Role of Additives with Biodiesel in the Performance of Diesel Engine as a Future Alternative Fuel: A Review

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Abstract: *In this paper, the classification and analysis of commercially available additives used with biodiesel by different researchers are discussed. Biodiesel is widely accepted as easily available, renewable, environment friendly and mainly alternative to petroleum diesel fuel for compression ignition engines in feature. Relatively poor cold flow property and high viscosity characteristics are limiting its application in diesel engine. Additives are chemical materials added in biodiesel to improve the desirable chemical properties for better performance of the engine. These additives become the most viable choice to improve properties of fuel and also to produce specified exhaust products that meets international and regional standard requirements. This paper covers a deep and through literature review of the different additive effects on biodiesel properties, engine performance and exhaust emission characteristics. Usage of additives in biodiesel is inseparable for the improvement of specific properties like cold flow, lubricity, fire point, fuel burning rate and viscosity etc. for the better engine performance and exhaust emissions control. It can be concluded from the literature that the available specific additives for biodiesel remain at their initial stage of improvement. Further research is needed to develop these additives in order improve the properties of biodiesel for better performance and exhaust emissions of the engine.*

Keywords: Biodiesel, Additives, Performance, Emissions, Properties, Alternative Fuel.

1. INTRODUCTION

Diesel engines are widely used to transport vehicles, trains, ships, irrigation pumps and to produce electric power. The combustion of fossil fuels produces emissions that affect the ecosystem and the human health. To overcome the stringent regulations of environment pollution made researchers to search for new and suitable future alternative fuels that are easily available, globally acceptable and technically feasible to use in diesel engines. The main advantages of using microalgae for biodiesel production are described in comparison with other available feed stocks, primarily palm oil more sustainable source of biodiesel in terms of food security and environmental impact compared to palm oil [1-2]. Alternative fuels are easily available, renewable and environment friendly. One of the promising alternative fuels considered to replace diesel without any modifications of engine is biodiesel. Particularly non-edible/edible oils, waste cooked oils and animal fats can be used to make biodiesel for feature fuel requirement in place of diesel fuel. Biodiesel fuel has better properties than petro-diesel fuel; it is renewable, biodegradable, non-toxic, and essentially free of sulphur and aromatics. Biodiesel seems to be a realistic fuel for future [3-4]. Biodiesel fuels can be derived from triglycerides (vegetable oils/animal fats), presents a promising alternative to substitute diesel fuels or from renewable oils and can be used in compression ignition engines in place diesel. These biodiesels have properties like diesel oils and reduced emissions from a clean burn due to their higher oxygen content in fuel [5-6]. Biodiesel properties are like diesel fuel; hence there is no need to modify the diesel engine when it is fuelled with biodiesel or biodiesel blends with diesel fuel. Additive is a chemical material added in base fuel to improve desirable chemical properties and function as a detergent or dispersed. Oxygenated additives like triacetin, diethyl ether etc. solve the problems occur prior to the burning and promote complete combustion of fuel in the combustion chamber which reduces engine deposits, smoke and other exhaust emissions [7-8].

Additives can be considered to improve combustion, fuel economy, decrease emissions and to make biodiesel quality equivalent to diesel fuel. The metal based additives, cetane number additives, antioxidant additives and oxygenated additives help in improving the quality of the biodiesel [9]. Alcohols lower the flash point slightly and reduce the viscosity and density of blend fuel marginally. With this fuel, ignition can start at lower temperature and able to burn completely to extract total energy content. The combustion rate of fuel is increased due to more oxygen availability in alcohol that results in reducing the levels of pollutants in exhaust gases [10]. Additives significantly improve the quality of biodiesel and its blends; enhance biodiesel properties, reduce from fuel system cleanliness with optimized performance and economy of fuel without modification of diesel engine [11]. Among the recent additives used in diesel and biodiesel fuels, the Fe nanoparticles have emerged as a novel and promising additive which results in the reduction of exhaust emissions including NOx and particulates and enhancement in the engine performance. Many researchers have focused their attention on fuel modification methods by using the nano-additives to achieve improved engine performance and reduced exhaust emission characteristics [12-13].

Particulate matter (PM) or smoke emission and oxides of nitrogen (NOx emissions) are the two important harmful exhaust emissions from the diesel engine. Fuel companies and the researchers around the world are devoted to reducing these emissions by different ways. Fuel modification, modification in combustion chamber design and exhaust after treatments are the important means to alleviate such emissions. In this context, engine researchers are hunting for suitable alternative fuels to the diesel engine. Among different available fuels, oxygenated fuel is such a kind of alternative fuel. Researchers studied the performance of Diethylene glycol dimethyl ether (DGME), dimethoxy methane (DMM), dimethyl ether (DME), diethyl ether (DEE), methyl tertiary butyl ether (MTBE), dibutyl ether (DBE), dimethyl carbonate (DMC), dibutyl maleate (DBM) oxygenated additives and concluded that the smoke content reduces by 35% at full load conditions using DMC20 blend, the oxygen content in the emission increases by 39% with DBM15, that results decrease in the percentage of unburnt hydrocarbons and carbon monoxide is 19 and 21 respectively. The blends of diesel with 15% DMC and DBM by volume is the best fraction for reduction of smoke and CO emissions without much affecting the performance of engine. Based on the results obtained, these additives are more effective for reducing the emission of diesel engine, alcohols (methanol and ethanol) and triacetin have played their role to reduce diesel emissions. These fuels can either be used as a blend with conventional diesel/biodiesel fuel or as an additive or directly as a neat fuel. The presence of oxygen in the fuel molecular structure plays an important role to reduce PM and other harmful emissions from the diesel engine [14-19]. DME was still more effective than ethanol in reducing aromatic species and particulate emissions when compared with the structure of an oxygenated compound blended with diesel fuel [20]. Dimethyl ether is a potential ultraclean fuel burns without producing smoke associated with diesel combustion and it can be produced from synthesis of gas or methanol. However, DME has a low viscosity as compared to diesel fuel and insufficient lubricity to prevent excessive wear in fuel injection systems, cylinder and piston surfaces. Clean burning blend fuels can be obtained with satisfactory properties by DME and diesel fuel. The viscosity of blends of DME with various fuels and additives, including low-sulphur diesel fuel, soybean oil, biodiesel and various lubricity additives were characterized with certain range of blend ratios. It was observed that none of the additives or fuels provides adequate viscosity when blended with more than 50% DME in diesel fuel [21].

