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Effects on Nano Additives on Performance and Emission Characteristics of Calophyllim inophyllum Biodiesel

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Abstract: The non-renewable energy sources are depleting at higher manner so there is more energy demand. Biodiesel is a replacement for diesel fuel in compressed ignition engines due to its significant environmental benefits. The use of biodiesel leads to reduction in PM,HC and CO emissions and the increase in fuel consumption and the increase in NOx emission on diesel engines without any modification. The addition of nano particles in biodiesel increases the thermal efficiency and decreases the NOx emission. The present investigation is to study the effect of Nano fuel additives (cobalt(II,III)oxide (Co3O4) and Titanium dioxide(TiO2)) on the performance and emission characteristics of Calophyllum innophyllum biodiesel (B100) in a single cylinder, four stroke, water cooled, compression injection diesel engine. The Nano additives are prepared by hydrothermal process.The obtained particle size range in below 100nm, The nanoparticles are characterized by using scanning electron microscope (SEM),zeta potential and X-ray diffraction(XRD). The Nano particles (150 mg/l) were dispersed in the biodiesel by an Ultrasonicator and Magnetic stirrer. According to the results of this experiment, additives are the best method for obtaining the reduction in the particulate matter (PM), carbon monoxide (CO) and unburned hydrocarbons (UHC) emissions but minimum increase in the nitrogen oxides (NO_x) emission. If the additives are added in the biodiesel at appropriate proportion, it will helpful to increase the engine combustion and performance characteristics. Nano additives are reduces the fuel consumption and improves the thermal efficiency during combustion the additives release the energy to the fuel.
Keywords: Calophyllum inophyllumoil, Biodiesel, Transesterification, NanoAdittives, Cobalt Oxide, Titanium dioxide, Comperssion Ingintion Engine.

1.Introduction

Biodiesel as an alternative fuel is one of the greatest choices among other sources due to having enormous potential to decrease pollutant emissions and to be used in compression ignition engines[1]Biodiesel is suggested to be an alternative fuel to petroleum-based fuel resulting in several environmental and social benefits and also economic. Biodiesel advantages contains bio-degradable, free from sulphur (< 0.001 %), non-toxic, and 60% less net carbon dioxide emissions.

Biodiesel is prepared by plantation of trees and shrubs such as Jatropha, Mahua, Pongamia, Calophyllum inophyllum, etc. The jatropha biodiesel has benefits of low fatty acid composition and the low phospholipids content. The farming and production of edible and non-edible plants based on high oil yielding plant, high yield of fruiting, fast growing plants, and saline soil. For getting a high amount of oil, the seeds should be chored properly after harvestation.[2]

Biodiesel is source of less emission of carbon dioxide (CO2), hydrocarbon (HC) and particulate matter (PM), which are the dominant factors while compared with diesel. The only problem in the case of biodiesel such as NOx emission is to be decreased. Many researches are doing research for reducing the NOx during and after the combustion process.

In order to overcome the complications associated with the biodiesel, use of chemical substances like fuel additives derived from organic and inorganic metals were used. A fuel additive generally improves the combustion efficiency and reduces the pollution. Metallic based compounds, such as iron, copper, manganese, barium, calcium and platinum etc., which have been helped as a combustion catalyst for hydrocarbon fuels. Current advances in nanoscience and nanotechnology allows production, control and characterization of nano energetic materials. Advanced nano materials are more effective than bulk materials because of its higher surface area. Additional important benefit of nano particle is its size, because there is no chance for filter clogging and fuel injector as in the case of micron sized particles.[3]

