaviour. Therefore, this review will provide a combination of the results for different fuels and their energy generation characteristics.

This review aims to establish the similarities, comparisons, contrasts, and deductions on the performance of these various fuel blends and consequently, shed light on any possible improvements. In addition, this paper will elaborate on fuel properties and emission characteristics to supplement the information gathered on the performance of the fuel blends.

1.1. Review procedure

This comprehensive report was prepared mostly by reviewing the published research papers or books published over the years. Among other sources, industrial reports, patents and academic reports were also considered. The main focus of this work is to compare and compile data from the above mentioned sources on engine and its performance when different type and quality of fuels are used. However, this review work did not intend to validate or to find the significance between different reports, instead the aim of this work was to present an inclusive report on different engine behaviours with different fuels and blends. Also, to do a qualitative analysis of engine's performance and its relation to emission of different gases to see how the engines' output varies when emission reduction is focused.

The whole process of reviewing has been shown in the flowchart below, where flow of the story can be found in a nutshell.

2. Literature review

2.1. Fuel properties and feasibility

Diesel engines have been used extensively and from early industrialisation due to their low cost, reliability, and longevity over gasoline

engines. It is considered the main source of power behind the mass transport, production and constructions around the world. However, several drawbacks are observed regarding their emission content, which is claimed to be a serious environmental problem such as acid rain, ground-level ozone, and particulate pollution, among others (Reşitoğlu et al., 2015).

This research focuses on the ideal fuel mix that would result in the best performance outcome of a DI engine. But the problem arises when mixing additives such as ethanol/bioethanol in diesel at low temperatures (Shahir et al., 2014). Therefore, mixing bioethanol in diesel requires careful deliberation to obtain an ideal fuel property mixture for DI diesel engine.

Although all alcohol blends in diesel fuel work in a similar manner, the composition of C/H/O, heating value, ignition, combustion, emission, etc. make the differences in their performance (Ghadikolaei et al., 2018). The best performance of an engine is obtained with certain percentage of biodiesel mix. A change in performance of an engine is obtained when, at least 5% of biofuel is used. Adding ethanol/bioethanol to diesel leads to changes in the properties of the mix in various aspects, such as viscosity, flash point, calorific value, and stability. Nevertheless, the mixture needs to satisfy certain standards in order to be useable in a DI engine (Yusoff et al., 2015). Some of the most important properties of the fuel mixture are further explained below:

2.1.1. Fuel quality enhancement through diesel-biodiesel-ethanol blends to increase engine performance

The methodology for diesel-biodiesel ethanol mixture involves various techniques to achieve the ideal solution (Torres-Jimenez et al., 2012). Some of the techniques adopted for the mixing of bioethanol with diesel are mentioned below:

- I. One of the focus was to control and maintain the temperature at which these fuel types are well mixed, since the synthetic diesel fuel temperature differs from that of biodiesel/ethanol. Therefore, obtaining a homogenous mixture of diesel-biodiesel-ethanol is very important and a wide variation in temperature would cause a fuel clog (Yilmaz et al., 2014).
- II. In a diesel-biodiesel-ethanol blends, ethanol has a characteristic 95% mass so the mixing is a challenge yet 95% ethanol makes the optimum fuel mixture to yields best physical and chemical properties. Although using this fuel mixture requires minor changes to the engine to suit the properties of ethanol (Tulliza et al., 2018). Even so, the diesel-biodiesel-ethanol mixture is hard to be used in compression-ignition (CI) diesel engines currently used nowadays (Sathiyamoorthi and Sankaranarayanan, 2017).

III. To achieve higher performance from an injection type engine running on biodiesel mix, not only appropriate volumetric ratio of diesel-biodiesel-ethanol is required but stability of that mixture is also equally important.

It is understood that the best ratio of diesel-to-biodiesel depends on their performance and emissions in different set up in an engine, and it is difficult to conclude with a specific figure (Che Hamzah et al., 2020). The performance and emission will further be elaborated in later section. The output performance of a fuel mix is evaluated through the particulate matter (PM) discharge from exhaust. For a biodiesel-ethanol/bioethanol mix, PM can be reduced to approximately 15% if low sulphur diesel was used (Cheenkachorn and Fungtammasan, 2010). The reduction of PM leads to improved engine performance and a 30% of reduction in emission was recorded when 10% of ethanol was used with pure diesel (Rajesh et al., 2014).

Moreover, mixing ethanol with diesel fuel enhances the properties of the cold stream (air stream) compared with supplying diesel fuel alone. Consequently, the heat produced by the engine reduces; this leads to an enhanced engine performance.

2.1.2. Properties of the mixture

The usability for a fuel mixture is usually defined by two characteristics i.e., viscosity and density and these characteristics are obtained during mixing of ethanol to diesel. During mixing, various other features of the fuel content are affected, such as consistency, lubricity, energy content, flash point, and calorific value (Kwanchareon et al., 2007). Since during mixing, among others, few parameters need to be considered, i.e., the amount of carbon present in the mixture, the amount of hydrogen present in the mixture, and the biodegradability of the fuel (Wojcieszky, 2018). However, focus is given on the mixture properties because it is the only way of improving the performance of a DI engine type (Hussan et al., 2013).

2.1.2.1. Stability of the fuel mixture. Since, stability of the mixture is important so it needs to be studied carefully all the way from its sub-atomic level to structural level. Identifying the ideal mixture for a DI engine type is useful because it ensures the ideal density and viscosity of the fuel mix which in turn improve the combustion characteristics (Elkelawy et al., 2018). The mixture is still unstable compared to pure diesel under certain conditions, especially when operated at a higher temperature (Ali et al., 2015).

Besides, the stability of the mixture is affected by the system temperature. In addition, the miscibility of the mixture is influenced by two main variables, which are temperature and moisture content of the mixture. These two factors in either fuel (ethanol or diesel) can fundamentally decrease the stability of the final mixture (Liu et al., 2016).

Speaking of the stability of the fuel mix, bioethanol and pure diesel become separated below 10 °C. To maintain the stability of the mixture at all times, three basic techniques to be considered. Firstly, co-solvent is added to both fuel types; then, isopropanol is mixed; lastly, an emulsifier is added to the mixture. These factors also help reducing the engine temperature while running, therefore, these factors must be ensured at all times (Yilmaz, 2012).

Alternatively, ethanol and diesel fuel mixtures can also be stabilized with the use of FAME. The FAME is blended into the mixtures through emulsification, a process of heating a mixture until it becomes splash blends. The dissolvability of ethanol in fuel type used, such as diesel, is influenced by its penetration content. The dissolved fatty acid methyl ester reacts as the main source that holds the content of the blend and enhances the blend of the diesel fuel by a number of hydrocarbons present. If the mixture is identified to be stable with all the measures taken into consideration, the carbon emission in the blend type will be reduced. This leads to a reduction in carbon footprint (Alptekin, 2009).

A biofuel mixture is usually identified to be stable when the added

emulsifier shows positive results. Among all suitable co-solvents, the ester is generally utilised due to its dissolvability. Co-solvent helps to stabilize the mixture and eventually leads to increase in 'elasticity' of the fuel mix with respect to water content and increases its stability (Shah et al., 2015).

The stability of fuel blends depends on environmental conditions, specifically on temperature. For higher temperature stability, its recommended that the ideal additive for diesel such as splash blend ethanol, must be kept at 5% (Shah et al., 2015). The power output from the engine increases with increased stability of the fuel blends which reduces the exhaust emission. Moreover, for a fuel mix, biodiesel as specific fuel source rather than bioethanol could be adequately utilised to maximise the performance of the engine (Geng et al., 2017).

To increase oxidative stability of a blend, 1000 mg/kg of butylated hydroxytoluene (BHT) was used as additive with biodiesel (El-Seesy et al., 2017). Water content also defines the stability of a fuel mix and therefore the engine performance.

Cloud point is another factor that impacts fuel blends stability and a blend can develop a cloud point by about 25 °C at just about 5% of the bioethanol present, although ethanol moisture content and bioethanol solvency do matter in this case. The miscibility of diesel and bioethanol is facilitated with the use of methyl ester as discussed earlier. Moreover, methyl ester from sunflower specifically, helps minimize the heat produced by the engine during operation and which increases the engine efficiency, resulting in an improvement of the performance (El-Seesy et al., 2017). The optimum fuel ratio in blends produces stable mixture as well as low PM which help to keep the engine temperature low during operation (Shameer et al., 2016).

2.1.2.2. Density of the mixture. Density determines some important characteristics in a fuel blend, such as viscosity, lubricity, pour point. Cetane number and warming quality are associated with the density of a particular fuel type used. Atomisation of a fuel and its burning qualities are usually affected by the density of a specific mixtures. The yield energy and its burning quality of a DI engine varies with respect to the density of the mixture (Shahir et al., 2014).

In certain cases, for most fuel types, higher density causes more resistance to the flow of mixture inside the DI engine (Torres-Jimenez et al., 2012). A comparison of various fuel blend types, such as biodiesel, diesel, and ethanol (Table 1) has shown similarity in their density, in fact its same with that of diesel fuel at temperatures between 0 °C and 80 °C (Sathiyamoorthi and Sankaranarayanan, 2017).

While the density of a fuel mix can be tailored according to need, a 20% bioethanol gives a stabilized blend, along with mixing at 15 °C. At a particular mix containing a specific percentage, for instance, 60% diesel, 20% bioethanol, 20% biodiesel, is comparatively denser than diesel fossil fuel (Yilmaz et al., 2014); (Sathiyamoorthi and Sankaranarayanan, 2017).

2.1.2.3. Calorific value. Calorific value is obtained by measuring the total heat energy produced by a specified quantity of fuel; in order to determine the sum of energy enclosed in a mixture. This is usually important when considering the adeptness of the mixture under certain conditions and to obtain the best alternative for diesel. Reducing the calorific value of a fuel influences positively on engine performance. Biofuels usually have lower calorific value than for traditional fuel such as diesel (Cheenkachorn and Fungtammasan, 2010).

Table 1
Medium sized diesel engine specification (vehicle).

Pickup truck engine	
Cylinder number – bore – stroke	4, 93, 92 (mm)
Displacement	2.499
Compression ratio	17.7:1
Rated power/Speed	58 (kW)/3900 (rpm)
Max torque/Speed	176 (Nm)/1800 (rpm)

The measuring of calorific value of biofuels mainly focuses on the three basic factors, i.e., biodiesels, bioethanol, and pure diesel. Therefore, calorific value of a mixture can be changed by altering the percentage of these three basic mixtures combinations. A high calorific value of the fuel mix would result in an increase energy production by the engine during combustion which can be lead to engine overheat and reduce performance. (Kulkarni et al., 2014).

