

NO_x Emission Reduction in Annona Biodiesel Engine by Means of Antioxidant Additives

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ABSTRACT

Biodiesel as an alternative diesel fuel prepared from vegetable oils or animal fats has attracted more and more attention because of its renewable and environmental friendly nature. Many recent studies shows that 20% proportion of biodiesel-diesel blend (B20) can substantially reduce the hydrocarbon (HC), carbon monoxide (CO) and smoke emissions. However, there is a slight increase in NO_x emission for B20 than that of diesel and it was a barrier to market expansion. The addition of antioxidant additives was the most effective method to mitigate the NO_x emission. Hence, in this paper experimental investigation has been carried out to mitigate the NO_x emission in Annona biodiesel (A20) operated diesel by addition of antioxidant additives. The antioxidant additives such as p-phenylenediamine, A-tocopherol acetate and L-ascorbic acid were used in the present investigation. In recent years Annona biodiesel has been considered as potential novel renewable energy source in India. Therefore in this experimental investigation was conducted to improve the A20 (7) (20% of annona methyl ester with 80% of diesel) with the help of antioxidant additives. It was evidently proved from the experimental investigation that use of antioxidant additive was effective in controlling the NO_x emission in diesel engine. Result shows that 250mg concentration of p-phenylenediamine additive with A20 blend was optimum for NO_x mitigation up to 25.7% when compared to that of diesel without any major modification.

KEYWORDS: Annona methyl ester, NO_x mitigation, Antioxidant additives, Emissions, Diesel Engine

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INTRODUCTION

Alternative fuels have been widely used in the internal combustion engines due to extensive research in finding alternative sources for fossil based fuels. Vegetable oils, biodiesel, simple alcohols such as methanol and ethanol and blended fuels are utilized in combustion engines. The CO, HC and smoke emissions were reduced but NO_x emission was increased with vegetable oil blends than that of diesel fuel. Further, the engine performance with vegetable oil blend or biodiesel was similar to that of diesel fuel [1, 2, 3, 4, 5, 6].

EFFECT OF BIODIESEL DIESEL BLENDS

The A20 blend shows better performance and lower exhaust emissions. Further, the CO, HC, and smoke emissions were reduced considerably. However, the NO_x emission was slightly increased for the various proportions of Annona methyl ester (AME) [7]. The brake specific fuel consumption (BSFC) for Ceibapentandra biodiesel blends (CPB10) was higher than that of diesel and CO, HC and smoke emissions were reduced for all biodiesel blends. Further, the NO_x and CO₂ emission were increased for CPB10 when compared to that of diesel [8]. The brake specific energy consumption (BSEC) of rice bran oil was higher than that of all blends at all loads and viscosity, better combustion and lesser emission than that of other blends of rice bran oil [9]. The Brake thermal efficiency (BTE) of

Jatropha biodiesel blends was lower and there is a slight increase in BSFC of Jatropha biodiesel blends than that of diesel. Further the HC, CO and smoke emissions were lower for Jatropha biodiesel blends than that of diesel but at the expense of increase in NO_x [10].

NO_x Mechanism

As the use of biodiesel has increased tremendously the rise in NO_x emission can became a significant barrier to market expansion. For pure 100% biodiesel increase the NO_x emission by 13% than that of diesel. During combustion, the NO_x is generated by three mechanism such as thermal, prompt and fuel. High combustion temperature (1700K) breaks the strong triple bond of nitrogen molecules and form high less reactive atomic nitrogen, then it reacts with the oxygen and generates thermal NO_x. Further the formation of free radicals in the flame front of the HC flames leads to the rapid production of prompt NO_x. The fuel NO_x is formed by the reaction of nitrogen bond in the fuel with the oxygen during combustion process. Among these three mechanisms, thermal and prompt NO_x are the dominant mechanisms in biodiesel operated diesel engine since biodiesel does not contain fuel bond nitrogen. The thermal mechanism is unaffected by fuel chemistry, whereas the prompt mechanism is sensitive to free radical in the reaction zone. Numerous reasons have been proposed for biodiesel NO_x effect; however the exact cause is still unclear. The development of improved NO_x reduction technology is therefore

critical to the global environment. Hence the antioxidants are very effective in controlling the NO_x emission and it has potential antioxidant properties to suppress the free radical formation. [11, 12, 13, 18, 19]

