Experimental investigation on direct injection diesel engine fuelled with graphene, silver and multiwalled carbon nanotubes-biodiesel blended fuels


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Abstract

In the present energy scenario of increased energy demand and rapid depletion of high energy non-renewable energy resources like petrochemical products the search for new renewable and alternative fuels has gained momentum. Increased pollution due to the excess use of such petroleum and diesel fuels for varied energy requirements is another important issue to be addressed. Due to their low emission characteristics and equivalent energy density biodiesel are becoming more useful in replacement for petroleum fuels. In the present work biodiesel derived from honge oil called HONGE oil methyl ester (HOME) was used as an alternative fuel as it was locally and abundantly available. Different metal and metal oxide nano-particles were then added to HOME to prepare novel hybrid fuel blends. Biodiesel-nanoparticles blends were prepared with the aid of an ultra-sonicator and the nanoparticles used were varied in the mass fraction of 25ppm and 50 ppm. Experimental investigations were carried out on a single cylinder four stroke diesel engine fuelled with biodiesel-nanoparticle blends to determine performance, combustion and emission characteristics. The result showed considerable enhancement in the brake thermal efficiency with reduced harmful exhaust emission from engine with addition of nano-particles to HOME.


Definitions/Abbreviations

<table>
<thead>
<tr>
<th>PM</th>
<th>Particulate matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>NOx</td>
<td>Nitric oxides</td>
</tr>
<tr>
<td>NPs</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>bTDC</td>
<td>Before top dead center</td>
</tr>
<tr>
<td>HSU</td>
<td>Hartridge smoke unit</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nano-tubes</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Multi Walled Carbon Nanotubes</td>
</tr>
<tr>
<td>HOME</td>
<td>HONGE oil methyl ester</td>
</tr>
<tr>
<td>HOME+50GRAPHENE</td>
<td>HONGE biodiesel with 50mg of graphene nanoparticles</td>
</tr>
<tr>
<td>HOME+50 MWCNTs</td>
<td>HONGE biodiesel with 50 mg of MWCNTs nanoparticles</td>
</tr>
<tr>
<td>HOME+50 SILVER</td>
<td>HONGE biodiesel with 50mg of silver nanoparticles</td>
</tr>
</tbody>
</table>

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1. Introduction

The diesel engines have advantages like durability, reliability and fuel economy compared to their counterpart gasoline engines. Diesel engines cause higher emission of particulate matter (PM), carbon monoxide (CO), Hydrocarbon and Nitric oxides with various global hazards such as climate change, ozone layer depletion, greenhouse effect, global warming, smog, acid rain water bodies and hence reduce air quality. Focus on energy security, environmental concerns, foreign exchange savings and socio-economic issues enable use of renewable fuels and are gaining prominence. Many researchers have contributed their work towards reduction of hazardous tail pipe emission from the engine using different methods such as engine modification, fuel alteration, and exhaust gas treatment. Fuel alteration may include use of biodiesel produced from vegetable oils as an alternative fuel to diesel. Recent works on novel hybrid fuels report use of nanoparticles in liquid injected fuels as additives since they exhibit better enhanced properties when compared to their bulk form. Adding such catalytic reactivity materials like metal and oxide materials in biodiesel may enhance the properties of the base biodiesel. This could be due to special properties of nano-particles like magnetic, optical, electrical and thermal properties [1]. Nano-particles have higher surface to volume ratio and their higher surface area is more relevant for catalytic reactivity and improved magnetic properties as compared to their bulk form. Adding some metal and metal oxide nanoparticles to biofuel will improve the engine performance as well as reduce the harmful gases from engine exhaust [2]. It is also reported that adding aluminum nano-particles to ethanol and diesel could enhance the ignition properties due to the heat built up with in the fuel and reactive nature of aluminum nanoparticles [3]. Size of nanoparticles may also affect the parameters like combustion process, ignition delay, burning rates of fuel. Aluminum nanoparticle additives to biodiesel resulted in faster burning, improved combustion and ignition delay as well [4, 5]. Improvement in the performance of engine and decreased emission of harmful gases to environment has been reported in the literature with the use of these nano-particle additives [6]. It is reported that addition of cerium oxide nanoparticles to biodiesel enhanced surface area to volume ratio. The flash point of biodiesel, which is an indication of the volatility, was found to increase with the inclusion of such additives. The viscosity of biodiesel was found to increase with the addition of cerium oxide nanoparticles to biodiesel. The viscosity and the volatility were found to hold direct relations with the dosing level of the nano-particles [7, 8]. The linear burning rates of nitro-methane have been studied at high pressures, exploring the effects of potential nano-structured catalyst support material additives, including aluminum oxy-hydroxide, amorphous silicon oxide, and functionalized graphene sheets. Of these, graphene proved to be the most promising one in terms of maximizing the nitro-methane reaction rates [9]. This is attributed to the effect of enhanced heat transfer by radiation and thermal conductivity of graphene being an exciting material. It has a large theoretical specific surface area (2630 m²/g), high intrinsic mobility (200000cm²/vs), high Young’s modulus (1.0 TPa) and thermal conductivity (5000/ WmK) [10]. Performance and the emission characteristics of a diesel engine operated on alumina-diesel blends have been experimentally investigated [11]. They observed a substantial enhancement in the brake thermal efficiency and reduced harmful pollutants compared to that of neat jatropha biodiesel and diesel and better combustion was reported to be responsible for this observed trend. Use of Carbon nano-tubes (CNT) indicated that suspended CNT in a base fluid will enhance the surface-area-to-volume ratio and settling time. The same
team [12] have critically reviewed the applications of nano-particle/nano-fluid in diesel engines and concluded that adding suitable proportion of nanoparticles/CNT to the conventional fuels such as diesel will reduce the evaporation time, which in turn favours shorter ignition delay. Owing to the potential properties of nano-particles of CNT, its subsequent effects on the performance, emission, and combustion characteristics of a single-cylinder, direct-injection diesel engine using CNT blended water–diesel emulsion fuel has been reported. Nano-particles can function as a catalyst and an energy carrier, as well. In addition, due to the small scale of nanoparticles added, the stability of the fuel suspensions markedly improved [13]. Silver nanoparticles for engine application have not been reported in the literature. Their nodal metal properties like thermal, optical and high reactivity due to the large surface to volume ratio has been presented in the literature [14, 15].