2.1.2.4. Lubricity and viscosity. Lubricity and viscosity of a fuel blend determine the nature of atomisation process, the splash blend attributes, and the quality of ignition. The optimum viscosity of a mixture is received at temperatures between 15 °C and 19 °C; beyond 19 °C, the mixture becomes less viscous but yields higher performance. A lower than required viscosity may cause leakage due to its higher flow rate to fuel pump and reduce the engine performance (Hussan et al., 2013).

A denser fuel blend compared to pure diesel may lead to various other factors, such as:

1. Comparatively low atomisation;
 2. Increased deposits in DI engine; and
 3. Lower rate and higher energy consumption in fuel circulation.
- Therefore, to mitigate the above-mentioned factors, the density should be kept low at all times for enhanced engine performance. (Ali et al., 2015).

2.1.2.5. Pour point. Pour point is the minimal temperature at which a fluid is capable of flowing. If pour point increases, it develops crystals in the mixture which increase its melting temperature. Pour point depends on many factors, therefore, the ratio of components in a fuel blend doesn't controls the value. For example, for a mixture of 15% biodiesels and 85% diesel, the pour point is same with a 90% diesel and 10% biodiesel mix which is again similar to that of pure diesel (Shah et al., 2015). Bioethanol has lower pour point and its mixing yields a fuel blend with lower pour point that helps reduce the chance of engine overheating during operation (Geng et al., 2017).

2.1.2.6. Surface tension. The surface tension of the fuel mixture is also responsible for combustion in DI engine and as surface tension increases so is the consistency of the fuel mixture (El-Seesy et al., 2017). Overall, surface tension reduces the emission produced by the engine (Shameer et al., 2016).

2.1.2.7. Flash point. The flammability of a mixture is characterised by its flash point and the temperature limits. But flash point doesn't directly impact the combustion characteristics of the fuel; rather, a higher flash point signifies the safety aspect of the fuel such as handling, transportation, and storage. Biodiesel, in this consideration is safer as its flash point is greater than 120 °C (EN 14214); while for diesel it is 55 °C (EN 590) and 16 °C for bioethanol (Shahir et al., 2014).

Flammability limit is relatively more important when considering refuelling, damage, or leaks in the fuel system k (Yusoff et al., 2015).

PBDF generates insufficient vapour to reach its lower flammability limit at ambient temperature. Ethanol exhibits intermediate flammability limit of gasoline and fossil diesel and the flashpoint of diesel-ethanol blends was found to be within 12 °C and 15 °C; which is close to that of pure ethanol (Torres-Jimenez et al., 2012).

2.1.2.8. Content of the fuel oxygen. Oxygenated fuel naturally enhances the burning of fuel and reduce the discharge of a diesel engine, although this discharge depends particularly on the engine load but due to better combustion discharge of thick gases, oxides of carbon usually reduced for oxygenated fuel. An oxygen rich fuel blend increases the hydrocarbon emission along with deposition inside the engine wall, causing the engine to be inefficient; as a result, the engine wears out quickly (Doğan, 2011). So, oxygen content in fuel blends should be maintained at its minimum to

reduce the emission and for improved functionality of the engine (Yilmaz et al., 2014).

2.1.2.9. Cold filter plugging point (CFPP). Biodiesel fuel blends functions are dependent on the climate the engine operated (Sathiyamoorthi and Sankaranarayanan, 2017). Therefore, CFPP is an important criterion for quality controlling of biodiesel blends since this parameter tells much about the fuel mixture properties at low temperature. CFPP is determined by a number of additives the mixture contains for instance, at approximately 5% of ethanol, the CFPP reduces comparing to 10% of it. (Cheenkachorn and Fungtammasan, 2010). Since CFPP indicates crystal formation in a fuel mixture at low temperature, a higher value should be avoided as it would gradually decrease of the engine efficiency.

2.2. Emission characteristics

Researchers have used different methods to report on the emission of diesel engine based on its conditions for using biofuel blends and pure diesel on reducing engine's emission. Different types of exhaust gas from a diesel engine was observed such as: carbon dioxide (CO₂), carbon monoxide (CO), sulphur dioxide (SO₂), nitrogen oxides (NO_x), and hydrocarbon (HC). The amount of emissions is dependent on factors such as fuel type, engine speed, cetane number, and load at the engine.

2.2.1. Emission of carbon monoxide (CO)

Emission of CO was detected and it is dependent on the biofuels by volume percentage. Different mixture ratios (80% diesel: 20% biodiesel), (80% diesel: 15% biodiesel: 5% bioethanol), (80% diesel: 10% biodiesel: 10% bioethanol), (80% diesel: 5% biodiesel: 15% bioethanol) were studied for this case to compare the emission. At a high speed of over 2300 rpm, the CO emissions were high for the biofuel's mixture compared with that of pure diesel due to the difference in the air to fuel ratio. When this ratio is relatively low, amount of CO increases due to less of the oxygen content that requires completing the combustion (Geng et al., 2017); (Hua et al., 2017). Inversely, higher level of oxygen content in biodiesel and bioethanol will reduce the CO emission. Interestingly, both biodiesel and bioethanol are 12% and 35% higher in oxygen than in pure diesel. A study of biodiesel and bioethanol blends impact on exhaust due to variable engine functions revealed that CO emission were very much related to the fuel characteristics than engine operation set ups (Park et al., 2012). Inversely, the fuel content is also responsible for emission gas. For example, when 1-butanol and 1-pentanol content increases in biodiesel blend volume of CO increases due to the higher latent heat of vaporization and low ignition properties of those alcohols (Nanthagopal et al., 2018). The low ignition and high latent heat of vaporization caused a reduction in cylinder temperature, which led to decrease in combustion properties and increase in CO (Saravanan, 2015). Alternatively, for a CI engine the investigation was done for fuel variants with different engine loading.

The three-engine loading were: small (0%–40%), medium (40%–80%) and high (over 80%). The result evaluation shows that at small and medium load, the highest amount of CO emission was measured from diesel fuel. The CO emission of the biofuel blend observed to be lesser than diesel fuel at small and medium load due to the high level of oxygen content (Barabás et al., 2010).

Another study on CO emission from a diesel engine for using of more integrated blends which are Fuel A (60% diesel, 30% biodiesel, 5% ethanol, and 5% butanol) and Fuel B (40% diesel, 50% biodiesel, 5% ethanol, and 5% butanol) and pure diesel were tested at full load conditions. Fig. 1 shows the result obtained on the CO emission.

It is clear that lower CO emission was obtained for Fuels A and B in comparison with the diesel emission. The result is attributed to the higher oxygen concentration of Fuels A and B than in diesel, which further approves the previous discussion on fast and complete combustion (Keskin et al., 2016).

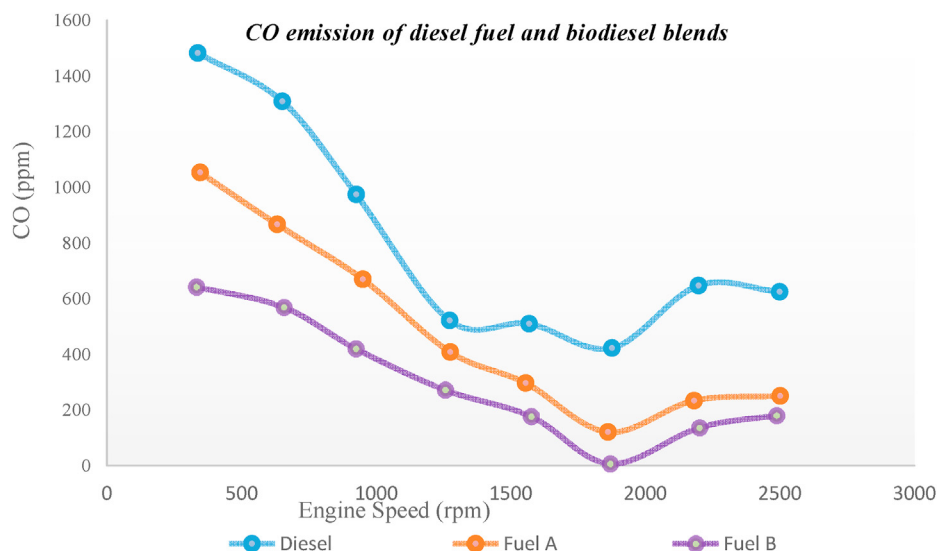


Fig. 1. The CO emission of the diesel fuel and blend's fuel at different speed of a diesel engine (Constructed based on data taken from Keskon et al., 2016 and Barabas et al., 2010).

2.2.2. Emission of carbon dioxide (CO_2)

Both fuels condition and engine setup cause variation in CO_2 emission. The emission of CO_2 a DI engine which is operated at a constant speed of 1500 rpm, full load, and constant angle of diesel injection and was fuelled with: diesel-ethanol (DE) and biodiesel-ethanol (BE) with variable volumetric fraction of ethanol fuel shows that the emission decreased with increasing volumetric fraction for both fuels. The biodiesel-ethanol blends produced lower emission of CO_2 compared to diesel-ethanol (Tutak et al., 2016).

The oxygenated biodiesel-ethanol fuel has less carbon in its molecules whereas ethanol contains more H_2O which results in less CO_2 emission.

Fig. 2 portrays the comparison made on both DE and BE with increasing ethanol volumetric fraction. It further consolidates the fact that the BE has less CO_2 emission compared to DE fuel.

In an inclusive investigation with five different fuel blends containing a different percentage of ethanol fraction shows that as the ethanol increase in fuel blend, the CO_2 emission decreases since carbon-hydrogen ratio reduces in the blend and oxygen increase with the increase of ethanol. The addition of ethanol to the blend causes the cetane number, heating value, and kinematic viscosity of fuel blends to be reduced which helped the reduction in gas emissions (Yang et al., 2019).

A fuel blend of 84% (volume) diesel, 025% hydrous ethanol, 4.75%

anhydrous ethanol, and 11% biodiesel, which was called as diesohol-biodiesel blend was tested in a heavy-duty DI engine to find out the emission characteristics. Detailed specification of the DI engine is listed in Table 1.

The particle exhaust the engine shows that diesohol-biodiesel blend produced less CO_2 than by regular diesel since higher oxygenated fuel helped improve the combustion process (Cheenkachorn and Fungtam-masan, 2010).

