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A Preparation and Performance Investigation of Al_2O_3, TiO_2 and Gr Nanoparticles Dispersed Waste Fish Oil (WFO) Biodiesel

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Abstract

In the present work, an attempt has been made to improve the combustion of diesel oil. Biodiesel derived from waste fish oil along with ethanol was used for this purpose. The esterification process was undertaken to synthesize the biodiesel. TiO_2, Graphene (Gr), and Al_2O_3 were added to the diesel blends to improve the turbulence in the engine. The fuel mixture consisted of 20% waste fish oil, 5% ethanol, 50 ppm of particulate matter and the rest was commercially available diesel oil. The magnetic stirring method was adopted to prepare the mixture. The B20-Al_2O_3 biodiesel had a viscosity of 4.99 cSt and a density of 0.875 gram/cc. The flash point was found to be the least for the ethanol added biodiesel and it increased in the case of the nanoparticle added biodiesel. Heavy mining engines like generators, compressors, and locomotives can run on the produced biodiesel as an alternative fuel.

Keywords: *Biodiesel, Esterification, Waste Fish Oil*

1.0 Introduction

Locomotives and automobiles that ferry goods and people extensively rely on petroleum derivates to power them. The concentrated form of energy in fossil fuels made them the preferred source of energy and has increased their utilization exponentially. The drawbacks of fossil fuels are exhaustibility, non-judicious utilization and cartelization to keep the fuel costs high. The high fuel cost in the recent past has significantly affected affordability, especially in a country like India. India is the second largest importer of petroleum after China.

Compared to other gasoline fuels, diesel, a petro-chemical byproduct, has maximum energy density. This property of the derivative makes it desired to be used as a fuel in heavy-duty vehicles that run on CI engines. Further, diesel is also the preferred choice of fuel in the case of axillaries equipment used in power generators, and various agricultural equipments. Diesel engines are thought to be more efficient and reliable and perform better than petrol engines. Hence, the usage of diesel fuel is higher than that of other petroleum fuels which provides motivation to explore various methods to increase the efficiency with which diesel oil can be productively used.

Kara *et al.*,[1] evaluated the possibility of using disposal fish oil as a biofuel feedstock. The biofuel was produced by purifying waste fish oil using a two-stage

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esterification phase. A four-stroke single-cylinder, the water-cooled diesel engine was used in their experiments. All investigations were performed at a constant rotational speed. The characteristics, efficiency, and emission properties of different blends [B10, B20, B40, B60, and B100] added to diesel were tested. This study showed that bio-diesel derived from Dairy Waste Scum (DWS) was a viable substitute for traditional diesel that produces the preferred fuel properties. The investigation provided a new method for lowering the cost of producing bio-diesel and the problems associated with waste fish oil disposal. Moreover, compared to other biodiesels that are made from edible and non-edible fats and oils, the cost of waste fish oil is very competitive. Biodiesel having different blends ratios combusted in engines showed a reduction in the emissions of CO, HC, CO_2, and NOx. According to the experimental data, the B20 blend ratio is substantial for coated engines when compared to diesel and other blends. The study shows that the qualities of DWS-based bio-diesel are a beneficial substitute for petroleum-based diesel fuel having 20% ethanol.

An impact of Al_2O_3 nanoparticles added to waste cooking oil on the combustion performance, and emission characteristics of a diesel engine were investigated by Kumar *et al.*,[2] Bio-diesel blends were prepared with the aid of an ultra-sonication. The nanoparticles were added in the mass fraction of 25 ppm, 50 ppm, and 75 ppm. The experimental results showed increased brake thermal efficiency for the B20+Al_2O_3 (75 ppm) at all the loads compared to the diesel oil used. The specific fuel consumption and emission of CO and HC were lowered for the B20+Al_2O_3 (75 ppm) blend compared to the pure diesel oil for all the loads. The NO_x emissions were reported to be lower for the diesel than that of the B20+Al_2O_3 blend.

