A Review on Performance of Biodiesel in Engines with and without Addition of Nanoparticles

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Abstract:

Increased energy requirement in sectors like power generation, transportation and others together with dependence on fossil fuels will face problems due to depletion of it. Due to these broad attention has been given to biodiesel production as a substitute to petro-diesel. Fatty acid methyl or ethyl esters derived from vegetable oils or animal fats are turning out to be great alternative because of its renewability, biodegradability and highly oxygenated nature properties. But using biodiesel, there are most disadvantages such as higher density, lesser heating value, high fuel consumption and high oxides of nitrogen. To avoid the above disadvantages, the fuel additives help in playing a very important role in minimizing the drawbacks of biodiesel and in maintaining international fuel standards. In this review article there is a comparative study to find out the most important variables that influence the transesterification reaction, effects of additives for biodiesel and its blends and efforts to recover the combustion and performance and to diminish the emissions. The effects of the additive nanoparticles on the individual fuel properties, the engine performance and emissions are studied, and comparisons of the performance of the fuel with and without the additive are also presented. The reviews conclude that the uses of additive to the second generation of biodiesel are the best in improving the combustion performance and emission reduction.

Keywords: Bio-diesel, Non-edible Seeds, Transesterification, performance and emission, fuel additives.

1. Introduction

Depletion of fossil fuel resources, their harmful emissions when used in engines and increased energy requirement for sectors like transportation, energy generation has resulted in a need to search for new alternative energy sources. The increased environmental pollution and stringent emission norms are considered to be the main reason for need of new energy source. To address these issues, biofuels promise a ray of hope, as they have practically no sulphur and aromatic contents and thus no emissions of SO_2 and polycyclic aromatic hydrocarbons. The term biofuel is as such referred to solid, liquid, or gaseous fuels that are produced from plant matter and residues, agricultural crops, municipal wastes and agricultural and forestry by-products. Production of biofuel from biomass is one way to reduce both the consumption of crude oil and environmental pollution. Majority of liquid biofuels is produced in the form of bioethanol (around 80%) and the rest constitutes biodiesel. Development of biofuels as a renewable energy for transportation is a critical towards achieving self-reliance of energy security. It is very necessary to develop the source of renewable energy and increase its utilization to reduce dependency on fossil fuels and environmental pollution issues. Biodiesel has become an attractive for environmental benefits such as non-toxic and eco-friendly and these are made from the renewable resources and it possesses high biodegradability and lubricating property which makes it even better fuel. Biodiesel making process is dependent on variables such as free fatty acid percentage, catalyst concentration, alcohol to oil molar ratio, reaction temperature and reaction time. A new technology, i.e. transesterification reaction has been applied to produce a renewable fuel ‘‘biodiesel’’ derived from various raw materials such as vegetable oil/plant oils both edible as well as non-edible and animal fats oils. Production of Bio-diesel from edible oil crops is not desirable as there are many concerns regarding the use of food crops as feedstock for fuel production and has created famous debates about food v/s fuel. The high price of biodiesel derived from food grade vegetable oils makes it non-viable to compete economically with fossil - based diesel. Less expensive, non-edible vegetable oil / plant oil as potential feedstock for biodiesel production is one of the key resource of the renewable bioenergy.

Biodiesel and its blends with diesel were employed as a fuel for diesel engine without any modifications in the existing engine. Because, using the biodiesel in CI engines can reduce the hydro-carbons (HC), smoke and carbon monoxide (CO) emissions. But oxides of nitrogen (NOx) will increase due to the oxygen (O_2) content is present in biodiesel causes a NOx formation. In order to overcome the problems associated with the biodiesel use of chemical substances like fuel additives derived from organic, inorganic and metals were used. A fuel additive generally improves the combustion efficiency and reduces the pollution. The relatively very small diameter of nanoparticles increases the chaotic movements and reduces the settling velocity of particles which improve the dispersion stability of nanofluids. These additives could lower the oxidation temperature as well improves cetane number of the fuel, which in turn improves the ignition characteristics. Recent advances in nanoscience and nanotechnology enables production, control and characterization of nanoscale energetic materials. Nano materials are more effective than bulk materials because of its higher surface area. Generally, addition of some metal and metal oxide in the form of nano-powder to the base fuel may enhance the properties of the fuels. This is due to the interesting properties of nanoparticles like higher specific surface area, thermal conductivity, catalytic activity and chemical properties as compared to their bulk form.

1.1 Biodiesel

Biodiesel is a very essential for vehicular fuel. Biodiesel has worthy properties as a diesel fuel, so it is capable for using in diesel engines. Biodiesel can be derived from a number of various vegetable oils and animal fat feedstock. Biodiesel is one of the current favourites to be the next generation fuel. Biodiesel is defined by ASTM as a fuel comprised of alkyl (methyl, ethyl or propyl) esters of long chain fatty acids derived from different animal fats and vegetable oils. Biodiesel is formed by the process of chemical known as transesterification and also esterification. Neat oil produced from these natural sources are chemically processed by “trans-esterification”, in which the alcohol is added to the neat oil under mild condition in presence of a base catalyst. During esterification process, the triglycerides present in the oil gets transformed into alkyl esters and glycerol. The trans-esterification process is carried out in the temperature range of around 50^{o}C to 80^{o}C with the addition of methanol or ethanol. The base catalyst commonly used are sodium hydroxide (NaOH) and potassium hydroxide (KOH).