2.2.3. Emission of nitrogen oxides (NO_x)

The nitrogen oxides are one of the main emissions produced from a DI diesel engine. This emission is resultant from the reaction between nitrogen and oxygen gases during the combustion of the engine. This emission might have serious impacts on the environments. Therefore, many researches had been done to establish the effect of using biofuels on reducing this emission. The effect was investigated with a fuel blends which was a mixture of diesel and fish oil-biodiesel with the proportion of 20–40%. Additionally, two of these fuel blend's cetane number was improved by adding 0.5% and 1% of ethanol by volume. The fuel blends used in a DI engine at a constant speed of 1500 rpm with different engine loads. The results show that the NO_x emission portrayed a decreasing trend with increasing ethanol volume in the blends. The increase in

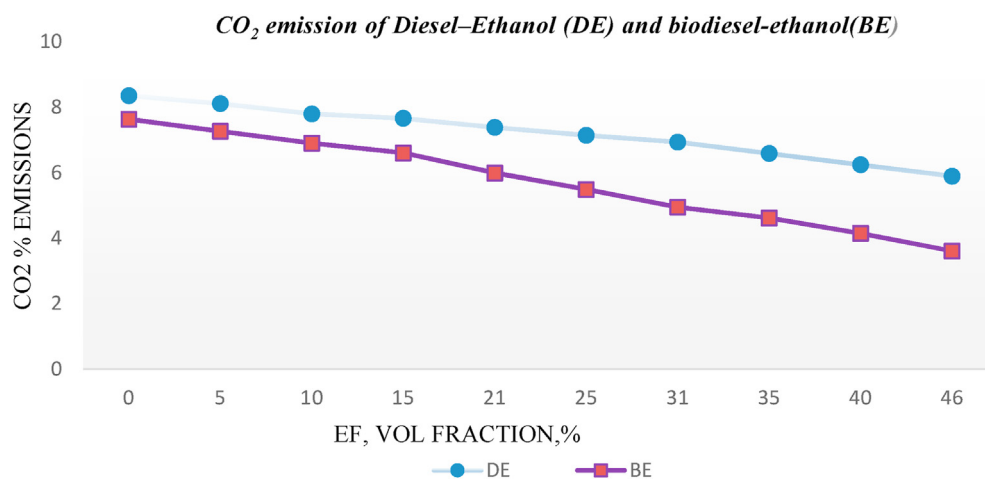


Fig. 2. The CO_2 emission of Diesel-Ethanol (DE) and biodiesel-ethanol (BE) as the ethanol fuel volumetric fraction increasing (Adapted from Tutak et al. (2017)).

ethanol volume resulted in reducing the ignition delay and combustion temperature which helped to reduce the NO_x emissions. It was observed that the NO_x emission decreases by 3.7% and 4.5% as the ethanol volume increases in blends by 0.5% and 1%, respectively (Kirankumar et al., 2015).

Another study on fuel types (diesel fuel, biodiesels, and biodiesel-ethanol blends) with maximum torque and rotation in a DI engine shows a detailed emission characteristic. The blends contained 5%, 10%, and 15% of ethanol by volume. The result reveals that the NO_x emission of diesel fuel increases with engine load increase, however, emission from the blends is 15% lower than that of diesel at full engine load and it further decreases with volume of ethanol increases (Anbarasu et al., 2013). Therefore, to prevent separation of diesel and ethanol in a DI engine during operation, hexanol was used as an additive to a fuel blend with 20%, 25%, 35%, and 45% ethanol and the effect on NO_x emission was compared with the same form of diesel fuel in the same engine set up. The result of the experiment shows that the NO_x emission of different blends of ethanol is decreasing and as the ethanol volume increases, a further decrease in NO_x emission was observed (Sathiyagnanam et al., 2010).

A different study conducted by other researchers to investigate the emission of NO_x from diesel-butanol blends that range from 5% to 20% of butanol in a DI diesel engine at 1500 rpm and the blends were denoted as B5, B10, B15 and B20 following the butanol percentage. Fig. 3 shows the result obtained for the NO_x emission from this experiment. It can be seen that the NO_x emission obtained for the diesel fuel is higher than that of the butanol blends. As the amount of butanol increased, the NO_x emission was found to have decreased due to the availability of excess oxygen in the blends. This result agrees with the other studies discussed earlier, in which the biofuel blend with higher oxygen content helps in enhancing the combustion and reduction in NO_x emission (Liaquat et al., 2012).

The emission of the NO_x can be affected by different factors such as oxygen content and combustion temperature. The addition of ethanol to the blends helps to decrease the combustion temperature, in which the ethanol has good cooling ability.

2.2.4. Emission of hydrocarbon (HC)

HC emission has several impacts on the environment, which leads to several investigative studies done on the effect of using biofuels to reduce this type of emission.

The HC emission of biodiesel blend was tested with pure diesel and its mixture with 5% coconut biodiesel blend, and 15% coconut biodiesel focusing on biodiesel's oxidation capabilities. The engine used in this investigation was at 100% load with speed variation from 1500 to 2400 rpm at an interval of 100 rpm. (Choi et al., 2015). The result showed that

the oxygen content in fuel blends improved the fuel oxidation, as a result the amount of HC emission was found to have reduced. Additionally, the high amount of cetane number in biodiesel blends resulted in reduced ignition delay and less HC emission is obtained (Choi et al., 2015). The result shows an obvious improvement through the use of biodiesel blends compared with 100% diesel fuel.

Table 2 shows the cetane number of diesel fuel and biodiesel blends using in this research, in which the cetane number of the blends is higher than the 100% diesel fuel. As the biodiesel volume increasing in the blends, the amount of cetane number also increases, which leaves a positive impact on reducing the emission of HC (Choi et al., 2015). The lower value of cetane number in a diesel blend with 10% and 20% by volume of n-butanol led to a delay in the ignition, in which the combustion became unstable that resulted in the higher amount of HC emission. This study proves that HC emission is influenced by the amount of cetane number in the blends, where an increased cetane number will enhance the ignition of the engine and produce less HC emission (Parthasarathi et al., 2014). A similar result was reported for a fuel blend of 50% diesel, 40% ethanol, and 10% surfactant (de Oliveira et al., 2017).

Table 2 shows, in details, the changes in cetane number with the fraction of biodiesel used in fuels blends.

In a different approach, organic compounds have also been blended up alongside biodiesel and tested with diesel fuel. One such approach was by adding diglyme to the biodiesel blends, as a result the BTE was found to be increased due to the enhanced oxygen content in the blends, which improved combustion. Although it was still lower than that of pure diesel, the addition of diglyme is reported to have improved the cetane number and enhanced the engine performance while reducing the temperature of the exhaust gas. This additive improved the premixed combustion phase and ignition timing. Thus, the engine required less fuel for desired output and emitted less HC and CO. on the down side though, increased oxygen content contributed to excess NO_x emission. (Varuvel et al., 2018).

Results on improvement in BTE was reported by Devarajan et al. (2018) for Neem biodiesel. The thermal properties of the fuel blends were further improved with the addition of oxide nanoparticles, which helped in the complete combustion of fuel through the supply of excess oxygen. Moreover, for the same reason emission characteristics in exhaust gas was significantly improved (Devarajan et al., 2018).

Other researchers have also made comparison of diesel and deoxygenated vegetable oils and reported that biodiesel blends were able to improve the combustion characteristics and aided in complete combustion because of their comparatively low viscosity and higher calorific values. Moreover, the fuel blends perform better by reducing the exhaust gases, such as HC and CO, significantly under both half-load and full-load

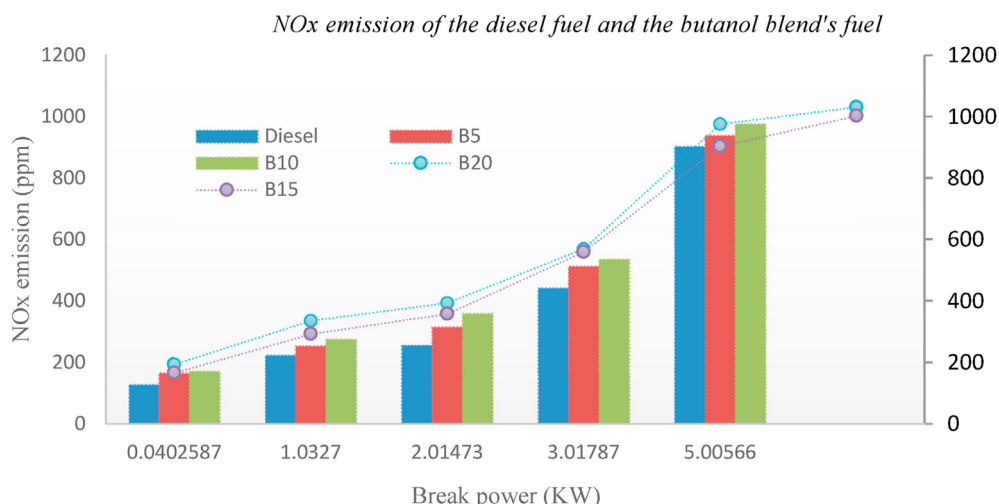


Fig. 3. The quantity of NO_x emission from diesel and its blend's at various power generation (Constructed with data adapted from Liaquat et al. (2012)).

Table 2

The cetane number of the diesel fuel and biodiesel blends.

Fuels Used in the experiments							
	Diesel	Fraction of biodiesel	(Fraction) type of additive	HC/CO	NO _x	Effi	References
Cetane number	51	5% biodiesel (95%) diesel	15% biodiesel	↓	↑	↓	Choi et al. (2015)
	51.5	Ethanol	40% Ethanol	↓	↑	—	de Oliveira et al. (2017)
	50	5–8	46	↑	↓	↑	Adam et al. (2018)
	47	Palm biodiesel	50% Palm biodiesel	↑	↓	↑	Adam et al. (2018)
	57.5	Rubber Seed oil	Diglyme	↓	↑	↑	Varuvel et al. (2018)
	52	45	126	↓	↑	↓	Devarajan et al. (2018)
	48	100% Biodiesel	100% Biodiesel + Ag ₂ O	↓	↑	↓	Devarajan et al. (2018)
	55	57	57	↑	—	↓	Pattanaik and Misra (2018)
	47.14	Jatropa Oil	Jatropa Oil biodiesel	↑	—	↓	Pattanaik and Misra (2018)
	—	48.13	48.13	↓	—	↑	Pattanaik and Misra (2018)
	48	Deoxydenated Palm oil	Deoxydenated Keranja oil	↓	—	↑	Pattanaik and Misra (2018)
	58.2	55.8	55.8	↑	↓	↑	Prakash et al. (2018)
	47	Castor Oil	Castor Oil 70%	↑	↓	↑	Prakash et al. (2018)
	28	38	38	↑	↓	↓	(Sanjid et al., 2016); (Sanjid et al., 2014)
	51	5% Kapok biodiesel	5% Moringa Biodiesel	↑	↓	↓	
	59	51	51				

Legend: ↑ Decreasing trend; ↓ Increasing trend; — No data; Effi. = Efficiency.

engine conditions (Pattanaik and Misra, 2018).