The effect of fuel oxygen on PM and other exhaust emissions of different biodiesels with oxygenated fuels like ethanol, DMC and DMM were reduced with all biodiesels compared to that of diesel fuel. THC emissions with all biodiesels were observed to reduce from 45-67%. Similarly, PM, CO emissions were also reduced by 4-16% with all biodiesels. On the other hand, NOx emissions were increased with the addition of fuel oxygen content in biodiesel. The results of experiments conducted with three oxygenated fuels, that are 10-30% of ethanol with PME, 10-20% of DMC and 10-20% of DMM addition with CME biodiesel concluded that reductions in PM, THC and CO emissions, whereas NOx emissions were increased due to the high oxygen content in the fuel [22]. The potential of using diethyl ether as supplementary fuel in diesel engine with diesel fuel to improve its characteristics were studied. The engine characteristics with blends of 2%, 5% and 10% of diethyl ether with neat diesel fuel was concluded that the 5% blend of diethyl ether showed slight improvement in thermal efficiency, brake specific fuel consumption with low in the smoke level and oxides of nitrogen, unburned hydrocarbon, carbon monoxide and ignition delay along with increase in carbon dioxide emissions due to its higher Cetane number of DEE additive [23]. The addition of 5% diethyl ether with neat diesel slightly improves the thermal efficiency and reduces the smoke, carbon monoxide and the hydrocarbon emission levels in a single cylinder direct injection diesel engine. It is also reported that the nitrogen oxide emission level slightly increases with 5% blend fuel due to better combustion with high oxygen availability in the additive. The exhaust gas temperature found to be higher for diethyl ether blend fuel [24].

The characteristics of karanja biodiesel with 5%, 10%, 15% and 20% by volume of diethyl ether (DEE) shows improved physicochemical properties such as heating value, viscosity, specific gravity, distillation profile including cold starting problems were found according to the ASTM standards with higher efficiency, NOx emission reduced significantly along with smoke reduction with 15% DEE in biodiesel [23]. The use of Jatropha oil as an additive with diesel fuel that increases brake thermal efficiency as the load increases on the engine. The 2.6% jatropha oil acts as additive in diesel that gives higher efficiency at all loads on the engine. The observation is that the 2.6% of jatropha oil mixed into the diesel fuel enhances the performance of engine and reducing the exhaust temperature and the NOx emission [25].

2. MAKING OF BIODIESEL

The high viscosity, acid composition, free fatty acid content, as well as formation of gum due to oxidation, polymerization during storage and combustion, carbon deposits and thickening of lubricating oil and/or the use of vegetable oil blends are causing the main problems in diesel engines. To come out of the problem vegetable oils must undergo the process of transesterification to improve the properties and that can be used in diesel engines. Biodiesel is the product of any oil or animal fat produced in the process of transesterification as methyl or ethyl esters. Biodiesel is biodegradable, non-toxic, free from sulphur, renewable and can be produced from agriculture and plant resources to be a future alternative fuel [26].

2.1 *Preparation of Biodiesel*

Sample of Jatropha oil methyl ester (Biodiesel) is prepared from raw Jatropa oil by transesterification process. Initially Jatropha oil is filtered to remove solid waste particles and heated up to 105^{0}C temperature for some time to remove water content from the oil. In acid treatment methanol of 120ml and 2ml of concentrated highly pure sulfuric acid (H_2SO_4) per litre of oil is added and heated with magnetic stirrer nearly at 62^{0}C for about half an hour in a closed conical flask. After attaining brown colour, the mixture can settle down in a decanter. The settled glycerin at the bottom of decanter is removed from methyl ester. Sodium methoxide was prepared by mixing thoroughly 200ml of methanol (20% by volume) with 6.5 grams of sodium hydroxide (NaOH) per litre of oil. The formed solution is added to the oil obtained from acid treatment, then stirred continuously at 62^{0}C for about one hour in the base treatment and then allowed to settle down in decanter. The settled glycerin at the bottom of decanter is separated from methyl ester. The collected Jatropha oil methyl ester (JOME) is bubble washed with pure water and orthophosporic acid (H_3PO_4) to remove soap content, acid and methanol. The washed JOME is heated further above 100^{0}C for some time to remove water content. The prepared biodiesel can be used in diesel engine along with additives as per the requirement to study the properties and performance of engine as an alternative to diesel fuel. [27-28].

2.2 *Biodiesel properties*

The researchers have shown that physical properties of biodiesel can be improved with the addition of additives to solve the problems like viscosity, cold flow, energy release rate, lubrication, combustion rate, performance and engine life. In this regard number of additives has been tried for improving the efficiency and exhaust emissions of the engine. Diesel oil is a fuel derived from petroleum and consists of mainly aliphatic hydrocarbons which contain 8-28 carbon atoms with boiling point in the range of 130-370°C. It is a blend of fractions with hydrocarbons heavier than the hydrocarbons in gasoline with a lower H/C mass ratio that determines the high carbon compounds emission per unit heat energy delivered in the combustion of engine. A reduction in fuel consumption with high performance and improvement in the quality of diesel fuel have been the object of study by various researchers that motivated the increasing demands mainly in the transport and electric power generation sectors. Commercially available diesel fuel is a combination of fossil diesel and several types of additives, which are added in different quantities to perform the following specific functions. The fuel additives that are used with diesel, biodiesel and their blends improve the fuel properties and hence show the following benefits in the engine performance and operation with low emissions as far as possible [29].

i. Reduce pernicious emissions,
ii. Improve fluid stability over a wider range of working conditions,
iii. Improve the viscosity index by reducing the rate of viscosity change with temperature,
iv. Improve ignition by reducing its delay time with lower flash point of fuel,
v. Reduce wear with agents that adsorb onto metal surfaces,
vi. Suppression of corrosion of fuel tanks, channel lines and wear of fuel system equipment in the diesel engine.
vii. Improvement in fuel cetane, octane numbers for smooth running of engine.
viii. Improvement of cold flow and boosting utilization of biofuel.
ix. Improve engine performance with fuel economy and low emissions.

