EFFECT OF ANTIOXIDANT ADDITIVES ON ENGINE PERFORMANCE AND EMISSIONS OF A DIESEL ENGINE FUELLED WITH CANOLA OIL METHYL ESTER DIESEL BLENDS

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Abstract : This study has been Scarcity of conventional petroleum fuels has promoted research in alternative fuels for internal combustion engines. Worldwide energy demand has been growing steadily during the last five decades and most experts believe this trend will continue to rise. The conventional petroleum fuels for internal combustion engines will be available for few years only, due to a tremendous increase in population .Biodiesel is a green fuel produced from renewable resources, and offers clean combustion over conventional diesel fuel. However, several authors report to increase in NO_X emissions for biodiesel compared with conventional diesel fuel. In the previous paper results shows that engine performance i.e., brake specific fuel consumption (BSFC) blend B20 was decreased and brake thermal efficiency increased compared to blends like B5, B10, B15, B25. In the present study, antioxidants like ethylenediamine, P-phenylenediamine, L-ascorbic acid are mixed in proportions (500ppm, 750ppm and 1000ppm) with B20 fuel and tested engine performance and exhaust emissions on a single cylinder, four stroke, water cooled diesel engine with canola oil methyl ester diesel blends at constant speed with varying loads . According to engine performance test results, brake specific fuel consumption (BSFC) of B20 with antioxidants decreased and brake thermal efficiency increased compared to those of B20 without antioxidants. With the addition of antioxidants additives NOx were decreased and HC emissions and CO emissions were slightly increased compared to B20 but almost nearly equal to diesel. As the concentration proportion of additives increases in Blend B20 the more NO_x reduces .So,1000ppm concentration of B20 fueled with P-Phenylenediamine reduced 40% NO_X followed by EDA as 32% and last by L-A as 21% respectively and nearly equal to diesel.

***KEY WORDS* - Biodiesel, canola oil, additives, P-phenylenediamine (PDA), ethylenediamine (EDA), L-ascorbic acid, performance and emissions, ppm.**

I. INTRODUCTION

Biodiesel, which is an oxygenated diesel fuel made from vegetable oils and animal fats by converting the tri-glyceride fats to esters via various transesterification process. Biodiesel, as a renewable alternative fuel for diesel engines, in place of diesel fuel has been progressively performed to study its engine performance and exhaust emissions. Among all radical formations during combustion of biodiesel, hydroperoxyl (-OOH), hydroxyl (HO-), alkoxyl (RO-) and peroxyl (ROO-) radicals have significant impact on NO_x formation. NO_X is the major cause of smog, ground level ozone also a cause of acid rain. These radicals react with N_2 and N_2O from air to form nitrogen oxides. Furthermore, antioxidants can reduce free radical formation by four routes as chelating the metal catalysts, chain breaking reactions, reducing the concentration of reactive radicals and scavenging the initiating radicals. NOx is generated during combustion by three mechanisms: thermal, prompt and fuel. Thermal NO_x Is generated by oxidation of nitrogen at elevated temperatures(above 1700K),while prompt NO_x is generated by the formation of free radicals in the flame front of hydrogen flames .Thermal and prompt are the dominant mechanisms for the NO_x generation .Antioxidants inhibit oxidative process by donating a electron or hydrogen atom to a free radical. Many studies show that more complete combustion of biodiesel and their blends of diesel fuel, especially B20, can slightly reduce unburned hydrocarbon (HC), smoke capacity and CO emissions and increases NOx emissions but increases break specific fuel consumption (BSFC) and increases brake thermal efficiency. However, biodiesel can increase NO_x emissions due to its high oxygen content of chemical structures and increases break specific fuel consumption.

Various types of biodiesel such as cotton seed oil, jatropha, sunflower, canola oil are reviewed and among them canola oil biodiesel plays a vital role in the replacement of diesel with its characteristics. Its scientific name is Brassica napus, canola is Canada oil contains low acids.'CAN' stands for CANADA ,'O' stands for OIL ,'LA' stands for LOW ACID. It has 6% low acids those are saturated and poly unsaturated fats. The major advantages are high calorific value, easy availability because the canola plant will grow in any environmental conditions in India. As India is an agricultural country, if the cultivation of canola plants is made by farmers it will be very useful to the farmers and also to our India economy. Higher yield with < 2% erucic acid and relatively shorter duration of crop and safe for human consumption also.

