ORIGIONAL ARTICLE

Impact of antioxidants on NO$_x$ emissions from a mango seed biodiesel powered DI diesel engine

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KEYWORDS
Mango seed oil; Antioxidant; Engine emissions; Biodiesel; NO$_x$ emission

Abstract
The uses of biodiesel in diesel engines result in reduction of exhaust emissions, though many researchers described that the biodiesel produces higher NO$_x$ emissions than diesel, which is detract from the inflation of the market for these fuels. The aim of the present study was to analyze the experimental exploration of the three antioxidants DEA (Di-Ethyl Amine), PHC (Pyridoxine Hydro Chloride) and TBHQ (Tert Butyl Hydro Quinone) on engine emission and performance of a single cylinder diesel engine fueled with methyl ester of mango seed. The experiment is conducted with different antioxidant concentrations of mango seed methyl ester mixtures (100, 250, 500 and 1000 ppm). The results exhibited that PHC is effectual in controlling NO$_x$ emissions than TBHQ and DEA.

1. Introduction

Eloquent population growth and modification in lifestyles are resulting in increased energy consumption. The electricity generation and transportation sectors are the main consumers of energy. The diesel engine plays an indispensable part of both of these sectors throughout the world. The diesel fuel has protein requisition because of its high fuel efficiency over gasoline [1]. There is prominent interest in worldwide for the replacement of diesel fuel by biodiesel in order to minimize the harmful diesel exhaust emissions from engines. Nevertheless, the biodiesel results in a recognizable increase (10%) in NO$_x$ emissions when compared to diesel [2]. NO$_x$ causes human health and also affects the environment resulting ground level ozone forming potential [3]. There is less research conducted on biodiesel NO$_x$ emissions compared to diesel NO$_x$ emissions. Biodiesel is elucidated as mono-alkyl esters of long-chain fatty acids prepared from plant oils, animal fats and other lipids. The biodiesel has much advantage over diesel fuel. i.e., superior lubricity and biodegradability, lower toxicity, no sulfur or aromatic content, positive energy balance and reduced emissions. On the contrary, biodiesel has higher level of olefinic compounds, which can be corrosive and attributed to the presence of oxygen moieties, increased polarity of biodiesel and auto-oxidation [4]. Besides the criterion for formation of NO$_x$ is highly dependent upon the chemical and physical properties of fuel (cetane number, bulk modulus, iodine number, fatty acid composition, density, aromatic contents etc.), pressure and temperature of inlet air, fuel injection advance, fuel/air equivalence ratio, compression ratio, and percentage of waste gas in fresh inlet air [5]. Biodiesel degenerates mainly owing to its auto-oxidation in the presence of atmospheric oxygen. One practical solution is to resist the biodiesel against
auto-oxidation without modifying the fuel properties to treat them with antioxidants [6]. The antioxidants considerably slow down the biodiesel degradation process. According to the mode of action, antioxidants are differentiated as follows: free radical terminators, metal-ion chelators or oxygen scavengers. Free radical terminators are primary antioxidants. They donate one or more of an electron (or) hydrogen atom ($\text{RO}^-$) to a free radical derivative. The primary antioxidants combine with peroxy radicals and break the auto-catalytic cycle. The secondary antioxidants are peroxide decomposers. It is implemented by removing the oxidative catalyst and prevents the initiation of oxidation. Both phenolic and amine antioxidants are generally used antioxidants [7].

$$\text{ROO}^- + \text{AH} \rightarrow \text{ROOH} + \text{A}^-$$  
(1)

$$\text{RO}^- + \text{AH} \rightarrow \text{ROH} + \text{A}^-$$  
(2)