2. Preparation of blends for present study

The novel hybrid biodiesel-nanoparticle blends for the present study were prepared by using homogenizer and ultrasonicator. Multi walled carbon nanotubes, Graphene and silver were selected as nanoparticles additives to HOME owing to their improved properties like higher thermal conductivity, mechanical and magnetic properties. Nanoparticles are weighed to predetermine mass fraction of 50 mg and were then added to 1 litre of HOME. For better mixing of nanoparticles with biodiesel the blends were kept in an ultra-sonicator for about 30 minutes to ensure proper dispersion of these nanoparticles in biodiesel. Ultrasonicator is regarded as the best method to disperse nanoparticles in biodiesel as it allogarates nanoparticles in nanometer range. The blends were prepared with 50mg of respective nanoparticles and were named as biodiesel+50ppm nanoparticle (HOME+50GRAPHENE, HOME+50MWCNTs and HOME+50SILVER). The blends were kept in a static condition to check their stability as they tend to settle down due to their density after some time. To test the stability of the nanoparticles present in biodiesel, the blends were kept in a borosilicate glass overnight. The problem of nanoparticles settling was minimized with the help of homogenizer, which restricted the settling down of nanoparticles for longer time.

3. Properties of the novel fuel blends

Table 1 shows the specifications of the nanoparticles used for present work. The properties of the novel hybrid blends prepared were determined and are shown in Table 2.

4. Heat Release Rate Calculations

The heat release rate of the fuel causes a variation of gas pressure and temperature within the engine cylinder, and strongly affects the fuel economy, power output and emissions of the engine. It provides a good
insight into the combustion process that takes place in the engine. Determining the optimum heat release rate is particularly important in engine research. A computer program was developed to obtain the heat release rate.

**Table 1. Properties of nanoparticles used for present study**

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Parameters</th>
<th>MWCNTs Nanoparticles</th>
<th>SILVER Nanoparticles</th>
<th>GRAPHENE Nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Manufacturer</td>
<td>Intelligent Pvt. Ltd</td>
<td>Karnataka University Dharwad</td>
<td>Karnataka University Dharwad</td>
</tr>
<tr>
<td>2</td>
<td>Bulk/ true density – g/cc</td>
<td>0.05-0.17</td>
<td>0.04</td>
<td>-----</td>
</tr>
<tr>
<td>3</td>
<td>Average particle size (APS) – nm</td>
<td>10-30 length 1-2μm</td>
<td>150</td>
<td>22.5-26</td>
</tr>
<tr>
<td>4</td>
<td>Surface area (SSA) m²/g</td>
<td>350</td>
<td>385</td>
<td>492</td>
</tr>
<tr>
<td>5</td>
<td>Purity - %</td>
<td>95</td>
<td>97</td>
<td>99.7</td>
</tr>
<tr>
<td>6</td>
<td>Thermal conductivity –W/mK</td>
<td>3180</td>
<td>430</td>
<td>4840-5300</td>
</tr>
</tbody>
</table>