Effect of Antioxidant Additives

The L-ascorbic acid antioxidant additive was mixed in various proportions such as 100–400 mg with methyl ester of cottonseed oil (MECSO). The NO_x and HC emissions for LA300 with MECSO were reduced by 9.31% and 23.62% respectively. Further, the CO and smoke emissions were higher to all the mixtures of antioxidant additive with MECSO when compared to that of neat biodiesel [11]. The various antioxidant additives such as L-ascorbic acid, α -tocopherol acetate, butylatedhydroxytoluene, p-phenylenediamine and ethylenediamine were used. The NO_x emission for 0.025%-m concentration of p-phenylenediamine was reduced by 43.55% when compared to other antioxidants additives at 0.025%-m concentration. Further, the HC and CO emissions were slightly increased with the addition of antioxidant additives [12]. The antioxidant additives, N, N'-diphenyl-1, 4-phenylenediamine (DPPD) and N-phenyl-1, 4-phenylenediamine (NPPD) were tested in a diesel engine. The maximum NO reduction for DPPD and NPPD additives were 9.35% and 4.06% respectively when compared to that of B20 at 75% load. Further, the aromatic amine antioxidants were reduced the NO emission below the level of conventional diesel engine [13]. The four synthetic antioxidants such as butylatedhydroxyanisole (BHA), butylatedhydroxytoluene (BHT), tert-butylhydroquinone (TBHQ) and 2-ethylhexyl nitrate (EHN) were tested on a Land Rover turbocharged DI diesel engine. The highest NO_x emission reduction was found at EHN followed by BHT and BHA. The lowest NO_x emission was observed for TBHQ [14]. The oxidation stability increases with the increase of antioxidant additive proportion and the NO_x emission of BHT100 with MENO is reduced by 19.99% at full load condition when compared to that of neat biodiesel. However, the HC, CO and smoke emissions for all antioxidant mixture were increased slightly. Further, there is no variation in BTE with the addition of antioxidant additive in the biodiesel [15].

The EHN is a promising antioxidant additive for controlling the NO_x emission at the expense of increasing the CO and HC emissions. Further, the BHA is also capable of decreasing the NO_x and HC emission by 2.73% and 39.12% respectively at 1000 ppm concentration when compared to that of canola oil methyl ester (B20) without additive [16]. The NO_x emission for BHA and BHT antioxidants were reduced by 9.8–12.6% when compared to that of palm methyl ester (B20). However, the CO and HC emissions were reduced for both antioxidants additives with B20 by 8.6–12.3% and 9.1–12.0%, respectively when compared to that of B20 [17]. The NO_x emission for MENO + P200 was reduced by 35% when compared to that of neat diesel. Further, the HC emission for MENO+P200 is reduced by 31% at full load when compared to that of neat diesel, but CO_2 , CO and smoke emissions for all concentrations were found to be increased [18]. The NO_x emission for MENO + AT100 was reduced by 25.95% at full load when compared to that of neat biodiesel. Further, the HC, CO and smoke emissions increases with increasing antioxidant concentration whereas there is no significant variation in BTE and BSFC [19]. The addition of BHT and MBEBP antioxidants to callophyllum inophyllum (CB30) resulted reduction

in BSFC by 0.43% and 0.57%, respectively and increase in BTE by 0.36% and 0.45% respectively when compared to that of neat biodiesel. Further, the NO_x emission for both BHT and MBEBP blends were reduced by 5.91% and 5.27% respectively, but there was a significant increase of HC, smoke and CO emissions [20]. The antioxidant was effectively controlling the NO_x emission. Further, the addition of 0.15%-m DPPD additive in JB5, JB10, JB15 and JB20 showed NO_x emission reduction of 8.03%, 3.503%, 13.65% and 16.54% respectively, when compared to that of biodiesel blends without antioxidant additive [21]. The addition of butylatedhydroxyanisole was effectively controlling the NO_x emission, but the other antioxidants were not reducing the NO_x emission [22]. The performance characteristics for soybean biodiesel operated diesel engine were not influenced by the addition of antioxidants. Further the addition antioxidant additives with soybean biodiesel was reduced the NO_x emission efficiently decreased more than that of biodiesel fuel without antioxidant additive [23].