Antioxidants are added to oxidizable organic materials to retard oxidation and to prolong the useful life of the substrates [8]. Typically, the mixture of antioxidant and biodiesel fuel conquers the peroxy free radical formations by reaction with aromatic amines. These peroxy free radical formations are the focal source for the higher biodiesel NO$_x$ emissions. A free radical is the unpaired electron of a molecule which regulates the oxidation reaction rate [9]. The term ‘stabilization factor’ denotes the effectiveness of antioxidant and it is expressed as $F = \frac{IP_{o}}{IP_{x}}$, where, $IP_{o}$ is the induction period in the presence of the antioxidant and $IP_{x}$ is the induction period in its absence. Hess et al. [10] narrated the effect of antioxidant additives to 20% soy biodiesel on NO$_x$ emissions and found that the NO$_x$ was reduced by the addition of BHT (Butylated Hydroxy Toluene) and BHA (Butylated Hydroxy Anisole). Ryu [11] described the effect of antioxidant addition to soybean biodiesel. Tert-butyl hydroquinone (TBHQ) was the best antioxidant among the free antioxidants tested. There was no change in smoke, HC (or) NO$_x$ compared to the diesel fuel with TBHQ. Kivevele et al. [12] evaluated that biodiesel dosed antioxidant PY showed a lower BSFC compared to the stabilized biodiesel, but little effect on CO, HC and NO$_x$ emissions. Varatharajan and Cheralathan [13] studied the impact of antioxidants on NO$_x$ emissions of jatropha biodiesel containing 0.025%-m (0.025%-molar concentration) of the additives a-tocopherol acetate, BHA, BHT, l-ascorbic acid and p-phenylenediamine reduced the maximum of 43.55% compared to the neat biodiesel in NO$_x$ emissions. In another paper, Varatharajan and Cheralathan [14] investigated the effect of two aromatic amine antioxidants [N,N-diphenyl-1, 4-phenylenediamine (DPPD) and N-phenyl-1,4-phenylenediamine (NPPD)] added to soybean biodiesel. They found a 9.35% reduction of NO$_x$ emission with a forfeiture of 9.09% and 10.52% increases in CO and HC emissions. Ileri and Kocar [15] defined the effect of addition of four antioxidants with different concentrations (500, 750 and 1000 ppm) to 20% canola biodiesel in a turbocharged direct injection (TDI) diesel engine. They established that 2-Ethyl Hexyl Nitrate (EHN) reduces NO$_x$ emission adequately (4.63%) due to the presence of nitrogen present in the antioxidant. Increasing the concentrations with EHN resulted in lowering NO$_x$ emissions, but the opposite effect was observed with BHT. They also initiated increasing observed reduction of BSFC with TBHQ antioxidant. Gan and Ng. [16] examined the prospective of biodiesel with antioxidants as an alternative fuel in non-pressurized, water-cooled combustion chamber. Butylated hydroxy anisole (BHA), butylated hydroxy toluene (BHT) and tert-butyl hydro quinone (TBHQ) are mixed with different concentrations (250, 500, 750 and 1000 ppm) in B10 and B20 fuel blends for exhaust emission tests. They ramificated that BHA is a promising antioxidant for decreasing NO and CO concurrently in the combustion of biodiesel blends. TBHQ is also competent of limiting NO formation but at the expenditure of higher degree of incomplete combustion. The objective of this study is to investigate the NO$_x$ fueled with mango seed biodiesel blends. The antioxidant additives are chosen based on the cost, availability and effectiveness, using the optimized concentration designated from the previous work. All the additives are purchased from Lab chemicals at Chennai, India.