1.1.1 Biodiesel Feedstocks

Selecting the appropriate feedstock is a vital issue to ensure low production cost of biodiesel. As much as possible the biodiesel feedstock should fulfil two requirements for production of biodiesel which are low production costs and large scale production. In general, biodiesel feedstock can be categorized into four groups: (i) edible vegetable oil: soybean, palm oil, sunflower, safflower, rapeseed, coconut and peanut; (ii) non-edible vegetable oil: jatropha, karanja, mahua, linseed, cottonseed, argemone Mexicana, neem, camelina and beauty leaf tree/polanga etc.; (iii) waste or recycled oil: cooking oil, frying oil, vegetable oil soapstocks and pomace oil; and (iv) animal fats: beef tallow, pork lard, yellow grease, chicken fat and by-products from fish oil. Among those, non-edible vegetable oils, waste or recycled oil as well as animal fats are regarded as the second generation biodiesel feedstocks. The algae have been considered as third generation biofuel and an emerging non-edible oil of growing interest because of their high oil content and rapid biomass production.

1.1.2 Biodiesel Production

Transesterification is regarded as one of the best techniques to convert oil into biodiesel, as it has the most promising solution to the high viscosity problem among other approaches due to its low cost and simplicity. Furthermore, this technique has been identified as a widely available technique for industrialized biodiesel production due to its high conversion efficiency and low cost. In transesterification process, alcohol is reacted with vegetable oil in the presence of appropriate catalyst. The technology of biodiesel production includes transesterification of oils (triglycerides) with alcohol which gives biodiesel which is chemically-known as fatty acid methyl ester (FAME) as the main product and glycerol as the by-product. The triglyceride is converted step-wise into diglyceride, monoglyceride, and finally, glycerol, during which one mole of alkyl ester is removed in each step. The main transesterification reaction variables include: methanol/oil molar ratio, catalyst concentration, reaction temperature and reaction time are optimized for high biodiesel conversion and quality. Methanol to oil ratio is varied from 3:1 to 12: 1, while catalyst concentration is varied from 0.25 % to 1.25 %. The kinematic viscosity and biodiesel yield changes with change in reaction temperature. Reaction temperature varied between 55-85ºC for different experiments. The biodiesel yield decreases with the increase in reaction temperature. The biodiesel yield was highest and kinematic viscosity was smallest under the optimum reaction temperature and the lower limit is based on room temperature. To obtain pure methyl ester, the product is washed with hot water to separate from soap formed during reaction. The biodiesel sample is to be tested to determine the fuel quality. The important fuel property parameters that are investigated include: cetane number (ASTM D613), kinematic viscosity (ASTM D445), density (ASTM D1298), calorific value (ASTM D240), flash point (ASTM D93), pour point (ASTM D97), cloud point (ASTM D2500), oxidation stability (EN 14112), acid value (ASTM D664), lubricity (ASTM D6079), carbon residue (ASTM D4530), iodine value (EN 14111) and sulphated ash content (ASTM D874).

1.2 Fuel Additives

At present for vehicular fuels, combustion of numerous chemical additives is used to improve the quality of biodiesel fuel and diesel fuel to convene up the most wanted performance level. Additives will help out the petroleum to recover its engine combustion, performance and emission environmental standards. Therefore, fuel additives in diesel, biodiesel and their blends improves the fuel characteristics The additives selection will be based upon the drawbacks of biodiesel fuel such as density, toxicity, viscosity, economic feasibility, additives solubility, auto ignition temperature, flash point, and cetane number for the fuel blending process. The fuel additives are broadly classified as refinery products, distribution system products, and automotive performance enhancement products.

Therefore, fuel Additives are being alienated in terms of their application and drawbacks are listed out.

- **Metal based additives**
- **Oxygenated additives**
- **Cetane number improver additives**

- **Antioxidant additives**
- **Ignition promoter additives**
- **Lubricant additives etc.**

1.2.1 Nano-Particles as Additives

Addition of some metal and metal oxide in the form of nano-powder to the base fuel may enhance the properties of the fuels. This is due to the interesting properties of nanoparticles like higher specific surface area, thermal conductivity, catalytic activity and chemical properties as compared to their bulk form. Moreover, nano-particles as additives in diesel as well as biodiesel as new hybrid fuel blends. The properties of nano-particles such as size, thermal conductivity and chemical properties affect the performance and emission characteristics of engine. Reduced size of the nano-particles increased specific surface, surface to volume ratio, and surface area improving catalytic reactivity and magnetic properties as compared to their bulk form. Hence metal and metal oxide nano-particles addition to biofuel will improve the performance as well as reduce the harmful gases from engine exhaust. Addition of cerium oxide nano-particles to biodiesel may also be effective as they enhanced surface area to volume ratio. Flash point of biodiesel, which is an indication of the volatility, was found to increase with the inclusion of such additives making them safer fuels. The viscosity of biodiesel was found to increase with the addition of cerium oxide nano-particles to biodiesel. The viscosity and the volatility were found to hold direct relations with the dosing level of the nano-particles.

Therefore, nano-particles can function as both catalyst and an energy carrier when used in base fuels in diesel engines. In addition, small scale of nano-particles, also facilitate stability of fuel suspensions when used with base fuels.

1.2.2 Nano particle blending:

The process of adding nanoparticles to the fuel is done with the aid of an ultrasonicator. The ultrasonicator technique is the best suited method to disperse the nanoparticles in the base fuel, as it facilitates possible agglomerate nanoparticles back to nanometer range. The required quantity of the nanoparticle for each sample was accurately measured using a precision electronic balance and was mixed with the fuel by means of a probe sonicator, passing ultrasonic waves for a time period of 30 minutes to produce a uniform suspension. The modified fuel was utilized immediately after preparation, in order to avoid any settling or for sedimentation to occur.