There is also an increasing trend to use blends with biomass products such as vegetable oil, ethanol and biodiesel by as an alternative fuel. Blends of diesel and biodiesel usually require additives to improve the lubricity, stability and combustion efficiency by increasing the Cetane number. Blends of diesel with ethanol (E-diesel) usually require additives to improve miscibility and reduce the knocking tendency in the engine [30]. Composition of diesel and the use of additives directly affect the properties such as density, viscosity, volatility, cetane number and behaviour of the fuel at low temperatures [31]. By increasing the concentration of additives ethanol and ethyl tert-butyl ether or tert-amyl ethyl ether, there is a reduction in the cetane number and an increase in hydrocarbons that leads to decrease of CO emission up to 20% in comparison with diesel fuel. The cetane number of fuel decreases with an increase of ethanol content in the fuel because of the low cetane number of this additive. The other factor that influences, the decrease in cetane number level causes the incomplete combustion of ethanol-air mixture. Factors causing combustion deterioration, such as high latent heats of evaporation, could be responsible for increased CO emission. Another reason for high CO emission is the increase in ignition delay of combustion. This leads to a lower combustion temperature at lower and medium loads on the engine [32].

Flash point of B20 decreases drastically at 5% alcohols and increases at higher percentages. Increase in flash point as blend concentration increase may be considered better with respect to safety in fuel handling and storage. In case of viscosity and density, cetane number and acid values decrease as the percentage of alcohol increases. Alcohols lowers the flash point slightly and reduces the viscosity by decreasing the density of blend fuel that can start ignition at lower temperature and able to burn completely. The combustion rate of fuel is increased due to more oxygen availability in alcohol that results in reducing the levels of pollutants in exhaust gases of the engine performance [33]. Additives for diesel fuel are also classified according to their design and specific purpose. Preflame additives are designed to correct problems that occur prior to burning that include dispersants, pour point depressants and emulsifiers, which act as cleaning agents. Flame additives are used to improve the following in the engine [34].

i. Increase combustion efficiency in the combustion chamber,
ii. Increase cetane number of fuel,
iii. Reduce the formation of carbon deposits on surfaces,
iv. Avoid reactions of oxidation, contamination of fuel and filters clogging by rust,
v. Avoid potential explosions caused due to changes in static electricity.

Post flame additives are designed to reduce smoke, emissions and carbon deposits in the engine [35]. The increase in crude oil prices, limited resources of fossil fuel availability and environmental concerns, there has been a renewed focus on vegetable oil and animal fat to make biodiesel. Increasing in usage of petroleum fuel will increase the local air pollution which magnifies the global warming problems caused by carbon dioxide. In the closed environment of underground mines, biodiesel has the potential to reduce the level of pollutants [36].

3. ADDITIVES

Biodiesel is alkyl ester of fatty acid and can be obtained by transesterification of any oils or fats from plants or animals with short chain alcohols of ethanol and methanol. The use of biodiesel or diesel blends with biodiesel in engine, performance is comparable with pure diesel fuel. But high viscosity, high density and low calorific value of biodiesel play an important role in increasing the fuel consumption. Additives are used to achieve the required fuel properties and to improve the performance, fuel property characteristics and to attain a good emission control of the CI engine without any modification. The basic requirements of fuel additives added to commercially available diesel or biodiesel fuels in varying quantities to perform the following specific functions [37, 29].

i. The additives should reduce the exhaust emissions,
ii. Increase the oxygen concentration in engine and in the particulates filter,
iii. Improve the fluid stability over wide-ranging conditions,
iv. Increase the viscosity index of fuel,
v. Reduction in ignition delay time and flash point,
vi. The chemical-to-chemical contact should be improved rather than the metal-to-metal contact under high-load conditions to reduce the wear agents that adsorb on the metal surfaces.

Environmental regulations have been the major concern to look for alternative fuels, at this stage the use of biodiesel presents a promising alternative fuel in the world. It is not only a renewable energy source, but can also reduce the dependence on imported oil and support agricultural subsidies in certain regions. Researchers studied following several aspects with the aim of making biodiesel and possibility to use as substitute to diesel fuel. These include:

i. Appropriate available raw material sources,
ii. Comparative studies between emissions of diesel and biodiesel fuels,
iii. Development of new catalysts and new technological routes for the biofuel production,
iv. Improvement of qualitative and quantitative methods for characterization.