Nanofuels are a fresh class of fuels, and the application of nanoscale energetic material in conventional fuel is an interesting concept, yet uncharted to its fullest potential. Very few studies have been carried out on the addition of several potential nanoparticles as additives to diesel, biodiesel and its blends. In this work, the literature survey on the effects of several nano additives such as metal, metal oxide, magnetic, carbon nanotube, nano organic additives, and mixed nanoadditives on engine performance are reported. Lenin et al, performed the experiments on a single cylinder air cooled Direct Injection diesel engine for evaluation of diesel doped with metal additives. The change in diesel fuel properties (viscosity, flash point and fire point) due to introduction of nano metal oxide additive was observed. The diesel fuel with nano metal oxide additive had presented a marginal increase in performance. Brake thermal efficiency was increased marginally as compared to conventional diesel fuel. For the DI Diesel engine, the hydrocarbon emissions were highest at lower load.[4] Fangsuwannarak et al, evaluated the performance and emission of a Four cylinder, four stroke vertical-in-line, water-cooled compression ignition pickup diesel engine at full load condition using commercial diesel, Palm Biodiesel and nanoparticle blended fuel .The nanoparticle used was TiO2. It was found that TiO2 had reduced the specific fuel consumption and increased engine power for pure diesel. However the NOx emission for commercial diesel blended with nanoparticle fuel is effectively reduced as compared to commercial diesel and B5 blended with nanoparticle. The blend of TiO2 based additive with diesel does not only provide the minimum CO2 emission but it was also led to the minimization of fuel consumption in comparison with diesel without additive.[5] Mehta et al, Investigated the burning characteristics, engine performance and emission parameters of a single-cylinder CI engine using nano fuels which were formulated by sonicating nano particles of aluminum, and boron in base diesel with Span80 as a surfactant for stable suspension. The nano fuels reduced ignition delay, longer flame sustenance and agglomerate ignition by droplet combustion mechanism test. Peak cylinder pressures decreased at higher load conditions. Specific fuel consumption was reduced with Al in comparison to diesel. At higher loads, the emission study showed a decline in CO along with a drop of in hydrocarbon emissions for A1 and Fe nano fuels.[6] Karthikeyan et al, evaluated the performance and emission characteristics of Promolin Stearin wax oil biodiesel blended with diesel and concentration of Zinc Oxide on a single cylinder air-cooled and direct injection diesel. The zinc oxide additive blends improved the calorific value but did not had any significant effect on the other properties. The BSFC was decreased and BTE was increased with the increase in the dosing level of ZnO in the fuel. The CO and HC had appreciably reduced with the increase of the nano particle dose, as compared to blend of biodiesel. The NOx emissions of all blended fuels did not have any considerable effect.[7] Ganesh et al, investigated the effect of nano fuel additive on the performance and emission characteristics of jatropha biodiesel (B100) in a single cylinder direct injection, air cooled diesel engine. It was observed that at 75% load operation, NOx reduction is about 47% in case of cobalt oxide nano-fuel additive. The cobalt oxide nano fuel additive shows a reduction in NOx emission at all load when compared with Magnaliumnano fuel additive. By adding magnalium to boidiesel the maximum reduction of about 66% CO emission was observed at 50% load. Also by adding cobalt oxide, there is a 50% reduction in CO emission at 75% load.[8] Ajin et al, conducted an experiment to investigate the catalytic activity of cerium oxide, especially in nanosized form. The performance tests were conducted on a naturally aspirated four stroke single cylinder water-cooled compression ignition engine. It was observed that viscosity, flash and fire point increases with addition of nanoparticle. Also found that hydrocarbon emissions were decreased on addition of catalytic nanoparticle. On the addition of cerium oxide nanoparticle in diesel,the NOx emissions were found to be decreased about a maximum of 30%.[9]

Calophyllum inophyllum

The Calophyllum inophyllum(Polanga) trees are widely dispersed throughout the tropics, including the Hawaiian, Indian Peninsula, and other pacific islands. They typically grow into 8 to 20 meters at maturity. Commonly it is called as Alexandrian Laurel, 'Indian laurel', Beauty leaf, Beach calophyllum, ,Pannay tree, Sweet Scented Calophyllum (in English), Burmese, Hawaii, Pongnyet, Kokani, Nagachampa, (in Marathi), Sultan Champa,Surpan (in Hindi), Nagam, Punnagam, Punnai, Pinmai, Pinnay, Namere (in Tamil) Oil from the nuts has been traditionally used for medicine and cosmetics and is today being made commercially in the South Pacific. The tree grows finest in direct sunlight, but grows slowly.

