# USE OF ANTIOXIDANT ADDITIVES FOR NO<sub>x</sub> MITIGATION IN COMPRESSION IGNITION ENGINE OPERATED WITH BIODIESEL FROM ANNONA OIL

by

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The many researchers pointed out that the biodiesel produces reduced carbon monoxide, hydrocarbon, and smoke emission. However there is a slight increase in  $NO_x$ emission for biodiesel when compared to that of conventional diesel. The addition of antioxidant additives is the effective method for mitigate the  $NO_x$  emission. Hence, in this research work the effect of antioxidant additives on  $NO_x$  emission in a annona methyl ester operated Diesel engine has been investigated. The antioxidant additives such as p-phenylenediamine, a-tocopherol acetate, 1, 4-dioxane, and *l*-ascorbic acid are used in this investigation. Results show that antioxidant additives are very effective in controlling the  $NO_x$  emission. Among different antioxidant additives, 0.010%-m concentration of p-phenylenedimineadditive is optimum for  $NO_x$  emission reduction up to 42.15% when compared to that of neat biodiesel.

Key words: *annona methyl ester*, *NO<sub>x</sub> mitigation, antioxidants, emission, Diesel engine* 

## Introduction

The performance, emission, and combustion characteristics of single cylinder direct injection Diesel engine was investigated using annona methyl ester (AME) as a fuel. It is found from literature 20% AME + 80% diesel blends showed better performance and lower emission when compared to that of Neat diesel [1]. The antioxidant additives along with biodiesel plays vital role in mitigating NO<sub>x</sub> and oxidation stability of fuel while using in a Diesel engine. The various types of antioxidants such as butylatedhydroxyanisole (BHA), butylatedhydroxytoluene (BHT), tert-butylhydroquinone, and 2-ethylhexyl nitrate (EHN) were used at various concentrations. The EHN antioxidant with B20 has presented the best reduction of NO<sub>x</sub>. However, formation of CO emissions have been increased with addition of each of the antioxidants to B20 [2, 3]. The antioxidants reducing NO<sub>x</sub> emission by adding N, N0-diphenyl-1,4 phenylenediamine (DPPD) antioxidant and also adding DPPD additive to all biodiesel and also reduces the exhaust gas temperature [4]. The antioxidant addition in biodiesel leads to lower NO<sub>x</sub> emission when compared to diesel [5]. Further, the oxidation stability for all antioxidants such as BHT and BHA having lowest effec-

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tiveness in biodiesel. By using naturally ageing process the biodiesel antioxidants sample were measured to find the oxidation stability, kinematic viscosity and acid value. The addition of antioxidants in biodiesel improves the oxidation stability, the rate of change of kinematic viscosity, was found to be less [6, 7]

The effect of diethyl ether (DEE), dimethyl ether, and ethanol as additives along with biodiesel showed significant performance and emission reduction characteristics. It has been found that HC, CO, and smoke emissions significantly lower and the  $NO_x$  emission was slightly higher [8].

The effect of antioxidant L-ascorbic acid (LAA) on performance and emission characteristics of AME showed NO<sub>x</sub> emission is reduction by 23.38% and other emission such as HC, CO, and smoke also reduced when compared to that of Neat diesel [9]. The effect of DEE on the performance and emission characteristics of single cylinder pongamia biodiesel and eucalyptus oil operated Diesel engine proved. It has been that the brake thermal efficiency is very close to Neat diesel and there is a considerable reduction in emissions such HC, CO, and smoke were achieved [10].

In this present study the effect of different antioxidants along with annona biodiesel operated Diesel engine were analysed to reduce the  $NO_x$  emission. The emission results of different antioxidants at various proportions of antioxidant mixtures were compared experimentally.

Property	AME			
Kinematic viscosity at 40 °C [cst]	5.18			
Calorific value [kJkg <sup>-1</sup> ]	39575			
Density at 15 °C [kgm <sup>-3</sup> ]	872			
Cetane number	52			
Flash point [°C]	76			
Fire point [°C]	92			

Table 1. Properties of Annona methyl ester

#### Materials and methods

The AME oil procured from Tamil Nadu Agricultural University, India, is used as test fuel and its properties of annona oil shown in tab. 1.

The antioxidants are used in this study p-phenylenediamine (PPDA), a-tocopherol acetate (AT), 1, 4- dioxane, and LAA. The specification of antioxidantadditives are given in tab. 2.

# Experimental set-up and testing procedure

The experiments are carried out in a single cylinder, water cooled, direct injection Diesel engine. The schematic diagram of engine set-up is shown in fig. 1 and the specification of test engine is shown in tab. 3. An electric dynamometer is used as loading device. A fuel and gas flow rate, load, speed, and exhaust gas temperature are measured in a appropriate devices. The  $NO_x$  emission is measured using NDIR based AVL gas analyser. Before taking the emission test a leak check is conducted in the digital gas analyser.