It is also presented that a critical analysis on the sources of oil, the catalysts, transesterification yields, comparative studies on emissions from fossil diesel and blends with biodiesel in variable proportions [38]. Additives play a very important role in meeting the international fuel standards and real-time problems which are associated with biodiesel. With the help of additives, the fuel properties can be enhanced and biodiesel in blend form can be used with diesel in the vehicles, which is able to increase the performance and reduction in exhausts emissions from the engine. The selection of biodiesel additives is mainly based on different properties of additives such as flash point, fire point, viscosity, density, calorific value, solubility etc. The use of additives in biodiesel also solves many technical problems which limit the acceptability of biodiesel as an alternative fuel in all working conditions of the engine [39]. Additives are mainly classified into:

1. Oxygenated Additives
2. Ignition Promoters
3. Lubricity Additives
4. Cetane Number Additives
5. Stability Additives
6. Metal-Based Additives
7. Depressants and Wax Dispersants

4. PERFORMANCE WITH ADDITIVES

4.1 Oxygenated Additives

The idea of using oxygen to produce a clean burning of diesel fuels is half a century old. Many researchers have reported that the addition of oxygenated compounds to diesel fuel will meet the prescribed environmental pollution regulations. Among all, the following are the commonly used high oxygen content Oxygenated Additives (Table 1).

It has been found that the exhaust emissions including PM, total unburnt hydrocarbon (THC), carbon monoxide (CO), smoke and engine noise were reduced with oxygenated fuels without any trade-off between exhaust components. Normally NOx emissions were reduced but in some cases increased on the conditions of engine operation. The reduction of emissions is entirely dependent on the content of oxygen in the fuel. It has been reported that combustion with oxygenated fuels is much faster than that of conventional diesel fuel; this is mainly due to the molecular structure of fuel and low volatility.

Table – 1. Oxygen quantity in additives

S No	Additive name	% of Oxygen
1	Diethylene glycol dimethyl ether (DGM)	35.82
2	Dimethoxy methane (DMM)	42.1
3	Diethyl ether (DEE)	21.0
4	Methyl tertiary butyl ether (MTBE)	18.18
5	Dibutyl ether (DBE)	12.3
6	Dimethyl carbonate (DMC)	53.3
7	Methanol	50.0
8	Ethanol	34.78
9	Triacetin	46.16
10	Ethyl aceto acetate (EAA)	36.9
11	Diethyl carbonate (DEC)	40.6
12	Diethylene glycol (DEG)	45.2
13	Dibutyl maleate (DBM)	41.6

The low volatile oxygenated fuel evaporates earlier and very good air-fuel mixing is achieved during combustion eventually resulted in lower exhaust emissions [40]. In the investigation of DME additive at 10, 20 and 30% in diesel fuel are noted that higher the DME content lower the amount of heat release during the premixed combustion. This is due to good at ignition and atomization characteristics that improves the engine combustion process, which reduce the smoke density significantly, especially at higher loads. Overall the emissions were reduced and performance increases by increasing the concentration of DME additive in diesel fuel [41].

Ethanol can be obtained from biomass by using the process of fermentation that contains 35% higher oxygen by weight. Ethanol can be produced from different feedstock such as sugarcane, sugar beet, sorghum, potatoes, sunflower, molasses, corn, wheat, cotton etc [42]. Oxygenated fuels are generated by addition of ethanol in diesel fuel is also called as Diesohol. The report is that addition of ethanol in small percentage in the blends of biodiesel increases the brake thermal efficiency, heat release, reduces the viscosity and smoke in the exhaust of the engine. Physical and thermal properties of ethanol-biodiesel-diesel blends improved drastically which helps in fuel combustion in the engine cylinder [43]. Oxygenated additives are considered for reducing the ignition temperature of particulates. However, the reduction of particulate emissions through the introduction of oxygenated compounds depends on the molecular structure, oxygen content of the fuel and on the local oxygen concentration in the fuel. To reduce particulate emissions, oxygen bearing compounds should be blended with diesel to produce a composite fuel containing 10-25% v/v of oxygenate. Therefore, the composition of diesel and the use of additives directly affect properties such as density, viscosity, volatility, Cetane number and behaviour at low temperatures [44]. The ignition temperature of particulates from seed-derived oils (SO) and from blends of SO with diesel fuel can be lower than that of particulate from neat diesel fuel. At low and medium loads on engine, ignition delay causes lower combustion temperature. Further, increase in concentration of oxygen in the combustion products from the blends may cause increase in NOx formation in the exhaust [45]. Oxygenated additives results in formation of a lubricant film on the surface that improves anti-wear properties. The increase in volatility of the mixture is also apparent to a lower flash point at ambient temperature. Although this does not have a direct effect on engine performance, such mixtures would be subjected to the legislation concerning of fuel handling and storage [21]. The 2-methoxyethyl acetate (MEA) and diesel can be easily mixed by small, with change in the fuel delivery system, engine power and fuel consumption. Experiments showed that MEA is a good oxygenated additive of diesel for C I engines and can be used to decrease smoke, HC and CO emissions [46]. The compounds of ethers, aldehydes, ketones, esters, alcohols and acids are in ascending order with respect to anti-wear effectiveness [47].

DMC oxygenated additive is generally used to improve combustion and reduce diesel engine emissions. Dimethyl carbonate promotes good blend fuel properties and reduces smoke as its concentration increases. However, DMC cannot be used as fuel in diesel engines directly due to its low cetane number and high latent heat of vaporization. Addition of 10% DMC in the diesel fuel promotes a smoke reduction of 35-50%, and some reductions in hydrocarbons, carbon monoxide were abtained with a slight increase in NOx emissions. The engine fuelled with DMC emitted almost smokeless exhaust gas because this oxygenated fuel has no C-C bonds in molecules [48]. In the combustion of diesel engines, DMC along with exhaust gas recirculation, initial ignition of DMC by diesel and fuelling with DMC almost emits zero level of smoke with low exhaust gas temperature. DMC fuelled engine has lower NOx emissions and 2-3% higher thermal efficiency than the engine operated with diesel at moderate and high loads [49].