2. LITERATURE REVIEW

2.1 Biodiesel Productions and Its Properties

Nabeel A. Adeyemi et al. [1]. Investigated on the Biodiesel Production. Particular focus is given to technical successes of biodiesel production from nonfood oils. Transesterification via the alkali/acid-catalyst route is the preferred alternative for biodiesel production. Catalyst types and amount, oil/ alcohol ratio, and temperature have been confirmed to be the most critical factors in biodiesel production. Process type and product quality is largely depended on feedstock. **M. M. K. Bhuiya et al.** [2]. Focused on prospects, importance, feedstocks, conversion process as well as performance and emission characteristics of second generation biodiesel. Results show the transesterification method is the most suitable method among the several possible methods for biodiesel production.

Nikul K Patel et al. [3]. Studied the identification of Non-edible Seeds as Potential Feedstock for the Production and Application of Bio-diesel. Mentioned that different kind of biodiesel is produced from non-edible seeds such as jatropha, neem, karanj, kusum, jojoba etc. and there are around 78 non-edible species identified for the production of biodiesel but testing on engine is done with only few of them. **Mushtaq Ahmad et al.** [4] also obtained an optimization study on biodiesel production from castor bean, hemp, neem and pongame was done in detail with one-step alkali transesterification process along with the fuel property analysis of these oils and their blends. By using an optimum ratio of 1:6 (Oil: Methanol) at 60 ºC. Biodiesel from these sources was analyzed for qualitative and quantitative characterization by using different techniques and it is concluded that the bioenergy from these species can be feasible, cost effective, environment friendly and it satisfied the ASTM and EU standard for biodiesel production. **K.M. Shereena et al.** [5]. found that a new technology, how transesterification reaction has been applied to produce a renewable fuel ‘‘biodiesel’’ derived from various raw materials. **Jesikha. M,** [6]. discussed about the Fatty Acid Methyl Esters Characteristic and Esterification of Some Vegetable Oils for Production of Biodiesel and results that vegetable oils have a wide variety of fatty acid composition, depending on their source. Among the fatty acids, oleic acid is particularly stable to thermal oxidation and although most sunflower oils have about 20% of oleic acid, high breed varieties may reach 80% content, so this oil has been a special for the synthesis of esters used as bio-fuels and lubricants.

Kumar, K. & Sharma, M. P. [7]. Investigated on diesel engine performance and emission characteristics that fueled with the raw oils of Jatropha, moringa and palm was investigated. In this study, 20% of biodiesel of each and 80% of diesel fuel (JB_{20}, MB_{20}, and PB20) has been used in diesel engine, because 20%biodiesel blend has the fuel properties like: density, kinematic viscosity, calorific value etc. similar to diesel and can be used in diesel engine without any engine modification. **Seung Hyun Yoon et al.** [8]. Discussed how various temperatures could affect the properties of biodiesel and its blends. It was performed to investigate experimentally the effect of temperature on the specific gravity, density, and dynamic and kinematic viscosity for diesel, biodiesel, and blending fuels over the temperature range of 0–200 °C. Results in the specific gravities and the density values are measured increased proportionally with the blending ratio of biodiesel. All viscosities of blends, diesel, and biodiesel decreased with increasing fuel temperature. At a fuel temperature of 200 °C, the differences in kinematic viscosity among the test fuels decreased rapidly. At a temperature between 0 and 10 °C, wax crystals are partially distributed especially in B100.

Shubham Gupta et al. [9]. Evidently exhibited the experimental investigation of bio-diesel of the basic fuel properties like calorific value, density, kinematic viscosity, flash point, fire point etc. of Argemone Mexicana oil and its ester. Results in Alkaline Transesterification was results into 80% yield; amount of catalyst (KOH) was the more significant parameter than volume of methanol. Maximum Biodiesel yield of 90% was found with optimum parameters.

Litty Koria et al. [10]. focused on production process in Datura stramonium Seed Oil. Results showed that optimization of catalyst concentration, alcohol to oil molar ratio, reaction temperature and reaction time has been carried out to determine the maximum conversion of oil to biodiesel, in a nonedible oil source, Citrullus colocynthis seed oil. Optimization of Biodiesel 82-85 % of Datura stramonium oil was converted to biodiesel using 1.0% NaOH catalyst concentration at a molar ratio of 7:1 at a reaction temperature of 65°C and with a reaction time of 2 hours.

Parmjit Singh et al. [11]. Investigated the optimization of biodiesel from argemone oil with different reaction parameters. Biodiesel was highest by single step transesterification of argemone oil with methanol in the presence sodium metal as a catalyst. The optimum condition for production of biodiesel were 1:6 oil to methanol ratio, sodium metal catalyst concentration 1.5% w/w of oil, reaction time 2 hour, reaction temperature 75ºC, and stirring speed 650 rpm. **Gopukumar S T** [13]. Carried out for Argemone Mexicana oil for its potential use as a biodiesel. Evaluated for blended of A.mexicana oil physical and chemical properties of (B10 and B20) falls within the range of ASTM and EN standard values. A.mexicana oil blend B20 is the most potent source of biodiesel. The acid value of blends is slightly higher than that of the ASTM standard but the iodine values and the saponification values are less than that of the petro diesel however it is within the range of ASTM standard for the biodiesel.