K. Srinivas et al[1] Performance and emission analysis of Waste Vegetable Oil and its blends with Diesel and Additive. The sources of fossil fuels aware depleting day to day and there are no more fossil fuels in the future, so there is a need for the search for the alternative fuels. In this paper, the performance and emissions of diesel and vegetable oil and diesel additive blended with waste vegetable oil is studied, where the fuel, namely methyl ester of waste experimental investigation carried on computerized four stroke single cylinder diesel engine with Ethanol and Ethyl Hexyl Nitrate as additives to the diesel-biodiesel blends McCormick et al [5], explored various ways for reduction of NOX emissions from biodiesel. They detailed cetane improvers like di-tert-butyl peroxide (DTBP) and ethyl hexyl nitrate (EHN) are effective for reducing NO_X emissions in B20 blends. On the contrary, increasing fuel density, number of double bonds and quantified iodine number are equalized with increasing NOx emissions. Gan and Ng examined the effect of antioxidants equally tert-butyl hydro quinone (TBHQ), Butylated hydroxyl anisole (BHA) and butylated hydroxyl toluene (BHT) are used in different concentrations as (250,500,750,1000ppm) in B10, B20 fuels. They examined that BHA is a covenanting antioxidant for reducing CO emissions in the combustion of biodiesel blends. TBHQ is equally terminating NO formation more than other additives. Varatharajan et a**l [4],** the effect of antioxidant additives on NOx emissions of Jatropha biodiesel in diesel engine was investigated. The antioxidant additives L-ascorbic acid , a-tocopherol acetate, BHT, P-Phenylenediamine and ethylenediamine additive was optimal as NOx levels were significantly decreased compared to neat Jatropha biodiesel. However, addition of biodiesel increased HC and CO emissions.

As stated above, many studies have been carried out in order to reduce NOx emission of biodiesel. In the present study, canola oil is transesterified with methyl alcohol and Blend B20 is observed to be behaving better performance among B5B5,B10,B15, B20 &B25.Effect of antioxidant additives like p-phenylendiamine, ethylenediamine and L-Ascorbic acid (500PPM, 750PPM, 1000PPM) on the engine performance and exhaust emissions of a diesel engine fueled with B20 were also investigated and the results were compared with B20 without antioxidant and diesel fuel..

II. ANTIOXIDANTS:

Antioxidants are the molecules that inhibit the oxidation of other molecules and used as fuel additives when creating fuel blends. Oxidation reaction produce free radicals leading to chain reactions and antioxidants terminate the chain reaction by disrupting radical intermediates. Some antioxidants are used as a stabilizer in fuel to prevent oxidation.

Examples of some antioxidants used are:

i) Butylated Hydroxyl Toluene (BHT)
ii) 2, 4 Dimethyl-6-tert-butylphenol
iii) P-Phenylenediamine
iv) Ethylenediamine

III. TRANSESTERFICATION OF CANOLA OIL

In this study, the base catalyzed Trans-esterification process is shown in fig2.1 is used to prepare biodiesel from Canola oil. For trans-esterification process 500 ml of Canola oil is heated up to 70oC to drive off moisture. Methanol of 99.5 % purity having density of 0.791 g/cm³ is used. Further 2.5 gram of catalyst KOH is added to Methanol and stirred the mixture continuously. The mixture was maintained at one bar pressure and 60°C for two hours. After completion of trans-esterification process, the mixture is allowed to settle under gravity for 24 hours in a separating funnel. The products formed during trans-esterification were Canola oil methyl ester and Glycerin. Canola oil methyl ester (biodiesel) is mixed, washed with hot distilled water to remove the unreacted alcohol; oil and catalyst and allowed to settle under gravity for 25 hours. The biodiesel which is separated is taken for characterization.R1, R2, R3 and R' represent various alkyl groups. The process of trans-esterification brings about drastic change in viscosity of vegetable oil. The biodiesel thus produced by this process is totally miscible with mineral diesel in any proportion.

Table 3.1: Specifications of the engine.