A comparative study was conducted to evaluate the effect of Triacetin [$C_9H_{14}O_6$] additive with biodiesel blends on DI diesel engine. Coconut oil methyl ester (COME) was used with Triacetin additive at various percentages by volume for all load ranges of the engine starting from no load to full load. The engine performance and combustion characteristics results shows that the engine knocking problem can be alleviated to some extent and the tail pipe emissions including PM, total unburnt hydrocarbon (THC), carbon monoxide (CO) and smoke, engine noise are reduced with this oxygenated blend fuels without any trade-off between exhaust components as compared to neat diesel in respect of engine efficiency. NOx emissions were reduced and in some cases increased depending on the engine operating conditions, among the all biodiesel blend fuels tried, 10% Triacetin combination with biodiesel shows encouraging results. For this blend fuel vibrations of the engine were measured in three directions of the engine cylinder and on the foundation, finally analysed to elicit information about the nature of combustion since the combustion itself is the exciter. The pressure signatures are tallied with time waves eliminating the time lag in between exciter (combustion in the cylinder itself) and the cylinder head vibration. Triacetin being an antiknock fuel, with 10% blend emanated as a best blend with its contribution to reduce cylinder vibration in vertical direction of the engine cylinder. The time wave resembles attenuated sine wave replete with pure harmonics indicating smoother combustion with lesser engine detonation. [50-53].

4.2 Ignition Promoters

The internal combustion engines operating with diesel fuel, it is concluded that cetane number of the fuel is one of the most important characteristics of combustion process. The decrease in the ignition delay time of fuel is detected is due to improved ignition of fuel. The ignition delay time is the time between the start of fuel injection and detectable ignition. Shorter ignition delay time has been directly correlated with a faster startup in cold weather, reduced NOx emissions and smoother engine operation. The commercial market considers several factors when selecting to use cetane improvers. These include:

i. Efficacy toward improving ignition properties,
ii. Hazards associated with storage and transport,
iii. Additional costs associated to dilute cetane improvers to allow safe transport
iv. Nitrogen content in the fuel.

Alkyl nitrates are characterized by relatively high efficiency and simultaneously many serious drawbacks. They are toxic, corrosive and worsen the colour of the fuels during storage [54]. The cetane number is a function of the composition and structure of hydrocarbons present in diesel. Cetane number decreases with increase in aromatic hydrocarbon content and increase with increase in n-paraffin and olefin contents in diesel [55]. The use of Cetane-improving additives is necessary to avoid difficulties in cold starting and the performance problems associated with low Cetane numbers. Ignition promoters have traditionally been given to alkyl nitrates (e.g., amyl nitrate, hexyl nitrate and octyl nitrate), but compounds like alkyl peroxides have also been proposed [56].

The ignition promoters based on compounds with organic peroxides have received the most attention. They are more stable in storage, heating and do not decompose on contact with water, olefins, and other compounds which can be present in commercial fuels [57]. The experiments conducted with nitrate derivatives of soybean oil was synthesized and evaluated as an alternative to 2-ethylhexyl nitrate (EHN), which currently dominates the Cetane improver market. The synthesized additive exhibited NOx-reducing capabilities like that when EHN used in a diesel fuel. They also provide significant lubricity and Cetane enhancement to fuels at the same concentrations. Depending on the product, these additives exhibit increased stability and lower volatility than EHN. Commercially competitive enhancements of both ignition related properties and lubricity were achieved in a single product [54].

4.3 Lubricity Additives

The fuel lubricity can be enhanced with the addition of lubricity additives. They comprise with the range of surface active chemicals. They have an affinity for metal surfaces, and form boundary films which prevent metal to metal contact that leads to wear under light to moderate loads. Research shows that the addition of lubricity additives is not necessary in low sulphur diesel-biodiesel blends once vegetable oil methyl esters enhance the fuel lubricity [58-59]. The mixture of fuel and additive provides a stable and substantially a film on the metal surface reduces the wear scar on the surface area [60].

The presence of mono and diacylglycerols in the range of 100-200 ppm provides sufficient anti-wear capacity to safely ensure normal operation of the motor injection system, even when using a low-sulphur diesel [61]. The lubricity of fatty compounds possesses better than hydrocarbons because of their polarity imparting oxygen atoms. Additionally, pure free fatty acids, monoacylglycerols, and glycerol possess better lubricity than pure esters because of their free OH groups. The order of oxygenated additives enhancing lubricity was obtained from studying various oxygenated C10 compounds. Another experiment shows that oxygen enhances lubricity more than nitrogen and sulphur with pure C3 compounds containing OH, NH_2 and SH groups. The addition of biodiesel improves the lubricity of low-sulphfur diesel more than pure fatty esters that indicate other biodiesel components cause lubricity enhancement at low biodiesel blend levels. The addition of polar compounds such as free fatty acids or monoacylglycerols improves the lubricity of low-level blends of esters in low-lubricity diesel. The result suggests that these species considered as contaminants resulting from biodiesel production and that are responsible for the lubricity of low level blends of biodiesel in low sulphur diesel [62]. Free fatty acids and diacylglycerols can also affect the lubricity of biodiesel but not so much as monoacylglycerols. Triacylglycerols almost have no effect on the lubricity of biodiesel [63].

Fatty acid methyl esters (FAMEs), commonly known as biodiesel, have successfully been used as diesel fuel lubricity improvers. The lubricity improvement observed from vegetable oil based methyl ester additives is greater than that observed when the methyl ester of only one fatty acid is added at the same concentrations. Studies show that fatty acid esters derived from vegetable oils have increased fuel lubricity with diesel at concentrations of less than 1%. The fatty acid composition of FAME mixtures may have an impact on their effectiveness as lubricity enhancers. Factors such as saturation, chain length and hydroxylation could influence the performance of these additives as lubricity enhancers [64]. Oils which contain a high concentration of hydroxylated fatty acids, such as castor oil, produce a FAME mixture with much more effective lubricity than oils that do not contain any hydroxylated fatty acids. The hydroxyl group is significant because it facilitates plasticization and adhesion of the oil esters. When the unsaturation of FAMEs increased, the lubricity enhancement also increased. In C18 series methyl stearate, methyl oleate, methyl linoleate, and ethyl linolenate, methyl linoleate shows the best performance as a lubricity enhancing additive and methyl stearate was the least performer. The increase of unsaturation reduces the cetane number and increases in chain length that improves the cetane number, besides increasing the number of double bonds and their position in the chain results in a lower cetane number. Biodiesel from palm oil blended with diesel oil in a proportion of 15% increase in brake power and reduced exhaust emissions compared to base diesel [65].