Vishwajit *et al.*,[3] conducted experiments to determine the performance and emission characteristics of graphene (Gr) nanoparticles blended with biodiesel. Honge Oil Methyl Ester [HOME] was used to make biodiesel from honge raw oil. Using a mechanical homogenizer and an ultrasonicator, graphene nanoparticles were uniformly dispersed into the biodiesel in mass fractions of 25 ppm and 50 ppm. The results revealed a significant increase in brake thermal efficiency and a significant reduction in harmful pollutants for the graphene nanoparticle. This was due to the Gr higher surface area for reactivity and higher thermal conductivity.

Ahmed *et al.*,[4] studied the effects of Graphene Nanoplatelet (GNPs) as a catalyst on the effectiveness, combustion, and exhaust emissions of a single-cylinder direct-injection diesel engine running on Jatropha Bio-diesel blend (JB20). GNPs were mixed with JB20 at concentrations varying from 25 to 100 mg/L in steps of 25 mg/L. The presence of GNPs in the JB20 blend increased the peak cylinder pressure and the rate of increase in pressure. Improved engine performance was seen from the reported values. Reduced ignition delay and faster combustion initiation were achieved with 50-75 mg/L GNPs. The engine also ran smoothly, with no negative effects on performance as a result of the GNP-enhanced fuels.

The effect of Titanium Oxide (TiO) nanoparticles and ethanol addition to diesel-biodiesel blends were investigated by Prabakaran *et al*[5]. They used a blend of 40% diesel, 30% biodiesel, 30% ethanol, and 250 ppm of TiO nanoparticles. Initially, there was an increase in the ignition temperature for the biodiesel blends due to the surplus oxygen levels. This was confirmed by the increased density and the viscosity of the blend. This effect was reduced by the addition of 30 percent ethanol to the mixture. Other differences observed included an increase in fuel consumption, cylinder pressure, and a decrease in heat produced relative to the diesel oil.

Venu *et al.*,[6] explored the role of Alumina (Al_2O_3) nanoparticles on Injection Timings (IT) of 23, 27, and 19 minutes before TDC. At a constant engine speed of 1500 rpm, 25 ppm of Al_2O_3 was mixed with 70% diesel, 20% biodiesel, and 10% ethanol solution and was introduced into the engine. Advancing the injection timing to 27 minutes prior to TDC reduced the ignition delay and CO_2 emissions. However, this caused an increase in the combustion timing, HC, CO, and NOx emissions. With ignition caused 19 minutes prior to the piston reaching TDC resulted in the cylinder pressure and heat release away from TDC. The injection timing and emissions of HC, CO, NOx, and smoke were reduced.

From the above findings, it is clear that Biofuels are a potential partial substitute for diesel. They are obtained from the processing of natural sources like vegetative and biological substances. However, the biofuels produced lack consistency in terms of certain physiological properties. Owing to this drawback they cannot be used in their entirety in CI engines. Their lower calorific value during ignition is upgraded by the addition of ethanol.

While compared to plain fuels, nanoparticle premixed fuels are reported to have high thermophysical properties. Nanoparticles have a larger surface-to-volume proportion, which allows for a wider area of contact throughout rapid oxidation and enhances the fuel's heat transfer functionality. The swirl created by the nanoparticles-diesel blends inside the combustor aids in improved combustion at the dead zones inside the combustion chamber. As a result, adding metal oxide nanoparticles to bio-fuels will optimize the performance of the engine while also reducing toxic fumes from the exhaust.

2.0 Materials and Methods

2.1 Preparation of Waste Fish Oil

Biofuel from waste fish oil is typically produced through the esterification and transesterification processes. This entailed the following steps.

2.1.1 Removal of Water from Oil

A specified amount of waste fish oil was heated to 50-60 °C to liquefy the semisolid scum, then the oil was allowed to settle to remove all solid impurities before being heated to 110 °C to evaporate all the water content and obtain pure fish oil for further processing.

2.1.2 Free Fatty Acid Test

In a beaker, 1g of fish oil was diluted with 10ml of methanol. Methanol was treated with 3-4 drops of phenolphthalein indicator. In a burette, 0.1 normal NaOH solution was added dropwise to the scum oil solution until the solution changed its color to pink. The amount of NaOH solution used to achieve the pink color was recorded. The fatty acid content of the oil was calculated using the following formula based on the amount of NaOH solution consumed.