V. N. ARIHARAN, S.T. [14] and **Dereje Dagne et al.** [16]. Showed the physical and chemical properties evaluated for the biodiesel blends falls within the range of ASTM and EN standard values. A.mexicana oil blend B20 is the most potent source of biodiesel. It is eco-friendly and protects the environment from the various hazards. Excess of oxygen content are present in and lower viscosity and density of fuel. Argemone Mexicana biodiesel blend B20 (biodiesel 20%+80% diesel by volume) has improved fuel properties for diesel engine and improved performance. **Rajeshwer Y. Rao1 et al.** [15]. Investigated on crystalline manganese carbonate for production seed oil from Argemone Mexicana. Manganese carbonate efficiently promotes the transesterification in methanol solutions and results showed that manganese carbonate as a promising alternative catalyst for the production of biodiesel. And the properties of the fuel satisfied the ASMT and EU standards.

2.2 Performance and Emission Characteristics of Biodiesel Fuels

Parmjit Singh et al. [11]. Investigated the optimization of biodiesel from argemone oil and the experiment were conducted using diesel and argemone blend with diesel at different samples under different load conditions at constant speed 1500 rpm. There was proper combustion and better atomization of fuel. The BSFC was decreased for AB20 at full load conditions even that of diesel fuel. Therefore, concluded that the argemone biodiesel blend AB20 (biodiesel 20%+80% diesel by volume) has improved performance. **Dereje Dagne et al.** [16]. Studied on Production of biodiesel from Argemone Mexicana Seed and investigated the performance in Diesel Engine. The brake torque and brake power was maximum for B20 than B0 at different speed and different gear conditions. The higher torque is registered to B0, however the percentage B20 increases the torque also increase throughout all the speed increment. The BSFC was decreased for B20 than B0 at different speed and different gear condition. This is due to excess of oxygen content are present in biodiesel and lower viscosity and density of fuel. **Nikhil Sutarand M.H. Attal.** [17]. The study looks for effect of compression ratio, fuel injection pressure and load. On an average the BTE increased by 13.33 % as compression ratio increased from 16 to 18 whereas BSFC reduced by around 14.2%. Thus higher compression ratio gives better engine performance. And CO_2 emission increased by 25.73%, NOx emission increased by 42.72%, the HC emission decreased by 50.94% and CO emission decreased by 45% as compression ratio increased from 16 to18. The smoke opacity reduced by 24.58 % averagely. Therefore, higher injection pressure is beneficial for engine performance. The NOx emission is increased by 21.83% and smoke opacity decreased by 34.56% when the diesel is replaced by B20 (20% biodiesel and 80% diesel) blend of argemone Mexicana biodiesel.

Kumar, K. & Sharma, M. P. [7]. Have studied the performance and emission characteristics of Jatropha, moringa and palm was investigated. In this study, 20% of biodiesel of each and 80% of diesel fuel (JB_{20}, MB_{20}, and PB20) has been used PB_{20}, MB_{20}, and JB_{20} reduced the brake power as 8.11%, 10.81%, and 1351% respectively and the BSFC increased for MB20, JB20, and PB20 by 8.60%, 8.14% and 6.98% respectively compared to diesel fuel at engine speed of 3500rpm. From all the biodiesel blends, palm (PB_{20}) shows higher performance than other biodiesel blends. **Mandeep Singh et al.** [18]. Experimental investigations on performance and emission characteristics of variable speed multi-cylinder compression ignition engine using Diesel/Argemone biodiesel blends of different samples at varying loads (0, 25, 50 and 75%) and speeds (2500–4000 r/min). It was observed that diesel/AOME blends show better results at higher loads as compared to lower load condition. Moreover, biodiesel blends show poor performance at lower loads and high speed conditions. All the tested blends AB10, AB20, AB30 and AB40 show better performance and emission characteristics than conventional diesel. AB30 shows maximum ITE and minimum ISFC and HC, CO and smoke are also minimum. However, AB30 blend shows higher emissions of CO2 and NOx as compared to diesel and other tested blends. Reduction in NOx and CO2 emissions were observed for AB40 fuel when compared with AB30. AB 40 shows improvement in performance and emission characteristics as compared to diesel but deterioration in performance characteristics when compared with AB30.

2.3 Effect of Nanoparticle Additive on Fuel's Physio-chemical Properties

Demirba et al. [23] and **Ajin C. Sajeevan and V. Sajith** [26]. Showed the importance of adding nano metal additives in biodiesel and its effect in improving the physio-chemical properties. The experimental investigations were carried out by varying the dosing levels of CeO_2 nanoparticles in the fuel (from 5 to 35 ppm). It shows that the flash point and fire point increase with the dosing level of cerium oxide nanoparticles in diesel. Even though kinematic viscosity increases with the catalytic nanoparticle addition in fuel, it was found to be decreasing with the addition of surfactant DDSA. **C. Syed Aalam et al.** [28]. Showed the enhancement of fuel properties with the addition of alumina nanoparticles with the Mahua biodiesel blend. ANP-blended biodiesel (MME20+ANP50 and MME20+ ANP100) showed an improvement in the calorific value and a reduction in the flash point compared to MME20. The peak pressure increases with the addition of ANP. The addition of ANP reduces the ignition delay period. The heat release rate also increases with the addition of ANP. **A.Selvaganapthy et al.,** [29]. Studied the zinc oxide nano additive added to diesel shows the ignition delay reduced, peak pressure and heat release rate increased due the presence of particles. **Shaafi and Velraj** [30]. Used alumina, ethanol and isopropanol as fuel additive for B20-Soybean biodiesel. They mixed 100 mg/l of AONP in D80SBD15E4S1 blend, and noticed a drastic decrease in viscosity and calorific value along with an increase in Cetane number.