Engine Make	single cylinder Diesel Engine
Type	Kirloskar, single cylinder, vertical, water cooled , 4-stroke diesel engine
Bore & Stroke	87.5 mm & 110 mm
Compression ratio	17.5:1
Fuel	Diesel engine
Rated brake power	5.2 kW(7HP)
Speed	1500 rpm
Ignition system	Compression Ignition
Ignition timing	23°bTDC (rated)
Injection Pressure	220 bar
Loading Device	Eddy current dynamometer
Software	"IC Engine Soft" Engine performance analysis software

TABLE 3.2. PROPERTIES OF B20 BLEND OF CANOLA OIL AND DIESEL WITH ADDITIVES AFTER TRANSESTERFICATION

Properties	P-PDA			EDA			L-Ascorbic acid		
	B20 +500	B20 +750	B20 +1000	B20 +500	B20 +750	B20 +1000	B20 +500	B20 +750	B20 +1000
Density(kg/m^3)	847	846	845	848	848.5	847.5	850	849	849.5
Calorific value (kJ/kg)	42690	42710	42720	42500	42580	42600	42480	42500	42510
Flash point (°C)	58	59	60	58	59	59	58	58	59
Fire point (°C)	62	63	64	61	62	63	61	61	62
Kinematic viscosity(cst) at 40^{o}C	3.27	3.25	3.23	3.25	3.24	3.22	3.24	3.23	3.21

IV. EXPERIMENTAL SET UP

Experiments are carried out in a single-cylinder, water -cooled; naturally aspirated direct injection diesel engine of 5.2 KW rated power coupled with an eddy current dynamometer. An eddy current dynamometer coupled to the engine is used as a loading device. The gas flow rates, fuel flow rate, speed, load and exhaust gas temperature are displayed on a personal computer. Exhaust emissions are measured with a NDIR (Non-Dispersive Infrared) based AVL Di Gas 444 gas analyzer. The analyzer provided a CO measurement range of 0 to 20% by volume with a resolution of 0.01%, NOx range of 0 to 5000 ppm with a resolution of 1 ppm and HC range of 0 to 20,000 ppm with a resolution of 1ppm. As the viscosity of canola oil is slightly higher than diesel fuel, less amount of fuel is injectedin to the combustion chamber. So in the present work the fuel injection pressure is increased to 200 bar and is kept constant throughout the experiment and maintained constant speed as 1500 rpm.

Fig 4.1. Schematic of experimental set up

V.EXPERIMENTAL PROCEDURE:

Experimental procedure is explained below.

1. The engine is started at no load condition and allowed to work for at least 10 minutes to stabilize.
2. The readings such as time taken for 10cc fuel consumption, ammeter & voltmeter readings etc. were taken as per the observation table.
3. The load on the engine was increased by 20% of FULL Load using the engine controls and the readings were taken as shown in the tables.
4. Step 3 was repeated for different loads from no load to full load at constant speed 1500rpm.

5. After completion of test, the load on the engine is completely relieved and then the engine is stopped.

The above experiment is repeated for at B20 blend with different proportions of three additives on the engine. The experimental procedure is similar as foresaid. A stationary four stroke, 3.7kW direct injection water cooled single cylinder diesel engine is used to conduct experiments. For the measurement of exhaust gas emissions, A AVL DIGAS-444 five gas analyzer is used and emissions will be shown on screen by placing a probe on exhaust pipe. All the readings were taken under steady running conditions..

VI. RESULTS AND DISCUSSION

In this section, oxides of nitrogen, carbon monoxide, hydrocarbons, brake thermal efficiency, brake specific fuel consumption are discussed by using canola oil methyl ester diesel blend.