Chemistry of Antioxidant

Addition of small amounts of antioxidants into the biodiesel suppress the free radical formation of the hydrogen is released from the weak OH (phenols, hydroquinones) and NH (aromatic amines, diamines) blends of antioxidant [13]. Lipid oxidation reaction, such as these in biodiesel, are initiated by the formation of peroxides. A requirement for this reaction is free radicals, which is formed from oxygen present in the atmosphere. The most effective way to inhibit the oxidation of biodiesel is to limit its exposure to oxygen by adding antioxidants to the FAME that can dispose of the formed oxygen radicals. The hydroxyl (-OH) group of the antioxidant is active so that hydrogen is abstracted from -OH by donating a hydrogen to hydroxyl. This condition leads to a quaternary live structure of the antioxidant, which is significantly more stable than the radicals [20].

Reaction: $\text{OH} + \text{ROO} \cdot \rightarrow \text{R-O} \cdot + \text{ROOH}$ [17]

Table 1 depicts the effect of biodiesel-diesel blends on engine performance such as brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), exhaust gas temperature (EGT) and exhaust emissions such as hydro carbon (HC), carbon monoxide (CO), oxides of nitrogen (NO_x), and smoke

Table 1. Effect of biodiesel-diesel blends on engine performance and exhaust emissions.

Type of Engine	Single Cylinder 4 stroke Diesel Engine	Single Cylinder 4 stroke Diesel Engine	Single Cylinder 4 stroke Diesel Engine	Single Cylinder 4 stroke Diesel Engine
Feed stock	Jatropa Biodiesel (J20)	Rice bran oil (B25)	Ceiba Pentandra biodiesel	Annona Methyl ester
BTE	Decrease	Decrease	Decrease	Decrease
BSFC	Increase			
EGT	-	-	-	Increase
HC	Decrease	Decrease	Decrease	Decrease
CO	Decrease	Decrease	Decrease	Decrease
NO_x	Increase	Increase	Increase	Increase
Smoke	Decrease	-		
References	[10]	[10]	[8]	[7]

Table 2 depicts the effect of antioxidant additives on NO_x, HC, CO smoke, BTE and BSFC.

Table 2. Effect of additives on engine performance and emissions

Type of Engine	Single Cylinder 4 stroke Diesel Engine	Single Cylinder 4 stroke Diesel Engine	Single Cylinder 4 stroke Diesel Engine	Land over turbo Charged D.I diesel engine	Single Cylinder 4 stroke Diesel Engine
Feed stock	Cotton seed methyl ester (B100)	Jatropha methyl ester (B20)	Soybean biodiesel (B20)	B20	Neem oil methyl ester (B100)
Types of additives	L-Ascorbic Acid (LA3000)	p-Phenylenediamine (250 mg)	N,N'-Diphenyl-1,4-phenylenediamine	2-Ethylhexyl Nitrate (EHN)	Butylated Hydroxytoluene (BHT)
BTE	-	-	-	-	No-variation
BSFC	-	-	-	-	No-variation
HC	Decrease (9.3%)	Decrease (43.55%)	-	Decrease	Decrease
CO	Increase	Increase	-	Increase	Increase
NO _x	Decrease	Decrease	Decrease	Decrease	Decrease
Smoke	Increase	-	-	-	Increase
References	[11]	[12]	[13]	[14]	[15]

Type of Engine	Single Cylinder 4 stroke Diesel Engine	Single Cylinder 4 stroke Diesel Engine	Single Cylinder 4 stroke Diesel Engine	Single Cylinder 4 stroke Diesel Engine	Single Cylinder 4 stroke Diesel Engine	Multi cylinder Diesel Engine
Feed stock	Canola oil methyl ester (B20)	Palm methyl ester (B20)	Neem oil Methyl ester (B100)	Neem oil Methyl ester	Calophyllum phyllanthoides biodiesel (compared)	Jatropha biodiesel blend
Types of additives	EHN 91000 ppm and Butylated hydroxyanisole	BHA (1000 ppm) BHT (1000 PPM)	p-phenylenediamine (200mg)	A-Tocopherol acetate (100mg)	BHT & MBEP	DPP D(150mg)
BTE	-	-	-	-	Decrease (0.36%)	-
BSFC	-	-	-	-	Decrease (0.43%)	-
HC	Increase	Decrease (8.6%)	Increase	Increase	Increase	Increase
CO	Increase	Decrease	Increase	Increase	Increase	Increase
NO _x	Decrease	Decrease	Decrease (35%)	Decrease (25.95%)	Decrease (5.9%)	Decrease (13.65%)
Smoke	Increase	Increase	Increase	Increase	Increase	Increase
References	[16]	[17]	[18]	[19]	[20]	[21]