Mehta et al., [31]. Investigated formulated by sonicating nano particles of aluminum (Al) having 30-60 nm, iron (Fe) 5-150 nm and boron (Bo) 80-100 nm in size in base diesel with 0.5wt% and 0.1wt% Span80 as a surfactant for stable suspension. The nano fuels reduced ignition delay, longer flame sustainable and agglomerate ignition by droplet combustion mechanism test. Peak cylinder pressures decreased at higher load conditions and were registered as 55, 59, 60 and 62 bars for Al, Bo, Fe and diesel respectively**. Prabhu Arockiasamy et al.** [32]. Mentioned that the addition of 30 ppm Al_2O_3 and CeO_2 with Jatropha methyl ester improved the kinematic viscosity, density and calorific value as 4.25 Cst, 875 kg/m3 and 38.9 MJ/kg for JBD30A blend. JBD30C blend was found to have similar fuel property values as 4.30 Cst, 876 kg/m3 and 38.7 MJ/kg respectively. The addition of alumina with Jatropha biodiesel improved the fuel properties. **Karthikeyan et al.** [33]. Studied the effects of addition of zinc oxide nano particles in palm oil biodiesel. It was observed that the ZnO nano particles additives blends showed slightly improvement in calorific value and kinematic viscosity. No significant difference were observed in flash point, pour point, cetane number and sulphated ash due to the addition ZnO.

V. Sajith et al. [37]. Experimental Investigations on the Effects of Cerium Oxide Nanoparticle Fuel Additives on Biodiesel. Results show, the flash point, viscosity of bio diesel was found to increase with the dosing level of the nanoparticles, within the range analyzed (20–80 ppm). The cold temperature properties of bio diesel do not show significant variation and an improvement in the efficiency of the engine. **Abbas Alli Taghipoor Bafghi et al**. [38]. Effects of Cerium Oxide nanoparticle addition in Diesel and Diesel-Biodiesel blends. The tests revealed that cerium oxide nanoparticles can be used as additive in diesel and diesel-biodiesel blends to improve complete combustion of the fuel significantly. The major observations, an increasing trend for the flash point with the dosing level. Viscosity of the fuels decrease with an increase for all dosing levels.

H. K. Imdadul et al. [41]. A comprehensive review on the assessment of fuel additive effects on combustion behavior in CI engine fuelled with diesel biodiesel blends. Addition of additives in diesel, biodiesel and their blends has a great effect on fuel properties such as viscosity, flash point, fire point, pour point, calorific value etc. which inturns influences the combustion parameters. Metal-based additives such as FeCl3, CON, CNT, alumina nanoparticles showed an increased in HRR, CGP and PP with earlier start of combustion and decreased ignition delay.

2.4 Discussion on change in physio-chemical properties upon addition of nano metal additives

Addition of by varying the dosing levels of CeO_2 nanoparticles in the fuel the viscosity, flash point, kinematic viscosity and fire point increase with the dosing level of cerium oxide nanoparticles whereas, alumina (Al) nanoparticles shows reduction in the flash point.[26, 28, 30, 37 and 38]. The addition of alumina with Jatropha biodiesel improved the fuel properties like the kinematic viscosity, density and calorific value but for CeO_2 was found to have similar fuel property values to base fuel [32]. The ZnO nano particles additives blends showed slightly improvement in calorific value and kinematic viscosity and ignition delay reduced, peak pressure and heat release rate increased. But no significant differences were observed in flash point, pour point, cetane number and sulphated ash due to the addition of ZnO [29, 33]. Metal-based additives such as FeCl3, CON, CNT, alumina nanoparticles showed an increased in HRR, CGP and PP with earlier start of combustion and decreased ignition delay. The use of fuel-borne catalyst has the advantage of increase in the fuel efficiency and reducing harmful greenhouse gas emissions.

Addition of some metal and metal oxide in the form of nanopowder to the base fuel enhance the properties of the fuels. This is due to the interesting properties of nanoparticles like higher specific surface area, thermal conductivity, catalytic activity and chemical properties as compared to their bulk form. Therefore, to solve the problems (drawback) of the biodiesel fuels it is possible to use the appropriate nanoparticle metal or metal oxide additives further for enhancing the performance and emissions.

2.5 Effect of Nanoparticle Additive on performance and emissions

Vijay Kumar et al. [24]. Have studied on the impacts on combustion, performance and emissions of biodiesel by using additives in direct injection diesel engine. The additives are most important for biodiesel, but there are more investigations needed on non-edible oils and to enhance better evaluation. The additives must be utilized more for 2nd generation of biodiesel such as rapeseed, Pongamia, jatropha, neem, mahua, castor, linseed, and sterculia foetida. Therefore, the additives selection will be based upon the drawbacks of biodiesel fuel such as density, toxicity, viscosity, economic feasibility, additives solubility, auto ignition temperature, flash point, and cetane number for the fuel blending process.

