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# $NO_x$ EMISSION REDUCTION FROM DIESEL ENGINE USING VARIOUS ANTIOXIDANT ADDITIVES - A REVIEW

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**Abstract**

In the conventional CI engine diesel is used as a fuel which provides better power, efficiency and brake specific fuel consumption. But it increases the $CO_2$, CO, HC, $SO_x$ and $NO_x$ emission which affect the environment and human health. It causes global warming and greenhouse effect and sometimes acid rain too. Also, diesel fuel is non-renewable energy resource and increase our dependency for importing fuel on other countries. Scarcity of conventional petroleum fuels has promoted research in alternative fuels for internal combustion engines. Worldwide energy demand has been growing steadily during the past five decades and most experts believe this trend will continue to rise. The conventional petroleum fuels for Internal Combustion engines will be available for

few years only, due to the tremendous increase in population.
This study presents a detailed analysis of the effect of antioxidant on performance and emission characteristics of diesel engine fuelled with alternate fuels. It is observed that using alternate fuels in diesel engine emits lower CO, HC and emits higher NOx. Higher level of NOx emission can be reduced by adding various antioxidants in alternate fuels and its blend.

***Key Words*:**Antioxidants, engine emissions, fuel consumption..

# 1 INTRODUCTION

In developing countries like India, transportation is vital for everyday activities and in the growth of economic condition. In India, the consumption of petroleumderived fuel is about 30 million tons in the year 2017. During the lastsix decades, crude oil consumption rate in India have increased 16times because of faster growth of vehicle population, industrial growth and agricultural development. Due to increasing usage of petroleumderived fuels, the cost of the crude oil is increasing with the demand.The biodiesel is produced from different sources and it may eitherfrom conventional or non-conventional sources. Some biodiesel blendscan be directly used in engines without any modification, and some requires slight modifications like piston-cylinder coating, injection advance etc., to obtain the same performance to that of fossil fuel. Further, in Internal Combustion (IC) engines there is an increase in the exhaust emission such as carbon monoxide (CO), hydrocarbon (HC), $NO_x$, smoke etc. which cause damage to the environment and to the living medium present in the atmosphere. In order to meet out the present scenario, biodiesel usage will substitute the fossil fuel moderately [1].

### *A. Biodiesel production*

The transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol [2][3]. Almost all the biodiesel is produced in a similar chemical process using base catalyzed transesterification as it is the most economical process, requiring only low temperatures and pressures while producing a 98% conversion yield[2][3].

During the transesterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide [2][3]. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel, and crude glycerol [2][3]. In most of the production process, methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalyzed by either Potassium or sodium hydroxide. Potassium hydroxide has been found more suitable for the ethyl ester biodiesel production, but either base can be used for methyl ester production [2][3].

The figures below show the chemical process for methyl ester biodiesel. The reaction between the fat or oil and the alcohol is a reversible reaction, so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion [2][3].

