Effect of antioxidants on the performance and emission characteristics of a diesel engine fuelled by waste cooking sunflower methyl ester

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Abstract. Biodiesel is a renewable, biodegradable fuel produced from vegetable oils and animal fats. Nonetheless, its extensive utilization is impeded by the auto-oxidation resulting in degradation of the fuel. Adding antioxidants to the biodiesel is a potential solution, but it might have an effect on the clean-burning characteristics of the fuel. This paper investigates the effect of antioxidants on the performance and emission characteristics of a diesel engine fuelled by the waste cooking sunflower methyl ester. The fuel samples tested include B10, B20, B30 and B40, among which B20 produced the best possible results. Antioxidants 2, 6-ditert-butyl-4-methylphenol (BHA) and 2(3)-tert-butyl-4-methoxy phenol (BHT) of two concentrations 1000 ppm, 2000 ppm were added to B20 to evaluate the effectiveness. B20BHA1000 had the best effect with an average decrease of 5.035%, 2.02% in brake specific fuel consumption (BSFC) and exhaust gas temperature (EGT) compared to B20. Regarding the emission characteristics it was observed that B20BHA1000 had produced an increase of 7.21%, 27.79% in NOx and smoke emissions and a decrease of 33.33% in HC emissions when compared to B20. On the whole, without any requirement of alteration in the diesel engines, B20 blends with antioxidant can be utilized as fuel.

Keywords: Antioxidants, Biodiesel, Emission, Performance, Diesel.

1. Introduction
Biodiesel production and demand is gaining acceptance off late as an outcome of the ever increasing consumption of energy in electricity generation and transportation sector, exhaustion of fossil sources, environmental deterioration and the emission limitations lay down by various environmental agencies across the globe. It is anticipated that world’s biodiesel production will reach 41917.17 million litres by 2020 according to the OECD–FAO [1]. Biodiesel can be termed as a non-petroleum based diesel fuel that is built with mono-alkyl esters of long chain fatty acids. Over the years the feed stock primarily
utilized for its production was animal fats and vegetable oils. The generated fuel must comply with ASTM D6571 stipulations for it to be employed in diesel engines. Currently, feedstock predominantly used for the production of biodiesel is the waste cooking oil that is collected from various restaurants, industrial food producers etc. Despite the fact that production of feedstock i.e., raw oil employing agricultural practices is the greatest potential source, it is simply too expensive. Adding to this production of feedstock, conversion cost (raw oil to biodiesel) also comes into picture so, it is economically not viable to compete against diesel and replace it as its substitute. To overcome this problem waste cooking oil which is already used for cooking can be procured for free of cost or at a cheaper rate resulting in cost control [2].

Biodiesel possess certain advantages over petroleum diesel which include derivation from renewable source, biodegradability, improved flash point, less toxicity and free of aromatic and sulfur content [3-5]. Keeping aside these advantages, there are quite a number of disadvantages that need to be addressed. The important ones are the long term thermal stability and the low temperature flow properties. When it is stored for longer periods, maintenance of quality is significantly problematic as a result of its low cold filter plugging point. Air, fuel composition and storage conditions results in auto-oxidation which deteriorates the fuel properties [6].

In this work biodiesel production from waste cooking sunflower oil using alkali-catalyzed transesterification and determination of its fuel properties was done. An experimental investigation to find out the best possible biodiesel percentage in the blends was carried out. In addition to that an experimental study to analyse the effect of antioxidants BHA, BHT on the performance and emission characteristics of a diesel engine was also conducted.

Quite a few researchers have conducted investigations on the possibility of waste cooking sunflower methyl ester as a substitute to diesel in CI engines by carrying out the performance, emission and combustion tests. Bjorn S. Santos et al. (7) carried out a performance evaluation and emission analysis on two diesel engines employed with sunflower methyl ester (SFME) as engine fuel. It was observed that when the engine was fuelled with 100% SFME, there was a loss in the power and torque delivery whereas BSFC was greater. B5 and B20 exhibited minor loss of power but identical BSFC with respect to diesel. The CO emissions were on the lower side whereas the NOx, CO2 and HC concentrations were higher for both 100% SFME and SFME-diesel fuel blends. Sudhir Ghai et al. (8) has done an investigative study analysing the performance and emission characteristics with SFME as fuel. Regarding the performance characteristics an increase of 1.5-4% in BTE and identical BP were observed with the blends of SFME. In relation to emissions, HC and smoke opacity values were reduced because of the inbuilt oxygen in the biodiesel. Higher NOx emissions were produced as a result of higher temperatures during combustion in diffusion phase and as the biodiesel is sulfur free there was no SOx emission. F. Moreno et al [9] evaluated the possibility of SFME as a fuel for CI engines. It was concluded that blends B25 and B50 produced the optimum performance results with torque, power delivery almost similar and BSFC values slightly higher, compared with diesel. Pertaining emissions, B25 and B50 produced lesser HC, CO concentrations than of diesel. It was also observed that the NOx emission values were little less to that of pure diesel.