P.Jayanthi1 et al. [19]. Have studied on the effects of copper oxide added to for Linseed oil based biodiesel on performance and emission characteristics of a direct injection diesel engine operated at a constant speed of 1500 rpm at different operating conditions. Results show that maximum increase in brake thermal efficiency was found to be B20+ 80 PPM CuO and also reduces specific fuel consumption at full load conditions. The copper oxide additive is effective in control of hydrocarbon (HC), carbon monoxide (CO), smoke and oxides of nitrogen (NOx) at full load conditions. **Prabu** [20]. Investigated on three types of test fuels are prepared, with two different additives that is Alumina and Cerium Oxide, the prepared samples are denoted as B20 (containing 20% biodiesel and 80% diesel in volume percentage), B100A30C30 (containing 100% biodiesel in volume percentage, 30 ppm Alumina, and 30 ppm Cerium oxide), and B20A30C30 (containing 20% biodiesel and 80% diesel in volume percentage, 30 ppm Alumina, and 30 ppm Cerium oxide). Results showed that at the maximum of 12% improvement in BTE is observed for B20A30C30 test fuels, followed by 9% improvement in BTE for B100A30C30test fuel, compared with B100. The NO emission drastically reduced for the B20A30C30 test fuel with percentage reduction of 30%, when compared with B100 due to the combined effect of Alumina and Cerium oxide nanoparticles. At the maximum of 60% reduction of CO, 44% reduction of UBHC and 38% reduction of smoke opacity are observed for B20A30C30 test fuel due to the improved Oxidation–Reduction process by addition of nanoparticles. Among the nanoparticles dispersed test fuels B20A30C30 shows significant improved of performance and emission characteristics of the engine.

Mojtaba Saei Moghaddam. [21]. Investigated on engine fueled with Diesel nitrogenated additives Nitro-Methane (NM) and Nitro-Ethane (NE). The addition of nitrogenated additives to the standard diesel fuel caused brake thermal efficiency (BTE) increased. Overall, NE has been found to be promising fuel additives in compare with another additive, capable of providing high thermal efficiency, low soot levels and decreased viscosity but have high level of NOx at at the maximum torque speed (1500rpm). Nitrogenated additives increased brake thermal efficiency (BTE), in all modes, the average smoke reduction rates of NM- Diesel and NE-Diesel were 16.2% and 35.7% of that of sole Diesel respectively.

Shiva Kumar et al. [22]. Studied on pongamia biodiesel blends of B20 with ferrofluid as the additive with various volumetric proportions were used as fuel. The results are BSFC of a biodiesel -diesel blend showed higher value compared to neat diesel due to its lower calorific value and higher viscosity. The addition of ferrofluid improved the performance of B20 with giving the maximum BTE and lesser BSFC. CO and HC emission were found to be reduced by 35.8% of CO emission and HC emission was reduced by 22.9% at full load condition. The NOx emission is found to be reduced for fuel blend with additive. The blend with 1% volumetric additive showed the maximum reduction in NOx emission and maximum reduction in smoke emission. **D. Ganesh and G. Gowrishankar.** [25]. Studied the effect of Nanofuel additives [Magnalium (Al-Mg) and cobalt oxide (Co_3O_4)] on the performance and emission characteristics of Jatropha biodiesel (B100) in a single cylinder, air cooled, direct injection diesel engine. Results is a significant improvement in efficiency compare to neat biodiesel operation without additive. Nearly 1% improvement in thermal efficiency for magnalium additive compare to B100 without additive. Cobalt oxide showing 75% reduction in HC at 75% load and with magnalium, there was a reduction of HC emission around 70% at 50% load. There is about, 47% reduction in NOx was observed with cobalt oxide Nano-fuel additive. Reduction in CO emission was observed with cobalt oxide and magnalium Nano-fuel additive. Cobalt oxide showing 50% reduction at 75% load, because cobalt oxide acts as an oxygen buffer and donates surface lattice oxygen.

Ajin C. Sajeevan and V. Sajith [26]. The experimental investigations were carried out by varying the dosing levels of CeO_2 nanoparticles in the fuel (from 5 to 35 ppm). The results of the load test on the diesel show that the efficiency is increased up to 5% and a reduction of HC and NOx emissions by 45% and 30%, respectively, especially at higher load and the reduction in the emissions is proportional to the dosing level of nanoparticles in the diesel and optimum dosing level of 35ppm of catalytic nanoparticles was observed. **R. Sathiyamoorthi et al.** [27]. Studied the performance, emission and combustion characteristics using Neem oil biodiesel with nano additive CeO_2 . Shows brake thermal efficiency for nano particles blended BN20 is higher than that of BN20 and diesel fuels and the harmful gases like, CO, HC, smoke and NOx emissions reduce significantly due to the addition of nano additive in the BN20 fuel blend. The cerium oxide additive influences the better combustion process which yields the peak pressure and heat release rate than BN20 and diesel fuel blends.

C. Syed Aalam et al. [28]. Effects of nano metal oxide blended Mahua biodiesel. In this investigation, aluminium oxide nanoparticles were added in different proportions (50 and 100 ppm) to a biodiesel blend (MME20) to investigate the performance, emission and combustion of the CRDI system assisted diesel engine. With the addition of aluminium oxide nanoparticles, there is a considerable reduction in fuel consumption compared to biodiesel operation. A minor increment in BTE was observed and reduced HC and CO emissions up to 26.04% and 48% compared with a biodiesel blend (MME20). **K. Krishna et al.** [35]. Investigated the effects of Alumina Nano Metal Oxide Blended Palm Stearin Methyl Ester Bio-Diesel The test were performed at constant speed of 1500 rpm using different Nano Biodiesel fuel blends (psme+50 ppm, psme+150 ppm, and psme+200 ppm). Results showed that the break thermal efficiency was almost same for diesel and palm stearin methyl ester blended with alumina (50ppm), the carbon monoxide (co) emissions were decreased by 39.21% blended with 50ppm compared to diesel. The NO_X emissions were decreased by 9.70% for 50ppm alumina nano particle blended with palm stearin methyl ester compared to diesel and 50ppm alumina can be used as additive with biodiesel which showed reduction in emissions as well as compatible performance characteristics with diesel.