Free Fatty Acid content (FFA) = 28.2×(Normality of NaOH)×(Titration Value)

2.1.3 Acid Catalysed Esterification

The oil in the Batch Reactor was heated in the temperature range of 60-64 °C. A beaker was then filled with 240 ml of methanol and 25 ml of sulphuric acid (Figure 1(a)). The methanol acid mixture was gradually poured into the reactor containing oil. The batch reactor stirs the oil,

(a) Esterification **(b)** Transesterification **(c)** Separation **(d)** Washing

Figure 1. Preparation of waste fish oil.

methanol, and acid mixture, and prevents solidification. After 90 minutes of stirring, the mixture is poured into a separating funnel and was allowed to settle for 60 minutes. This is known as the Acid-Catalyzed Esterification process. With the progress in time inside a separating funnel, two distinct layers form: the top layer was known as esterified oil, and the bottom layer is the acid ester. The acid ester is separated from the esterified oil, and a free fatty acid test for 1 gram of esterified oil was performed. If the Free Fatty Acid (FFA) value is less than 4, the separation step was skipped. If the FFA value is greater than 4, the next step esterification, known as transesterification or base-catalyzed transesterification, was performed.

2.1.4 Base Catalysed Esterification

The esterified oil acquired from acid-catalyzed esterification was heated to 70°C. In a batch reactor, 240 ml of methanol and 7 grams of NaOH pellets were added and continuously stirred until the NaOH pellets dissolved. The heated esterified oil is then transferred to the esterification setup's batch reactor as shown in Figure 1(b). A mixture of methanol and NaOH was slowly poured into the batch reactor containing scum. The remaining procedure followed was akin to the acid transesterification described above.

2.1.5 Separation

Following the completion of the reaction, the solution was transferred into a separatory funnel for approximately 12 hours to allow for phase separation. As methyl ester is poorly soluble, glycerin that formed settled at the bottom (Figure 1(c)). Reacted glycerides should be preferentially attracted to the glycerin phase and then removed when the phase is separated from the separating funnel due to their polarity.

2.1.6 Drying

Water in fuel causes the following issues: (i) corrosion of the engine fuel systems. (ii) Bacterial activity. Drying separates the intertwined water from the biodiesel. Washing with water increases the water content of biodiesel. Drying aids in the removal of the dispersed and dissolved water in biodiesel, guarding against poor combustion and smoke emissions leading to optimal engine performance. The biodiesel was dried by heating it in a beaker to about 110°C, (Figure 1(d)). The drying process also removes any traces of methanol.

2.2 Bio-Diesel Blend Preparation

The waste fish oil was mixed with diesel to obtain the bio-fuel. To achieve a uniform mix, biodiesel (20% and 5% ethanol) is blended with diesel oil (75%) using a magnetic stirrer (Figure 2 (a)) operating at a speed of about 750-800 rpm. The blend thus obtained is known as B20E5 as it contains 20% biodiesel and 5% ethanol in a 75 percent diesel base.

Aluminium Oxide, Graphene, and Titanium Oxide were added (50 ppm) to the biodiesel mixture. The mixture thus obtained was ultrasonicated for 30 minutes to ensure uniform dispersion, followed by 1 hour of

(a) Magnetic stirring of B20 blend **(b)** Alumina nanoparticle B20 blend **(c)** Graphene nanoparticle B20 blend **(d)** Titanium Oxide nanoparticle B20 blend

Figure 2. Bio-diesel blend preparation.

stirring with a magnetic stirrer. The prepared blends of bio-fuel are shown in Figure 2(b), (c) and (d) for alumina, graphene, and TiO_2 bio-fuel respectively

3.0 Result and Discussion

Following blends were prepared; the notations are shown in the following Table 1.

The flash and fire point were investigated for pure diesel and other bio-diesels using Pensky Martens apparatus. The bar chart shows the average of five readings of the flash and fire points (Figure 3).

The flash and fire points of the bio-fuels were found to be higher in comparison to the diesel oil. Among the biofuels, the flash and fire points increased in the order of DBE, DBE-A, DBE-G, and DBE-T respectively.

