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Effect of Graphene Nano Material Added *Pongamia pinnata* Biodiesel Combustion on Durability of CI Engine Components and Lubricating Oil Performance

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Abstract

An alternative, lasting and renewable fuel for Compression Ignition (CI) engines is biodiesel. However, because of its lesser heating value compared to diesel, engines running on biodiesel, produce lower torque and have excessive Brake Specific Fuel Consumption (BSFC). Furthermore, the brake power and thermal efficiency of CI engines powered by biodiesel are decreased. Burning biodiesel increases emissions such as Carbon Dioxide (CO_2) and Nitrogen Oxides (NOx), but decreases emissions such as Carbon Monoxide (CO) and Total unburned Hydrocarbons (THC). Nanomaterial additives can be added to biodiesel to overcome these limitations. This study investigates the effects of adding graphene nanomaterial to Pongamia pinnata biodiesel on lubricating oil performance and the longevity of CI engine components.

Major Findings: *The findings show that the lubricating oil drained from engine running on Graphene Nano Material-Added Pongamia pinnata Biodiesel (GNMAPBD), has a greater concentration of wear components such as chromium, copper, magnesium, iron, zinc, lead and aluminum. Additionally, lubricating oil characteristics deteriorate more quickly in engines powered by GNMAPBD than in engines powered by diesel. While the lubricating oil's ash content is reduced, its density and moisture content also increases.*

Keywords: *CI Engine, Durability, Graphene Nano Material Added Pongamia pinnata Biodiesel (GNMAPBD), Lubricating Oil*

1.0 Introduction

Compression Ignition (C.I) engines have played a pivotal role in global power systems since their creation by Rudolf diesel. These engines find extensive applications in various fields, such as power generation, construction, marine, transportation, irrigation pumps and military operations, owing to their dependable performance[1-4]. The rising count of vehicles on the road, fueled by population expansion and enhanced living conditions, has markedly heightened the need for fossil petroleum fuels[5]. Nonetheless, diesel engines significantly impact environmental pollution by releasing harmful substances including Carbon Dioxide (CO_2), Hydrocarbons

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(HC), Particulate Matter (PM), Carbon Monoxide (CO), Nitrogen Oxides (NOx), and smoke[2]. The swift exhaustion of fossil fuels and their detrimental emissions have prompted an immediate inquiry into alternative fuels. Biodiesel has surfaced as a compelling alternative owing to its advantageous characteristics, such as elevated oxygen content, and increased kinematic viscosity[6]. This material boasts qualities such as biodegradability, non-flammability, non-explosiveness, non-toxicity, renewability, and a positive impact on the environment[7]. The combustion of biodiesel results in reduced emissions when compared to traditional diesel. Animal fats and vegetable oils serve as prevalent sources for biodiesel production, positioning it as a lasting alternative fuel for CI engines. Nonetheless, the utilization of biodiesel generally causes reduced brake thermal efficiency and brake power, accompanied by inflated brake-specific fuel consumption.

To lower emissions and improve engine performance, nanomaterials have been incorporated as additives to biodiesel. The materials enhance the thermo-physical characteristics of the fuel, including the thermal conductivity, mass diffusivity, and surface-to-volume ratio. Furthermore, the properties related to physics and chemistry, like flash point, fire point, pour point and kinematic viscosity, demonstrate significant enhancement[8]. Improved thermo-physical and thermo chemical characteristics result in shorter ignition delay, which enhances combustion efficiency. Enhanced combustion leads to greater brake power and brake thermal efficiency, simultaneously lowering brake-specific fuel consumption. Additionally, exhaust gas temperature along with emissions such as CO_2, CO, PM, Total Hydrocarbons (THC), and smoke are reduced[9]. Durability, characterized by an entity's capacity to function until it encounters a limiting condition, plays an essential role in performance of an engine[10]. Investigations into durability examine elements like the wear and degradation of components of engine, the carbon accumulation on cylinder heads and pistons as deposits, the coking of injectors, and the corrosion of engine parts which come in contact with biodiesel[11]. There has been a scarcity of studies focused on the durability of engines utilizing biodiesel, A. K. Hasannuddin *et al.* conducted an investigation on the durability of a single-cylinder C.I engine, operating it for 200 hours using diesel and emulsion fuels (E10 and E20). The investigation revealed no unusual wear in engines utilizing emulsion fuels. Nonetheless, a marginally increased viscosity was recorded for lubricating oil derived from the engine that runs on emulsion-fuel compared to lubricating oil derived from the engine runs on diesel[12]. Levent *et al.* investigated how rapeseed methyl ester influences the wear of ferrous components and crankcase oil. The findings showed a decline in the effectiveness of lubricating oil, characterized by a decline in viscosity and base number because of significant fuel dilution, which contributed to heightened wear on engine components[13]. Avinash *et al.,* examined the impact of *Karanja* biodiesel on the longevity of engines. The wear of components was comparable to that seen with diesel, but the rate of lubricating oil deterioration was greater in the engine using *Karanja* biodiesel[14]. Schumacher *et al.* studied the impact of 2% biodiesel on the longevity of engine components following 110,000 miles of use. They noted less wear in engines operating on biodiesel in comparison to those utilizing diesel fuel[15]. Yong *et al.* investigated how small proportions of Biodiesel (B2) affects the longevity of heavy-duty diesel engines. Following 500 hours of operation at full load and 1,000 hours under transient cycles, there was minimal wear observed on the primary components, with a slight improvement in tribological performance noted in engines fueled by biodiesel[16]. Gopal *et al.* carried out a 256-hour durability assessment on engines utilizing *Pongamia* oil. Engines fueled by *Pongamia* methyl ester exhibited elevated levels of wear metals and notable deterioration of lubricating oil when compared to those using diesel[17]. The existing literature suggests that there is a lack of thorough investigations into the effects of incorporating nanomaterials into *P. pinnata* biodiesel on engine durability. Thus, the primary objectives are to analyze the wear and tear of engine components that come in contact with biodiesel and assess the performance of lubricating oil under these conditions.