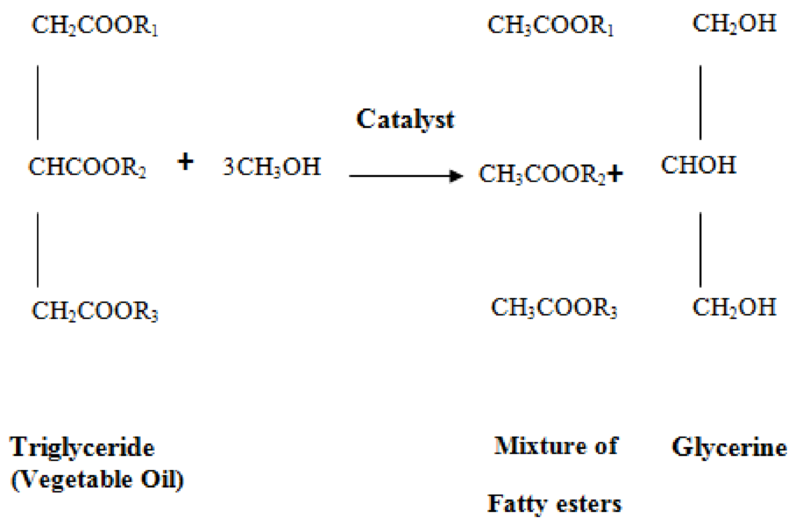


Figure 1. Transesterification process

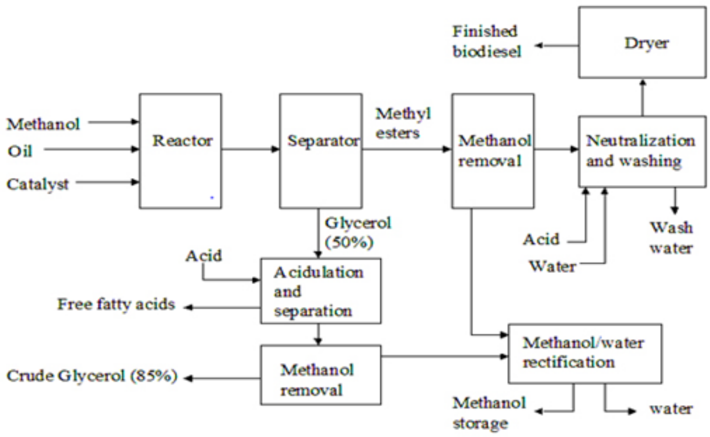


Figure 2. Process flow chart of biodiesel production

***B. Sources of biodiesel***

Typical raw materials of biodiesel are rapeseed oil, canola oil, soybean like oil, sunflower oil and palm oil. Beef and sheep tallow and poultry oil from animal sources and cooking oil are also sources of raw materials. There are various other biodiesel sources: Almond, Andiroba (Carapaguianensis), Babassu (Orbignia sp.), Barley, Camelina (Camelina sativa), Coconut, Copra, Cumaru (Dipteryxodorata), Cynaracardunculus, Fish oil, Groundnut, Jatrophacurcas, Karanja (Pongamiaglabra), Laurel, Lesquerellafendleri, Madhucaindica, Microalgae (Chlorella vulgaris), Oat, Piqui (Caryocar sp.), Poppy seed, Rice, Rubber seed, Sesame, Sorghum, Tobacco seed, and Wheat. Various oils have been in use in different countries as raw materials for biodiesel production owing to its availability. Soybean oil is commonly used in United States and rapeseed oil is used in many European countries for biodiesel production, whereas, coconut oil and palm oils are used in Malaysiaand Indonesia for biodiesel production. In India and southeast Asia, the Jatropha tree (Jatrophacursas), Karanja (Pongamiapinnata), and Mahua (M. indica) is used as a significant fuel source [1][4].

## 2 ANTIOXIDANT ADDITIVES

There are five antioxidant additives available for reducing the NOx emission in diesel engines using the Jatropha biodiesel which are, P-Phenylene Di Amine (PPDA), ButylatedHydroxy Toluene (BHT), ButylatedHydroxyanisole (BHA), Tetra-Butyl hydroquinone (TBHQ), Ethylene Di Amine (EDA) etc.

***A. P-Phenylene Di Amine additive***

P-Phenylene Di Amine (PPPD) is an organic compound having the C6H4 (NH2)2 formula. PPPD derivative of aniline is a gray solid, but samples can blacken due to the oxidation of air. PPPD is used as an element of engineering polymers and mixtures as well as an additive for reducing the NOx emission.

***B. Butylatedhydroxytoluene additive***

Butylatedhydroxytoluene (BHT) known as dibutylhydroxytoluene, is a lipophilic organic composite, and possess the antioxidant properties because it is a derivative of phenol [5]. BHT is widely used for reduction the fuel oxidation, oil and other resources where free extremists must be controlled.

***C. Butylatedhydroxyanisole additive***

Butylatedhydroxyanisole (BHA) is a mixture of two isomeric organic compounds i.e. 2-tetra-butyl-4-hydroxyanisole and 3-tetra-butyl-4-hydroxyanisole. BHA prepared from 4-methoxyphenol and isobutylene. The main use of BHA is as an antioxidant and protective in food packaging, animal feed and petroleum products. BHA usually used in medicines.

***D. Tert-Butylhydroquinone additive***

Tert-Butylhydroquinone (TBHQ) is an organic compound which is a type of phenol. TBHQ is derived from hydroquinone, replaced with a tetra-butyl group. TBHQ is used as acorrosion resistor in biodiesel fuel. TBHQ minimize the evaporation rate and increase the stability of biodiesel fuels.

***E. Ethylene Di Amine additive***

Ethylene Di Amine (EDA) is the organic compound having the

C2H2 (NH2)2 formula. EDA is a colorless liquid with an ammonia-like odour is a powerfully basic amine. EDA eagerly reacts with moisture in moist air to produce a corrosive, poisonous and frustrating mist, to whicheven small revelations can cause serious injury to health.