2. Experimental setup

Experiments are carried out in a single-cylinder, water-cooled, naturally aspirated direct injection diesel engine of 5.9 KW rated power coupled with an eddy current dynamometer. The schematic diagram of the experimental setup is shown in the Fig. 1. An eddy current dynamometer coupled to the engine is used as a loading device. The engine has hemispherical combustion chamber, with over head valve arrangements operated by push rods. The load can be increased or decreased on the dynamometer, by switching on or off the load resistances. The energy assimilated by the dynamometer is dematerialized by a resistor bank. The engine can be loaded by introducing an electric current into the dynamometer. This current relinquishes the dynamometer resistance to spinning. The engine remunerates by adding more fuel to increase the power. The power developed by the engine is to overcome the resistance from the dynamometer and retain a set speed on the engine controller. The water required for engine cooling is supplied from an over head cooling water tank. The engine is loaded by introducing an electric current into the dynamometer. Fuel consumption is measured with the help of a sensor and data acquisition system. Fuel consumption is measured manually with the help of a digital stopwatch and burette. The fuel from the tank is furnished to the engine through a graduated burette, using a two-way valve. The fuel embraced in the burette is supplied to the engine, when the valve is set in a position the fuel, is sent to the engine directly. The fuel flow rate of the engine can be measured, when the valve is set at position and the time for 10 cc of fuel consumption is noted. The air flow to the engine is dispatched to through the cubical air tank. The air tank consummates the purpose of regulating the flow of air to the tank. The inlet of the air tank is contributed with an orifice, and the air flow rate is measured using the mass air flow sensor. The specification of test engine and the dynamometer details are listed in Table 1 and 2 respectively. The engine crank angle can be measured by a 11 bit 2050 step crank angle encoder which is mounted on the cam shaft. The position of top dead center (TDC) can be sensed by a crank angle encoder with TDC. The output from the crank angle encoder and pressure transducer is connected to a charge amplifier. The thermocouples are contributed for the necessary measurement of temperature at different locations. The engine is instrumented with a piezoelectric transducer to measure the combustion process. The non-contact proximity sensor is employed to measure the speed.
of the engine. The AVL Di Gas 444 gas analyser and the automatic NETEL NPM CH 1 smoke meter probes are inserted into engine exhaust tube. Exhaust emissions are measured with a NDIR (Non-Dispersive Infrared) based AVL Di Gas 444 gas analyser. The constituents present in the exhaust gas are hydrocarbon (HC), NO\textsubscript{x} in parts per million and carbon monoxide, carbon dioxide and oxygen in percentage volume will be displayed in the digital gas analyser. The analyser provided a CO measurement range of 0–20% by volume with a resolution of 0.01%, NO\textsubscript{x} range of 0–5000 ppm with a resolution of 1 ppm and HC range of 0–20,000 ppm with a resolution of 1 ppm. The instrument range and accuracy are represented in Table 3. The experiments are conducted with different antioxidant concentrations of biodiesel fuel mixtures (100, 250, 500 and 1000 ppm) in addition to neat biodiesel and diesel fuel. The antioxidant additives PHC, DEA and TBHQ are accurately weighed using a high-precision electronic weighing balance and added to measure quantity of mango seed biodiesel. To make 100 ppm of antioxidant mixture 100 mg of the antioxidant is added to 1 l of the biodiesel. A 3000 rpm speed mixer is used to prepare a homogenous mixture of the antioxidant and fuel. The instrument used uncertainty is illustrated in Table 4. Before taking the emission test, a leak check has to be conducted in the gas analyser. The purpose of the leak check is to discharge the residual gases through the gas analyser’s exhaust tube. AVL smoke meter is employed to measure the smoke intensity and it works based on the principle of absorption/obscuration of light. A green LED driven by a pulsating constant source emits a light beam having peak spectral intensity between 550 and 570 mm wavelengths. The beam elapses through a smoke cell and onto a silicon photo detector which continuously senses the intensity of light incident on it, and transforms it onto an electric signal, and that is operated by precise signal handling circuits. The properties of tested fuel and antioxidants are listed in Table 5 and 6 consequently. In each load levels, the measurements of fuel pressure, fuel consumption, coolant temperature, exhaust flow rate, exhaust gas temperature, NO, HC, CO and smoke emissions are recorded and carried out.