On the other hand, Prakash et al. (2018) tested different biodiesels from various sources and reported that biodiesel and their several blends (pine oil or castor oil methyl ester or a mixture of diesel and neat castor oil), and higher percentage of biodiesel will cause higher emission due to their higher viscous properties, which causes poor atomisation. In fact, these blends or biofuels in higher ratios did not help in reducing the smoke and pollutants; instead, the exhaust temperature was higher than that of pure diesel. Therefore, all biodiesels are deemed unfeasible and not environmentally friendly, and in many instances, they increase the environmental burden by increasing the level of emission (Prakash et al., 2018).

Although, biodiesel does improve combustion characteristics and engine efficiency to some extent, additives such as nanoparticles and antioxidants are capable of achieving the same goal with minimal quantity and effort. Evidence shows that the amount of HC emission obtained for a 50-50% Diesel-Ethanol (D50E40) blend was higher compared to that from a diesel fuel, which provides an important information about the relation between the cetane number of fuel and emission measured from a DI diesel engine. This claim is evident from Fig. 4 as it clearly shows the HC emission of the diesel fuel is lower than that of D50E40 fuel blend. (de Oliveira et al., 2017).

Similarly, another study reported on fuel blends containing 7% biodiesel, 5% diesel fuel and 30% hydrous ethanol volume fraction showed an increase in HC emission, as the ethanol volume increased in the blends. The ethanol in these blends was found to have caused poor vaporization affecting the mixture formation. The quality of the combustion was also affected, whereby it resulted in higher HC emission (Venu and Madhavan, 2016).

2.2.5. Emission of particulate matter (PM)

Smoke is the visible form of particulate matters and its emission is resulted due to various factors which includes both engine set-up and fuel properties. Usually the emission from a diesel engine consists of very tiny solid particles of unburnt/partially burnt fuels, fuel droplets, ash, fuel vapours etc and form smoke. These are consequential to the environment. DI diesel engines, particularly, are considered to produce excess smoke, therefore, here, in a comparative study the answer was sought through other researchers' findings.

The definitive result of reduced smoke from a DI engine for biofuel blends was reported by (Swamy et al., 2015). The researchers claimed that higher cetane number and oxygen content in the fuel blends reduced due to better combustion of the fuel. Likewise, Singh and co-researchers reported that due to adding of ethanol in blends availability of O₂

Hydrocarbon emission versus Break power

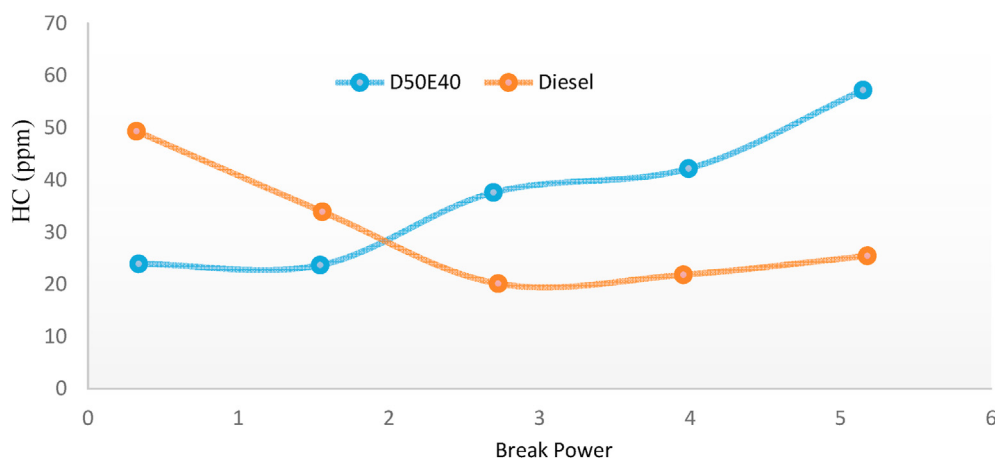


Fig. 4. The hydrocarbon emission versus break power of the DI diesel engine of diesel fuel and D50E50 blend's fuel.

increased which helps to complete combustion and reduced delay in ignition and smoke emission (Singh et al., 2012). The relation between higher cetane number and better combustion quality was confirmed by researchers, who claimed that increasing of cetane number leads to reduce ignition delay, and ultimately improving the cold start and lowering the white smoke formation (Sahafi et al., 2018).

Addition of oxidizing agents to ethanol blends can improve the combustion process further and therefore will reduce the PM. Alternative fuels which are capable of providing excess oxygen to fuel mix help to achieve PM reduction. Polyoxymethylene dimethyl ether (PDE) is an alternative fuel that provides oxygen and acts as co-solvent which helps to stabilize the biodiesel blends. When mixed at certain volume with diesel/ethanol blends this alternate fuel helps to reduce the PM emission by almost 87%. The interesting thing however, is that the PDE also works as catalyst when mixed with diesel and ethanol. The PM reduction increases linearly with the ethanol volume percentage blended in the fuel mixture when PDE is added (Liu et al., 2019).

Diesel mixed with jatropa or moringa oil methyl ester showed to have reduced the whole spectrum of emissions properties from a diesel engine running on full load at 1000–4000 rpm. Just about 10% of jatropa and moringa oil methyl ester blended with diesel reduced the hydrocarbon emission by 16% and 12% respectively which reduced soot formation (Rahman et al., 2014). The relatively high oxygen content in the blends is due to the methyl ester which contributes to higher combustion temperature and prevents escaping of unburnt substances from the engine. Interestingly, an opposing result was reported for HC emission when 20% of first- or second-generation biodiesel (macadamia, rice bran and waste cooking oil) were blended with pure diesel and when butanol was added to it. The higher the butanol content the higher was the emission for these cases. The presence of ester molecule due to butanol causes bigger fuel droplets because of its molecular size. The droplets are bigger than that for pure diesel and therefore, the evaporation rate reduces which contributes to higher HC emission. But particulate matters for the same blend was found to be reduced in opposite trend than what is reported for HC emission. The reduction of PM was reported to be about 16% for the same first-generation biodiesel blend which consists of 5% butanol, 20% macadamia oil and 75% diesel. Additionally, as the engine speed increases the PM emission decreases and the emission was found to be insignificant after rotation reached to 2000 rpm (Rahman et al., 2017). This finding starkly contrasted by the results of having higher smoke at higher engine load for a diesel engine when pine biodiesel was used. The researchers found that high viscosity of biodiesel increased smoke emission because vaporization for the blends was poor which subsequently reduced atomisation and led to incomplete combustion. But

when an additive (1,4-dioxane) was used with the same biodiesel blends smoke emission was reduced up to 23% (Mebini Samuel et al., 2020). The availability of oxygen in the blends due to additives or ethanol increases which helps to remove the droplets from the emission and after all, blended fuels have lower sulphate or lead contents so the PM emission is reduced (Gugulothu, 2020) (Cheung et al., 2009). In fact, the relationship between available oxygen mass in biodiesel/biofuel and the PM emission with or without the addition of oxidizing agents was consistently established (Guan et al., 2017). The reducing trend of soot and other particulates matters in emission by using biodiesel in single-cylinder DI diesel engines was found to be a common phenomenon and was agreed unanimously by many researchers (Joshi et al., 2017); (Dawodu et al., 2014).

2.3. Engine performance based on bioethanol fuel blends

A 80-20% and 70-30% (v/v) of diesel with ethanol mixtures were applied in a four-cylinder DI engine at full load conditions with gradual increase of engine speed and to relate engine output with fuel composition. As the percentage volume of ethanol increases, the power produced (horsepower) decreases as shown in Fig. 5. As a consequence of ethanol volume increases in the mixture, fuel consumptions also increases due to the compensation for low calorific value of ethanol as shown by Fig. 6 which is extracted from (Arapatsakos, 2009). The reduction in power output due to added ethanol in fuel mixture was further confirmed by measuring the minimum BSFC value for pure diesel, 7.5% and 10% ethanol in the same engine set ups at 490 rpm and the values were found to be 450 g/kWh, 1000 g/kWh, and 2000 g/kWh, respectively.

In terms of BTE, a single cylinder water-cooled, four stroke DI engine perform better when ethanol in fuel mix is less than 50%. In fact BTE increases as volume of ethanol increases and the maximum value is obtained at 50-50% diesel ethanol blend (Ganesh and Kumar, 2010).

In an experiment, to evaluate the biofuel's efficiency on a four-cylinder engine, two separate blends B10 (90% diesel 10% biodiesel) and E20B10 (70% diesel, 20% ethanol and 10% biodiesel) were tested under different load conditions of the engine. As the load increase, the BSFC values for both types of fuel blends were found to decrease, and FCE values for B10 was found to be higher at low load conditions; whereas E20B10 surpassed B10, as the engine approached higher speeds and full load conditions (Guido et al., 2013). The lower stoichiometric air to fuel ratio due to the presence of ethanol in E20B10 and a lower radiation heat loss than that of B10 helped the engine to perform better at higher speed. The effects of ethanol and/or methanol fuel blends on the performance and exhaust emissions of a single cylinder, four-stroke DI engine provides valuable information about the thermal efficiency of the fuel. At different

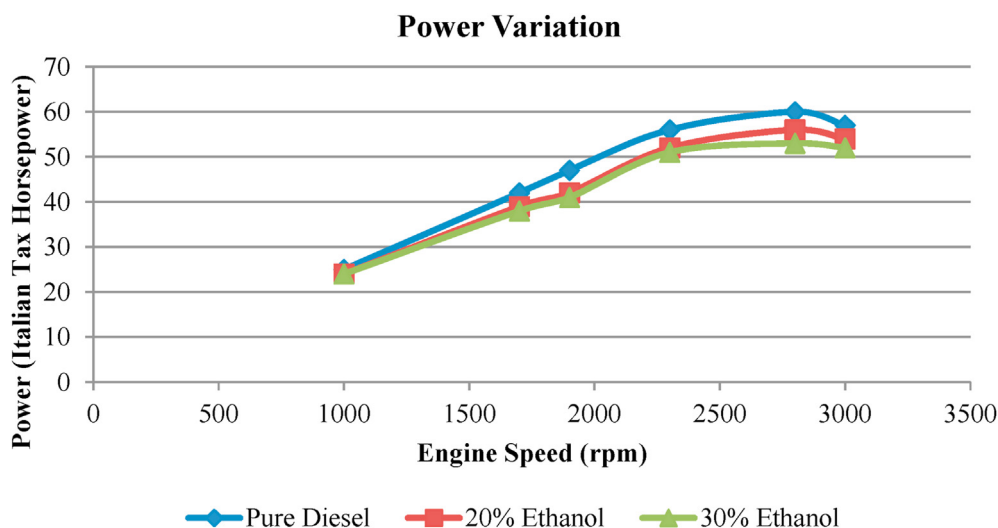


Fig. 5. Effect on power output by different fuel types fuel and blends [Excerpt from Arapatsakos, 2009].