Varatharajan et al. (10) had done an investigative study to know antioxidants effect on NOx emission of diesel-jatropha blends. Biodiesel treated with 0.025%–m level of p-phenylenediamine produced best emission results and an average reduction in NOx by 43.55%. The addition of antioxidants improved HC and CO emissions when scrutinized against pure biodiesel and blends. α–tocopherol, L-ascorbic acid and BHT produced an increase in BSFC but ethylenediamine and p-phenylenediamine produced a reduction compared to pure biodiesel.

Erol Ileri et al. (11) conducted an investigation to study the effect of antioxidants 2-Ethyl Hexyl Nitrate EHN), Tert-Butyl Hydro Quinone (TBHQ), Butylated Hydroxy Toluene (BHT) and Butylated Hydroxy Anisole (BHA) on the engine’s performance and exhaust emission values employed with canola-diesel blends. With respect to BSFC, 1000ppm of TBHQ produced optimum result with a reduction of 10.19% on comparison with fuel sample without antioxidants. B20 along with EHN produced the best average NOx with a decrease of 4.63%. Regarding the NOx emissions, the
antioxidants efficacy was in the sequence of EHN > BHT > BHA. Contradictory behaviour was shown by the TBHQ additive. However, treating B20 with antioxidants caused an increase in CO value.

Thomas T. Kivevele et al. (12) conducted an investigative study to find out the influence of antioxidants on biodiesel storage stability, combustion, emissions and performance characteristics. According to the results, antioxidants efficacy was in the sequence of (Pyrogallol, PY) > (Propyl Gallate, PG) > (Butylated Hydroxyanisole, BHA). Treating biodiesel with antioxidants caused a reduction in BSFC and BTE. Effect of antioxidants on emissions as well as combustion characteristics of the engine running on biodiesel was minimal.

2. Materials and methods

2.1 Biodiesel production

Biodiesel from waste cooking sunflower oil was produced by using the alkali-catalyzed transesterification process. The waste cooking sunflower oil was heated to a temperature of around 60°C and while doing so methanol (25% v/v oil) and 1% (w/w oil) potassium hydroxide (KOH) were mixed together. As soon as the temperature of waste cooking sunflower oil reached 60°C, the methanol and KOH mixture was made to react with waste cooking sunflower oil with temperature being maintained around 60°C for 2 hours and stirring speed at 1500 rpm which results in the formation of biodiesel. The produced biodiesel was then transferred into a separation funnel where it was kept stagnant for 5-6 hours so that the glycerine which is denser than biodiesel gets settled at the bottom. The lower layer, which included glycerine and various impurities was then drawn off. Biodiesel was later washed with pure water to remove any traces of remaining glycerine and impurities by heating it at 60°C. As done previously the bottom layer which included water and impurities was drawn off. It was done till the biodiesel obtained a neutral pH of 7. At the end of the process, biodiesel was heated to 100°C to remove any water and excess alcohol.

2.2 Experimental setup

The investigative study was carried out on a 5.5 kW GREAVES GL-400 single cylinder, four stroke, direct injection diesel engine. The engine was coupled to a 50kW eddy current dynamometer. The engine throttling and the dynamometer settings were operated by using a load cell connected to the dynamometer. K type thermocouple was utilized to measure exhaust temperature. The fuel tank was provided with a flow measurement system. The emissions of NOx, HC and CO2 emissions were measured using AVL-MEXA 584L five gas emission analyser and the smoke emissions measurement was done with the help of AVL 415S smoke meter.