2.0 Materials and Methods

2.1 Biodiesel

Pongamia pinnata oil is extracted from P. pinnata tree seeds[18-20]. It is found in humid and subtropical environments where annual rain fall ranges from 0.5

to 2.5 m and maximum and minimum temperatures range are from 27° C to 38° C and 1° C to 16° C respectively[21]. *P. pinnata* biodiesel is produced by 2 steps transesterification process. The transesterified *P. pinnata* oil which is *Pongamia pinnata* Oil Methyl Ester (PME) has been collected from "Biodiesel Information and Demonstration Centre, Biotechnology Engineering Department NMAMIT, NITTE".

2.2 Nano Material Used

The nano material utilized in this work is graphene. The nano material produced from graphite has a diameter of less than 5 microns, featuring a very high aspect ratio and consisting of 2-4 layers of aggregates of sub-micron platelets. When this is optimally blended in small amounts with host matrices such as polymers and metals, the thermal, mechanical, and electrical properties are enhanced without a significant rise in the cost of the final products. It is generated using specialized techniques and tailored machinery, subsequently employing modified Hummer's method. The material has a thickness ranging from 2 to 5 nm, with lateral dimensions of 5 microns. Its specific surface area measures 220 m^2/g, while the bulk density is recorded at 0.08 g/cc. The porosity is noted to be 1 nm, and the atomic oxygen content stands at 0.5%, with a purity exceeding 98%. The material exhibits a thermal conductivity of 3000 W/mK in one direction and 6 W/mK in the perpendicular direction to the surface. The material exhibits a tensile modulus exceeding 1000 GPa, a tensile strength greater than 5 GPa, and electrical conductivity values of 10^7 siemens/m and 10^2 siemens/m when measured parallel and perpendicular to the surface, respectively.

2.3 Fuel Preparation

This study explores the durability of a CI engine runs by using Graphene Nano Material added *Pongamia pinnata* Biodiesel (GNMAPBD) and compares it with the durability of a CI engine runs by using conventional diesel. To formulate one liter of GNMAPBD, begin by combining 40 ppm of graphene nanomaterial with 0.16 g of surfactant in 5 ml of Deionized (DI) water. The mixture is subjected to ultrasonic treatment in an ultrasonicator for duration of 20 minutes. Subsequently, the treated mixture is blended with 200 ml of *P. pinnata* biodiesel and agitated using a magnetic stirrer for duration of 20 minutes. The resulting mixture is subsequently combined with 800 ml of diesel to yield one liter of GNMAPBD. This particular formulation, comprising 20% biodiesel and 40 ppm of nanomaterial, was selected due to its documented capacity for delivering optimal performance[22]. The diesel utilized in this study was sourced directly from the supplier, remaining unaltered. Table 1 summarizes the essential fuel properties of diesel and GNMAPBD.