**Table 2. Nanoparticles blended fuel properties**

<table>
<thead>
<tr>
<th>Type of fuel</th>
<th>Flash point, ºC</th>
<th>Kinematic Viscosity, cSt @ 40 ºC</th>
<th>Net calorific value, MJ/kg</th>
<th>Density @15 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel</td>
<td>56</td>
<td>3</td>
<td>43</td>
<td>840</td>
</tr>
<tr>
<td>HOME</td>
<td>170</td>
<td>5.6</td>
<td>36.016</td>
<td>880</td>
</tr>
<tr>
<td>HOME+50</td>
<td>158</td>
<td>5.8</td>
<td>35.50</td>
<td>900</td>
</tr>
<tr>
<td>GRAPHENE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOME+50</td>
<td>164</td>
<td>5.8</td>
<td>35.10</td>
<td>900</td>
</tr>
<tr>
<td>MWCNTs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOME+50</td>
<td>168</td>
<td>5.9</td>
<td>34.95</td>
<td>905</td>
</tr>
<tr>
<td>SILVER</td>
<td></td>
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</tr>
</tbody>
</table>

The heat release rate at each crank angle was calculated by using first law analysis using ensemble pressure versus crank angle history obtained from 100 cycles using the following expression given below:

\[
Q_{app} = \frac{\gamma}{\gamma - 1} [PdV] + \frac{1}{\gamma - 1} [Vdp] + Q_{wall}
\]

Where,
- \(Q_{app}\) - Apparent heat release rate (J)
- \(\gamma\) - Ratio of specific heats \(C_p\) / \((C_p - R)\)
- \(R\) - Gas constant in \((J / kmol-K)\)
- \(C_p\) - Specific heat at constant pressure \((J / kmol – K)\)
- \(V\) - Instantaneous volume of the cylinder \((m^3)\)
- \(P\) - Cylinder pressure (bar)
- \(Q_{wall}\) - Heat transfer to the wall (J)

The heat transfer was calculated based on the Hohenberg equation (Hohenberg 1979) given below and the wall temperature was assumed to be 730 K [16].

\[
Q_{wall} = h \times A \times [T_g - T_w]
\]

\[
h = C_1 V^{-0.06} P^{0.8} T^{-0.4} (V_p + C_2)^{0.8}
\]

Where,
- \(h\) - Heat transfer coefficient in \(W/m^2 K\)
- \(C_1\) & \(C_2\) - Constants, 130 & 1.4
- \(V\) - Cylinder volume in \(m^3\)
- \(P\) - Cylinder pressure in bar
- \(T\) - Cylinder gas temperature in \(K\)
- \(V_p\) - Piston mean speed in \(m/s\)
- \(A\) - Instantaneous Area \((m^2)\)

**5. Experimental set up**

Performance, combustion and emission tests were conducted on a single cylinder four stroke single cylinder water cooled direct injection compression ignition engine with a displacement volume of 662 cc, compression ratio of 17.5:1, developing 3.7 kW at 1500 rev/min using the base fuel and
nanoparticle-biodiesel blends. Figure 1 shows the experimental set up. The specification of the engine used is given in table 3. The engine was always operated at a rated speed of 1500 rev/min. The engine had a conventional fuel injection system. The engine was always operated at a rated speed of 1500 rev/min. The engine had a conventional fuel injection system. Injector was provided with three holes each having an orifice diameter of 0.3 mm. The injector opening pressure and the static injection timing as specified by the manufacturer was 205 bar and 23° btdc respectively. Earlier experiments conducted on biodiesel (home) engine operation showed that retarded injection timing of 19°btdc and increased injection pressure of 230 bar resulted into comparable performance with diesel operation. Hence injection timing and injection pressure of 19°btdc and 230 bar were fixed for home-nanoparticles blended fuel operation. The governor of the engine was used to control the engine speed. The engine was provided with a hemispherical combustion chamber with overhead valves operated through push rods. Cooling of the engine was accomplished by circulating water through the jackets on the engine block and cylinder head. A piezoelectric pressure transducer was mounted with the cylinder head surface to measure the cylinder pressure. The emissions like unburnt hydrocarbons, carbon monoxide, nitric oxides were measured by five gas analyzer and smoke by hartridge smoke meter during engine steady state operation.