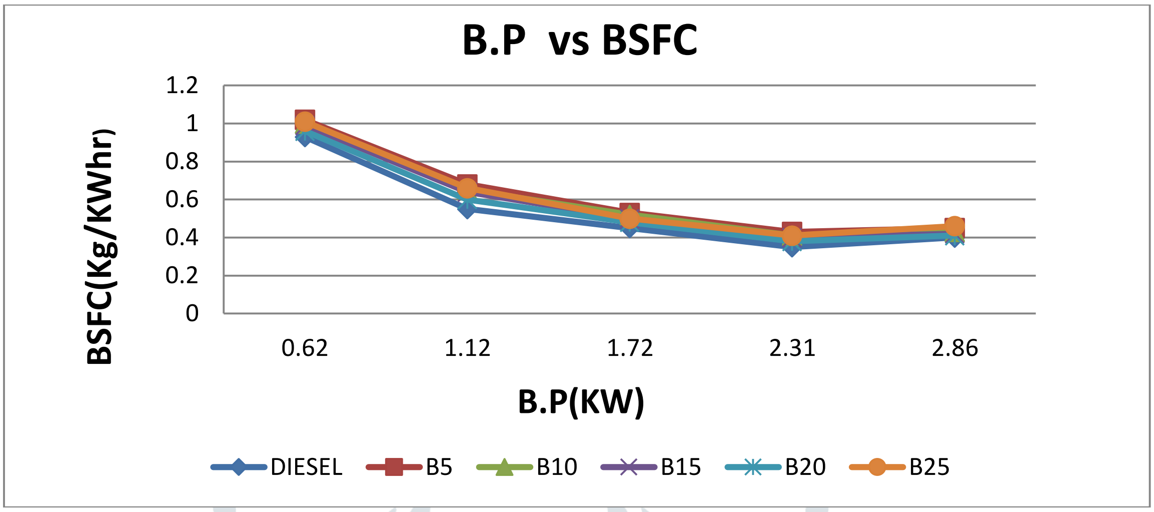

Fig 6.1

Fig 6.1 shows the variation of BSFC with respect to various B.P of the engine

Among the five concentrations tested, blend B20 is observed to be behaving better performance i.e, the BSFC is low and BTH is high compare with to blends among B5, B10, B15, B20 and B25 . In this present study, at B20 concentration with addition of additives of 500ppm, 750ppm and 1000ppm concentrations of P-PDA, EDA AND L-ASCORBIC ACID on engine performance and exhaust emissions of diesel engine are tested and compared results at 80% load with and without additives in biodiesel and diesel.

(i) PERFORMANCE PARAMETERS:

A) BRAKE THERMAL EFFICIENCY:

The results show the variation of Brake thermal efficiency with respect various B.P of the engine.

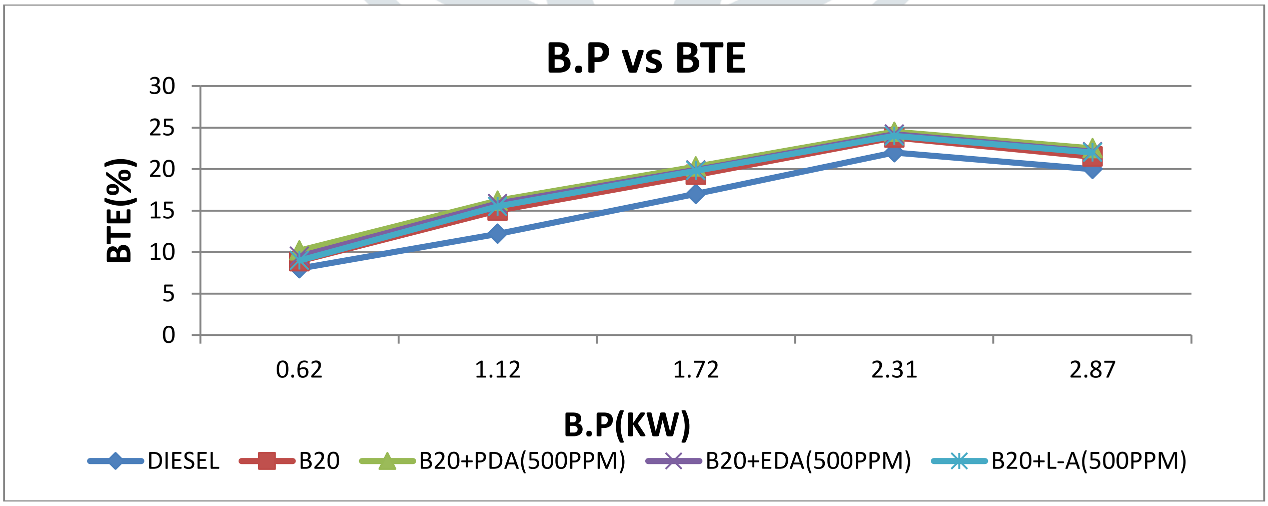

Fig 6.2

Above Fig shows that 500ppm P-PDA additive was found to be most effective antioxidant for increasing of BTE OF B20 than other additives .The BTE of Blend B20 was increased by 500 ppm of P-PDA,EDA AND L-A are 0.029%, 0.016% and 0.008% respectively with respect to Blend B20 but nearly equal to diesel.