2.4 Experimental Setup

The experimental configuration designed to assess the durability and performance of the internal combustion engine utilizing graphene nano material enhanced *P. pinnata* biodiesel comprises several essential elements as shown in Figure 1. The fuel tank serves the purpose of storing fuel, which is subsequently transferred through a burette to ensure accurate measurement of fuel consumption throughout the test. The fuel enters the engine combustion chamber *via* the fuel injector. The

Table 1. Properties of diesel and GNMAPBD

S. No.	Parameter	Diesel	GNMAPBD
1	Density	0.830 g/ml	0.850 g/ml
2	Pour point	-10° C	-6° C
3	Flash point	52° C	85° C
4	Fire point	57° C	93° C
5	Total acid number	0.7 mg KOH/g	3.9 mg KOH/g
6	Kinematic viscosity at 40° C	2.2 cSt	3.8 cSt

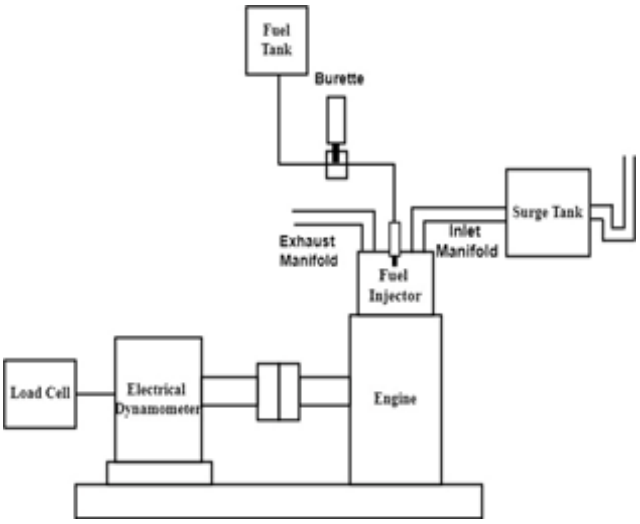


Figure 1. Experimental setup.

air necessary for combustion is delivered through the inlet manifold, which is linked to a surge tank designed to stabilize the intake airflow and minimize pressure fluctuations. The exhaust manifold serves to gather the exhaust gases generated by post-combustion and channels them into the exhaust system. The mechanical output of the engine is linked to an electrical dynamometer, which quantifies the engine's power output and facilitates load control throughout the experiment. Furthermore, a load cell is incorporated into the system to quantify the torque generated by the engine, facilitating precise computation of performance metrics. This configuration guarantees a methodical evaluation of engine performance, fuel efficiency, and durability when tested with both traditional diesel and GNMAPBD.

3.0 Results and Discussion

To study the impact of GNMAPBD, on durability of CI engine components, to which the fuel comes in to contact and lubricating oil degradation, 250 hours of long duration experiment was carried out on a single cylinder, Direct Injection (DI), water cooled, four stroke, compressed ignition engine (Kirloskar made AV1, 1500 rpm and BP of 3.7 kW) in two phases at 80% load. Figure 1 shows the experimental setup. In phase-I, the engine was assembled with new piston, piston pin, piston rings, gudgeon pin, diesel injector, high pressure pipe, fuel line pipe, oil pump with filter and cylinder head assembly. Using conventional diesel, the engine was run for 250 hours. The new lubricating oil (SAE 20W 40) was filled to engine as instructed by engine manufacturer. The first phase of the durability test was conducted for 250 hours using diesel fuel. At every 50 hours, by following the standard sampling procedure, the samples of lubricating oil were fetched from engine for analysis of different tribological wear assessment and properties of lubricating oil. In phase-II, the engine components used in the first phase were replaced by new set. Now the engine is running for 250 hours again using GNMAPBD to compare its effect on durability of engine components that come in contact, and lubricating oil degradation with diesel. The effect of GNMAPBD on durability of CI engine is studied in 2 sections; in the 1st section, effect of GNMAPBD on engine components is discussed and in the 2nd section, deterioration of lubricating oil is discussed.

3.1 Effect of GNMAPBD on Engine Components

The samples of lubricating oil fetched from the engine, at the interval of 50 hours for diesel and GNMAPBD fuelled engine were tested in atomic absorption spectrometry, to identify the amount of wear metals like chromium, iron, magnesium, copper, zinc, lead and aluminium present in the samples according to ASTM D7740-11 test procedure. Readings were tabulated and graphs are drawn and explained for all the wear metals.