Advantages of Calophyllum inophyllum:

1. It has high survival potency in nature, still productive upto 50 years.
2. It has high Calorific value.
3. It does not compete with food crops.
4. It has high eroil yield than Jatropha curcas
5. Its trees serve as windbreaker at the sea shore.
6. Its biodiesel meets the USA STMD6751and European Union EN 14214 biodiesel standards.
7. Its biodiesel can be used as a potential substitute for diesel as other plant/seed feedstocks have been used or proposed to be used.
8. Its biodiesel is compatible with diesel and possesses better lubrication capability.

(a) (b) (c) (d) (e)

Fig 1.CalophyllimInophyllum Tree, Fruits and oil (a)Flowers, (b) Fruits, (c)Dried Fruits, (d)Kernal, (e) Extracted oil

2. Materials and Methods

2.1.Biodiesel Production

Calophyllum inophyllum oil, which is converted to calophyllum inophyllum methyl esters (CIME) by transesterification process. Calophyllum inophyllum (hone) oil contains 19.58% free fatty acids. The methyl ester is produced by chemical reaction with Calophyllum inophyllum (honne) oil with an alcohol (methyl), in the presence of base catalyst (Sodium Hydroxide). A two stage process is used for the transesterification of Calophyllum inophyllum oil. The first stage process (acid catalyzed) is to reduce the free fatty acids (FFA) content in oil by esterification with methanol (99% pure) and acid catalyst(H_2SO_4) sulfuric acid (98% pure) in one hour time at 57ºC in a closed reactor vessel. The calophyllum inophyllum oil is first heated upto 50ºC then 0.7% (by wt. of oil) sulfuric acid is to be added to oil and methyl alcohol about 6:1 molar ratio (by molar mass of oil) is added. Methyl alcohol is added in excess amount to speed up the reaction. This reaction was happening with stirring at 650 rpm and temperature was controlled at 55-57ºC for 90 min. The fatty ester was separated after natural cooling. At second level, the separated oil from the separating funnel is to be produced to transesterification. Methoxide (methanol + sodium hydroxide) is added with the above ester and heated to 65°C. The similar temperature is maintained for 2 hours. with continuous stirring, and then, it undergoes natural cooling for 8 hours. Glycerol will deposit at the bottom of the flask, and it is separated out by a separating funnel. The remaining in the flask are the esterified vegetable oil (biodiesel). The separated biodiesel from the said method contains various impurities like traces of unused methanol, glycerol, soap particles, etc. Water washing is carried out to eliminate all impurities. Air bubble wash is one of the methods normally suggested in the laboratory level. In this method, the contaminated biodiesel is placed in a beaker initially. Water is added gradually through the side wall of the beaker (both are immiscible).

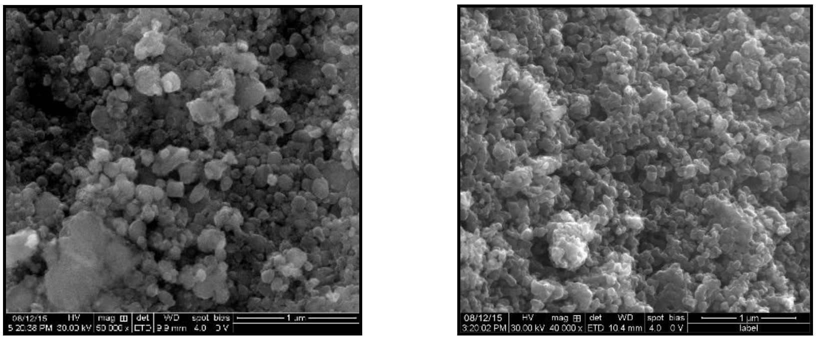
Table 1 Properties of biodiesel

Properties	**Units**	**Diesel**	**Biodiesel**
Density @ 15^{0}C	Kg/m^3	810	868.6
Kinematic Viscosity @40^0 C	Cst	2-3.5	3.7
Calorific Value	MJ/Kg	42.5	36.86
Flash Point	^{0}C	75	122
Fire Point	^{0}C	80	132
Cetane Number	--	40-50	52