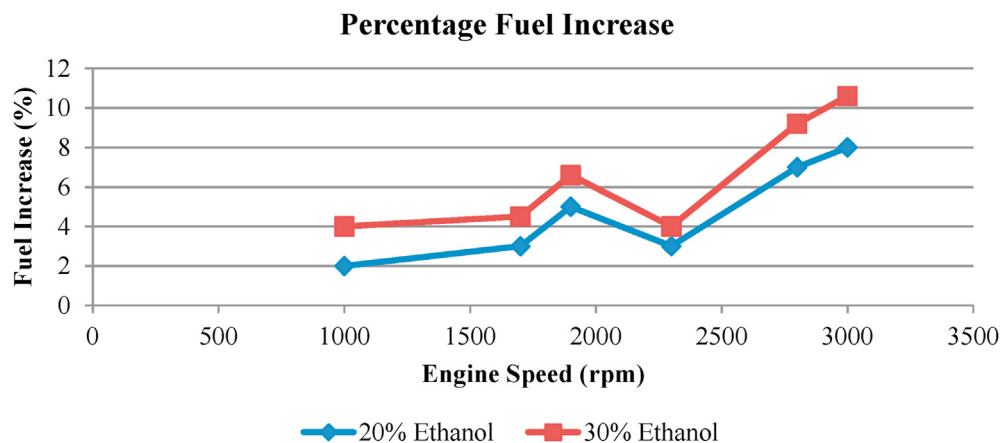


Fig. 6. Percentage increase of fuel consumption per engine rotation [Excerpt from Arapatsakos, 2009].

engine speeds, the BSFC values of diesel-ethanol fuel mixes are higher than pure diesel. As the volume ratio of ethanol in the fuel mix increases, the BSFC values increase as well. Decrease in BTE value with ethanol content increasing indicates that energy derived from the fuel was not efficiently converted to mechanical output (Sayin, 2010).

Next, a more detailed study was conducted with pure diesel, 95% diesel and 5% ethanol fuel mix, as well as 90% diesel and 10% ethanol fuel mix to determine the effects of ethanol-diesel fuel blends on a heavy-duty DI diesel engine (Rakopoulos et al., 2008). The engine was set at 1200 and 1500 rpm with 20%, 40% and 60% load for both rpm set, corresponding to different BSFC. Both BSFC and BTE values were found to be increasing as the volume ratio of ethanol in the fuel mix increases at all these specific engines set up conditions. The results were similar to the studies carried out later and reported by (Praptijanto et al., 2015) and Sayin (2010). The difference between these blends became more prominent as the load increased (Guido et al., 2013). This phenomenon can be explained through the lower cetane number of ethanol which contributes to a better percentage of constant volume combustion (Ganesh and Kumar, 2010). This result implies that heat losses are much lower when fuel blends with higher volume ratios of ethanol are used.

The heat loss can be confirmed further by trying with different diesel ethanol fuel blends and in a DI engine at same engine speed and rotation which shows that fuel blends with higher ethanol volume ratio possess longer ignition delay compared with pure diesel fuel. The duration of premixed combustion and the amount of heat released from the process increases when ethanol volume ratio increases (Ren et al., 2008). This undesirable phenomenon leads to longer ignition delay, in addition to the increase in oxygen content, which promotes the formation of excessive flammable mixture and causes problems to the engine eventually.

Since pure diesel produces lowest brake power value, so in a quest to find a suitable fuel blend which can generate this same value closest to pure Diesel biodiesel-diesel mixture with butanol and diethyl ether as additives were used. The result shows that the fuel mix of 80% diesel, 15% biodiesel, and 5% ethanol produces the second lowest brake power values among other fuel sources (Imtenan et al., 2014). Although, ethanol in the fuel mix had improved the BTE when compared with pure diesel and the 80% diesel with 20% biodiesel fuel mix (Arapatsakos, 2009).

Similarly, from other investigation on the effects of ethanol as additives to the biodiesel-diesel fuel blends in a DI engine with different engine load and reported that BTE was higher in ethanol added fuel than that for pure diesel-biodiesel fuel mix. The increased oxygen content due to ethanol which is readily available for combustion may have helped. (How et al., 2014).

Equivalent results were obtained when a HSDI diesel engine was used to determine its performance and emission with 5%, 10%, and 15% volume ratios of ethanol (Rakopoulos et al., 2007). The test was conducted at four separate load conditions and at 2000 rpm which shows

that the ignition delay for neat diesel is lower than the 15% ethanol blend (Rakopoulos et al., 2007). This result mirrors the work by Imtenan et al. (2014), whereby ignition delay was found to have increased with increased volume ratio of ethanol in the fuel mix. Besides, the cumulative heat lost when 15% ethanol blend was used was found to be slightly lower compared to the neat diesel fuel. So, 15% ethanol fuel blend promotes better thermal efficiency. To establish a relation between BTE and fuel types with variable engine speed it was reported that increasing of ethanol ratios can cause the thermal efficiency of the engine to go high or low than for pure diesel (Rakopoulos et al., 2007), (Rakopoulos et al., 2008). Saying claimed that this difference in thermal efficiency also depends engine load (Sayin, 2010). This result was slightly contrasted because higher ethanol volume ratio was reported to cause higher BTE when compared with that for neat diesel (Ganesh and Kumar, 2010). Besides, the thermal efficiency of a CI engine was also recorded to be reduced due to the combustion of biodiesel/ethanol blends as an effect of lower calorific value of the fuel mix (Gad et al., 2018); (Zheng et al., 2016). Due to lower calorific value and higher latent heat of vaporization for some biofuel mix in-cylinder temperature reduces which causes less in-cylinder pressure that leads to reduced efficiency (Kumar et al., 2016).

Due to lower calorific value more fuel is needed for required output. However, high biodiesel was found to generate higher cylinder pressure due to its high viscosity and increased mass of fuel per stroke, although there were no changes in ignition delay for reformulated biodiesel fuel because of high in-cylinder temperature (Sharma and Ganesh, 2019). Besides, the reduction of torque occurs as ethanol volume increases in the fuel, therefore, pumping more fuel compensates the LHV of the fuel blend. This increased fuel volume did not affect the engine power output for 5% or less ethanol blend with a different engine load, although the BSFC was increased to 2% for different loading (Pradelle et al., 2019). Pumping of excess fuel caused to increase the BSFC for the biofuel when compared with that of diesel which causes more deposits to build up in/out of the injector nozzle, which in turn, adversely affect the power output of the engine (Hoang and Le, 2019). BSEC, after all, is a more precise way to compare the fuels and the engine performance due to different fuel blends, and with increasing load on the engine, the BSEC reduced due to increased conversion of power that occurred at increased load (Ashok et al., 2017).

The performance and emission characteristics of a DI diesel engine were measured with many variations of diesel-ethanol blends under two supply systems which are the LPSS and HPSS. From the study, it was found that diesel-ethanol blends are more suited to be used under the HPSS (pressure = 1.0 bar) as the problem of power drop when the blends are used under LPSS (pressure = 0.1 bar) is significantly reduced (Tutak et al., 2016). It is clearly indicated in the ignition delay, thermal efficiency and mean effective pressure curves, whereby the curves for HPSS are able to portray a better relationship between the parameters and the

increasing ethanol volume ratio when compared with LPSS curves. This phenomenon was observed due to the availability of fuel blends to fill up the chamber of the injection pump at a better rate under HPSS. This pressure supply system is also found to be better than LPSS, as fuel blends with higher percentage volume of ethanol can only be operated at HPSS, as indicated in the study, the best ethanol volume ratio under LPSS is found to be 30%. With any ratio higher than that value of ethanol, the combustion process will begin to degenerate (Subbaiah et al., 2010).

To understand the relation between engine performances, emission and BTE with different fuels and its blends, pure diesel, pure biodiesel, biodiesel-diesel blend, and three different diesel-biodiesel-ethanol blends were studied. As far as the BTE is concerned, the experimental values for this parameter at increasing load for the conventional diesel fuel were the lowest among the fuels tested. The maximum BTE values at every load condition were exhibited by E30 fuel blend (50% diesel, 20% biodiesel, and 30% ethanol). This result can be attributed to the lower fuel density and viscosity due to the addition of ethanol. The presence of ethanol has appeared to decrease the exhaust gas temperature of the diesel-biodiesel blend (Subbaiah et al., 2010). This is evident when comparing the values between fuel blends, whereby the E10 (70% diesel, 20% biodiesel and 10% ethanol), E20 (60% diesel, 20% biodiesel and 20% ethanol), and E30 blends have exhaust gas temperatures of lower values than the B20 blend (80% diesel and 20% biodiesel) for all load conditions. This is caused by the low heating and high evaporative heat properties possessed by ethanol. Low boiling point of ethanol improves the evaporation properties of a fuel mix so BTE enhances. The BTE value also increases as heat losses in combustion cylinder decrease due to lower flame temperature of ethanol (Imdadul et al., 2016).

A research was done on the effects of PFR and EGR of ethanol on the performance and emissions of a single cylinder, four stroke, water cooled, DI diesel engine (Pandey et al., 2015). The results don't suggest any linear relationship with PFR and EGR values to engine performance. For example, BSFC value increases whereas BTE value decreases when PFR increases while the EGR ratio stays at 0%. In contrast, an increase of PFR ratio together with the EGR ratio leads to an increase in BSFC and BTE when compared with the 0% EGR ratio (Pandey et al., 2015). Thermal efficiency increases when PFR ratio is increased at high load conditions and a higher EGR ratio helps to reduce the cooling of premixed fuels which occur due to the high latent heat of vaporization of bioethanol compared to pure diesel fuel. The reduction of cooling further increases thermal efficiency. In fact, all types of biodiesel blends reduce the BTE due to poor volatility and viscous properties. This phenomenon can be resolved by using oxygenated additives to the fuel blends, which are effective in increasing BTE than any other pure or unadulterated mixture. Metal based additives, as evident from Table 3, are also reported to have reduced the viscosity and rise the flash point and increase the combustion of fuel (Rashedul et al., 2014).