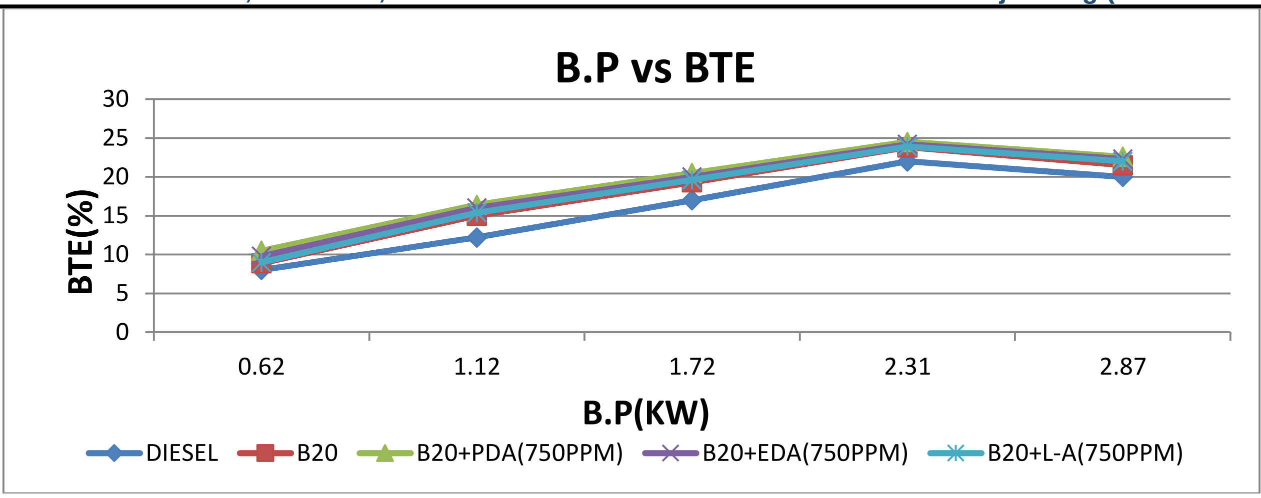

Fig 6.3

Above Fig shows that 750ppm P-PDA additive was found to be most effective antioxidant for increasing of BTE OF B20 than other additives .The BTE of Blend B20 was increased by 750 ppm of P-PDA,EDA AND L-A are 0.029%, 0.016% and 0.012% respectively with respect to Blend B20 but nearly equal to diesel.