The wear results of various types of additives improved fuel lubricity [58]. The biodiesel produced from four vegetable oils (canola oil, green seed canola oil, processed waste fryer grease and unprocessed waste fryer grease) using methanol and KOH as a catalyst were tested evaluated to find their diesel additive properties. From the results of four biodiesels produced the best choice to use as an additive was canola methyl ester, mainly due to the enhancement of the fuel's lubricity number. A useful effect of the lubricity in diesel fuel also was observed with biodiesel produced from rapeseed oil, sunflower oil, corn oil, used fried oil and olive oil at low concentrations (0.15-0.5% by volume). The esters of C8-C18 saturated and unsaturated fatty acids produced by the transesterification of vegetable oils with polyhydroxy alcohols can also shows considerable effect to use as lubricity additives [66].
The influence of adding low amounts of four specific types of biodiesel and two tertiary amides on the tribological behaviour of the steel-on-steel systems, lubricated with low-sulphur automotive diesel. With the experiments on engine, the wear results have clearly shown a specific behaviour of the components tested, which dissolved in selected base fuels at the concentration range of 0.05–10%. The conclusion is that a very small amount of the selected biodiesel types and tertiary amides dramatically improves the low sulphur diesel lubricity [64]. The fatty compounds possess better lubricity than hydrocarbons found in diesel, because of their polarity-imparting oxygen atoms. Additionally, pure free fatty acids, monoacylglycerols and glycerol possess better lubricity than pure esters. The oxygen content enhances lubricity more than nitrogen and sulphur. The addition of biodiesel improves the lubricity of low-sulphur diesel more than pure fatty esters [62]. The main purpose of the oxygen compounds is to reduce adhesion between contacting asperities and to limit friction, wear and seizure. This can be achieved because they adsorbed or reacted with the rubbing work surfaces of engine parts in movement [67]. Even less than 1% of biodiesel from jatropha oil improves the lubricity in ultra-low sulphur diesel and is a superior lubricity enhancer [68].

4.4 Cetane Number Additives

Cetane number measures the readiness of the fuel to auto ignite when injected into the engine and is one of the most significant properties to specify ignition quality of any fuel for internal combustion engines. An increase in cetane number decreases the delay between injection and ignition. One of the undesirable effects of running on a low cetane number fuel is an increase in engine noise. In general, aromatics and alcohols have a low Cetane number [69]. Cetane number value also affects the NOx and particulate matter emissions from diesel, biodiesel and diesel-biodiesel blend in engines as noted by several researchers. For instance, a diesel blend consisting of 46% Fischer-Tropsch diesel fuel, a diesel base stock containing 10% aromatics and 1 vol % di-tert-butyl peroxide or 0.5 vol % 2-ethyl-hexyl nitrate (EHN), in all cases, the reduction of the NOx emissions came from the increase in Cetane number of the fuel [70]. NOx results increase from advancing the injection time of biodiesel and diesel-biodiesel engines as compared to diesel [71-72]. A high cetane number leads to a reduction of both NOx and particulate matter emissions [73]. Some strategies have been proposed to overcome this effect, such as detection of the presence of biodiesel in the fuel and retarding of the static injection time or by blending biodiesel with other fuels or additives [74].

The effect of 2-EHN antioxidant additive addition on NOx emission with B20 biodiesel blend increased the cetane number of the fuel, leading a shorter ignition time and thus to a decrease in NOx emissions. The cetane number of biodiesel ranges from 48 to 67 depending on several parameters such as oil processing technology and climate conditions where the feedstock (vegetable oil) is collected and mainly the fatty acid composition of the base oil [75-76]. It is well-known that the overall properties of biodiesel are determined by the properties of several fatty acids which, in turn depend on the structural features of fatty acids chain length, degree of un-saturation and branching of the chain. Among these properties, cetane number is especially affected by the structural features of the various fatty esters [77]. The presence of double bonds in fatty acids will lower the cetane number value and then strategies are addressed to shift the fatty pool of a vegetable oil toward saturated moieties which improve the ignition quality of the derived biodiesel, but the oxidative stability may compromise cold flow properties [78]. As per the relation between cold flow and oxidative stability (cetane number) the design of optimal fuel for all environments can be a quite difficult task. However, information obtained from simulated mixtures of oil can provide insight for the ideal fatty acid composition for fuel. Additives can play an important role, in this case, providing adjustment of the cetane number value that could not be fitted only by the composition of the diesel-biodiesel blends. To get oil with an increased oxidative stability and cetane number combining oleic acid and stearic acid was proposed. Such fuel could be used in warmer rather than cooler climates because of the decreased cold flow associated with increased saturated fatty acid content. In addition, to combine oxidation stability (cetane number) with enhanced lubricity, it is suggested to use the mixture of oleic acid and ricin oleic acid in soybean oil [79].

Oleo chemical carbonates have recently found increasing interest in commercial applications, including as biodiesel additives due to direct synthesis in addition to their properties [80]. The physical and fuel properties (cetane number, low-temperature properties, kinematic viscosity, lubricity and surface tension) of five straight-chain C17-39 and three branched C17-33 oleo chemical carbonates to evaluate their potential as biodiesel additives. These compounds showed cetane numbers ranging from 47 to 107 depending on carbon chain length and branching. With the same number of carbons, the cetane numbers of carbonate were lower than those of fatty alkyl esters with an interruption of CH_2 chain by the carbonate moiety. The carbonates did not affect cold flow or lubricity properties significantly at concentrations up to 10,000 ppm. It was concluded that the properties of carbonates resembled those of fatty alkyl esters with similar trends resulting from compound structure and therefore were promising as cetane number additives.