2.3 Experimental procedure

After achieving steady working state the diesel fuel was replaced with fuel sample to be tested and the return line was disconnected while doing so to drain the diesel fuel. After running the engine for few minutes to make sure any diesel traces are completely removed the fuel consumption rate was measured. Engine’s operating was 2300 rpm whereas the load conditions varied from zero to full load condition with an increase of 25% every single time. A load cell linked to the eddy current dynamometer was employed to alter the load condition. The same procedure was repeated for all the remaining fuel samples without antioxidants (B10, B20, B30 and B40 and fuel samples with antioxidants (B20BHA1000, B20BHA2000, B20BHT1000 and B20BHT2000). For accurate, reliable readings the performance and emission tests were performed three times.

The engine specifications used for the investigative study are given in Table 1. The properties of the fuel are tabulated in Table 2.
Table 1. Engine Specifications.

| Parameter                      | Specification          |
|--------------------------------|------------------------|
| Model                          | Greaves GL-400         |
| Maximum engine output (kW @rpm)| 5.5 kW @3600 rpm       |
| Stroke                         | 86 mm                  |
| Bore                           | 63 mm                  |
| Displacement                   | 395 cm³                |
| Compression ratio              | 18:1                   |

Table 2. Properties of fuels.

| Properties                               | Diesel | WSME |
|------------------------------------------|--------|------|
| Density (kg/m³)                           | 820    | 878  |
| Calorific value (kJ/kg)                   | 44800  | 38200|
| Cetane Number                            | 49     | 54.4 |
| Kinematic viscosity (mm²/s) (40°C)        | 2.3    | 4.1  |
| Flash point (°C)                          | 46     | 191  |
| Fire point (°C)                           | 52     | 197  |
| Oxidation stability (hours) (ASTM D2274)  | 16     | -    |
| Acid Number (mg KOH/g)                    | 0.04   | 0.19 |

Figure 1 Schematic diagram of test setup

Components: 1. Test rig 2. Emission analyser 3. Smoke meter 4. Exhaust probe 5. Engine 6. Coupling 7. Dynamometer 8. Dynamometer control panel 9. Measuring burette 10. Fuel tank
3. Results and discussions

3.1. Brake specific fuel consumption (bsfc)

Figure 2 indicates the variation in brake specific fuel consumption (BSFC) of biodiesel blends (B10, B20, B30 and B40) at load conditions starting from zero to full load condition with a step of 25% increase. It was seen that as the load increased, quantity of fuel necessary to run the engine for each unit energy output reduces at higher loads [12]. Overall it was found that the BSFC for all biodiesel blends treated with antioxidants and without antioxidants have greater value with respect to diesel. This can attributed to lower heating value and higher density of the biodiesel blends [13, 14]. The average BSFC value of diesel was 0.2690 kg/kW-hr and that of blends were B10 (0.286 kg/kW-hr), B20 (0.297 kg/kW-hr), B30 (0.3188 kg/kW-hr) and B40 (0.3397 kg/kW-hr). From the figure 3 it can be seen that antioxidant addition (BHA, BHT) of two concentrations (1000, 2000 ppm) helped to improve the BSFC of B20. Among the two additives BHA1000 had the best effect with an average decrease of 5.035% compared to that of B20 without additive.

3.2 Exhaust temperature

Figures 4, 5 depict the variation in exhaust temperature of different biodiesel blends (B10, B20, B30 and B40) without antioxidants and (B20) with antioxidants against different load conditions. Exhaust temperature is a very good parameter for the indication of combustion temperature inside the cylinder which helps in understanding NOx emissions [15]. The reason for higher exhaust gas temperature may be the higher ignition delay and poor atomization which contributes to the presence of unburnt mixtures even in the diffusion combustion phase [16]. It is seen from figure 4 that there is just a slight difference in the exhaust gas temperature of pure diesel and various biodiesel blends at all loads. The peak value of exhaust temperature was found for B40 at full load. The maximum increase (10.61%) in exhaust temperature when compared with diesel was found for B40 at no load condition. Addition of BHA, BHT
Figure 4. Variation in EXHAUST TEMPERATURE of WSME blends without antioxidants

Figure 5. Variation in EXHAUST TEMPERATURE of B20 with antioxidants

Figure 6. Variation in NOx of WSME blends without antioxidants

Figure 7. Variation in NOx of B20 with antioxidants
**Figure 8.** Variation in HC of WSME blends without antioxidants

**Figure 9.** Variation in HC of B20 with antioxidants

**Figure 10.** Variation in SMOKE OPACITY of WSME Without antioxidants

**Figure 11.** Variation in SMOKE OPACITY of B20 with antioxidants
caused a decrease in the exhaust temperature when compared to that of without antioxidants. The highest decrease (3.22%) was found for B20BHA1000 when compared with B20 at no load and 25% load condition.