OVERVIEW

As discussed in the above mentioned literature review, although there have been a number of studies on biodiesel performance, emissions and their highlighted problem was higher NO_x in the exhaust. It has been seen from the literature review that while using 20% biodiesel there was a decrease in performance and increase in the NO_x emission. Hence, most of the researchers have attempted to find the various methods for reducing the NO_x emission. The addition of antioxidant additives in biodiesel will be effective for reducing the NO_x emission. The objective of this study is to test the feasibility of annona biodiesel in India and suggest an appropriate solution of the future of biodiesel. Therefore, in the present investigation antioxidant additives have been used along with A20 blend for effectively controlling the NO_x emission.

MATERIALS AND METHODS

Test Fuel

The AME was used as test fuel in this study. The chemical composition of AME was C - 76.38%, H-11.26%, O - 12.39% and C/H- 6.16%. The custard apple seeds obtained were subjected to hot press at 85°C to produce raw oil. The little brown colour custard apple oil was filtered and the biodiesel was obtained through transesterification process using methanol as alcohol and NaOH as catalyst. EN14214 standard test methods were taken as reference in measuring the obtained values. The properties of A20 with diesel were tested as per the ASTM standards and compared to diesel as given shown in Table.3. The AME contains 49.6% saturated methyl ester and 50.1% unsaturated methyl ester. The free fatty acid (FFA) compositions (%w/w) of AME contains such as lauric - 0.40%; myristic-0.18%; Palmitic -17.57%, stearic-16.60%; oleic-45.83%; and lindic-17.79%. The rancimat method was used to determine the oxidant stability of A20 with antioxidant additives. The lower percentage of saturated fatty acids in AME correlated with lower NO_x and good oxidant stability.

Table 3. Properties of A20 and diesel [7]

Property	Standard Method	Diesel	A20
Kinematic viscosity in cst at 40°C	ASTM D613	3.10	3.52
Calorific value in KJ/kg	ASTM D240	43200	42475
Density at 15°C in kg/mm ³	ASTM D941	830	838.40
Cetane Index	ASTM D93	46.40	47.52
Flash point (°C)	ASTM D445	56	60
Sulphur content (%)	ASTM D4294	0.01	0.001
Iodine number	EN 14111	-	112
Oxidation Stability at 110°C (h)	EN15751	-	6.90

PREPARATION OF BIODIESEL BLEND AND ANTIOXIDANT ADDITIVE

The P-phenylenediamine (PPDA), α -tocopherolacetate (AT) and L-ascorbic acid (LA) were selected for this present investigation because of its properties, oxidation stability, availability, cost and rate of suppression of NO_x emission. These antioxidants were effectively controlling the free radical formation, since it determines the reaction rate and prompt NO_x formation in the engine. The properties of the antioxidants such as PPDA, AT and LA were given in Table 4. All additives were accurately weighed for using high precision electronic balance and added to the measured quantity of annona methyl ester.

To make 50mg of antioxidant mixture 0.005%-m of antioxidant was added to 1 kg of biodiesel. A speed mixer was used to prepare a homogenous mixture of test fuel. The same procedure was followed for all other test mixtures of annona methyl ester with 50 mg, 150 mg, 250 mg, 350 mg and 450 mg concentrations.