3. Results and discussion

The effect of antioxidant additives on NO, HC, CO and smoke intensity is investigated in this study. The exhaust emissions of

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Table 1 Specification of the engine.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Parameters</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Make</td>
<td>Kirloskar</td>
</tr>
<tr>
<td>2.</td>
<td>General details</td>
<td>Single cylinder, four stroke, water cooled, port injection</td>
</tr>
<tr>
<td>3.</td>
<td>Bore</td>
<td>87.5 mm</td>
</tr>
<tr>
<td>4.</td>
<td>Stroke</td>
<td>110 mm</td>
</tr>
<tr>
<td>5.</td>
<td>Cubic capacity</td>
<td>0.661 lit</td>
</tr>
<tr>
<td>6.</td>
<td>Rated output</td>
<td>5.9 kW at 1800 rpm</td>
</tr>
<tr>
<td>7.</td>
<td>Compression ratio</td>
<td>17.5:1</td>
</tr>
<tr>
<td>8.</td>
<td>Inlet valve open BTDC</td>
<td>4.5 Deg.</td>
</tr>
<tr>
<td>9.</td>
<td>Inlet valve close ABDC</td>
<td>35.5 Deg.</td>
</tr>
<tr>
<td>10.</td>
<td>Exhaust valve open BBDC</td>
<td>35.5 Deg.</td>
</tr>
</tbody>
</table>

Table 2 Details of the dynamometer.

<table>
<thead>
<tr>
<th>Make</th>
<th>SAJ Test plant Pvt. Ltd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rating</td>
<td>11 kW</td>
</tr>
<tr>
<td>Speed</td>
<td>9000 rpm</td>
</tr>
<tr>
<td>Torque</td>
<td>50 N m</td>
</tr>
<tr>
<td>Type</td>
<td>Eddy current</td>
</tr>
<tr>
<td>Effective radius of arm</td>
<td>0.5 m</td>
</tr>
</tbody>
</table>
engine are influenced by the addition of antioxidants with biodiesel. The performances and emissions of antioxidant mixtures and neat biodiesel are discussed in this section.

3.1. Effects of NO emissions

NO$_x$ is the most detrimental pollutant at the combustion stage. It is very familiar that the higher combustion temperature, longer combustion duration inside the combustion chamber and ample local oxygen concentration are the main factors for NO$_x$ formation [17]. Figs. 2 and 3 indicate the NO reduction percent of different antioxidant concentrations relative to B100 and B20 fuel at full load (5.9 KW), 80% load (4.72 KW), 60% load (3.54 KW), 40% load (2.36 KW) and 20% load (1.18 KW) respectively. Antioxidant addition to the B20 fuel reduces up to 80% load (6.53%) and then it starts increasing, and for B100 fuel the NO emission reduction increase linearly with the concentrations.

The antioxidant activity is defined by the ration $F/\ln[H]$, where $F$ is the antioxidant activity and $\ln[H]$ is the acceptor reacting with alkoxyl and peroxyl radicals [18]. The antioxidant activity does not depend on the antioxidant concentration. For B100 fuel, we found 18.19%, 14.4% and 16.3% reduction in emission respectively, when the fuel is loaded with PHC, TBHQ and DEA respectively. PHC is the most effective antioxidant, giving more than 20% decrease in measured NO emissions at all engine loads. For B20 fuel, the NO produced by PHC additive and base fuel at 80% load is 2.19 and 2.30 g/kw hr respectively. For B100 fuel the NO emissions are 4.14 and 2.92 g/kw hr respectively. As shown in Fig. 4 biodiesel fuel emits more NO than the conventional diesel fuel.

Fennimore mechanism [19] illustrates that NO formation is initiated by reactions of hydrocarbon radicals [CH, CH$_2$, C2, C and C$_2$H] with molecular nitrogen. Brezinsky et al. [14] derived increased formation of CH radicals during biodiesel combustion leads to increased NO$_x$ formation for biodiesel fuel. The similar result is obtained by Dunn [20] and he perceived increased antioxidant activity (less than 1000 ppm) at lower loadings and constant or decreased antioxidant activity at higher loadings.
3.2. Effects of CO and HC emissions

Carbon monoxide is generated due to the absence of fuel-borne oxygen in their molecular structure. The effect of antioxidant additives with biodiesel fuels on CO emissions is shown in Fig. 5. CO is generally configured during combustion, whenever charge is burned with an insufficient air supply with low flame temperature [21]. It is seen that CO emission increases with the increase in antioxidants. The increase in CO emission can be described by the hindrance formed by the antioxidants through the conversion of CO to CO$_2$. At 80% load, the PHC additive has about 7.94% and 14.44% more CO emissions than the neat B20 fuel and neat biodiesel respectively. But, the CO emission with the addition of antioxidant is well below than the petro-diesel.

