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# Mitigation of $NO_x$ Emissions from Cotton Seed Oil Methyl Ester Fuelled Direct Injection CI Diesel Engine Using Antioxidant Additives

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**Abstract—***Biodiesel offers cleaner combustion than conventional diesel fuel including reduced particulate matter, carbon monoxide and unburned hydrocarbon emissions. However, several studies point to slight increase in NOx emissions (about 10 - 20%) for biodiesel fuel, compared with conventional diesel fuel. As the use of biodiesel has increased tremendously, the increase in NOx emissions could become a significant barrier to market expansion. For universal acceptance of biodiesel, it is desirable to reduce these NOx emissions, at least to levels observed with petro diesel combustion. Many researchers proposed some possible reasons for the increase of NOx in biodiesel fuel.Some studies have pointed out that the increased formation of prompt NOx is responsible for biodiesel NOx effect. The treatment of biodiesel with antioxidants is a promising approach, because it reduces the formation of hydrocarbon free radicals, which are responsible for prompt NOx production in the combustion process.*

## 1. INTRODUCTION

There is considerable interest worldwide in the replacement of petrodiesel by biodiesel in order to reduce the harmful diesel exhaust emissions fromengines. However, the use of biodiesel results in a noticeable increase (about 10%) in NOx emissions when compared to conventional diesel [1]. The biodiesel market in the US is expected to reach 6,453 million litres in 2020 and 45,291 million litres globally [2]. As a consequence, the increase in NOx emissions could become a significant barrier to biodiesel market expansion. The nitrogen oxide compounds not only have direct effects on human health, but also affect the environment and have ground level ozone-forming potential. When compared to diesel NOx, a relatively small amount of research has been conducted on biodiesel NOx emissions.

NOx is generated during combustion by three mechanisms: thermal, prompt, and fuel. High combustion temperature (1700 K) breaks the strong triple bond of nitrogen molecules and form highly reactive atomic nitrogen which reacts with oxygen and generates thermal NOx. According to prompt mechanism, formation of free radicals in the flame front of hydrocarbon flames leads to rapid production of NOx. The fuel NOx is formed by the reaction of nitrogen bound in the fuel with oxygen during combustion.

Thermal and prompt NOx are the dominant mechanisms in biodiesel fuelled engines since; biodiesel does not contain fuel-bound nitrogen. Many researchers proposed some possible reasons for the increase of NOx in biodiesel fuel; however, the exact cause of the biodiesel NOx effect is still under investigation. The National Renewable Energy Laboratory of USA (NREL) [3] has suggested that the increase in NOx is not driven by thermal NOx formation and therefore may involve some pre-combustion chemistry of hydrocarbon free radicals. This would result in an increased formation of prompt NOx. Thermal mechanism is largely unaffected by fuel chemistry, where as prompt mechanism is sensitive to free radical concentrations within the reaction zone.

Brezinsky et al. [4] have reported that the amount of acetylene production from the unsaturated constituents of biodiesel is the primary contribution to the increased NOx formation. The acetylene forms CH radical which is responsible for prompt NOx formation. Other authors concluded that the effect of biodiesel on NOx emissions is mainly due to elevated combustion temperature. Lin [5] suggested that the rich oxygen content of biodiesel leads to complete combustion but results in high combustion temperature and NOx formation. In contrast, Lu et al. [6] reported that port injection of oxygenated fuel ethanol in a biodiesel fuelled engine significantly reduces NOx. The advanced injection timing due to high bulk modulus of biodiesel, longer fuel penetration into the engine cylinder, decreased radiative heat transfer due to reduced soot formation, shorter ignition delay and higher heat release rate of biodiesel fuel are the other factors that influence the thermal NOx formation [7].

Knothe et al. [13] found more NOx emissions with biodiesel fuelled engine fitted with EGR (a method to reduce thermal

NO)when compared to conventional petro-diesel fuelled engine. This shows that thermal NO has less effect on biodiesel NOx emissions. Furthermore, Mueller et al. [5] concluded that changes in prompt NO formation may play an important role in biodiesel NOx effect. Recently, Somand Longman [14] of Argonne National Laboratory found higher prompt NO formation in biodiesel combustion.