Based on previous knowledge the compounds used to enhance octane number have a negative effect on the Cetane number and vice versa. Amines of various structures as potential diesel additives with the aim of stating impact of the structure of these compounds on diesel and biodiesel fuel quality, mainly on cetane number and on cold-flow properties. It was found that as the chain length increased, the amine enhanced the cetane quality; methylation seemed to increase the cetane number than ethylation [81]. The mono-dianol polyamides enhance the cetane number and have good cold-flow performance therefore, these can be used as additives for both diesel and biodiesel fuels. The tertiary methylated fatty amines have the additional advantage of being produced from renewable starting materials (fatty acids) [82]. Dimethylamino ethylene showed the best performance, but its oxidation stability must be evaluated in more detail because of its olefinic nature. DME as an additive to biodiesel and diesel-biodiesel blends due to its high cetane number. However, even small additions of DME (25%) into diesel fuel significantly reduce the viscosity of the final mixture, showing that viscosity is the limiting factor in blending DME with diesel fuel [16].

4.5 Stability Additives

Oxidation of biodiesel is one of the major factors to assess the biodiesel fuel quality. Oxidation stability is an indication of the degree of oxidation, potential reactivity with air that can determine the need of antioxidants. Normally reaction occurs in the presence of unsaturated fatty acid chains and double molecule bond, which reacts with the oxygen available in air as soon as it exposed. The chemical composition of biodiesel is more prone to oxidative degradation than diesel fuel [83].

The researchers focused special attention on the stability of biodiesel during its storage and use. Esters of unsaturated fatty acids are particularly unstable to the action of light. When exposed to air during storage, autoxidation of biodiesel may cause degradation of fuel quality by affecting properties such as kinematic viscosity, acid and peroxide values. One approach for increasing the resistance of fatty derivatives against autoxidation is to treat them with antioxidants. The influence of different synthetic and natural antioxidants on the oxidation stability of biodiesel from rapeseed oil, sunflower oil, used frying oil and beef tallowhas been experimented. The four synthetic antioxidants pyrogallol (PY), propylgallate (PG), tert-butylhydroquinone (TBHQ) and buty-lated hydroxyanisole (BHA) produced the highest enhancement of the induction period. The induction periods of methyl esters from rapeseed oil, used frying oil and tallow could be improved significantly with PY, PG and TBHQ. A satisfactory correlation was found between the improvement of oxidation stability and fatty acid composition. Different synthetic phenolic antioxidants can improve the oxidation stability of biodiesel prepared from different feed stocks. At antioxidant concentrations of 1000mg/kg, an improvement in oxidation stability could be achieved with all antioxidants tested. The efficiency of antioxidant varied as per the concentrations from 100 to 1000mg/kg depending on the different type of biodiesels [84]. The influence of antioxidants on biodiesel fuel critical parameters showed no negative impacts on viscosities, densities, carbon residues, CFPP and sulphated ash contents of different biodiesel samples. However, in terms of acid values, a noticeable increase could be observed at antioxidant levels of 1000mg/kg. At lower antioxidant concentrations, increase was much lower and acid values remained within the required limits [85].

The stability of biodiesel on the effects of storage condition, biofuel composition and antioxidants on the degradation of biofuels was studied. To further enhance stability, addition of the antioxidants was effective but in some cases, it also adversely affected the stability of biofuels [86]. The effectiveness of TBHQ, BHA, butylated hydroxyl - toluene (BHT) and PG in mixtures with soybean oil fatty acid methyl esters (SME). PG, BHT and BHA were most effective. Phase equilibrium studies were also conducted to test the physical compatibility of antioxidants in SME-diesel blends. It was recommended for BHA or TBHQ for safeguarding biodiesel from effects of autoxidation during storage. BHT is also suitable at relatively low loadings. PG showed some compatibility problems and it may not be readily solubilised in blends with larger SME ratios [87].

4.6 Metal-Based Additives

The metal-based additives may reduce diesel emissions by two ways. First, the metals either react with water to produce hydroxyl radicals, which enhance soot oxidation, or react directly with carbon atoms in the soot, thereby lowering the oxidation temperature [88]. The metal in the additives used for combustion of fuel in the engine, acts as a nucleus for soot deposition. The addition of metal-organic additive is emitted in the particulate phase as oxide, on soot particles or for minimum nano sized particles by homogeneous nucleation of the additive [89]. In case of ferrocene additives carbon particles are condensed on additives and are totally burned in the following stages of the process. Additionally, ferrocene reduces carbonaceous matter in combustion by more efficient burnout rather than by the inhibition of soot formation. Ferrocene vapour leads to particle formation early in the flame that is below the soot inception point of an unseeded flame [90]. Smoke suppressant additives reduce emissions of black smoke with the exhaust gases from diesel engines. Black smoke is formed in engine overloading and in malfunctions of fuel system. Some metal compounds can cause soot to burn, primarily barium, manganese and calcium compounds are proposed as smoke-suppressant additives [56]. The effect of barium fuel additives on carbonaceous particulate (soot) emissions is reducing carbonaceous particulate emissions by barium. Various investigators have reported 20-75% reductions in visible smoke emissions from diesel exhaust by using barium fuel additives [91].