2.4. Engine performance based on biodiesel fuel blends

The following factors are integral in assessing the performance of a CI diesel engine running on biodiesel and biodiesel blends.

2.4.1. Engine power output and general running performance

Biodiesel, due to its reduced amount of energy per unit volume when compared with PBDF, gives lower torque and power output values. The values were found to be between 3% and 5% lower (Murillo et al., 2007) (Sharma et al., 2008). But even with this lower torque the power generated by the engine was similar to that with diesel fuel (Dwivedi et al., 2011). In fact, the difference was less than 1% (Roskilly et al., 2008). A low concentration of rapeseed oil biodiesel blend had shown performance that could be feasible for a mass use, in fact, 20% rapeseed oil and 80% diesel blend produced merely the required BTE for the engine (Kousoulidou et al., 2010). The experiment also showed that diesel would release more heat and higher pressure per unit volume, which can be attributed to the calorific values of the different fuels and blends.

Table 3

Effect of metal nano additives in the fuel mix and their effect on engine performance.

Nano fuel additives	Effect on engine performance and power output
Al ₂ O ₃	The high surface area of nanoparticles helped in rapid combustion by rapid atomisation and increase evaporation rate which caused a low heat release rate in respect to high engine load and crank angle. The exhaust temperature was decreased more than that by TiO ₂ through reducing the temperature at the combustion chamber (Sungur et al., 2016).
FeCl ₃	The BTE increased more than 3% at various load and different operating condition of a DI diesel engine. The combustion characteristic also enhanced (Kannana et al., 2011).
TiO ₂	Nano titanium increases both BTE and brake specific fuel consumption by better mixing of fuel and nanoparticles. The addition of nano also increases the density and viscosity of the fuel, this changed property, in turn, shows poor burning for other researchers (D'Silva et al., 2015).
Graphene oxide	Decrease fuel consumption, increase engine efficiency through catalytic activity and reducing dynamic viscosity so power output increases. Graphene nanoparticles cause an increase in exhaust gas temperature which indicates an increase in cylinder gas pressure (Hoseini et al., 2018).
ZnO	At full engine load, the BTE increases to 30% due to its catalytic activity. Large surface provides high energy for fuel oxidation acceleration. The oxygen in this nano material reduces the air requirement for full combustion, therefore, increase the fuel-air equivalence ratio and increase the efficiency (Ashok et al., 2017).
Graphene nanoparticles	About 2000 times higher increased combustion and higher cylinder pressure. Due to the higher cetane number, the evaporation rate of fuel increased which reduces the ignition delay. The large surface area of the additives enhanced the heat transfer to fuel which in turn, improved the combustion characteristics of the fuel and increased the peak pressure (El-Seesy et al., 2018).
CeO ₂	Longer and more complete combustion due to CeO ₂ ability to behave as an oxygen buffer. Flashpoint and BTE increased by 1.5% at the optimum additive level to biodiesel. Cold properties were reported not changed. (Sajith et al., 2010).
CeO ₂ +CNT	Brake thermal efficiency increased, while the fuel consumption decreased. Reduced ignition delay (Selvan et al., 2014).
SiO ₂	SiO ₂ shows the lowest thermal conductivity among the other two nano additives; for instance, Al ₂ O ₃ and carbon nanotubes. Al ₂ O ₃ was found to generate maximum cylinder pressure and shortest ignition delay among all (Chen et al., 2018).

Ozsezen and Canakci, in a study on WPOME and COME biodiesel showed a decrease in the maximum power output compared with PBDF. The reduction value was a result of the WPOME and COME having lower heating values of 8.9% and 8.2%, respectively, than PBDF. Meanwhile, both WPOME and COME had the same energy content, where the experiment result showed slight variations in the cylinder gas pressure between the two fuels. The variations in the cylinder gas pressure dispersions are a result of different biodiesels from different sources, having differences in BSFC values and fuel properties (Ozsezen and Canakci, 2011).

The neat biodiesel usually experiences a shorter combustion delay than diesel fuel and oxidised biodiesel (Monyem and Gerpen, 2001). If the injection timing is retarded the ignition delay in all the fuels would be reduced (Shahid and Jamal, 2008). Researchers illustrated of how biodiesel presents superior values in properties such as density and viscosity, compared to PBDF and suggested recipe for further improvement with the addition of bio-ethanol which would allow for an increase in the amount of biofuel content while bringing forward the reminded properties in the prescribed limits of commercial diesel (Barabás et al., 2010); (Aydin and Ilklic, 2010). While biodiesel-diesel-ethanol blends have the capability to improve engine performance, it would require a certain composition to be maintained and a maximum of 5% ethanol would keep the mixture optimum. Therefore, an increase in the amount of fuel-ethanol in the biodiesel-diesel blend would result in a decrease in

efficiency of the engine. In fact, lower percentages of ethanol work better and smooth for diesel engine, whereas, a blend with 10% or more ethanol would create knocking effects and increase in vibration, which leads to shock in the engine block and eventually, reduces the engine longevity (Taghizadeh-Alisaraei and Rezaei-Asl, 2016).

A higher biodiesel blend ratio requires higher injection pressure due to the large surface tension of biodiesel (Hwang et al., 2014). This pressure can be reduced by cooling the intake air temperature, injection timing retardation, EGR, and optimisation of piston bowl design (Al-Dawody and Bhatti, 2013). While these strategies were suggested with the purpose of reducing NOx emissions, they would also be able to alleviate some of the problems posed by using a higher injection pressure. Additionally, these strategies would be accompanied by an increase in the fuel consumption, therefore, putting a strain on the need to find both an effective injection system to mitigate consumption while simultaneously increasing performance (Shahid and Jamal, 2008).

Researchers demonstrated how EGR, which could be an ideal way of reducing emissions, would result in a decrease in the combustion pressure and therefore a reduction in the amount of torque the engine would be able to produce (Yoon et al., 2014). These results were further confirmed, in part, by experiments performed by other researchers and was concluded that if BD20 blended fuel was used with EGR in the mid-range speed of the engine, it would have no negative impact on engine performance while simultaneously reducing the NOx emissions (Saleh, 2009).

An investigation with methanol-biodiesel which is derived from keranji indicates a slight delay in onset of combustion and in dynamic injection, also the maximum pressure rate rises at all loads along with an increase in ignition delay (Thangaraja et al., 2012). Yet, engine performance can be improved through alcohol fumigation, which involves the addition of alcohol (in this case, methanol or ethanol) to the air intake manifold. A decrease in BTE has been related directly with the increase of ethanol fumigation, although this was not the case when the highest load applied on the engine. (Cheng et al., 2007). Results showed This result entails that at high loads, fumigation methanol would be a viable option, as it would cause an increase in BTE. Nevertheless, a contradictory result would be expected of the BTE at lower loads.

2.4.2. Engine fuel efficiency

The efficiency of an engine running on biodiesel engine is usually between 3% and 5% compared to an engine running on PBDF. It should be noted that the engine efficiency drop-off in biodiesel engines is similar in magnitude to the power output drop-off of biodiesel engines when compared with PBDF engines (Dwivedi et al., 2011). The efficiency was found to be heavily dependent on engines and therefore, a generalisation of results cannot be achieved unanimously (Hribernik and Kegl, 2007). Besides that, when fuel efficiency of biodiesel was investigated by comparing two marine craft engines, reported results were as predicted. The biodiesel engine had a higher fuel consumption per unit of energy they generated therefore, more fuel has to be supplied to the engine (Roskilly et al., 2008). The higher affinity for fuel is a result of the lower calorific value of the biodiesel as shown in the FOBAS analysis (Rehman et al., 2011); (Roskilly et al., 2008). Moreover, a modified blend with pentanol instead, showed an increase in engine performance by 10% by improving the ignition quality and brake power. The short combustion duration and high heat helps to increase BTE but the reduction of heat loss with decreasing temperature at the initial stage for the pentanol blend had increased the BTE (Imdadul et al., 2016) (Barabás et al., 2010).

Speaking about fuel consumption rate, fuel consumption when using blends of rapeseed and diesel doesn't show any improvement regardless of the proportions in the blend (Kousoulidou et al., 2010). Similar result was found when soybean and castor oil biodiesel were used as the specific fuel capacity increased as the biodiesel content in the fuel increased. Both castor oil and soybean oil showed the same specific fuel consumption. Therefore, it can be concluded that to improve the specific fuel consumption of the system using biodiesels, fuel injection system

optimisation would be required (Valente et al., 2010).

Sunflower oil and olive oil were blended in proportions up to 50% in another study and the results suggested that the two types of biodiesel performed in an equivalent way. While the emissions were improved, the amount of volumetric fuel consumption was also found to have increased (Singh and Singh, 2010). The outcome of this experiment may indicate that regardless of the raw material of biodiesel used, results are expected to remain similar or have minor effects on efficiency and performance. Experimental results show that fuel consumption of various biodiesel blends would be higher with reduced loads because of the blends having a higher specific gravity value. This higher value, ultimately, would reduce with the progress of the combustion process since as heat increases the fuel to become less viscous (Leahey et al., 2007); (Rehman et al., 2011).

In a separate study, other researchers investigated the use of olive oil methyl ester on combustion efficiency using a DI diesel Perkins engine. The experimental results indicate that there was no drop-in efficiency for testing with two different fuels i.e., waste olive oil methyl ester and PBDF. The use of blends such as a biodiesel-methanol blend do have the ability to increase the BTE of the engine at higher loads (Dwivedi et al., 2011); (Thangaraja et al., 2012). The lower heating value of biodiesel increases the BTE as the ignition delay increases and more pre-combustion occurs (Zhu et al., 2010).