Antioxidant	Formula	CAS number	Molecular weight [gmol <sup>-1</sup> ]	Melting point [°C]	Boiling point [°C]	Density [gcm <sup>-3</sup> ]
P-pheylenediamine	$C_6H_8N_2$	106-50-3	108.14	145-147	267	1.0
A-tocopherol acetate	$C_{31}H_{52}O_3$	59-02-9	430.71	2.5-3.5	200-220	0.950
1.4-dioxane	$C_4H_8O_2$	123-91-1	88.10632	11.8	101	1.03
L-ascorbic acid	$C_6H_8O_6$	50-81-7	176.13	190	553	1.69

Table 2. The specification of antioxidants additives

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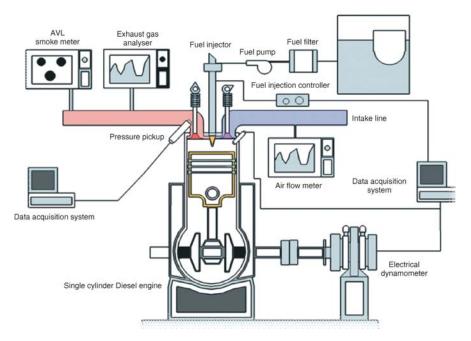


Figure 1. The schematic diagram of engine set-up

The NO<sub>x</sub> emission is analysed at different proportions of antioxidants at a constant speed of 1500 rpm. The experimental uncertainties are shown in tab. 4. All additives are accurately weighed using high precision electronic machine and added to measured quantity of annona biodiesel to make 0.010%-m of antioxidant mixtures. A speed mixture is used to prepare a homogenous mixture of antioxidant and test fuel. The experiments were carried out after through engine and calibration of measuring instruments same test procedure was followed for all the test mixtures (MEAO + 0.010%-m, MEAO + 0.020%-m, MEAO + 0.030%-m, and MEAO + 0.040%-m).

Type of engine	Kirloskar SV1, 1-cylinder, 4-storke, 661 cc Diesel engine	
Maximum brake power	5.2 kW	
Rated speed	1500 rpm	
Compression ratio	17.5:1	
Lubrication system	Forced feed system	
Bore diameter and stroke length	87.5 × 110 mm	
Cooling system	Water cooled	
Injection pressure	210 bar	

Table 3. Specification of the experimental engine

## **Results and discussions**

## Comparison of NO<sub>x</sub> emission

Temperature plays a vital role in  $NO_x$  formation. It is also depends upon the compression ratio, equivalence ratio, geometry of the combustion chamber, fuel injection advance, pressure, and temperature of the inlet air. Figure 2 shows the variation of  $NO_x$  emission with brake power (BP) for different antioxidant concentrations of PPDA. It can be seen from graph that

S.No	Instruments	Variation	Accuracy	Uncertainties
1	Gas analyzer	CO 0-10%, CO <sub>2</sub> 0-20%, HC 0-10000 ppm, NO <sub>x</sub> 0-5000 ppm	+0.02% to -0.02% +0.03% to -0.03 % +20 ppm to -20 ppm +10 ppm to -10 ppm	+0.2 to -0.2 +0.15 to -0.15 +0.2 to -0.2 +0.2 to -0.2
2	Smoke	HSU 0-10	+0.1 to -0.1	+1 to -1
3	Temperature indicator	0-900 °C	+1 °C to −1 °C	+0.15 to -0.15
4	Speed	0-1000 rpm	+10 rpm to -10 rpm	+0.1 to -0.1
5	Load	0-100 kg	+0.1 kg to -0.1 kg	+0.2 to -0.2
6	Burette for fuel measurement		+0.1 cc to -0.1 cc	+1 to -1
7	Digital stop watch		+0.6 to -0.6 second	+0.2 to -0.2
8	Manometer		+1mm to -1mm	+1 to -1
9	Pressure pickup	0-110 bar	+ 0.1 to -0.1	+0.1 to -0.1
10	Crank angle encoder		$+1^{0}$ to $-1^{0}$	+0.2 to -0.2

Table 4. List of instruments and its range, accuracy and percentageuncertainties

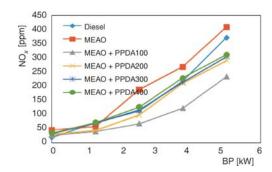


Figure 2. Variation of NO<sub>x</sub> emission with BP for different antioxidant concentrations (PPDA)

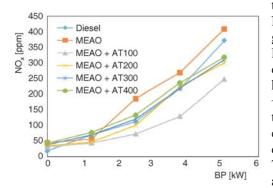


Figure 3. Variation of  $NO_x$  emission with BP for different antioxidant concentrations (AT)

 $NO_x$  emission increases with increase of engine load. The  $NO_x$  emission decreases with the percentage of PPDA with the MEOA, up to of MEAO + PPDA100 of antioxidant mixture after that it increases. Further, it is also seen that  $NO_x$  emission of MEAO + PPDA100 of antioxidant mixture is decreased by 42.15% when compared to Neat diesel fuel. This is due to the reduction in the formation of free radicals by PPDA. The free radicals play a key role in prompt NO formation during the combustion of biodiesel within the flame.