The two major causes of HC emissions in diesel engines are (i) mixing of fuel-fuel is leaner than the lean combustion limit during the delay period and (ii) under mixing of fuel-fuel leaves the fuel injector nozzle late in the combustion process at low velocity [22]. Fig. 6 illustrates the effect of antioxidant additives with biodiesel fuels on HC emissions. HC emission increases with the addition of antioxidant, but it is lower than petro-diesel. At 80% load the increase in HC emissions for B20 and B100 fuels is 6.94% and 12.35% respectively. Peroxyl (HO$_2$) and hydrogen peroxide (H$_2$O$_2$) radicals are formed during oxidation and it is converted into hydroxyl (OH) radicals by absorbing heat (Eqs. (3) and (4)).

\[
\text{H}_2\text{O}_2 \rightarrow 2\text{OH} \quad (3)
\]
\[
\text{HO}_2 \rightarrow \text{OH} + \text{O} \quad (4)
\]
Figure 3  Effect of antioxidant additives on NO\textsubscript{x} emissions for B100 fuel.

Figure 4  Variation of NO with brake power.

Figure 5  Effect of antioxidant additives with biodiesel fuels on CO emissions.
The antioxidant reduces the concentration of peroxyl and hydrogen peroxide radicals. The increase in HC emission is due to the reduction in free radicals and has a significant effect on the formation of OH radicals and the oxidation of CO and HC [23].

3.3. Effects on smoke emissions

The effect of antioxidant additives with biodiesel fuels on smoke emissions is shown in Fig. 7. The PHC additive increased the smoke by 10.4% and 8.2% when compared with the B20 and B100 fuels respectively for 80% load conditions. But, the increase in smoke emissions is well below than the diesel level. This increase in smoke level may be the reduction of oxygen availability, increase of C–C bonds and increase in aromatic content due to the antioxidant addition.

3.4. Effects on brake thermal efficiency

The variation of brake thermal efficiency with different loads for the antioxidant fuel mixture is shown in Fig. 8. At full load, efficiencies are slightly lower than the neat biodiesel, but at part loads change in brake thermal efficiencies are indistin-

4. Conclusions

The aim of this experimental work was to investigate the effect of antioxidants on engine out NOx emission from mango seed biodiesel fueled DI diesel engine. From the experimental observation, the following conclusion can be drawn.

(1) The antioxidants and biodiesel mixtures reduced the nitrogen oxides. Among the antioxidants tested, the phenolic derived additive Pyridoxine Hydro Chloride (PHC) delivered highest reducing activity of NO emissions compared to the DEA and TBHQ antioxidant additives. At 80% load, the maximum NOx reducing activity for B20 fuel was 18.19% and B + 250 ppm of PHC produced the lowest NOx emissions.

(2) Prompt NO could be the major reason for the biodiesel NOx effect. To control the prompt NO modification in the engine design and minimize the formation of sub-stoichiometric regions within the flame could be done.

(3) The antioxidant mixtures produced slightly higher CO and HC emissions. The PHC additive of 250 ppm delivered higher CO emission about 7.94% for B20 fuel and 14.44% for B100 fuel. The HC emission is increased about 6.94% for B20 + 250 ppm of PHC fuel and 12.35% for B100 + 250 ppm of PHC fuel. This increase in CO and HC emissions is more prominent in B20s, because they possess less fuel–borne oxygen than B100s.

(4) Smoke also slightly increased with the addition of antioxidants owing to the reduction in oxidative free-radical formation. But, these emissions are well lower than the diesel emission levels.

(5) The brake thermal efficiency with antioxidant is found to be insignificant. Moreover, slight reduction in BTE (0.6%) is observed at full load of the antioxidant mixtures. This reduction in brake thermal efficiency can be attributed to the combined effect of their lower heating value and higher viscosity.

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References