It is ensured that the equivalent amount of water is added above the level of biodiesel. Air is made to pass through the biodiesel and water since the bottom of the beaker with the help of a bubbler. The air will then take away all contaminations from the biodiesel; they will travel up as the bubbles move up, and they are added in the water. The traces of glycerol and soap particles make the water to become like soap water. Once the water develops like soap water, the bubbler is stopped. After allowing some time for contaminations to settle, the biodiesel is drained from the separating funnel, and pure biodiesel will be straightly used, with or without blending, in the engine.

2.2. Nano Particles Preparation

Hydrothermal method is helped for the preparation of the nano particles and it is the chemical synthesis route. Hydrothermal synthesis is the reaction carried out at high temperature and high pressure. 0.25gm.of Cobalt Chloride (Co_3O_4) is added to 20 ml. distilled water at molar concentration of 0.1 is used for the reaction. The surfactant is help to reduce the surface energy and to reduce the reaction rate. 0.5gm. in 15 ml. distilled water at 0.1molar concentration of CTAB is worn as the surfactant and it is added to the precursor solution. Sodium hydroxide is used as the reducing agent. The reducing agent of 0.05 gm. is taken and added to 15 ml distilled at 0.1 molar concentration and it is added to the precursor mixture drop by drop. The reaction mixture of 60 ml is the transferred to Teflon lined auto clave. Then the auto calve is kept in the hot air oven at 180°c for the duration of 6 hours. The auto clave is taken out from the oven after the desired duration and allowed to air cooled. Then impurities are removed from the sample using ultra-centrifuge and the sample is collected using whatman filter. Then the nanoparticles are kept in the hot air oven at 80°c over the duration 2 hrs. for drying. Thus the cobalt oxide nanoparticles are prepared.



(a) (b)

Fig 2. SEM Images (a) Cobalt Oxide Nanoparticle (b) Titanium dioxide Nanoparticle

Titanium butoxide of 0.6gm.is mixed with 20 ml. distilled water at 0.1 molar concentration is used as the precursor for titanium oxide synthesis. The CTAB of 0.5gm.in 15ml. distilled water at 0.1molar concentration is used as the surfactant and mixed to the precursor solution. 0.1 molar concentration sodium hydroxide of 0.05gm. was taken and added to 15 ml. distilled water as reducing agent and added to the precursor mixture drop wise. The 60 ml. of the solution is converted to the Teflon lined autoclave. The auto calve is kept at 180^{oc} for 12 hours at the hot air oven. The auto clave is allowed to air cooled after the desired duration. The sample is washed and collected using ultra centrifuge and whatman filter. Then the nanoparticles are dried at 80^{oc} in hot air oven for 2 hrs. Thus the titanium dioxide nanoparticles are prepared.

The characterization of the nanoparticles are done to obtain its properties. Zeta sizer is helped for the stability and size analysis, nanoparticle structure were found using XRD and nanoparticle morphology were found using SEM and XRD. The dispersion studies are to be carried out after adding the nanoparticles to bio diesel. As the size of the nanoparticles are less than 100 nm, they are more stable and the will not agglomerate and settle down. Thus the nano-fluid with high stability are obtained. The nanoparticles are then added to the bio diesel with the help of ultrasonicator and the dispersion studies are carried out. The nano particles we have are less than 100nm so it won't agglomerate and settle down . Thus we obtain the highly stable nano-fluid.

3. Experimental Procedure

Experiments were executed in the thermal engineering laboratory, Department of Mechanical engineering, Sri Ramakrishna engineering College, Coimbatore.