Table 1. Notations for fuels prepared

Fuels	Notation
Diesel	D
75% Diesel + 20% Bio-Diesel +5% Ethanol	DBE
75% Diesel + 20% Bio-Diesel +5% Ethanol + 50ppm Al_2O_3	DBE-A
75% Diesel + 20% Bio-Diesel +5% Ethanol + 50ppm Graphene	DBE-G
75% Diesel + 20% Bio-Diesel +5% Ethanol + 50ppm TiO_2	DBE-T

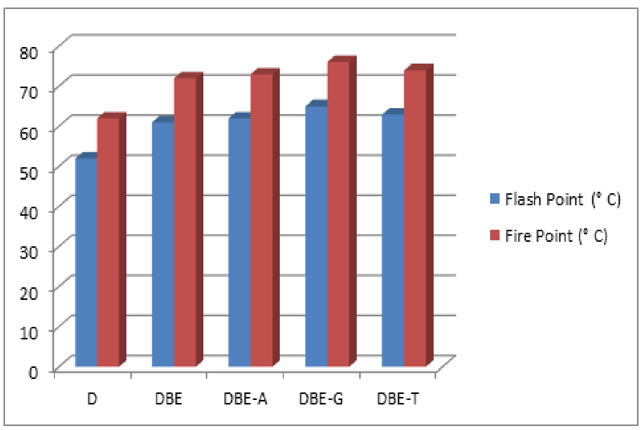

Figure 3. Flash and fire point for the fuels.

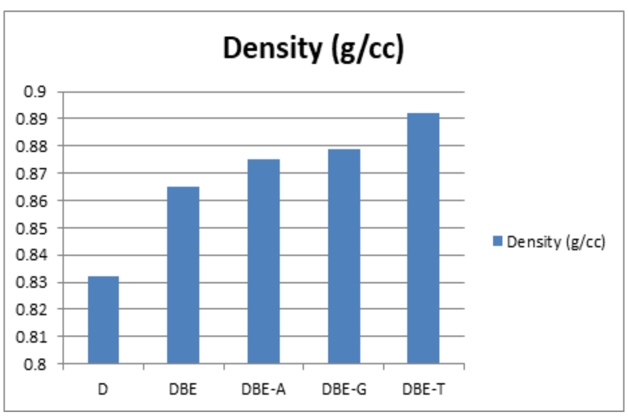

Figure 4. Density for different fuel.

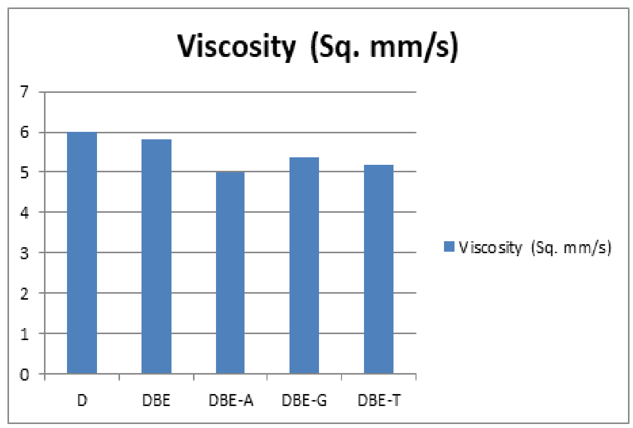

Figure 5. Viscosity for different fuel.

The density measurements proved that the bio-fuels were heavier compared to the diesel oil (Figure 4). The lower and higher densities were found in diesel and DBE-T bio-fuel respectively.

Viscosity measurements were obtained using a Redwood viscometer. The measured viscosity is shown in Figure 5. Lower viscosity was found for the DBE-A compared to the other fuels.

4.0 Conclusion

Waste fish oil biodiesel was produced successfully through the esterification and transesterification processes.

The particles such as TiO_2, Gr, and Al_2O_3 were mixed uniformly to the diesel blends via a magnetic agitator to improve the turbulence in the engine. The B20-Al_2O_3 biodiesel had a viscosity of 4.99 cSt and a density of 0.875 gram/cc. The flash point was found to be the least for the ethanol added biodiesel and it increased in the case of the nanoparticle added biodiesel. The produced biodiesel can be used as a substitute fuel for heavy mining engines, including compressors, generators, and locomotives.

5.0 References

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