CH and OH radicals are continuously formed during combustion reactions. The formation of CH radicals is an indicator of low temperature pre-combustion reactions and the formation of prompt NO. And the presence OH radicals indicate high temperature reactions and thermal NO [10]. Additions of small amounts of antioxidants into the fuel suppress free radical formation by reacting with peroxyl radicals to form new inactive radicals so interrupting the propagation step. The hydrogen donating ability of a chain breaking antioxidant has a very important effect on its antioxidant activity. The hydrogen is released from the weak OH (phenols, hydroquinones) and NH (aromatic amines, diamines) bonds of antioxidants. In general phenolic antioxidants (TBHQ, BHT, BHA etc.) are added to biodiesel to prevent degradation. They are so effective in controlling free radicals at room temperature but their antioxidant activity decreases rapidly with increasing temperature. The quantum-chemical study of an aromatic amine N, N′-diphenyl-p-phenylenediamine (DPPD) indicate that it retains itsantioxidant activity even at increased temperatures [11].

The purpose of this study was to evaluate the effects of N′-diphenyl-1,4-phenylenediamine(DPPD) antioxidant on NOx and other emissions of a DI diesel engine powered by Cotton seed oil methyl ester(CSOME).

**Table 1: Specifications of test fuels**

| Properties | CSOME | Diesel Indian oil |
|---|---|---|
| Density at 15 °C kg/m3 | 830 | 822 |
| Viscosity at 40 °C mm/s2 | 6.0 | 2.5 |
| Flash point °C | 110 | 66 |
| Pour point °C | 4 | 12 |
| Calorific value kJ/kg | 39600 | 43400 |
| Cetane number | 52 | 43 |

**Table 2: Specifications of test antioxidant**

| Antioxidant | Specifications | |
|---|---|---|
| N,N′-diphenyl 1,4phenylenediamine (DPPD) | CAS number<br>Molecular weight<br>Chemical formula<br>Melting point °C | 74-31-7<br>260.34<br>C18H16N2<br>144 |

The specifications of the test fuels and antioxidants and biodiesel are presented in Tables 1 and 2 respectively. The chemical structures of the antioxidant is given in Fig. 1. The antioxidant DPPD contains NH substituent.

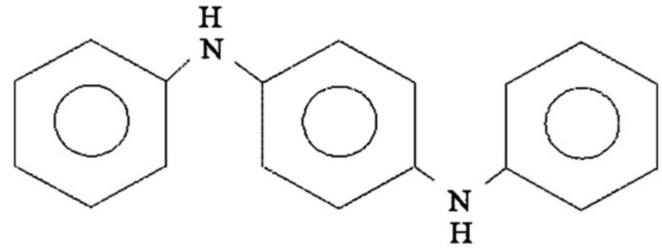


**Fig. 1: Fig. example.**

## 2. EXPERIMENT DETAILS

The engine used in the present study is the computerized Kirloskar-make 4 stroke water cooled single cylinder diesel engine of 5.2 kW rated power. The schematic diagram of the experimental setup is shown in Fig. 2. The engine was directly coupled to an eddy-current dynamometer equipped with a load controller. The fuel flow rate, speed, load, exhaust gas temperature and gas flow rate were displayed on a personal computer.

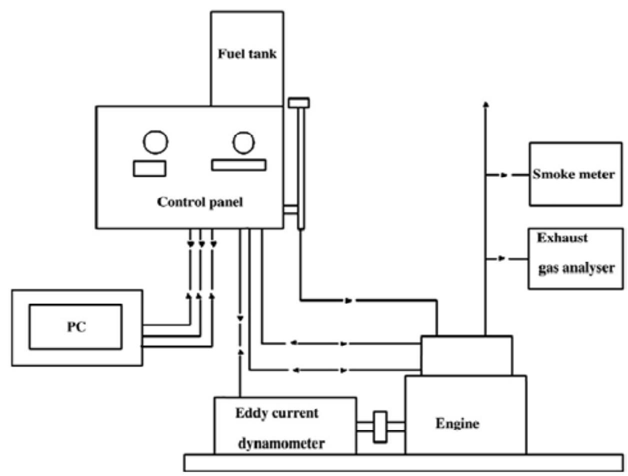



**Fig. 2: Schematic diagram of experimental setup**

The specifications of the engine are given in Table 3. The cylinder pressure was measured by a Piezo sensor of PCB Piezotronics Model M111A22 and the signal of the cylinder pressure was acquired for every 1°CA. Exhaust emissions were measured with an AVL DiGas 444 five gas analyser. The analyser provided a NO range of 0 to 5000 ppm with a resolution of 10 ppm, CO measurement range of 0% to 20% by volume with a resolution of 0.01%, and HC range of 0 to 20,000 ppm with a resolution of 10 ppm. The accuracy of the instrument is 10%, 5% and 0.5% of the indicated value for the measurement of NO, HC and CO respectively. As for smoke measurement, the automatic NETEL NPMCH1 smoke meter was employed. The smoke intensity was measured as light absorption coefficient (m−1). The display range, scale resolution, repeatability, response time and warm up time of smoke meter are 0–9.99 m−1, 0.01 m−1, 0.1m−1, 0.3 s and 3 minutes respectively.