Table 2. Engine Specification

1	Maker	Kirlosker
2	Type	Four stoke,water cooled ,direct injection diesel engine
3	Number of Cylinder	Single
4	Rated Power	3.5kW @1500rpm
5	Bore Diameter	87.5mm
6	Stroke Length	110mm
7	Compression Ratio	17.5:1
8	Dynamometer	Eddy current type
9	Dynamometer Arm length	0.185mm
10	Injection Timing	23^{o}bTDC
11	Injection Pressure	200 bar

The experimental study was carried out to investigate the performance and emission characteristics of a compression ignition engine with calophyllum inophyllum methyl ester using additives($B100CO_3O_4$ and $B100TiO_2$) and relating it with that of diesel. Technical specification of diesel engine is elaborated in Table 2. The diesel engine was primarily started with diesel and then with the produced test fuels. Speed of the engine was maintain constant speed at 1500 rpm under varying load conditions to measure the performance parameters such as brake thermal efficiency, brake power(BP), brake specific fuel consumption (BSFC) and exhaust gas temperature and also to measure the emission parameters like carbon monoxide(CO), unburnt hydrocarbon(HC) and nitrogen oxide(NO) emissions for both diesel and the prepared test fuels with the help of AVLDIGas 444 analyzer.

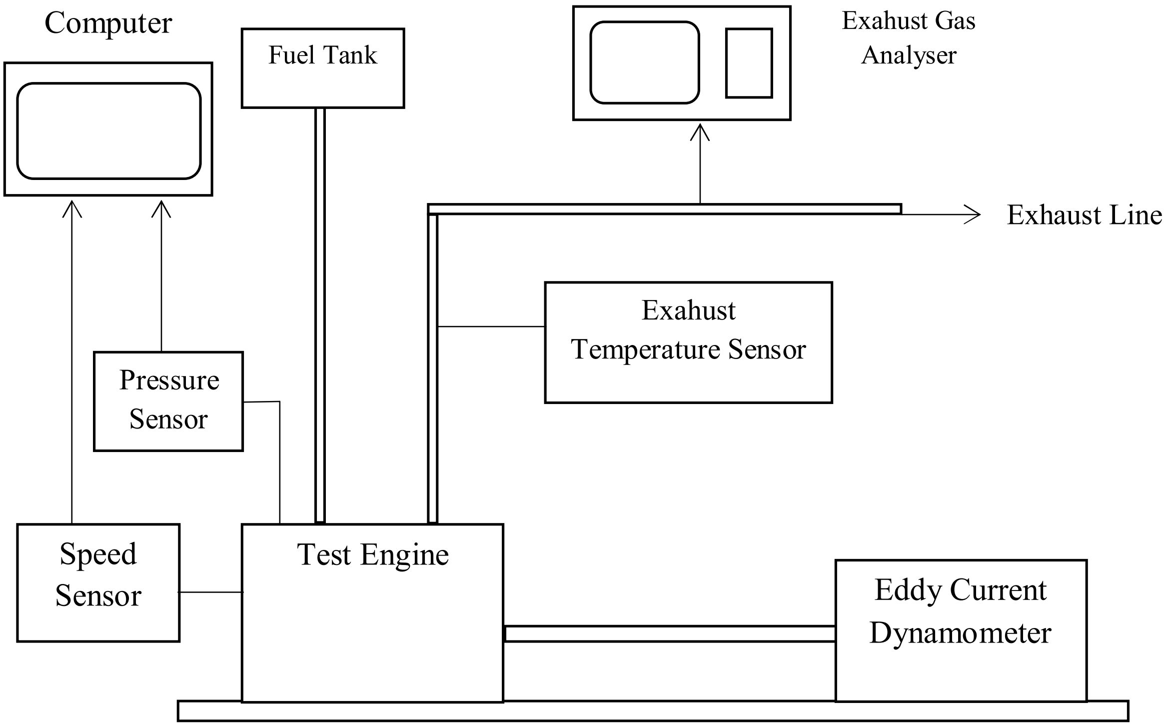


Fig 3.Schematic Diagram of Experimental Setup

4. Results and Discussion

4.1.Brake thermal efficiency

The IC engine brake thermal efficiency is the ratio of the thermal energy in the fuel to the energy delivered by the engine at the crankshaft. It importantly depends on the manner in which the energy is converted as the efficiency is normalized respect to the fuel calorific value. The brake thermal efficiency indicates the ability of the combustion system to receive the experimental fuel and offers comparable means of assessing how efficient the energy in the fuel can be transformed into mechanical output. It was marked in the study that for all test fuels the brake thermal efficiency