Fig. 3: shows the experimental set up

Table 3. Specification of the compression ignition engine

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Parameters</th>
<th>Engine specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Type of engine</td>
<td>Kirlosker make Single cylinder four stroke direct injection diesel engine</td>
</tr>
<tr>
<td>2</td>
<td>Nozzle opening pressure</td>
<td>200 to 205 bar</td>
</tr>
<tr>
<td>3</td>
<td>Rated power</td>
<td>5.2 kW (7 HP) @ 1500 RPM</td>
</tr>
<tr>
<td>4</td>
<td>Cylinder diameter (Bore)</td>
<td>87.5 mm</td>
</tr>
<tr>
<td>5</td>
<td>Stroke length</td>
<td>110 mm</td>
</tr>
<tr>
<td>6</td>
<td>Compression ratio</td>
<td>17.5 : 1</td>
</tr>
</tbody>
</table>

6. Results and Discussion

This section explains the performance, emission and combustion behaviour of diesel engine using HOME-nanoparticle blended fuels.

6.1 Brake Thermal Efficiency

Figure 4 below shows the variation of brake thermal efficiency with Brake power for nanoparticle blends of MWCNTs, Graphene and silver nanoparticles respectively and HOME. The HOME resulted in inferior performance due to its higher viscosity (nearly twice diesel) and lower volatility and lower calorific value compared to diesel. However the brake thermal efficiency of the HOME- nano-particle blended fuels improved compared to neat HOME.
operation. This could probably be attributed to the better combustion characteristics of HOME- nanoparticle blends. In general, the nano-sized particles possess high surface area and reactive surfaces that contribute to higher chemical reactivity and act as potential catalyst.

Brake thermal efficiency of Graphene nanoparticles blended biodiesel was found to be higher compared to MWCNTs and Silver nanoparticles blended biodiesel. This could probably be attributed to the better combustion characteristics of Graphene blended biodiesel. In general, the Graphene nanoparticles possess high thermal conductivity, surface area and reactive surfaces that contribute to higher chemical reactivity to act as a potential catalyst. In this perspective, the catalytic activity of HOME+50GRAPHENE could have improved due to the existence of high surface area and active surfaces provided by graphene nanoparticles.

Fig. 4: Variation of Brake Thermal Efficiency with Brake power

6.2 Smoke opacity

Figure 5 shows the variation of smoke opacity for different nano-particle biodiesel blended fuels combinations. HOME resulted in higher smoke opacity compared to HOME-nano-particle blended fuels due to their heavier molecular structure and lower volatility. However smoke opacity was reduced for HOME+50GRAPHENE as compared to the HOME+50MWCNTs and HOME+50SILVER blends, due to shortened ignition delay of HOME+50GRAPHENE blended fuel. The typical ignition delay values for the biodiesel and nano-biodiesel blended fuels vary from 12 to 14°CA.

6.3 Hydrocarbons

Figure 6 shows the variation of Hydrocarbon emissions from the engine when fuelled with HOME and different nanoparticles blended fuels. Nanoparticles act as oxidation catalyst and lowers the carbon combustion activation temperature and thereby enhances hydrocarbon oxidation, promoting complete combustion. Thus HC emission for HOME operation is higher compared to that of HOME+Nanoparticles blended fuels. Lower thermal efficiency of the HOME operation with incomplete combustion resulted in the observed trend. However HC emissions were marginally lower for the HOME+50GRAPHENE blended fuel than HOME+50MWCNTs and HOME+50SILVER blended fuels. This could be due to higher catalytic activity and improved combustion characteristics of HOME+50GRAPHENE blended fuel, which leads to improved combustion.