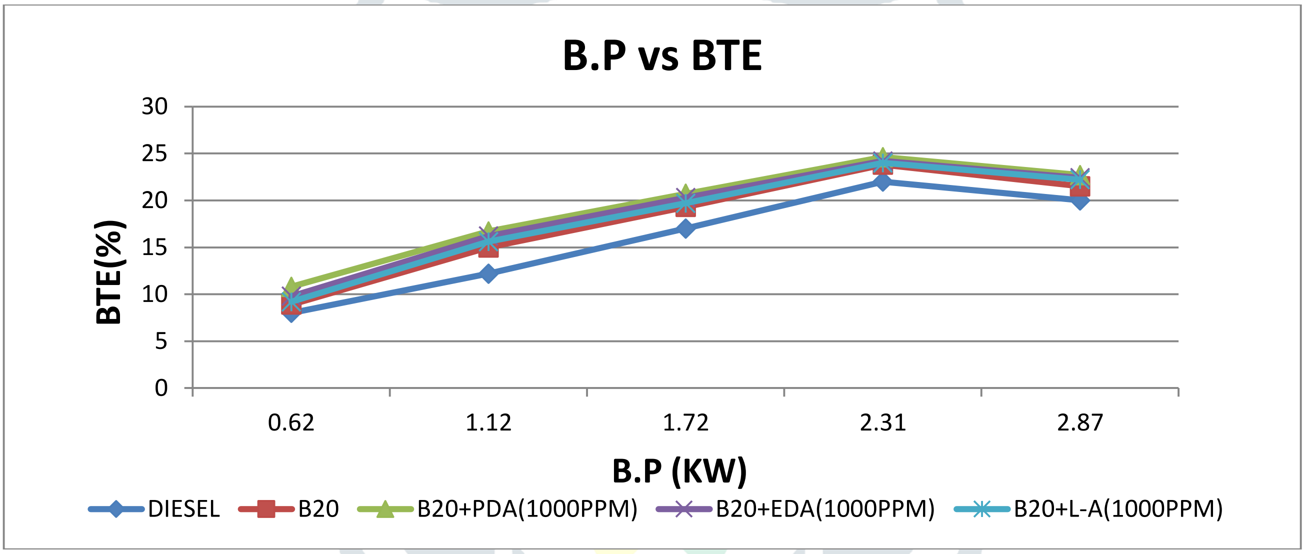

Fig 6.4

Figs 6.2, 6.3 and 6.4 show the variation of B.P with BTE.

Above Fig shows that 1000ppm P-PDA additive was found to be most effective antioxidant for increasing of BTE OF B20 than other additives .The BTE of Blend B20 was increased by 1000 ppm of P-PDA,EDA AND L-A are 0.033%, 0.021% and 0.019% respectively with respect to Blend B20 but nearly equal to diesel.

It is clearly seen in the figs that the brake thermal efficiency of diesel and blend B20 with and without antioxidants additives increases with increase in load up to 75% load and then decreases. As the additives proportions increases in B20 the BTE slightly increases but not as much as diesel i.e nearer to diesel efficiency.

B) BRAKE SPECIFIC FUEL CONSUMPTION (BSFC):\

The results shows the variation of BSFC with respect to various B.P of the engine. Effect of antioxidant concentration on BSFC of B20 containing 500ppm, 750ppm, 1000ppm of EDA, L-A, PDA antioxidant additives.

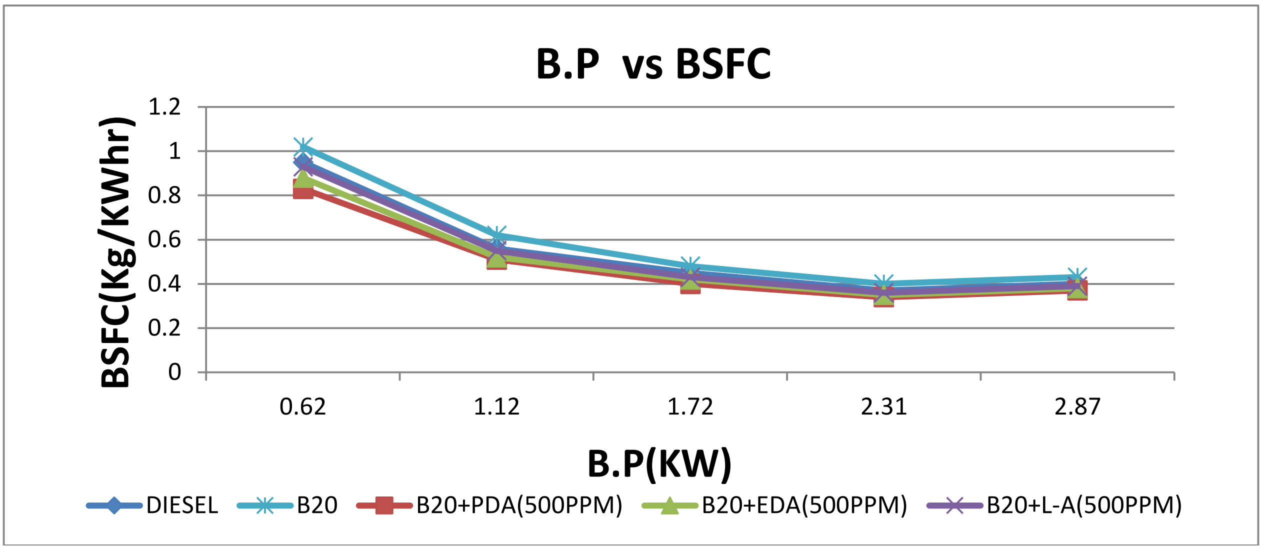

Fig 6.5

Above Fig shows that 500ppm P-PDA additive was found to be most effective for reduction of BSFC of B20 than other additives .The BSFC of Blend B20 was reduced by 500ppm of P-PDA,EDA AND L-A are 17.6%,14.2% and 11% respectively with respect to Blend B20 but nearly equal to diesel.