improved with improve in brake power. Fig shows the variation of the brake thermal efficiency of the pure biodiesel, biodiesel with additive and diesel with brake power. The results show that the brake thermal efficiency of the engine is upgraded by the addition of the both cobalt oxide and titanium dioxide nanoparticles individually added in the biodiesel.The nanoparticles in the biodiesel helps the complete combustion when compared to the pure biodiesel. Thus the brake thermal efficiency is improved. The cobalt oxide blended with biodiesel shows 7 % increase in brake thermal efficiency when compared with pure biodiesel.

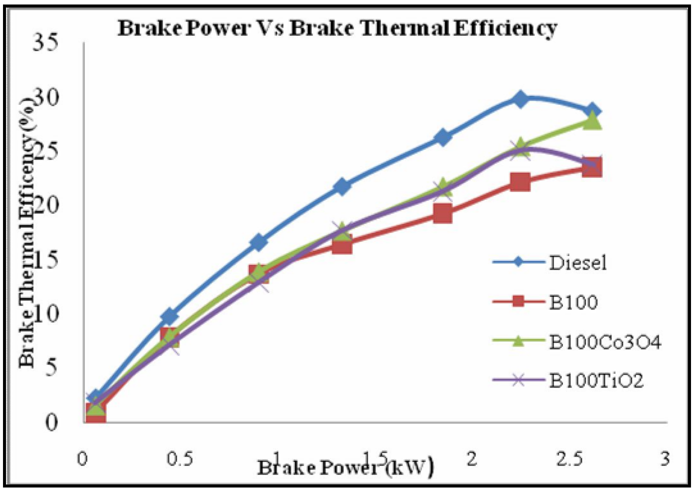


Fig 4. Variation of Brake Thermal Efficiency with Brake Power

4.2.Brake-Specific Fuel Consumption

The BSFC defined as the fuel flow rate per unit of power output is a measure of the efficiency of the engine in using the fuel provided to produce work. It is desired to obtain a lower value of BSFC meaning that the engine takes less fuel to produce the same amount of work. The BSFC of diesel engine depends mainly on the relationship between the volumetric fuel injection system, viscosity, fuel density, and energy contents.

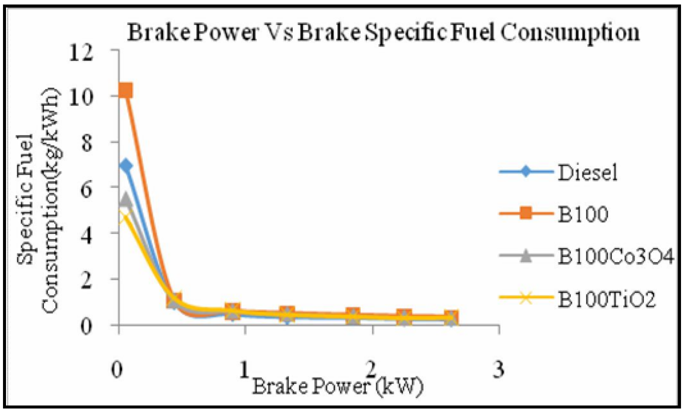


Fig 5. Variation of Brake Specific Fuel Cosumption with Brake Power

Fig 6.shows the variation of brake specific fuel consumption with brake power for pure biodiesel, biodiesel with nanoparticles and diesel. The brake specific fuel consumption of nanoparticles with biodiesel is lower than the pure biodiesel foe all load conditions. The cobalt oxide with biodiesel resulted in 4 % reduction in brake specific fuel consumption due to the catalytic chemical oxidation of fuel. The addition of titanium dioxide with biodiesel also resulted in 2 % reduction in brake specific fuel consumption. The nanoparticles acts as oxygen buffer so complete combustion occurs. Due to this the fuel consumption decreases compared to pure biodiesel.