Figure 3 shows that variation of  $NO_x$  emission with BP for different antioxidant concentrations of AT. From the graph it is observed that  $NO_x$  emission increases with the increase of engine load due to higher combustion temperature. For MEAO + AT100 mixture  $NO_x$  emission reduces by 24.83%. The  $NO_x$  emission reduction is higher at MEAO + AT100 and lower for MEAO + AT400. This is due to the nitrogen content in the antioxidant additive. A tocopherol acetate is a chain-breaking antioxidant and it has ability to donate its phenolic hydrogen to free radicals. Thus,  $NO_x$  emission reduced with the addition of antioxidant additive.

Figure 4 shows that variation of  $NO_x$  emission with BP for different antioxidant concentrations

of 1, 4-dioxane. From  $NO_x$  emission decrease with increasing additive 1, 4-dioxane with MEOA. Further, it can be observed that  $NO_x$ emission for MEAO + 1,4-Dioxane100 is decreased by 16.87% when compared to MEAO at full load. This is due to reduction in cylinder temperature which in turn reduces the  $NO_x$ emission.

Figure 5 shows that variation of  $NO_x$  emission with BP for different antioxidant concentrations of LAA. It can be seen from graph that  $NO_x$  emission increases with increase of engine load. The LAA produced small amount of  $NO_x$  reduction 6.56% of MEAO + LAA100 mixture antioxidant additive. The LAA is a radical-trapping antioxidant, effectively scavenges reactive NO species such as NO, NO<sub>2</sub>, and N<sub>2</sub> to prevent nitrosation of target molecules.

Figure 6 shows that variation of  $NO_x$  emission with BP for different antioxidants concentration of 0.010%-m with neat MEAO. It is seen that significant reductions in  $NO_x$  emission is observed by using different antioxidants. However, optimum reduction is found at 0.010%-m concentration of additives. The result indicate that the highest  $NO_x$  emission reduction is found at PPDA and followed by AT, 1, 4-dioxane, while LAA had the lowest. Hence, the  $NO_x$  emission can be reduced by formation of free radicals present in the antioxidant additives.

#### Conclusions

The experimental work shows that the potential benefit of antioxidant additions annona biodiesel operated Diesel engine. The main conclusion of this present work can be summarized:

- The antioxidants are quite effective in controlling the NO<sub>x</sub> emission mitigation.
- Among different antioxidants, PPDA showed optimum NO<sub>x</sub> emission reduction of 42.15%, when compared to other different antioxidant additives.
- The NO<sub>x</sub> emission reduction efficiency of antioxidants is observed in the order PPDA > AT > 1, 4-dioxane > LAA.

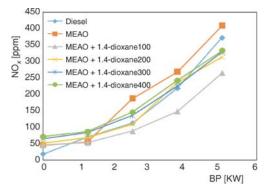


Figure 4. Variation of NO<sub>x</sub> emission with BP for different antioxidant concentrations (1, 4- dioxane)

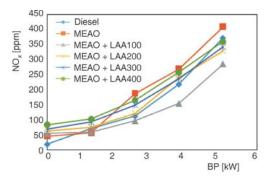


Figure 5. Variation of NO<sub>x</sub> emission with BP for different antioxidant concentrations (LAA)

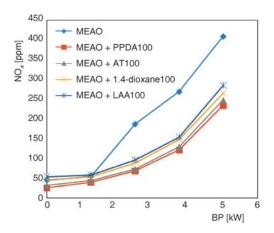


Figure 6. Variation of  $NO_x$  emission with BP at different antioxidants concentration of 0.010%-m

#### Acronyms

- AME annona methyl ester
- AT a-tocopherol acetate
- BHA butylatedhydroxyanisole
- BHT butylatedhydroxytoluene
- BP break power
- CAS chemical abstracts service
- CR compression ratio
- DEE diethyl ether

- DI direct injection
- DPPD N0-diphenyl-1.4 phenylenediamine
- EHN 2-ethylhexyl nitrate
- IP injection pressure
- LAA l-ascorbic acid
- MEAO methyl ester of annona oil
- NDIR non-dispersive infrared detector
- PPDA p-phenylenediamine acetate

#### References

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