**Table 3: Specifications of test engine.**

| Parameter | Specification |
|---|---|
| Model | Kirloskar TV-1 |
| Type | Single Vertical cylinder,four stroke,constant speed,bowl in piston,DI Diesel Engine |
| Capacity | 661 cc |
| Bore and stroke | 87.5mm*110mm |
| Compression ratio | 17.5:1 |
| Speed (constant) | 1500 rpm |
| Rated power | 5.2 kw |
| Loading type | Eddy current dynamometer |
| Injection pressure | 200bar |

Experiments were conducted with different antioxidant concentrations of biodiesel fuel mixtures (0.010,0.015,0.025,0.050,0.01%-m) in addition to neat biodiesel and diesel fuel. In each load levels, the measurements of exhaust gas temperature, fuel consumption, fuel pressure, coolant temperature, exhaust gas flow rate, combustion pressure, NO, HC, CO and smoke emissions were carried out and recorded.

## 3. RESULTS AND DISCUSSIONS

The effect of aromatic amine antioxidant additive on NO, CO, HC and smoke emissions of cotton seed oil methyl ester fuelled diesel engine were systematically investigated in this study. The NO measurements were repeatable within each engine run, with replicate measurements varying by 3–6 ppm. The exhaust emissions of engine are greatly influenced by the addition of antioxidants with biodiesel. The results of performances and emissions of test antioxidant mixtures are compared with neat biodiesel and discussed in this section, as follows.

### 3.1. Effects on NOx emissions

The NO emissions during combustion of test antioxidant mixtures were compared to neat biodiesel and diesel. The changes in NO emissions that resulted from the antioxidant addition were found to be significant.

Fig. 3 shows the NO reduction percent of different antioxidant mixtures relative to neat biodiesel and B20 fuel at full load (5.198 kW), 80% load (4.146 kW), 60% (3.095 kW) load, 40% load (2.07 kW) and 20% load (1.021 kW) respectively. From the Fig. it can be seen that, antioxidant addition with B20 fuel reduce the NO emission up to a certain concentration and beyond the limit emission of NO increase with antioxidant loadings. At 80% load, the maximum NO reduction percent of DPPD additive is 27.63% and at full load 24.51% . As shown in Fig. 3 for B20 fuel, the NO emission reduction increased linearly with the concentration of DPPD additive. Similar trends were obtained by Dunn [19] and he observed increased antioxidant activity at lower loadings (less than 1000 ppm) and constant or reduced activity at higher loadings. The possible reason for the inverse relationship between treatment rate and amount of NO reduction is that all the p-phenylenediamine based antioxidants contain nitrogen in its chemical structure and at higher loading, the excess antioxidant reacts with oxygen and forms additional NO. The antioxidant efficiency is defined by the ratio F/ [In H]. Where F is the antioxidant activity and In H is the acceptor reacting with alkoxyl and peroxyl radicals. This ratio does not depend on the antioxidant concentration [12]. For B20 fuel, we found 27.63% and 24.51% reductions in NO emission, respectively, when the fuel was loaded with DPPD. DPPD was the most effective of the antioxidants studied, giving more than 25% decrease in measured NO emissions at all engine loads. The comparison of specific NO emission of cotton seed oil methyl ester with the best antioxidant additive to B20 is DPPD. For B20fuel, the NO produced by DPPD additive and base fuel at 80% load was 12.79% and at full load is 14.36% respectively.