4.3.Emission Analysis

4.3.1.Carbon monoxide

The Carbon monoxide (CO) emission depends upon the strength of the mixture, availability of oxygen and viscosity of fuel. Carbon monoxide (CO) is a toxic gas developed from the incomplete combustion of any fuel that does not contain oxygen. Normally, several factors such as engine speed, type of fuel, injection timing, injection pressure and air/ fuel ratio have an effect on Carbon monoxide (CO) emissions. Fig shows the influence of the nanoparticles with biodiesel on carbon monoxide emissions. The nanoparticle blended fuels showed complete combustion due to the shorten ingnition delay, this the degree of fuel-air mixing and uniform burning occurred. Hence there was a rduction in carbon monoxide emission for nanoparticles blended biodiesel. By adding cobalt oxide there is a 30% reduction in carbon monoxide emission at initial load. The titanium dioxide blended biodiesel shows 25% increase in carbon monoxide emission at full load. Comparing the both additives, cobalt oxide shows good results in reduction of carbon emission.

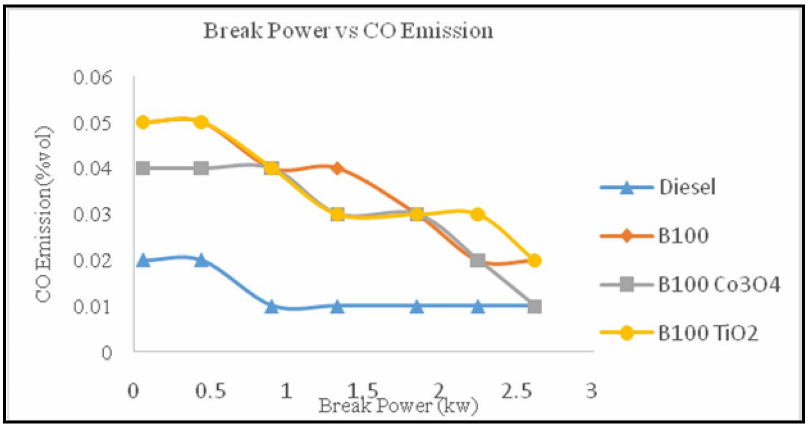


Fig 6.Variation of Carbon Monoxide with Brake Power

4.3.2.Hydrocarbon

Unburned HCs mainly result from the incomplete combustion of fuel, oxygen content of fuel and flame quenching in crevice regions of the IC engine and at cylinder walls. Figure 5 shows the variation of the hydrocarbon emission for nanoparticles blended biodiesel, pure biodiesel and diesel. The higher cetane number also helps reduce the HC emissions. The nanoparticles improved the oxygen content in the biodiesel. The emission of Hydrocarbon (HC) is decreasing with increase of loads. The hydrocarbon emission of pure biodiesel decreased on the addition of nanoparticles at all load condition. Cobalt oxide blended biodiesel resulted in 80% reduction in hydrocarbon emission at full load condition. Similar trend was noticed with titanium dioxide blended biodiesel. In that hydrocarbon emission reduced 70% at full load condition.