Shaffi and Velraj [30]. Analyzed the influence of nanoparticle additives with diesel-soybean biodiesel blend in the diesel engine. Alumina nanoparticles along with ethanol and isopropanol (surfactant) were mixed with diesel-biodiesel blend. The amount of NOx was same upto 50% load for diesel and nano blended fuel and beyond that it increased than neat diesel. UBHC was very high by 25% than neat diesel and B20, and it was increasing uniformly as the load was increased. **Mehta et al.,** [31]. Investigated the burning characteristics, engine performance and emission formulated by sonicating nano particles of aluminum (Al) having 30-60 nm, iron (Fe) 5-150 nm and boron (Bo) 80-100 nm in size in base diesel with 0.5wt% and 0.1wt% Span80 as a surfactant for stable suspension. Specific fuel consumption was reduced by 7% with Al in comparison to diesel. Exhaust gas temperature of Al, Fe and Bo rose by 9%, 7% and 5% respectively, resulting into increase in brake thermal efficiencies by 9%, 4% and 2% as compared to diesel at higher loads. A wet whatman filter paper was adopted to collect the soot particles and increase in weight by 12%, 9% and 8% was observed for Fe, Bo and Al nano fuel respectively as compared to diesel. At higher loads, the emission study showed a decline of 25-40% in CO (vol. %), along with a drop of 8% and 4% in hydrocarbon emissions for Al and Fe nano fuels respectively. Due to elevated temperatures a hike of 5% and 3% was observed in NOx emissions with Al and Fe.

Prabu Arockiasamy et al. [32]. discussed the combustion and emission characteristics of Jatropha biodiesel with addition of alumina and CeO2 nanoparticles as additives. Nano particles were added to the biodiesel using ultrasonicator. Both blends were stable without any phase separation upto 48 hrs. BTE increased upto 5% for both the samples. JBD30A showed 9% reduction in NOx, 33% reduction in UBHC, 20% reduction in CO and 17% reduction in smoke opacity than neat biodiesel. JBD30C showed 7% reduction in NOx, 28% reduction in UBHC, 20% reduction in CO and 20% reduction in smoke opacity than neat biodiesel. **Karthikeyan et al.** [33]. Studied the effects of addition of zinc oxide nano particles in palm oil biodiesel and the results indicate that there was increase in BTE, NOx, EGT, found that the maximum cylinder pressure with ZnO nano particle additive and decrease in emissions of CO, HC and smoke. **C.Srinidhi, Dr. A Madhusudhan.** [34]. Investigation Fuelled with Nickel Oxide Nano Fuel-methyl Ester. It is observed that the rise in brake thermal efficiency due to nano particles was on average of 6.2% with respect to original base blends (i.e. B10, B20 and B30). The rate of specific fuel consumption was lowest for B20 blend of Diesel-palm oil methyl ester and NiO nanoparticle dosing level of 40ppm. The usage of nanoparticle depreciated the brake specific energy consumption by 5.119% and B20 blend with Nickel Oxide nanofuels with dosing level of 40ppm proved a better alternative to conventional fuel for diesel engine.

Rolvin D'Silva et al. [36]. Investigated the Performance and Emission Characteristics of pongamia pinnata methyl ester with Titanium Dioxide and Calcium Carbonate Nano additives. It is observed that the fuel sample with titanium dioxide nanoparticles shows better result. There is 2.05% increase in brake thermal efficiency and 5.7% reduction in BSFC at most of the loads. Among emissions, the unburnt hydrocarbons and smoke are found to be less in case of fuel sample with TiO2 nanoparticles. NOx emissions are slightly higher at higher loads when TiO2 nanoparticles are used. Hence titanium dioxide nanoparticles with concentration of 100ppm in the B20 sample shows better performance and emission characteristics.

V. Sajith et al. [37] and **Abbas Alli Taghipoor Bafghi et al**. [38]. Analyze the Performance Characteristics of a CI Engine with Cerium Oxide nanoparticle fuel additives on Biodiesel. Emission levels of hydrocarbon and NOx are appreciably reduced with the addition of cerium oxide nanoparticles. promotes the oxidation of hydrocarbon and reduction of nitrogen oxide, thus acting as an effective catalyst, when added in the nanoparticle form.

Arul et al. [39]. Examined the performance and emission characteristics of a single cylinder four stroke DI diesel engine fuelled with ceria nanoparticle added diesel. The results showed an improvement in BSFC and BTE of diesel-biodiesel-ethanol blend with the addition of ceria nanoparticles. **Joshua marcus paul, Gowdham** [40]. Studied the emission characteristics of Cerium Oxide Nanoparticle Blended Emulsified Biodiesel. It is concluded that the use of biodiesel in conjunction with petroleum diesel improves the fuel properties and leads to lower HC and CO emissions. This is due to the high surface to volume ratio of cerium oxide leading to better mixing of air and fuel however; the NOx emission is slightly increased.

2.5.1 Discussion on performance parameters

The additives are most important for diesel/biodiesel fuels to enhance the performance and reduce the emissions, but there must be the additives selection based upon the drawbacks of biodiesel fuel such as density, toxicity, viscosity, economic feasibility, additives solubility, auto ignition temperature, flash point, and cetane number for the fuel blending process.