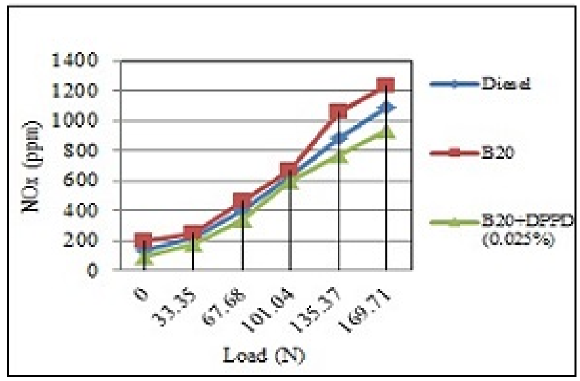



**Fig. 3: Load vs NOx Emission**

### 3.2. Effects on CO and HC emissions

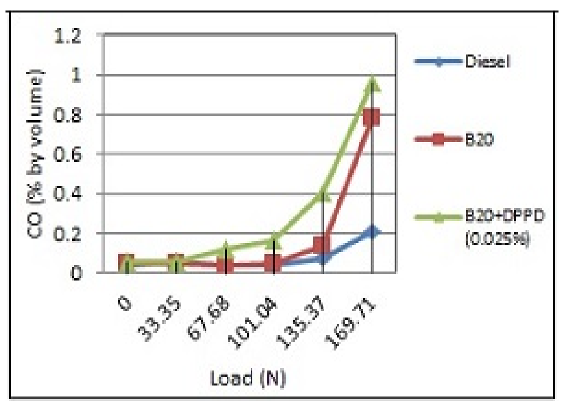
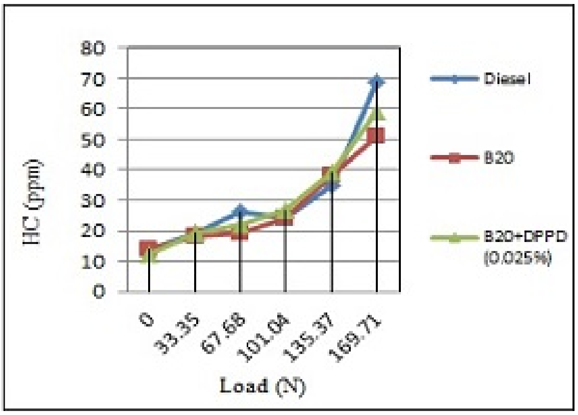



**Fig. 4: Load vs CO emission**

Fig. 4 shows the influence of the DPPD antioxidant additive on the brake-specific CO emissions at various loads for B20. It can be seen that CO emissions increase with the addition of the antioxidants. At 80% load, the DPPD additive had about 11.03% more CO emissions than the neat B20 fuel and neat biodiesel fuel respectively. The variation of brake-specific HC emissions with load is shown in Fig. 5.




In the same manner as the CO emissions, the antioxidant addition was found to significantly increase HC emissions. The increase in HC emissions for B20 fuel was 2.63% and 13.55% respectively at 80% and 100% load conditions. However, the levels of CO and HC emissions with the addition of antioxidants were still below those for petro-diesel. The reason for the increase

in CO and HC emissions is explained as follows: Peroxyl (HO2) and hydrogen peroxide (H2O2) radicals are continuously produced during oxidation. These radicals are further converted into hydroxyl (OH) radicals by absorbing heat (Eqs. (5) and (6)). The OH radicals are responsible for the conversion of CO into CO2 and HC into H2O and CO2 . Treating biodiesel with antioxidants reduce the concentration of peroxyl and hydrogen peroxide radicals. This reduction in free radicals may have a significant effect on the formation of OH radicals and oxidation of CO and HC.

$$H_2O_2 \rightarrow 2OH \quad (1)$$

$$HO_2 \rightarrow OH+O \quad (2)$$

$$CO+OH \rightarrow CO_2+H \quad (3)$$

$$HC + OH \rightarrow HCHO \quad (4)$$

$$HCHO + OH \rightarrow H_2O + HCO \quad (5)$$

$$HCO+O_2 \rightarrow CO_2+HO \quad (6)$$

### 3.3. Effects on smoke emissions and EGT

Fig. 6 shows the characteristics of the exhaust smoke emissions of biodiesel fuel and its blend containing the DPPD additive.

The DPPD fuel mixture increased the smoke density by 12.5 % and 6.6% when compared with the B20 fuel respectively for 80% and 100% load conditions. It is important to note that the increase in smoke emissions were still below the level of diesel. Several factors may contribute to the increase of smoke opacity with antioxidant addition. The possible reasons for the increase of smoke are reduction of oxygen availability, increase of C—C bonds and increase of aromatic content due to the addition of antioxidants with fuels.