3.3 NOx emissions
Figures 6, 7 indicate the NOx emission variation of different test fuels without and with antioxidants. The most customary mechanisms put forth for the NOx formation were Zeldovich, Fenimore, N2O pathway, inbuilt nitrogen and NNH mechanism[10]. NOx is the primary detrimental emission that need to be administered right at the stage of combustion. It is well archived that increased temperature of combustion and prolonged duration of combustion in the chamber of combustion, adequate concentration of local oxygen and various others are the crucial factors in formation of NOx [17]. The NOx values for the biodiesel blends produced a mean increase of B10 (11.63%), B20 (15.76%), B30 (27.95%), B40 (29.5%) compared to that of diesel. Since biodiesel is oxygenated and endowed with a shorter ignition delay owing to greater CN, it is implied that the blends will steer to enhanced combustion and accordingly higher NOx emission [18]. Antioxidant incorporation to the blends has exhibited a positive impression on bringing down the value of NOx. Among the antioxidants tested, the best was BHA1000 producing a mean decrease of 9.45% relative to B20. BHT1000 also produced a mean decrease of of 7.21% with respect to B20. This phenomenon was also promoted by the lower EGT. It can also be implied that Fenimore mechanism of NOx formation was hindered by the phenolic hydroxyl groups of the antioxidants [19].

3.4 HC emissions
Figures 8, 9 depict the variation in HC emissions of different biodiesel blends (B10, B20, B30 and B40) without antioxidants and (B20) with antioxidants against different load conditions. It was observed that HC emissions increased as the load increased. When the load increased, to cope up with required power, A/F ratio lowers contributing to higher HC emissions. At every load condition, the HC emissions of all blends were less than that of diesel fuel. This can be attributed to fuel borne oxygen [20]. A mean decrease of 16.24%, 27.28%, 30.74% and 35.79% was observed for biodiesel blends B10, B20, B30 and B40 respectively, in comparison to diesel. A slight increase in the emission was seen with the inclusion of BHA, BHT. Treating B20 with BHA, BHT might have reduced the concentration of peroxyl and hydrogen peroxide radicals which imposes a notable influence on the emergence of OH radicals and oxidation of HC [21]. B20BHA1000 had the minimum average increase of about 16.658% when compared with B20

3.5 Smoke emissions
Figures 10, 11 depict the variation in smoke emissions of different biodiesel blends (B10, B20, B30 and B40) without antioxidants and (B20) with antioxidants against different load conditions. It was seen that with increase in load condition the smoke opacity increased. At higher loads A/F ratio decreases resulting in more amount of fuel injection causing incomplete combustion. The smoke opacity for biodiesel blends was found to be less than that of diesel because of the fuel borne oxygen in biodiesel [10]. The highest value of emission was recorded at full load conditions with highest for diesel and lowest for B40. With antioxidant addition the smoke emission values slightly increased when compared to that of without additive. B20BHA1000 had a maximum increase of 27.79% when compared to that of B20 at half load condition.

4. Conclusions
The primary objective of this investigation was to examine the implication of antioxidants usage on the diesel engines performance and emission characteristics run with WSME blends. Based on the results the subsequent conclusions are implied.
Among the blends tested (B10, B20, B30, and B40), B20 produced the best possible results based on the difference between amount of biodiesel percentage increase to the improvement in performance and emission results when compared with other blends.

Regarding BSFC, among the two additives (BHA, BHT), BHA1000 had the best effect with an average decrease of 5.035% compared to that of B20 without additive.

With respect to EGT the influence of antioxidants was found to be minimal.

Addition of antioxidants to biodiesel resulted in the reduction of NOx emissions. Among the antioxidants tested, the best was BHA1000 producing a mean decrease of 9.45% relative to B20.

For HC emissions, B20BHA1000 had the highest decrease of about 33.33% when compared to that of B20. This reduction was attributed to reduction in the peroxyl and hydrogen peroxide radicals which might have hindered the formation of OH radicals.

With antioxidant addition the smoke emission values slightly increased when compared to that of without additive. B20BHA1000 had a maximum increase of 27.79% when compared to that of B20 at half load condition.

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