3.1.1 Iron

The comparison of variation of iron accumulated in the samples of lubricating oil with time of running for diesel and GNMAPBD fuelled engine is shown in Figure 2. Cylinder head, piston rings, camshaft, crankshaft, valve guide, cylinder block, wrist pin, piston rings, bearings, piston wear debris and rust from environment may be the sources of iron[17]. The accumulation of iron in the samples of lubricating oil fetched from an engine running on GNMAPBD fuel is high when compared to the accumulation of iron in the samples of lubricating oil fetched from engine running on diesel fuel. An average of 24.44% higher iron concentration is noticed in lubricating oil samples fetched from engine running on GNMAPBD

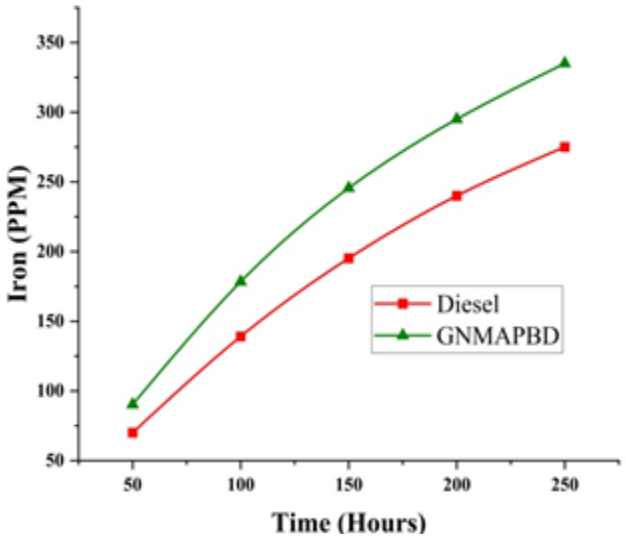


Figure 2. Comparison of deterioration of iron with time for diesel and GNMAPBD fuelled engine.

fuel in comparison to samples of lubricating oil fetched from engine running on diesel.

3.1.2 Copper

The comparison of variation of copper accumulated in lubricating oil samples with time of running for diesel and GNMAPBD fuelled engine is shown in Figure 3. Valve guides, piston rings, bearings, connecting rods, bushings, bearings, injector shields, and thrust valves are the possible sources of copper[17]. An average 35.83% higher quantity of copper is present in the samples of lubricating oil fetched from engine running on GNMAPBD fuel compared to the quantity of copper present in samples of lubricating oil fetched from engine running on diesel.

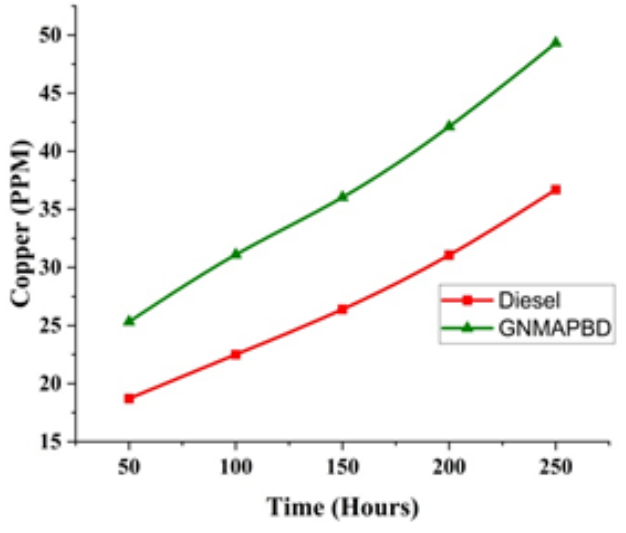


Figure 3. Comparison of deterioration of copper with time for diesel and GNMAPBD fuelled engine.

3.1.3 Chromium

The comparison of variation of chromium accumulated in lubricating oil samples with time of running for engine running on diesel and GNMAPBD fuel is shown in Figure 4. The possible chromium sources could be cooling system leakage, shaft, gear, rings wear and chromium plated liner[17]. The quantity of chromium present in the samples of lubricating oil fetched from an engine running on GNMAPBD fuel is an average 72.08% higher compared to quantity of chromium present in samples of lubricating oil fetched from an engine running on diesel.

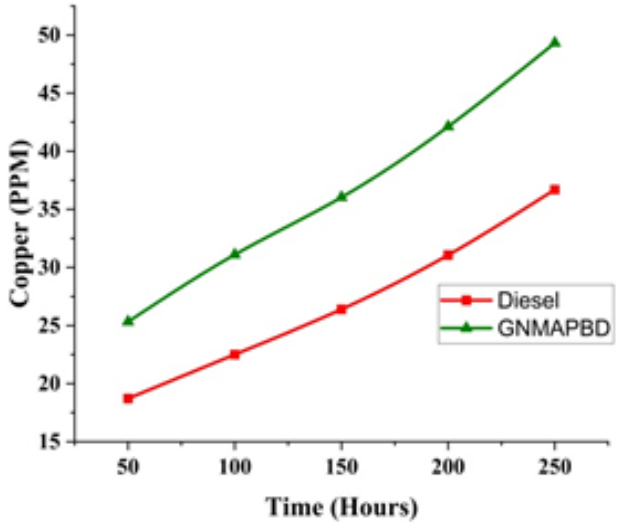


Figure 4. Comparison of deterioration of chromium with time for diesel and GNMAPBD fuelled engine.