2.4.3. Engine wear

Biodiesel engines are commonly understood to have reduced short-term wear on engines than PBDF engines. Extended engine life would also be expected for engines that run on biodiesel than PBDF. On the other hand, experiments conducted by Shehata and Razek (2011) reported how the combustion of S100 and B20 biodiesel had produced higher wall and exhaust temperatures during combustion (Shehata and Razek, 2011). The increased temperature is a direct result of incomplete combustion in the cylinder. Increased wall and exhaust temperature would result in an increased amount of engine and exhaust wear to some extent. A 20% biodiesel blend is suggested as safe for any internal combustion engine and crossing that threshold may cause serious maintenance problems and subsequently damage the engine (Shahid and Jamal, 2008); (Qi et al., 2010). However, about 12% biodiesel blended diesel has been reported to reduce the fuel consumption and significant heat release (Kousoulidou et al., 2010).

2.4.4. Residue and obstruction

There have been widespread reports of biodiesel leaving residue in engines and subsequent engine obstruction and clogging as a result. While this may indeed be the case, there is evidence to suggest that this phenomenon is a result of using biodiesels that are of low quality or biodiesel that has become oxidised. Should the biodiesel be of comparatively high quality, residue and deposits should not usually be a cause of concern (Dwivedi et al., 2011).

Monyem and Gerpen, in their research on long term testing with excessive oxidised biodiesel concluded that there was no case of filter plugging. While some researchers suggested that fuel plugging might be a result of the use of oxidised biodiesel, this was surely not the case for Monyem and Gerpen (2001). The fuel plugging was a direct result of interaction between biodiesel and the fuel additives in the diesel fuel, although it appears to be no difference in engine performance, when antioxidants was used in the fuel to potentially counter the effects (Ryu, 2010).

2.4.5. Omnifarious weather performance

PBDF, like their petroleum counterparts, is commonly known to experience operational difficulty in cold weather, which results in clogging and/or choking of filters. The use of flow improving additives, commonly known as "winter blends" of kerosene and biodiesel, has shown the ability to improve the operating range of biodiesel fuels at low temperatures. While pure biodiesel ordinarily operates comfortably at

temperatures about 5 °C, winter blends have been shown to further lower the operating temperature to −20 °C. Additives are typically known to reduce the engine operating temperature by about 5°C–8°C (Dwivedi et al., 2011); (Zheng et al., 2008).

An investigation to find out the performance of PUDF at stimulated high altitude with enriched oxygen showed that power output of different engines was determined mainly by the engine load and not by the use of oxygen enriched air (Perez and Boehman, 2010). What this entails is that even though the fuel used was PBDF, the same results would be expected in the use of biodiesels, which means that there would be little need for oxygen enrichment of the fuel at elevated temperature.

Biodiesel from Jatropha oil has properties close to PBDF, and it works better at higher load and gradually conserve the fuel consumption rate. The biofuel generates lower HC and CO gases but produces higher heat and increased NO_x production (Rehman et al., 2011). The higher oxygen content in the biodiesel enables this fuel to be used more effectively at higher altitude in low density oxygen environment.

2.5. Scope of improvements

This literature review covers a wide range of studies on biofuel efficiency and emission characteristics and it will now focus on five major themes, which have been frequently mentioned throughout this literature topic. These themes are an improvement of engine emission, consumption, performance, combustion, and efficiency.

2.5.1. Engine emission

Different types of fuel render in different emissions but the major gases are carbon monoxide (CO) and oxides of nitrogen (NO_x). However, the level of these emissions is different from one another.

Studies with single cylinder water-cooled engine, NA, DI diesel engine, show variation in the exhaust gas. The viscosity and density were considered as a factor for such studies. The test shows when biodiesel was used there was an increase in the oxide of nitrogen (NO_x) by 5% and a decrease in carbon monoxide (CO), and smoke by 4%. Even though the Exhaust Gas Recirculation (EGR) technique was applied to both diesel and biodiesel fuel to reduce the emission of NO_x, the study found that NO_x had a decreasing trend, while the opposite was observed for CO (Reşitoğlu et al., 2015).

One of the important key roles to improving the emission characteristics of blended fuel with diesel, such as biodiesel, is fuel injection pressure (Gumus et al., 2012). One particular study using Lombardini 6 LD 400, DI diesel engine to examine the exhaust emission by using four different injection pressures of 18, 20, 22, and 24 MPa. Unburned hydrocarbon in the emission, CO, CO₂ were measured.

The result shows that when injection pressure increased the percentage of CO, UHC and smoke were decreased. For NO_x emission, there was a slight decrease as the injection pressure increase, whereas, the NO_x increased when biodiesel increases. The reason behind the increasing of NO_x as biodiesel increasing is due to the chemically bound oxygen. In general, one of the solutions to improve the engine and to decrease the smoke, UHC, CO emission is to increase the injection pressure, but then CO₂, O₂, and NO_x would also increase (Gumus et al., 2012).

Engine emission can be summarized in few steps through different injection strategies. First, the increasing injection will decrease CO, HC, and smoke emission but it will increase NO_x as well. Although there is no evidence that injection pressure increases NO_x for diesel fuel, the vaporization increases for biodiesel with increased injection pressure (Mohan et al., 2013). The faster burning of biofuel due to higher fuel mists inside the cylinder naturally produces high temperature. Therefore, the O₂ content in the biodiesel boosts the production of NO₂ in the exhaust gas. On the other hand, the excessive heat in the cylinder causes high injection pressure and advancing in injection timing which lead cylinder pressure to build up due to longer ignition delay in some cases, so the sudden burst of heat causes excess NO₂ to be produced (Hwang et al., 2014). There are two ways to reduce NO_x emission either by using

pilot injection or multiple injections. Moreover, Table 4 shows some of the strategies found in different studies where different injections and exhaust gas composition was analysed. Speaking of exhaust gas reduction, NO_x and HC could be cut to almost half using a pilot injection process. Although, by using a double injection system, one-third reduction of particulates matters can be achieved without any increase in NO_x, provided that there is a considerable delay between successive injections. Moreover, putting the pilot injection prior to the main injection with reduced fuel quantity for ignition helps to suppress the possible increase of smoke and HC in the exhaust gas. In fact, the pre-combustion which is an effect of a pilot injection prior to the main injection, helps in combustion ignition, which enhances complete combustion of the main injection. The prior mixing of fuels shortens the main ignition delay and therefore, reduces smoke volume by improving air mixing in the cylinder. Apart from that, using split injection for biodiesel fuel is better in terms of NO_x reduction.

Therefore, biodiesel instead of pure diesel helps reducing the emission of the engine, however, not all emission gases are reduced, extra measures like additives and equipment can be used to achieve a considerable reduction in exhaust gases.

2.5.2. Engine consumption

Fig. 7 shows the result of three different variants of biodiesel and diesel fuels used in the experiment, where it can clearly be seen that the specific fuel consumption decreases when the engine speed increased until 2000 rpm; beyond this, the fuel consumption starts to increase. Interestingly, the amount of diesel consumption to bring the engine to the speed of 1500 rpm is less than that of biodiesel. Therefore, the specific fuel consumption is better with diesel than biodiesel. That is because biodiesel has less calorific value of about 10% lesser compared with diesel (Kaplan et al., 2006).

Another part to focus on the engine to improve its consumption is the combustion chamber shape. The combustion chamber is part of the engine, where the biodiesel, diesel, and other fuels are burned (Kim et al., 2017). To assess the improvement of the engine consumption, two different shapes of combustion chamber were used, as shown in Fig. 8. The experiment confirms that the egg shape has less fuel consumption because the egg-shaped bowl could refer to the less ignition time. Moreover, the egg-shaped has improved the emission, where it generates less NO_x and smoke compare with the previous shape.

In addition, adding nano-particles helps to improve the engine power by 6% and reduces the emission of CO by 20.5% and NO_x 13%, (Sarace et al., 2015). Addition of 10 and 20 ppm of nanoparticles into the net diesel had reduced the fuel consumption by approximately 3%. The fuel distribution in the chamber, ignition delay, and physical characteristics are the key factors that contributed to the reduction of fuel consumption due to the addition of nanoparticles. The nanoparticles in diesel fuel can increase fuel injection and puncture rate in the cylinder, which produces more mixture in the chamber. In general, adding nanoparticle can improve the ignition process and accelerate the fuel evaporation, which results in reduced fuel consumption.

2.5.3. Engine performance

An antioxidant is an interesting substance to be added to biodiesel to increase engine performance, although, emissions are also increased.

Table 4

Summary of affecting of different injection strategies on engine emission (Data taken from [Mohan et al., 2013]).

Injection strategies used	Type of Fuel used	NO _x	HC	CO	Smoke
Injection pressure	Diesel	–	ND	ND	–
Injection pressure	Biodiesel	+	–	–	–
High Injection pressure	Diesel	ND	ND	ND	–
Injection rate shipping	Diesel	–	ND	ND	+
Injection timing	Biodiesel	–	–	–	–
Split Injection	Biodiesel	–	ND	ND	ND

(–) Decreasing, (+) Increasing, (ND) No Data.

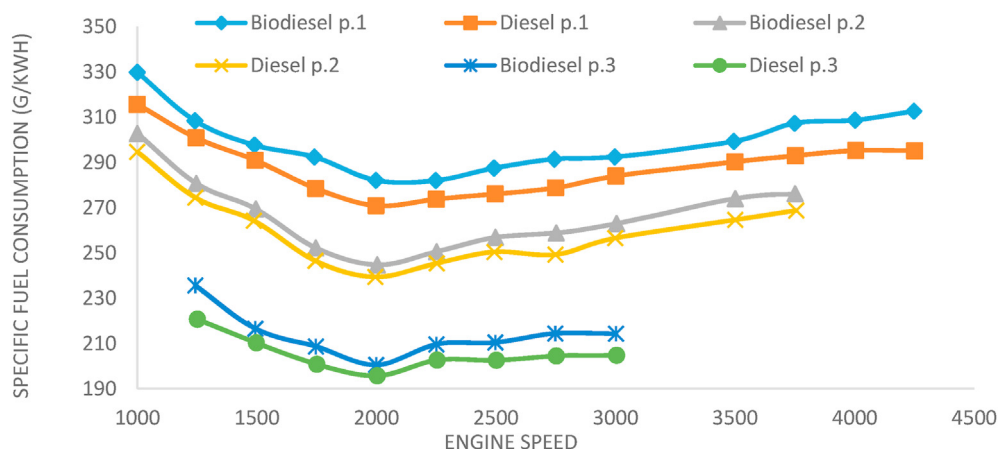


Fig. 7. Specific fuel consumption of biodiesel and diesel at different engine speed [Excerpt from (Kaplan et al., 2006)].