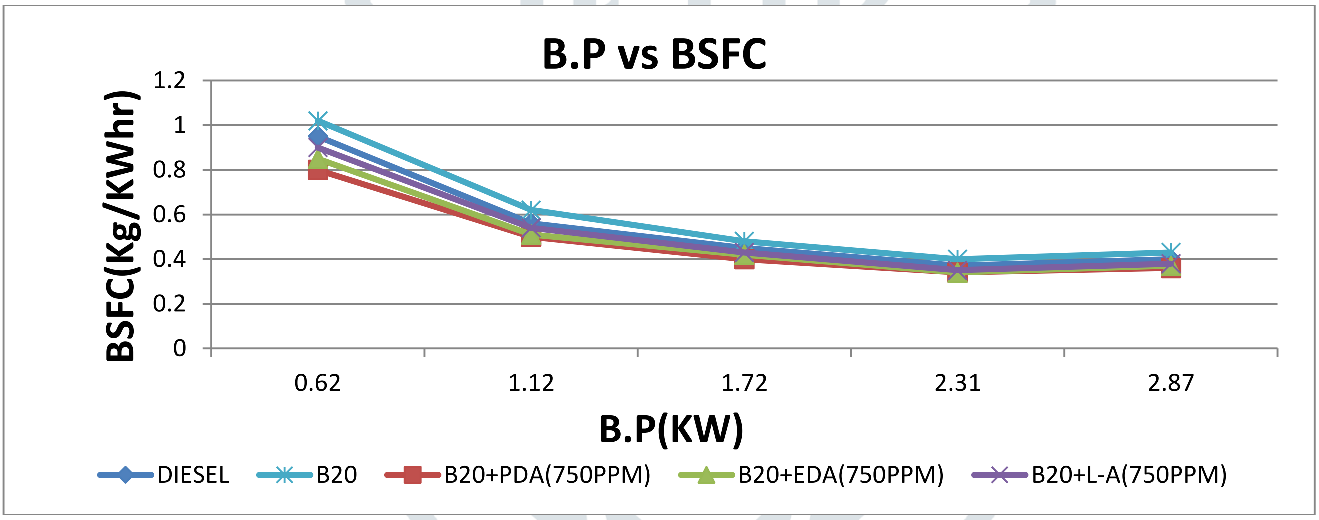

Fig 6.6

Above Fig shows that 750ppm P-PDA additive was found to be most effective for reduction of BSFC of B20 than other additives .The BSFC of Blend B20 was reduced by 750 ppm OF P-PDA,EDA AND L-A are 17.6%,17.6% and 14.2% respectively with respect to Blend B20 but nearly equal to diesel