# 3 EFFECT OF ANTIOXIDANT

It has been observed that biodiesel have poor oxidation stability [12]. Oxidation can alter the physical and chemical properties of fuel e.g., it can cause acidity and increasing viscosity due to formation of the insoluble gums that can plug fuel filters [12]. The use of antioxidant additives can help slow the degradation process and improve fuel stability up to a point [12]. By using the antioxidant it is possible to store biodiesel for longer time. Also, it has been observed that the addition of antioxidant can reduce the higher level of NOx emission caused by biodiesel. Synthetic antioxidants are more effective compared to natural antioxidants (vitamin E, -tocopherol and -carotene). Synthetic phenolic antioxidants namely BHA (Butylated hydroxyanisole), BHT (Butylated hydroxytoluene) and TBHQ (Tetra-Butyl hydroquinone) gives better oxidation stability and reduce NOx emission in biodiesel [12].

***A. Reasons for adding the additives***

The additives used for diesel engine are discussed and few reasons are listed out below [13].

- Enhanced the nagging properties and immovability of the fuel
- Shrinking the harmful emission from fuel combustion
- Developing the combustion and performance properties of the fuel
- Here to afford engine protection and cleanliness
- Saving the fuel from optimized engine economy and performance

- Protecting the petroleum tank, pipeline and other massively expensive corrosion

***Oxidation stability***

The oxidation of fatty acid chain is a complex process proceeded bya variety of mechanisms. Oxidation of biodiesel is due to the unsaturation in fatty acid chain and presence of double bonds in the molecule which offers high level of reactivity with $O_2$, especially, when it is placed in contact with air/water. The primary oxidation products of double bonds are unstable allylic hydro peroxides which are unstable and easily form a variety of secondary oxidation products. The oxidation of fatty acid chain is a complex process proceeded by a variety of mechanisms. Auto oxidation of fatty acid methyl ester is a free radical chain reaction and the chain reaction proceeds by three steps initiation, propagation and termination.

RH +I• R• + IH........... (1)

In the initiation step Eq. (1) initiator radicals (I•) react with thefatty acid methyl ester substrate (RH) and abstracts a hydrogen from a carbon atom of the fatty acid chain, to form a new fatty acid radical R• (carbon free radical). The initiator radical is formed by differentmechanism. Eq. (2) Thermal dissociation of hydroperoxides (ROOH) present as impurities at the elevated temperature. During storage the metals (M) present in the fuel as contamination will initiate the decomposition of fatty acid ester by catalyzing the reaction and it is given Eq. (3)

ROOH RO• + OH• ..........(2)
ROO + M2+ RO• + OH• + M3+ ..........(3)

Sometimes oxidation also initiated by light which is called photo oxidation of fatty acid esters [6]. In the propagation step the carbon free radical will react with the diatomic oxygen and forms peroxy radical at a higher rate and will not allow any alternative reaction. Theperoxy radical is reactive and quickly abstract hydrogen from another carbon radical and form hydroperoxide. The newly formed carbon free radical will react further with the diatomic oxygen and propagates the chain reaction. This addition of peroxy radical with oxygen will continues at a faster rate since it is a self-sustaining chain reaction.

R•+O2 ROO•................ (4)
ROO•+ RH ROOH + R•...........(5)

Termination of the chain reaction will occur only if the two freeradicals reacts to form a stable product as shown in the Eqn. (6) and(7).

R• + R• R-R (stable product).........(6)
ROO•+ ROO• Stable products ..........(7)

## 4 EXPERIMENTAL PROCEDURE

To carry out tests using biodiesel blends, the engine was run with diesel until a steady operating condition was achieved. Then the fuel was changed to biodiesel blend. After consumption of sufficient blend fuel, the data acquisition was started to ensure the removal of residual diesel in the fuel line. After each test, the engine was again run with diesel to drain all of the blend out of the fuel line. This procedure was followed for all blends. The test fuels were fossil diesel (B0), PME (B100), and 20% PME in diesel (B20). To determine the effect of antioxidant, 1000ppm of BHA and BHT were added to B20 (B20 + BHA and B20 + BHT). Test fuels were blended using a homogenizer device at a speed of 3000 rpm for 10 minutes. The engine was operated between 1000 and 4000 rpm with a step of 500 rpm at 100% load condition. The performance and emission measurements were triplicated. The results of each test were highly repeatable within that test series.