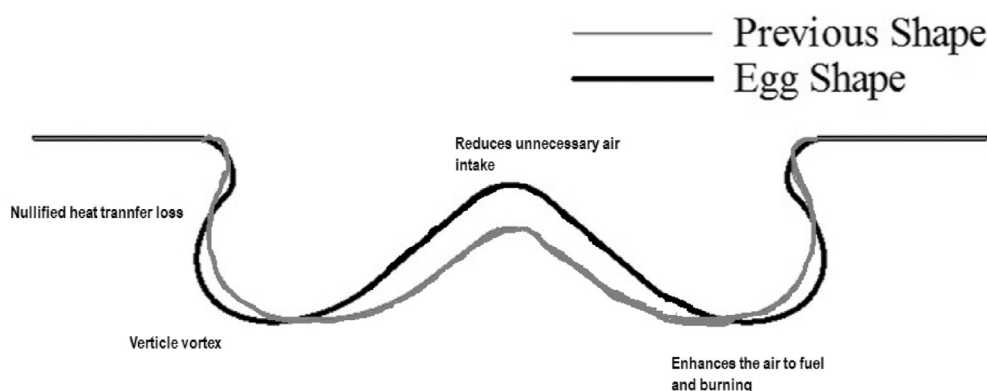


Fig. 8. The two shapes helped to understand the consumption of different fuels by different engines [(Kim et al., 2017) with permission].

Studies found that antioxidant has slight effects on engine performance and fuel properties, where there was an increase in engine performance and improvement in BSFC and brake power comparing to traditional biodiesel. The addition of antioxidant helps reduce the oxidative free radical and improve engine efficiency (Rashed et al., 2015); (Fernandes et al., 2015). However the efficiency reduces above 80 C for some antioxidant additives (Varatharajan and Pushparani, 2018). So, in-cylinder temperature may nullify the antioxidants effect on biodiesel stability and engine performance.

Özgür et al. (2015) investigated the improvement in engine performance by adding MgO and SiO₂ nanoparticle into biodiesel. Both the additive particles were used with high purity (>99.9%) and comparatively smaller size (<30 nm). The result shows that MgO increases the brake power by around 4.8%, SiO₂ increase the brake power by around 6.8%; while the maximum increase is by 2.4% compared with the base fuel. Moreover, the maximum engine torque is increased by 4.3% and 5.8% for SiO₂ and MgO, respectively. The maximum average torque is increased by 2.3%. Finally, the result of the study found a slight increase in engine performance through the addition of nanoparticles (Özgür et al., 2015).

Gumus and Kasifoglu (2010) found that a lower amount of biodiesel in fuel blend increases the torque and power of a single cylinder diesel engine due to higher availability in O₂ content and higher viscosity which led to pumping a large mass flow rate of fuel to the engine. In fact, an increase of biodiesel to 50% in a blend reduces the engine performance characteristics compared with diesel fuel (Gumus and Kasifoglu, 2010).

2.5.4. Engine combustion

Basha et al. reported on using the methyl esters of soybean oil blended with diesel, the ignition delay becomes shorter although the combustion characteristic is still similar to that of diesel. When methyl ester from jojoba oil in a fuel blend was used, ignition delay was reduced and ignition temperature was increased (Basha et al., 2009).

When FeCl₃ was used with biodiesel as fuel borne catalyst to evaluate the combustion characteristics of a diesel engine that runs at a constant speed of 1500 rpm and different operation conditions, the maximum cylinder gas pressure for biodiesel was found to be higher than that for diesel. For combustion of heat release rate, it was found to be negative during the ignition delay period due to cooling effect, which caused by the fuel vaporization and heat losses. Moreover, biodiesel has a maximum heat release rate due to increased accumulation of fuel, and shorter ignition delay (Kannana, G.R., Karvembub, R., Ananda et al., 2011).

An interesting study of using the fuel combination of ULSD-biogas-biodiesel for dual-fuel system in a four-cylinder CI engine at 2000 rpm exhibits the ignition delay at different engine load for two fuels: biodiesel and ULSD. Part of the result is illustrated in Fig. 9 which shows that biodiesel has better ignition delay than ULSD and ignition delay for both fuels works inversely with the engine. The ignition delay of dual-fuel combustion mode was found to be longer than in single-fuel operation because of biogas-biodiesel has a larger amount of biogas which contributes to higher specific heat capacity (Yoon and Lee, 2011).

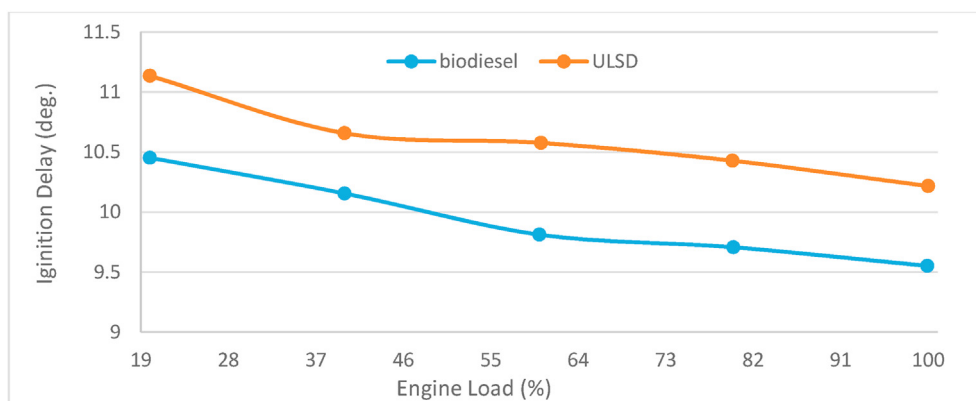


Fig. 9. The contrast of ignition delay in respect to increased engine load for biodiesel and ultra-low sulphur diesel fuel.

2.5.5. Engine efficiency

One of the solutions available to improve the effectiveness of the diesel engine is to adopt the Rankine cycle system. The main objective is to save fuel while getting more energy output. In fact, when H₂O and R245ca are used as medium thermodynamic efficiency increased due to high cycle pressure (Hountalas et al., 2012). Likewise, similar power output can be obtained by using lower recuperated heat amount from the exhaust gas. When the engine is fully loaded, the thermodynamic efficiency of steam and R245ca are 9.47% and 10.3%, respectively (Hountalas et al., 2012). Generally, the installation of the Rankine cycle is one of the solutions to reducing the fuel consumption of diesel engine.

Zheng et al. however, reached to a conclusion for single cylinder diesel engine operated at LTC and found that the fuel efficiency of the engine is affected by the combustion phase (up to 5%), as well as the thermal efficiency, both of which are substantially affected by the heat-release phasing more than the heat-release duration. Additionally, at LTC fuel efficiency was found to be around 42%–43% when using cylinder control techniques, where the efficiency achievable is approximately 40% (Zheng et al., 2016). The fuel efficiency of a diesel engine can be improved by fuel injection controlling, low load, and single shot with massive EGR.

Reddy and the team investigated the improvement of the ICE's efficiency by using secondary fuel similar in efficiency or has greater efficiency. The researcher used HO as secondary fuel in the study. Table 5 shows the comparison between conventional fuel and secondary fuel. From the above-mentioned table, a secondary fuel which is HO gas, has better efficiency, where 10 ml of the fuel took 114.2 s on average to be fully consumed, while diesel fuel is consumed in 102.4 s (Reddy et al., 2014). Therefore, biofuel efficiency can also be increased by adding fuel supplement and as previously explained, by adding antioxidants to it. For a concerted effort towards the positive changes in engine performance along with conserving clean environment more studies to be conducted on these fuel additives with different engine and environmental conditions.

3. Conclusions

Based on research findings, it is evident that increased biodiesel content improved combustion properties of the fuel mix, although in some cases, increased volume of ethanol in diesel reduces the power output. Higher ratio of biodiesel increases the density of the fuel blend which helps to increase the accumulation of matters inside the cylinder and causes the cylinder pressure to increase over time. HC and NO_x were also found to have been increased with the increase of biodiesel fraction. So, oxygenated biofuel additives such as, ethanol or ether can help improve the combustion of biodiesel by reducing viscosity and atomisation. Just like oxygenated additives, antioxidants have also been used to stabilize the fuel mix. Metal and metal oxide additives have shown better fuel combustion due to their catalytic properties and

Table 5

Time required for diesel and HHO to consume 10 ml of fuel (data taken from (Reddy et al., 2014)).

No.	Fuel consumed	Required Time (Diesel) (Second)	Required Time (HHO) (Second)
1	10 ml	104	115
2	10 ml	102	117
3	10 ml	102	113
4	10 ml	100	111
5	10 ml	104	115
Average 10 mL		102.4	114.2

simultaneously providing excess oxygen for combustion. So, low calorific value of biofuel mix could be compensated by the catalytic activities and boosting properties of nanoparticle additives. Among all the nanoparticles and their oxides reviewed, graphene oxide showed the lowest BSFC and maximum brake power. It also showed to have reduced emission for HC and CO.

Apart from the lower calorific value and low power output by biodiesel, its higher cetane number helps to reduce ignition delay thus reduce excess residue and discharge. However, conflicting results were reported by researchers for BTE with the usage of different fuel blends. This variation in BTE resulted from different combinations in engine type, load variation and rotation setup along with variation in fuel injection conditions. But BTE can be improved significantly through advancing injection timing and optimising in-cylinder pressure.

Due to low calorific value, more biodiesel is needed as compared to mineral fuels and increased volume of biofuels causes increased CO and HC emission. However, optimized operating condition of and fuel ratio could help reducing the emission of harmful gases and PM. Besides alcohols, synthetic organometallic additives can be used to increase O₂ content in fuel blends which will reduce the emission of various gases.

Although there are various works that have been done to understand the effect of biodiesel and fuel additives on engine efficiency, there is still a need to map and relate of a better fuel mixture, the heat release efficiency, cylinder pressure mapping, and the torque conversion to SEC for different fuel mixtures. The effect the nano additives on the exhaust gas subjected to pass through catalytic converter has to be evaluated as well. Moreover, the post combustion fate of those nano additives to be studied thoroughly, as well as their effect on other pollutants, such as SO_x.

The induction time above minimum standard for the nano additives is needed for better ignition delay and peak pressure in the cylinder. The optimum size of the additives within their nano realm also needs to be established. Although it is evident that nano additives help to improve engine efficiency and fuel consumption profile, a proper ranking through quantification of those additives effect is much needed.

So in closing, this review serves as a guide to the quest for designing a better and effective fuel mixture and formulation of additives for effective combustion and improved emission characteristics.

Declaration of competing interest

No conflict of interest.

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