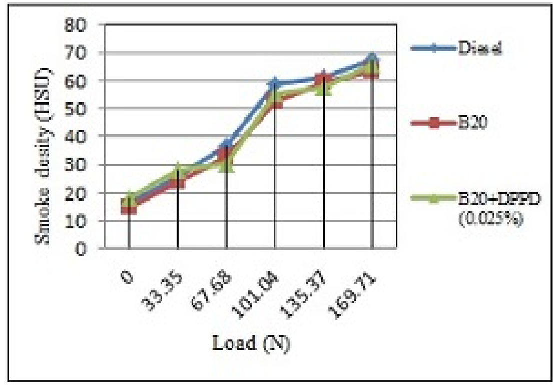



**Fig. 6: Load vs Smoke density**

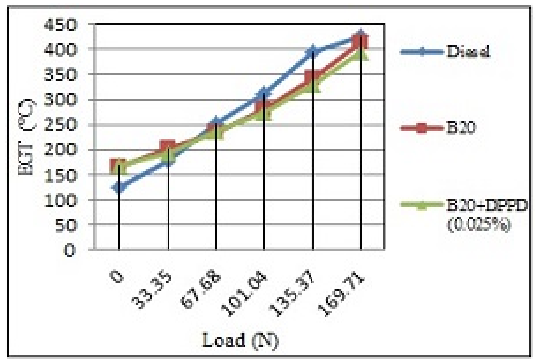



**Fig. 7: Load vs EGT**

### 3.4. Effects on brake thermal efficiency and SFC

The variation of brake thermal efficiency with loads for the antioxidant fuel mixtures is shown in Fig. 8.

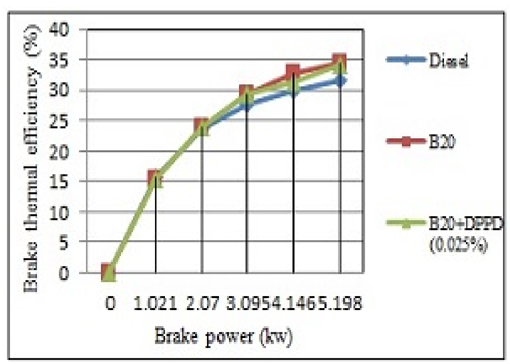
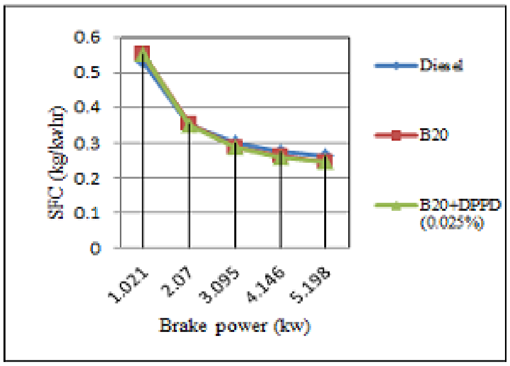



**Fig. 8: Brake power vs BTE**

At part loads change in brake thermal efficiencies due to antioxidants addition are insignificant but at full load, efficiencies were slightly lower than the neat biodiesel. At 80% load, the brake thermal efficiency produced by the DPPD and B20 fuel mixture was 31.28%, while the base B20 fuel had 32.70%. For B20 fuel, there is no significant change in brake thermal efficiency at 80% load but at full load, 0.26%

loss in BTE was observed. The reason for the reduction in thermal efficiency is possibly due to slight cylinder pressure reduction with the addition of antioxidants.




The SFC for B20 fuel at full load is 0.246 kg/kwhr and for B20 fuel with DPPD additive is 0.244 kg/kwhr. Therefore its total fuel consumption increases thus in-turn reduces the brake thermal efficiency.

## 4. CONCLUSION

The objective of this experimental work was to investigate the effect of p-phenylenediamine derived DPPD antioxidant on engine out NOx emissions from a biodiesel fuelled DI diesel engine. Based on the experimental results, the following conclusions can be drawn.

1. The test antioxidant and biodiesel mixtures produced lower emissions of nitrogen oxides.The tested antioxidant additive N,N′-diphenyl-1,4-phenylenediamine (DPPD) showed the highest activity in reducing NO in both B20 fuel. At 85% load, the maximum NO reduction percent relative to B20 fuel for DPPD additive was 28.63% and 24.% respectively and the corresponding reductions for neat biodiesel were 27.63% and 24.51% respectively. Moreover, the emission results show that the studied aromatic amine antioxidants additives reduced the NO emission below the level observed with petro-diesel combustion.

2. Increased formation of prompt NO could be the major reason for biodiesel NOx effect.

3. The antioxidant biodiesel mixtures produced slightly higher CO and HC emissions when compared with neat biodiesel. The DPPD additive increased the CO emissions over 11.03% with B20 fuel at full load conditions. Use of DPPD additive with biodiesel fuels leads to a significant increase in HC emissions by about 13.55% for B20 fuel.Smoke density also slightly increased with the addition of antioxidants with biodiesel. It should be noted however that these emissions are well below the diesel emission levels. The addition of antioxidants with biodiesel on engine brake thermal efficiency was also found to be insignificant. However, slight reduction in efficiency (0.26%) was observed with antioxidant fuel mixtures at full load.

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