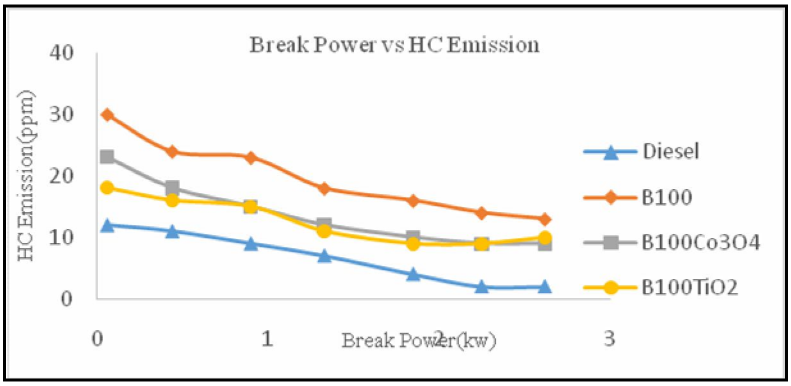


Fig 7.Variation of Hydrocarbon Emissions with Brake Power

4.3.2. Oxides of Nitrogen

The NOx emission related upon the oxidation of nitrogen at high temperature. The variation of the NO emissions of diesel, pure biodiesel and nanoparticles blended biodiesel is shown in Figure 8.Commonly the nanoparticles blended fuel reduces friction between the cylinder wall and piston thus the heat loose is arrested in the cylinder and result is considerable reduction in NOx.

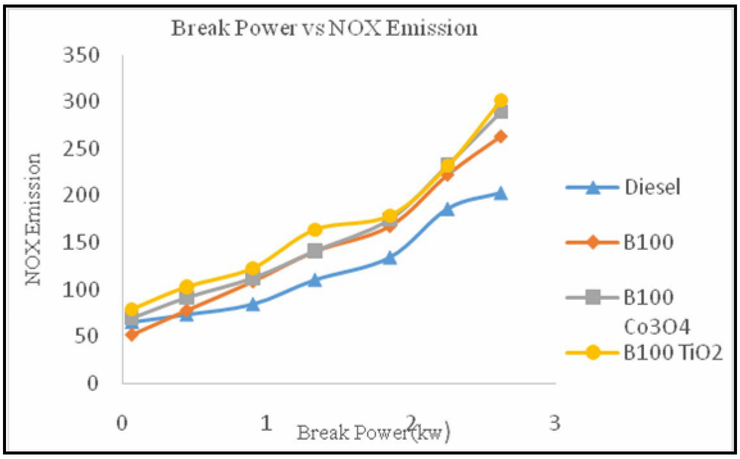


Fig 8. Variation of Oxides of Nitrogen with Brake Power

But the titanium dioxide blended biodiesel shows that increase in NOx emission at full load condition because the presence of fuel-bound oxygen promotes better combustion, resulting in higher cylinder temperature. At 50 % of load, the cobalt oxide blended biodiesel shows that NOx emission is almost close to the pure biodiesel NOx emission.

5. Conclusion and future work

The performance and emission characteristics of single cylinder,water cooled diesel engine using calophyllum inophyllum biodiesel and modified biodiesels (B100CO_3O_4 and B100TiO_2) were analysed. Based on the investigation, the following conclusions are,

- The Callophyllum inophyllum biodiesel (B100) having nearer Kinematic viscosity and Calorific value of the diesel values.
- Callophyllum inophyllum biodiesel (B100) having lesser thermal efficiency as compared with diesel. The nano additives blended biodiesel shows that increase in thermal efficiency slightly.
- The specific fuel consumption is decreases in the nano additives blended biodiesel.
- In HC emission cobalt oxide showing 80% reduction at full load. Titanium dioxide resulted that 70% reduction in 75% load.
- In NOx emission Cobalt oxide and titanium dioxide shows that increase gradually at all loads as compared with pure biodiesel.
- In CO emission the cobalt oxide blended biodiesel shows 30% reduction in CO emission at full load. Titanium dioxide blended biodiesel shows 25 % increase in CO emission at the full load condition.
- According to these Performance and emission analysis, the brake thermal efficiency was increased with nano additives. A problem was found that high NOx emission. It was found the mixing of nanoparticles with biodiesel to be advanced and it has a lot of promise for the future. We can also try different additives in calophyllum inophyllum biodiesel with different blends of diesel.

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