3.1.4 Zinc

The comparison of change in quantity of zinc in lubricating oil samples with time of running for engine running on diesel and GNMAPBD is shown Figure 5. The possible sources of zinc could be coolant leaks, brass components, neoprene seals, oil additives and lubricating oil itself[17]. An average of 13.49% higher zinc concentration is

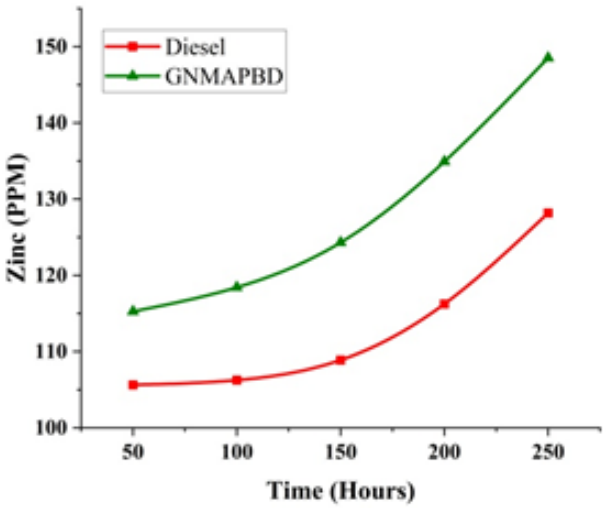


Figure 5. Comparison of deterioration of zinc with time for diesel and GNMAPBD fuelled engine.

noticed in samples of lubricating oil of engine running on GNMAPBD fuel compared to zinc concentration in the samples of lubricating oil fetched from an engine running on diesel.

3.1.5 Magnesium

The comparison of change in quantity of magnesium in samples of lubricating oil with time of running for engine running on diesel and GNMAPBD is shown in Figure 6. Wear of cylinder liner and gear along with addition as additive to lubricating oil are the sources of magnesium[17]. There is an average of 47.74% higher quantity of magnesium presence is noticed in the samples of lubricating oil fetched from an engine running on GNMAPBD compared to quantity of magnesium present in the samples of lubricating oil fetched from an engine running on diesel.

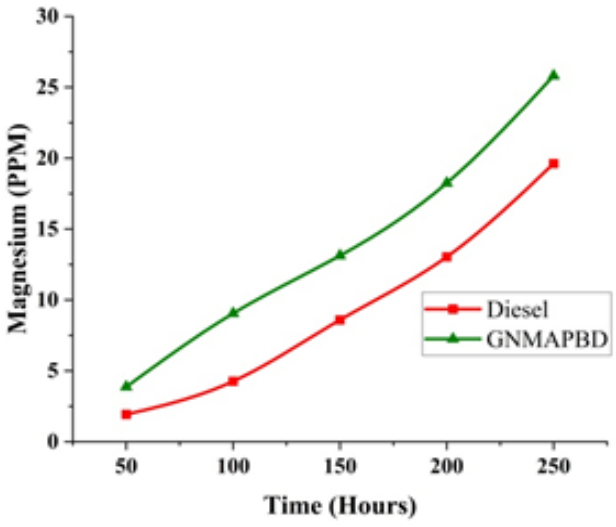


Figure 6. Comparison of deterioration of magnesium with time for diesel and GNMAPBD fuelled engine.

3.1.6 Lead

The comparison of change in quantity of lead exist in samples of lubricating oil with time of running for engine running on diesel and GNMAPBD fuel is shown in Figure 7. The sources of lead could be bearings, bearing cages, thrust bearings, bearing retainers, fuel blow by, *etc*[17]. About 32.18% more concentration of lead is noticed in samples of lubricating oil of engine running on GNMAPBD fuel compared to amount of lead in samples of lubricating oil fetched from an engine running on diesel.