Table 4. Properties of antioxidants additives[12]

Antioxidant	Formula	CAS number	Molecular weight g/mol	Melting point °C	Boiling point °C	Density g/cm ³
P-phenylenediamine	C ₆ H ₈ N ₂	106-50-3	108.14	145 to 147	267	1.00
α -tocopherol acetate	C ₃₁ H ₅₂ O ₃	59-02-9	430.71	2.50 to 3.50	200 to 220	0.950
L-ascorbic acid	C ₆ H ₈ O ₆	50-81-7	176.13	190	553	1.69

EXPERIMENTAL DETAILS

Experimental Setup

The experiments were conducted on single cylinder direct injection diesel engine which mounted rigidly on the floor as shown in Fig 1. One end of the engine was connected with eddy current dynamometer to apply load. The specification of the test engine as shown in Table 5. Initially, diesel fuel was filled in the tank and was supplied to the engine through the burette. The biodiesel- diesel blend was mixed separately kept in a small tank and supplied to the engine. The temperature of different parts of the engine like intake, exhaust, coolant temperature etc. were measured from the temperature sensors on the measuring board. The U tube manometer was used to measure the air level in the engine. The speed of the engine was measured using the speed sensor which senses the speed of rotating crank shaft. The smoke was measured using smoke meter. The carbon monoxide, oxides of nitrogen and unburned hydrocarbon emissions were measured using di-gas analyser. A computer was connected with the engine using Data Acquisition System (a sensors interface) which plots the graphs automatically according to the operation of the engine. A number of tests were carried out at a constant speed of 1500 rpm and variable loads. The loads vary from no load to full load, brake power was calculated using constant speed and the corresponding torque. The A20 blend with various antioxidant concentrations were used. The tests were repeated for three times and was averaged to ensure the reproducibility of data. Uncertainty analysis was done to prove the accuracy of experiments. The list of instruments and its range, accuracy and percentage uncertainties were shown in Table 6.

Gaseous emissions data including measures of CO, CO₂, NO_x and HC were measured at wet sample conditions according to SAE J816B specifications and procedures. Statistical analyses were also adopted and measures of performance were corrected to standard atmospheric conditions (SAE J816B). Gaseous emission data included non-dispersive infrared (NDIR) analysis of carbon monoxide (CO), carbon dioxide (CO₂) and hydrocarbons (HC) and chemiluminescent measurements of NO_x and oxygen (O₂). The emissions measurements were done according to specifications and procedures described on SAE Engine Test Code J816b.

All engine performance data were corrected to the standard atmospheric conditions given below.

The power correction factor used was (according to Turkish Standards, TS 1231).

$$K_d = f_a f_m,$$

where

$$f_a = \left(\frac{99}{P_a} \right) \left(\frac{T_a}{298} \right)^{0.7}$$

$$f_m = 0.036q_c - 1.14$$

$$q_c = \frac{q}{r}$$

T_a is ambient temperature (K), P_a is ambient pressure (kPa), q is fuel delivery rate (mg/cycle) and r is compressor pressure ratio (for naturally aspirated engines, r=1).

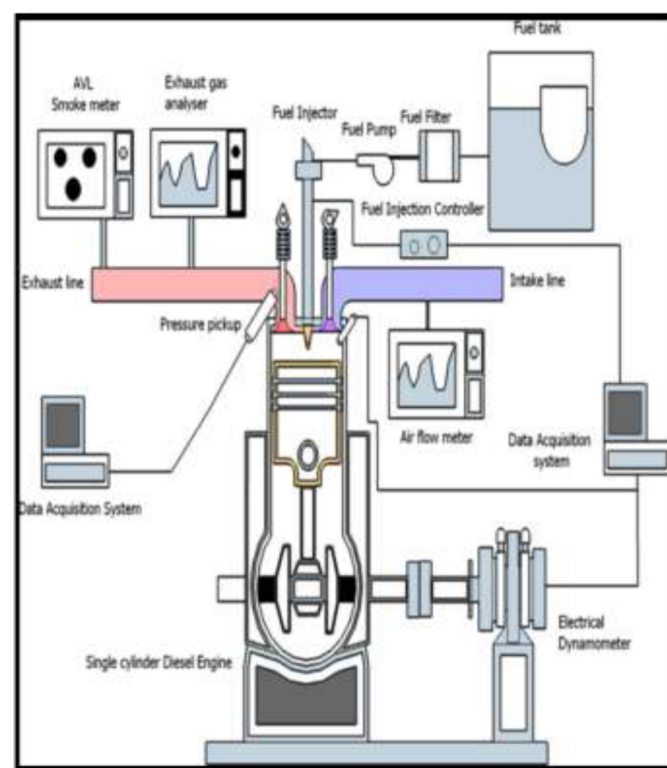


Figure 1. Schematic diagram of engine setup



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