Addition of nanoparticle additives providing high brake thermal efficiency when added with Nitrogenated (NE), CuO, CeO_2 and Al [19, 20 and 21]. The addition of Magnalium (Al-Mg) and cobalt oxide (Co_3O_4) and ferrofluid improved the performance by giving the maximum BTE and lesser BSFC [22 and 25]. The addition of CeO2 increased the BTE and reduced in BSFC As the dosing level of cerium oxide increases beyond 35 ppm a slight decrease in the efficiency was observed, especially at higher loads, which points to the optimum level of dosing of catalytic nanoparticles in diesel. [26 and 27]. With the addition of aluminium oxide nanoparticles, Mahua biodiesel there is a considerable reduction in fuel consumption and A minor increment in BTE was observed but the break thermal efficiency was almost same for diesel and palm stearin methyl ester blended with alumina (50ppm) [28 and 35]. Al, Fe and Bo in base diesel increased in brake thermal efficiencies by 9%, 4% and 2% and reduced BSFC [31]. Addition of alumina and CeO2 nanoparticles the BTE increased upto 5% for both [32]. zinc oxide nano particles in palm oil biodiesel increase in BTE and maximum cylinder pressure [34]. Titanium Dioxide and Calcium Carbonate Nano additives with pongamia pinnata methyl ester increase in brake thermal efficiency and reduction in BSFC at most of the loads [36]. Adding the nanoparticles with fuels will help in improving the fuel properties and thereby, improves the performance of CI engine.

2.5.2 Discussion on emission parameters

CuO added to for Linseed oil based biodiesel effective in control of hydrocarbon (HC), carbon monoxide (CO), smoke and oxides of nitrogen (NOx) at full load conditions [19]. B20 dispersed with two different additives that are Alumina and Cerium Oxide, the NO emission drastically reduced for the B20A30C30 and reduction for CO, UBHC and smoke opacity are observed for B20A30C30 test fuel [20]. Nitro-Methane (NM) and Nitro-Ethane (NE) low soot levels and decreased viscosity but have high level of NOx. Ferro fluid added with pongamia biodiesel blends of B20 increased CO and HC emissions whereas; it reduced NOx emission and smokes [22]. Magnalium (Al-Mg) and cobalt oxide (Co_3O_4) added to Jatropha biodiesel (B100) reduced all emissions [25]. CeO2 in diesel biodiesel blends CO, HC, smoke, in UBHC and NOx emissions reduce significantly due to the addition of nano additive in fuel blend especially at higher load and the reduction in the emissions is proportional to the dosing level of nanoparticles in the diesel and optimum dosing level of 35ppm of catalytic nanoparticles was observed [26, 27 and 32]. The cerium oxide nanoparticles present in the fuel promote longer and more complete combustion as compared to the base fuel, as cerium oxide acts as an oxygen buffer, releasing and storing oxygen depending upon the partial pressure of oxygen. Al_2O_3 with Mahua and Palm Stearin Methyl Ester Bio-Diesel reduced HC, CO and NOx emissions [28 and 35]. NOx was same upto 50% load for diesel and nano blended fuel and beyond that it increased than neat diesel with the addition of Al in neat biodiesel whereas, UBHC was very high [30]. Al, Fe and Bo a decline in CO and HC whereas due to elevated temperatures a hike in NOx emissions with Al and Fe [31]. ZnO and TiO2 increase in emission of NOx and decrease in emissions of CO, HC and smoke.

Generally, addition of nano particle additive, dosing levels and well dispersing of the added additive with biodiesel blend fuels can promote the physical and chemical properties of the fuels and that could leads to the enhancement of the performance and reduction in emissions of the fuels.

3. Conclusion

Production of biodiesel is very essential for reducing dependency on petrodiesel fuel and for reducing the drawback of using these fuels for those countries which are totally importing fuels from other country by partially substituting because biodiesel can be used instead of diesel fuels. However, there is a major drawback in the use of biodiesel as low heating value and NO_X tends to be higher. On the other hand, its relatively poor low-temperature flow properties are a characteristic of biodiesel which limits its application. Here, fuel additives become indispensable tools not only to decrease these drawbacks but also to produce specified products that meet the specification. A nano particle additive is playing a magnificent task in increasing the performance of the diesel engine, improving the combustion and reducing the emissions. A metal based additive will minimize the viscosity, pour point and increase the flash point properties of biodiesel fuel. The BSFC decreases significantly due to their catalyst effect by adding the metal based additives. The performance enhancement cannot be achieved with every amount of nanoparticle addition. Therefore, selecting optimal range (dosing levels) of nanoparticle addition is a key to get good results in the enhancement of performance and reduced emission in a CI engine. From the above discussion all different types of additives show that the utilization of additive on biodiesel and diesel fuels is having very good encouraged results found from the articles by researchers, but the selection of additive should be valid based upon the properties (drawbacks) of diesel and biodiesel in diesel engine and for biodiesel and its blends depends on the types of feedstocks.

Altogether, the performance, combustion and emission characteristics of a DI diesel engine are improved by incorporation of nanoparticles as additive in biodiesel diesel blend without any engine modification.

From this literature review, it can be concluded that the additives are most important for biodiesel, but there are more investigations needed on non-edible oils and to enhance better evaluation. Because, researchers have done very few investigations on 2nd generation by using additives. The additives must be utilized more for 2nd generation of biodiesel fuels.

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