The ferric chloride ($FeCl_3$) is a fuel borne catalyst (FBC) for waste cooking palm oil biodiesel. The ferric chloride metal based additive of 20 μmol/L in biodiesel resulted in a decreased brake specific fuel consumption of 8.6% while the brake thermal efficiency increased by 6.3% with lower nitric oxide (NO) emission and slightly higher carbon dioxide (CO_2) emission as compared to diesel. Carbon monoxide (CO), total hydrocarbon (THC) and smoke emission of FBC added biodiesel decreased by 52.6%, 26.6% and 6.9% respectively [92]. The metallic-based additives produced by synthesizing of resin acid with MnO_2 or MgO doped into diesel fuel at the rate of 8 μmol/lit and 16 μmol/lit for preparing test fuels. Both the additives improved properties of diesel fuel such as viscosity, flash point, cloud point and pour point. The fuels tested with metallic additives in a direct injection diesel engine at full load condition were obtained maximum reduction of 4.16% specific fuel consumption. Smoke opacity and CO emission decreased by 29.82% and 16.35%, whereas NO_x emission was higher and CO_2 emission remains unchanged as compared without additives [93]. It was observed that the use of additives significantly reduced the emission of particulates and carbonaceous particle [94]. Mg and Ni based additives reduced the flash point, pour point and viscosity of biodiesel fuel produced by animal fat, depending on the quantity of additive used [95].

Cerium oxide nanomaterials act as oxygen buffers causing simultaneous oxidation of hydrocarbons (HC) as well as the reduction of oxides of nitrogen. When the fuels tested on engine without changing the engine system from 0-100% load condition considerable enhancement in the brake thermal efficiency, improved brake-specific fuel consumption and decreased concentration of HC, NOx and smoke in the exhaust emitted from the diesel engine due to incorporation of aqueous cerium oxide in the test fuels [96]. The use of exhaust gas emissions can be reduced by exhaust gas catalytic converter but at the cost of lower engine performance. In the case of nano-particle additives use to improve performance of CI engine and reduce the main pollutants of that are oxides of nitrogen (NO_x) and particulate matter [97].

4.7 Depressants and Wax Dispersants

Petroleum distillate fuels containing n-paraffin waxes that tend to be separated from the oil at low temperatures. The wax generally crystallize as an interlocking on the surface, thereby trapping the remaining fuel and causing cold-flow problems such as clogging of fuel lines and filters in engine fuel systems. Several techniques have been used to minimize these problems caused by the wax deposition, and the continuous addition of polymeric inhibitors is an attractive technological alternative. The addition of copolymers such as polyacrylates, polymethacrylates, or poly (ethylene-co-vinyl acetate) (EVA) inhibits the deposition phenomenon; those copolymers are composed of a hydrocarbon chain, which provides the interaction between additives and paraffin, and a polar segment that is responsible for the wax crystal morphology modification necessary to inhibit the aggregation stage. Those copolymers are known as cold-filter plugging point (CFPP) additives or pour point depressants (PPDs). EVA copolymers present a good efficiency as diesel fuel CFPP additives [98-99].

The addition of PPDs has been proved to be efficient way to inhibit the wax deposition of diesel fuels. However, the complexity of oil is far beyond current commercial PPD products. So far, it mainly depends on syntheses of numerous compounds followed by repeating experimental measurements to improve the efficiency of PPDs. In molecular dynamic simulation the interaction between crystals plane of wax and EVA, and its derivatives with different branches based on the model of wax. The side-chain effects on adsorption energy and equilibrium adsorption conformations were studied under different kinds and numbers of branches. They concluded that side chains introduced by propylene were a benefit to the affinity between the EVA-type molecules and alkanes in the wax plane, comparing with those branches introduced by butylene. Molecular dynamic simulation calculations indicated that EVAP with one branch adjacent to the VA (vinyl acetate) group would be a better PPD additive than EVA in diesel fuels [100].

Metal solution additives used in diesel fuel as additives showed that the organic based manganese gave the greatest decrease in freezing point. These additives reduce the freezing point to 12.4°C at the rate of dosage of mol Mn/lit diesel fuel and established that the cetane number of diesel fuel without the additive was 46.22, whereas the cetane number was 48.24 for diesel fuel with the optimum amount of additive dosage. It was observed that the organic based manganese also drops the viscosity and flash point and improves the contents of the exhaust gases [101]. The performance of wax dispersant additives is especially important in countries with long winters. It was shown that traditional depressants (polyacrylates and copolymers of olefins and vinyl acetate) do not prevent separation during cold storage by reducing the solid point of the fuels. As a result, the fuel separates into two layers: an upper clear layer and a lower cloudy layer rich in waxes. Both layers are moveable, but when fuel is taken off the lower layer engine misses. Special additives such as wax dispersants or precipitators solve the problem. Their effect consists in the formation of very small wax crystals with high sedimentation stability [102].

The mechanism of additives action is that controls the sedimentation of paraffin crystals after their crystallization in diesel fuel. The chemical analysis of the crystals and detailed measurements of the sedimentation phenomenon give new insights into this complex process. Thus, the wax anti settling additives used for preventing wax crystal sedimentation which adsorbs onto surfaces of wax particles and provides them with enhanced colloidal stability. The settling rate is not related to the size of crystals or viscosity of the liquid medium, but to the ability of additives to prevent the aggregation of wax crystals [103].

CONCLUSIONS

- Biodiesel with additives is an added advantage to improve ignition and combustion performance of fuel that enhances power output.
- Properties of biodiesel can be improved with the addition of additives that helps in complete combustion, lubrication, less exhaust emissions, stable, more power output and longer life of the engine.
- Oxygenate additives can reduce PM emissions but increases NOx emissions of biodiesel with less power recovery.
- Metallic additives, emulsifier, additives of oxide, etc. seem to be useful in improvement of NOx emissions of biodiesel, but other emissions improve largely with small reduction in engine power output.
- The metal-based additives may be effective to reduce PM emissions of biodiesel due to catalyst effect and reduces CO emission but poor to improve HC and CO_2 emissions with biodiesel.
- A small quantity of alcohol (ethanol or methanol) addition into biodiesel and its blends with biodiesel have an advantage to reduce HC and CO emissions.

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