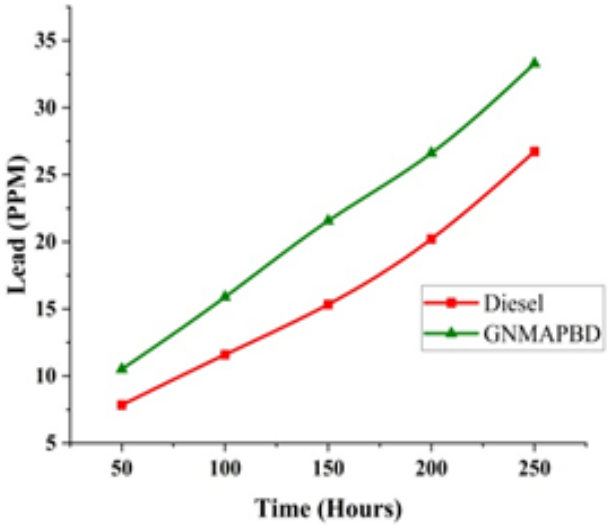


Figure 7. Comparison of deterioration of lead with time for diesel and GNMAPBD fueled engine.

3.1.7 Aluminium

The comparison of change in aluminum concentration in lubricating oil samples with time of running for engine running on diesel and GNMAPBD is shown in Figure 8. The Piston wear, crank case oil paint, push rods, oil pump, bearings, *etc*. may be the possible sources of aluminum[17]. The quantity of aluminum present in

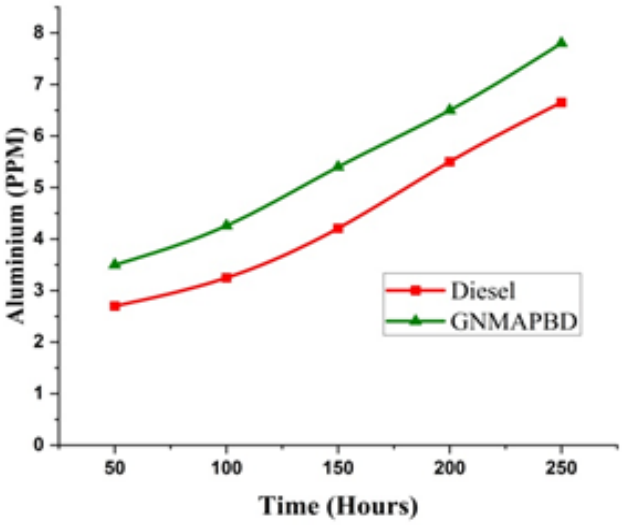


Figure 8. Comparison of deterioration of aluminium with time for diesel and GNMAPBD fuelled engine.

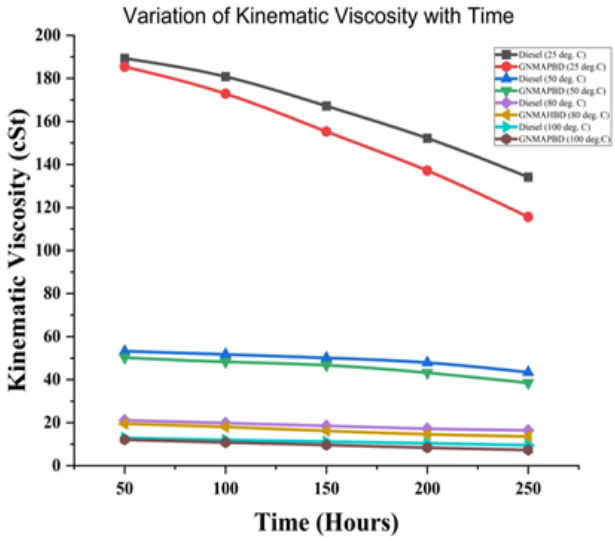


Figure 9. Comparison of variation of the kinematic viscosity of lubricating oil with time, for diesel and GNMAPBD fuelled engine at different temperatures.

the samples of lubricating oil fetched from an engine running on GNMAPBD fuel is 21.45% higher compared to the quantity of aluminum present in the samples of lubricating oil fetched from an engine running on diesel.

3.2 Effect of GNMAPBD Combustion on Performance of Lubricating Oil

3.2.1 Kinematic Viscosity

The lubricating oil viscosity has to be in a desired range when it is applied, because the efficiency of lubrication, engine durability and efficiency are affected by it. Film thickness, film formation and load carrying capacity of engine components are affected by the oil which does not have desired viscosity that leads to increased wear of bearings, reduced engine durability, poor oil economy, and low oil pressure. The reduction in anti-wear additives, formation of resinous products, contamination by insoluble and evaporation of lighter fractions increase viscosity where as fuel dilution and moisture addition decrease viscosity[23]. Therefore, with utilization, viscosity of the lubricating oil may either increase or decrease.