# 5 PERFORMANCE, EMISSION AND COMBUSTION CHARACTERISTICS OF BIODIESEL

***A.MOME can be used as substitute for diesel fuel***

SukumarPuhan et al. [6] have found that the CO and $NO_x$ emissions for mahua oil methyl ester (MOME), mahua oil ethyl ester(MOEE), mahua oil butyl ester (MOBE) were lower and $CO_2$ emissionwas slightly higher than that of diesel. They have concluded that theMOME can be used as potential substitute for diesel fuel when compared to that of other esters on the basis of performance andemission characteristics.

***B. Reduction of NOx emissions when compared with Diesel***

Saravanan et al. [7] have found that the CO and HC emission formahua ester were lowered by 26% and 20% respectively than that ofdiesel. They have concluded that the $NO_x$ emission was lesser by 4% formahua methyl ester when compared to that of diesel.

***C. Diesel without modification***

Soo-Young No [8] has observed that the use of jatropha, karanja, mahua, linseed, rubber seed, cottonseed and neem oil in CI engineshows reduction in HC, CO and PM emissions and higher NOxemission. They have reported that the diesel engine without anymodification can run successfully for 20% vegetable oil and 80% dieselfuel.

***D. Comparison of B10 and B20 with B0***

Mofijur et al. [9] have found that the reduction in BP for Jatrophamethyl ester (B10 and B20) were 4.67% and 8.86% respectively whencompared to that of B0. They have also found that the BSFC increaseswith the increase in percentage of biodiesel. They have reported thatthe reduction of HC emission for B10 and B20 was 3.84% and 10.25%and CO emission was 16% and 25% respectively when compared to thatof B0. They have concluded that the $NO_x$ emission of B10 and B20 was reduced by 3% and 6% respectively when compared to that of B0.

***E. Comparison of ALB10 and ALB20 with diesel engine***

Fattah et al. have observed that the CO, HC and smokeemission for Alexandrian laurel oil (ALB10 and ALB20) were reducedby 15.1226.84%, 9.2617.04% and 7.7813.28% respectively. Theyhave reported that the $NO_x$ emission for ALB10 and ALB20 were higherabout 2.12% and 8.32% when compared to that of neat diesel [10].

***F. HC emission of B7 and B100 with diesel fuel***

Enginozelik et al. have found that the BSFC is increased by12.21% for camelina biodiesel B7 fuel and 56.25% for B100. They havereported that the HC emission of B7 and B100 fuel were decreased37.5% and 68.8% respectively when compared to that of diesel fuel. Itis observed that the $NO_x$ emission of B7 and B100 fuel were found to behigher by 17.6% and 58.8% when compared to that of diesel fuel.

***G. Reduction of $NO_x$ emissions using Palm oil***

Mosarof et al. [11] have found that the palm oil produces betterengine performance, higher SFC and shorter ignition delay. They haveseen that the palm oil reduces HC, CO, CO2 and smoke emissionsconsiderably except $NO_x$ emission.

# 6 CONCLUSION

The objective of this review is to study the effect of diesel engine operating parameters such as CR, IP and IT, antioxidant additives on the performance and emission behavior of the diesel engine. According to the results;

- Most of the studies reports that the use of biodiesel will lead to loss in BTE due to the higher viscosity of the biodiesel that leads to poor atomization of biodiesel compared to that of diesel

- The BSFC of the biodiesel and its blends is higher than diesel due to the variation in heating value or caloric value of the biodiesel, to overcome the variation in caloric value more quantity of the fuel has to be injected to produce same power
- The majority of studies have shown that HC, CO and Smoke emissions were signicantly reduced, compared with diesel. The higher oxygen content of biodiesel and lower aromatic compounds has been regarded as the main reasons
- The majority of literatures agree that the NOx emissions will increase when using biodiesel. The reason for the increase in NOx emissions was higher oxygen content, higher cetane number, lower compressibility and associated variation in fuel injection characteristics and higher in cylinder gas temperature
- The most of researches showed that increase in operating parameters such as CR, IP and IT with B20 showed improved in BTE. Further, the HC, CO and Smoke emissions were reduced but increase of $NO_x$ emission was observed with increase of CR, IP and advanced IT
- The stability of most biodiesel was lower than the ASTM standard limit minimum of 6 hr induction period due to the presence of mono and poly unsaturated fatty acids. Further, it will be improved by the addition of suitable antioxidant additives antioxidants are also having effect in reducing the $NO_x$ emission from the engine without affecting the engine performance and emission characteristics. Further, the also antioxidants will reduce the prompt $NO_x$ emission rather than reducing the thermal $NO_x$. So, maximum that of 10% reduction in $NO_x$ emission can be achieved by the addition antioxidant with biodiesel

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