Fig. 5: Variation of Smoke opacity with Brake power
Figure 7 shows the variation of Carbon monoxide for different nanoparticle-biodiesel blended fuels. The CO emissions for HOME were higher compared to the HOME-Nano particle blended fuels. This could be due to their lower brake thermal efficiency as reported in Fig. 4 resulting in incomplete combustion. However CO emissions were marginally lower for the HOME+50GRAPHENE nanoparticles blended fuels compared to other nanoparticle biodiesel blended fuels (HOME+50MWCNTs and HOME+50SILVER). This could be due to the higher catalytic activity and improved combustion characteristics of HOME+50GRAPHENE blended fuels with improved combustion that resulted in better performance. Graphene nanoparticles have higher thermal conductivity; higher surface area for catalytic activity and showed better results as compared to the HOME+50MWCNTs and HOME+50SILVER blended fuels. The CO emissions associated with diesel fuel operation were lower than the biodiesel and nano-biodiesel blended fuels.

Figure 8 below shows variation of NOx for HOME-nanoparticles blended fuels. HOME showed higher NOx emissions compared to HOME-nanoparticles blended fuels. This could be due to lower heat release rates of HOME during premixed combustion phase, which lead to lower peak temperatures. The complete combustion may lead to increased temperatures inside the combustion chamber, with higher NOx formation. Furthermore, HOME+50GRAPHENE blended fuels produced higher NOx emission compared to that of HOME+50MWCNTs and HOME+50SILVER.
blended fuels. This due to their higher premixed combustion heat release rates and complete combustion being observed with HOME+50GRAPHENE blends. The premixed combustion phase refers to the start of combustion to the maximum pressure rise or heat release rate and is clearly seen in Figs. 9 and 10.

6.6 Cylinder pressure

Figure 9 shows the variation in pressure with crank angle for HOME-nanoparticle blended fuels. Combustion started later with biodiesel-nano-particle blended fuels in comparison to diesel. Increased catalytic activity observed with nano-particle blended biodiesel fuels resulted in reduced delay period with combustion starting earlier as well. HOME being common the properties of the nano-particles added to biodiesel resulted in the observed behaviour. Accordingly, graphene nano-particles have higher thermal conductivity and increased catalytic activity resulted in higher peak pressure.

Fig. 9: Variation of cylinder pressure with crank angle for 80% load

6.7 Heat release rate

Figure 10 shows heat release rate variation with crank angle at 80% load for nano-particle biodiesel fuel blends. It follows that for biodiesel a shorter premixed heat-release portion occurs, in spite of their increased ignition delay. The heat release rate for HOME- nano-particle blends was lower compared to diesel operation. The reduced heat release rate during premixed combustion phase and increased heat release rate were observed during diffusion combustion phase for both HOME and HOME-nano-particle blends. This leads to increased exhaust gas temperature. With blend of graphene and MWCNTs nanoparticles in HOME premixed combustion increased compared to HOME due to their increased catalytic activity, thermal conductivity and surface area. However increased catalytic activity observed with silver nano-particle blended biodiesel resulted in higher delay period with lower heat release rates. With the introduction of solid non-vaporizing particles of graphene, silver and MWCNTs into the cylinder the heat transfer physics within the cylinder would change definitely as is evident from higher peak pressure reported in Figures 9 and 10. Pure carbon is combustible; the reaction of C and O$_2$ to form either CO or CO$_2$ is relatively straightforward. The extra available carbon in the combustion chamber might cause certain reactions to be favoured over others.

Fig. 10: Variation of heat release rate with crank angle for 80% load

7. Conclusions

From the exhaustive experimental investigation carried out on diesel engine fueled with graphene, MWCNTs and silver nanoparticles– HOME, the following conclusions were made.
1. Use of HOME in diesel engine provides complete independence from petroleum fuel resources. HOME shows poor results in terms of reduced brake thermal efficiency, and increased emission of smoke, Hydrocarbons and carbon monoxides.

2. Addition of Graphene, MWCNTs and silver nanoparticles to HOME enhances the combustion characteristics and catalytic activity of the fuel, and thereby reduces the emissions and ignition delay during combustion process.

3. HOME+50GRAPHENE blended fuel shows better results as compared to the HOME+50MWCNTs and HOME+50SILVER blended fuel in terms of increased Brake thermal efficiency and reduced emission of smoke, Hydrocarbons, carbon monoxide.

4. Nitric oxide emissions of HOME were lower compared to HOME+GRAPHENE, HOME+MWCNTs and HOME+SILVER blended fuel. On the closure it can be concluded that higher dosage of nanoparticle addition i.e. more than 50 ppm to biodiesel could further improve the diesel engine performance. For this research on improved dispersion techniques of nanoparticles in liquid fuel needs to be undertaken.

8. References