The samples of lubricating oil obtained from the engine are tested at 25, 50, 80 and 100° C in this work. These viscosities are measured as per IS: 1448 (Part 25) method. The comparison of variation of viscosities of oil with time at different temperatures is shown in Figure 9. Because of fuel dilution into the oil with usage, the oil viscosity is decreased. The samples of lubricating oil fetched from an engine running on GNMAPBD fuel have been subjected to higher reduction in viscosity compared to samples of lubricating oil fetched from engine running on diesel. An average decrease of 6.95%, 7.87%, 11.93% and 13.92% is observed at 25, 50, 80 and 100° C respectively.

3.2.2 Ash content

The change in presence of ash in the samples of lubricating oil fetched from an engine running on diesel and GNMAPBD with time is shown in Figure 10. It is measured according to IS: 1448 (Part 4) method. The fuel which remains as non-combustible mixes with lubricating oil as ash. It is found either in solid or in liquid form[23]. The presence of ash in samples of lubricating oil fetched from an engine running on diesel is an average 15.86% higher compared to presence of ash in samples of lubricating oil fetched from an engine running on GNMAPBD.

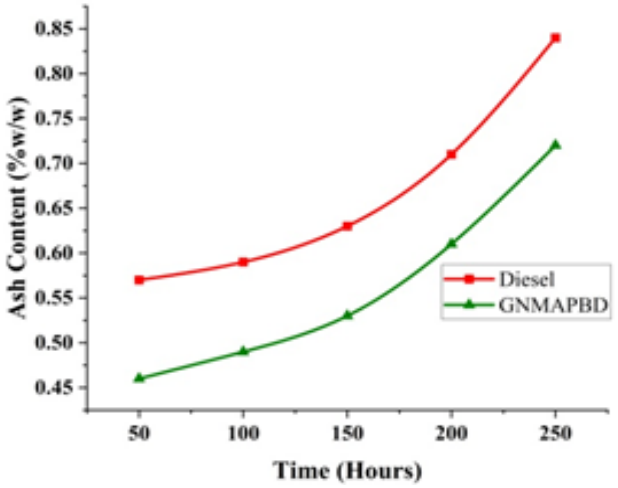


Figure 10. Comparison of change in ash content in lubricating oil with time for diesel and GNMAPBD fuelled engine.

3.2.3 Flash and Fire Point

The minimum temperature at which a lubricant can produce vapors that mixes with air which forms ignitable mixture is called as flash point. Similarly, the minimum temperature at which the ignitable mixture catches fire is known as fire point. For the longer operation of the engine, lubricating oil should have higher flash and fire point. They are measured as per IS: 1448 (Part 66) method. The comparison of flash and fire point of lubricating oil drained from an engine running on diesel and GNMAPBD is shown in Figure 11. Flash and fire point of lubricating oil drained from engine running on GNMAPBD fuel at 250 hours are 5.37% and 3.12% respectively lower than the lubricating oil drained from an engine running on diesel at 250 hours. Lubricating oil which has more Van der Waal's forces has more flash point as it requires more energy to vaporize the oil, which is highly desired[23].

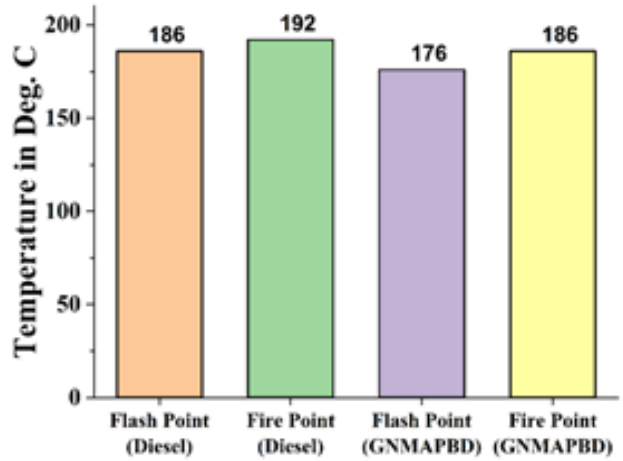


Figure 11. Flash and fire point comparison of lubricating oils of diesel and GNMAPBD fuelled engines at 250 hours.

3.2.4 Density

The density of lubricating oil should neither high nor low. The densities are measured as per IS: 1448 (Part 32) method. The higher density decreases the mobility, and its function will not be fulfilled. Similarly decrease in density enhances the friction between moving parts that causes more wear of the components of engine. The comparison of densities of the samples of lubricating oil fetched from an engine running on diesel and GNMAPBD is shown in Figure 12. The density of lubricating oil fetched from an engine running on GNMAPBD fuel is 10.625% higher compared to density of lubricating oil fetched from an engine running on diesel at 250 hours.

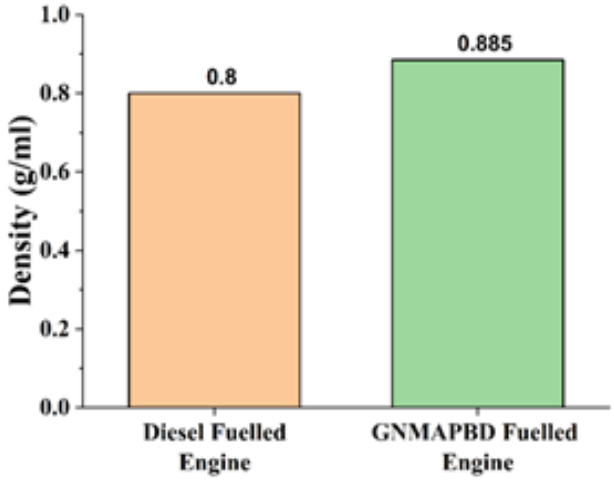


Figure 12. Comparison of densities of lubricating oils of diesel and GNMAPBD fuelled engines at 250 hours.

3.2.5 Moisture Content

The appearance of moisture in lubricating oil is unfavorable that diminishes oil film strength. The

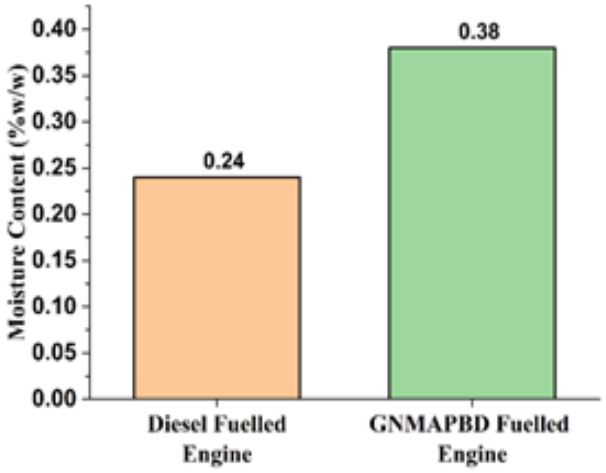


Figure 13. Comparison of moisture contents of lubricating oils of diesel and GNMAPBD fuelled engines at 250 Hours.

presence of moisture which increases oxidation reaction in lubricating oil will reduce the life of lubricating oil. The comparison of amount of moisture present in lubricating oil drained from an engine running on GNMAPBD and diesel is shown in Figure 13. These moisture contents are measured as per IS: 1448 (Part 40) method. The moisture content in lubricating oil drained from an engine running on GNMAPBD fuel is 58% higher compared to lubricating oil drained from an engine running on diesel at 250 hours.

4.0 Conclusions

The following conclusions are drawn after in depth analysis.

The presence of wear elements like chromium, magnesium, copper, zinc, iron, lead and aluminum in samples of lubricating oil fetched from an engine running on GNMAPBD is more compared to their presence in the samples of lubricating oil fetched from an engine running on diesel. The fuel dilution is more to the lubricating oil of engine running on GNMAPBD which deteriorates properties of lubricating oil; hence higher wear is noticed in GNMAPBD fuelled engine compared to an engine running on diesel.

With the utilization, the kinematic viscosity of lubricating oil decreases. The reduction in kinematic viscosity of lubricating oil of engine running on GNMAPBD is more compared to lubricating oil of engine running on diesel, because, the higher fuel dilution deteriorates lubricating oil properties due to water and impurities present in GNMAPBD. The amount of moisture present in the lubricating oil of GNMAPBD fuelled engine is more compared to moisture in lubricating oil of engine running on diesel. The flash and fire point of lubricating oil of engine running on GNMAPBD fuel are decreased.

The amount of ash present in the samples of lubricating oil fetched, from an engine running on GNMAPBD is less, compared to amount of ash present in the samples of lubricating oil, fetched from an engine running on diesel. The better thermo-physical properties of GNMAPBD, enhances combustion characteristics that results in improved combustion of fuel air mixture and thus reduces ash content.

The density of lubricating oil, drained from an engine running on GNMAPBD is more, compared to density of lubricating oil, drained from an Engine running on diesel. The increased wear element and impurities in biodiesel increases the density of lubricating oil.

5.0 Author Designation

K. S. Sudeep Kumar- Research Scholar
C. R. Rajashekhar- Research Supervisor

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