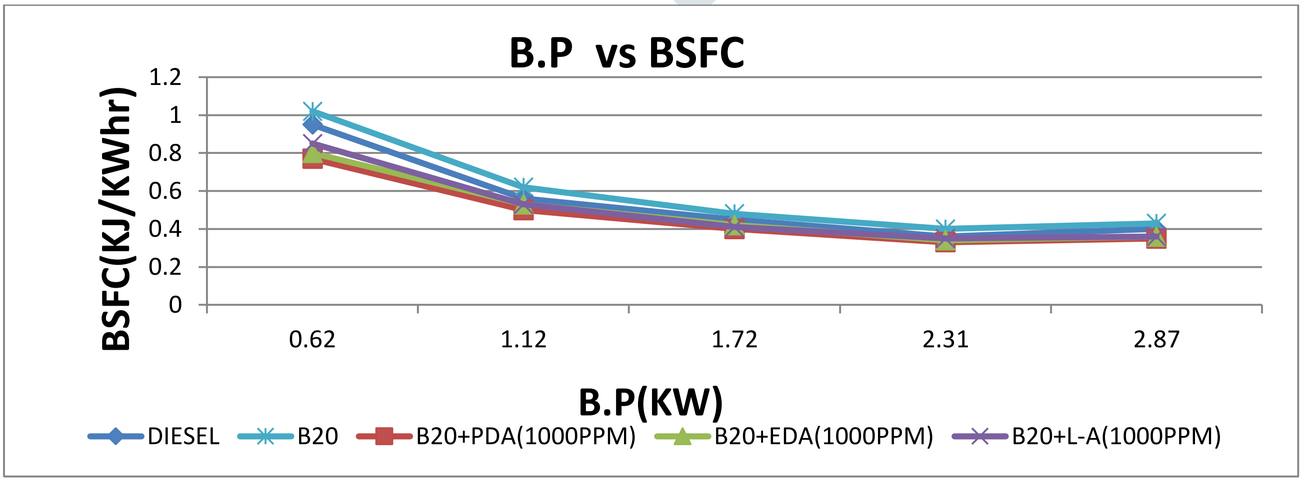

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Fig 6.7

Figs 6.5, 6.6 and 6.7 shows the variation of B.P with BSFC

Above Fig shows that 1000ppm P-PDA additive was found to be most effective for reduction of BSFC of B20 than other additives .The BSFC of Blend B20 was reduced by 1000PPM of P-PDA,EDA AND L-A are 21%,17.6% and 14.2% respectively with respect to Blend B20 but nearly equal to diesel.

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According to test results the BSFC of blend B20 is higher than that of diesel due to high viscosity of biodiesel and low heating value .With the addition of additives the flow capability of the fuel increases, viscosity decreases and calorific value increases. So, with the increase of additive concentration to B20 fuel the BSFC decreases. The general trend of the fig shows that as load increases, BSFC decreases up to 75% load and then again increases. As the additives proportions increases in B20, there will be slightly decrease in BSFC but as nearer to diesel.

(ii)EMISSION PARAMETERS

A) NO_X EMISSIONS :

The results show the variation of NO_x with respect various B.P of the engine.

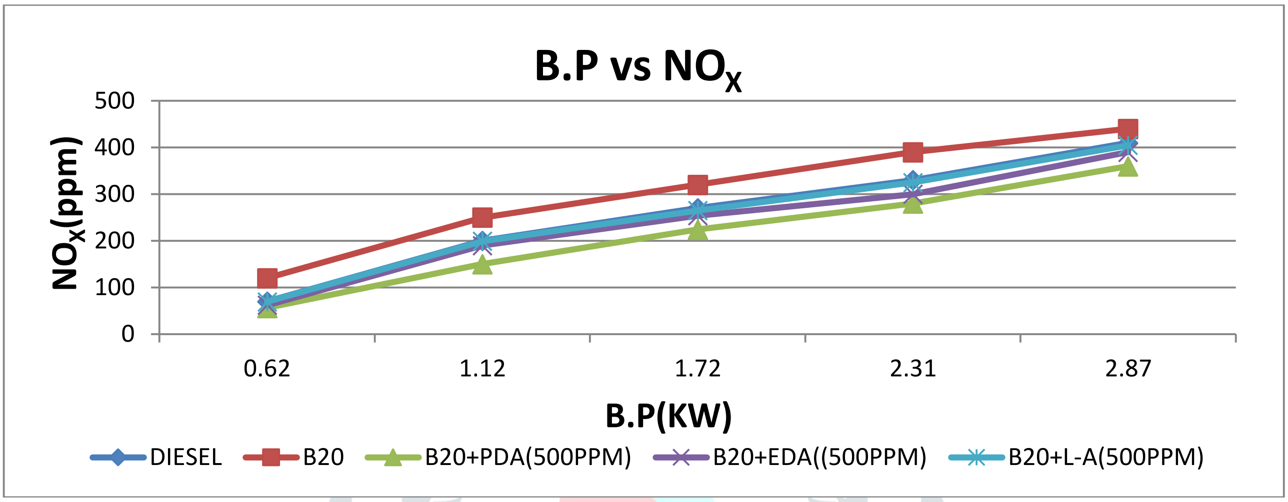

Fig 6.8

Above Fig shows that 500ppm P-PDA additive was found to be most effective antioxidant for reduction of **NO_X** emissions of B20 than other additives .The **NO_X** emissions Blend B20 was reduced by 500 ppm of P-PDA,EDA AND L-A are 34%, 30% and 20% respectively with respect to Blend B20 but nearly equal to diesel .

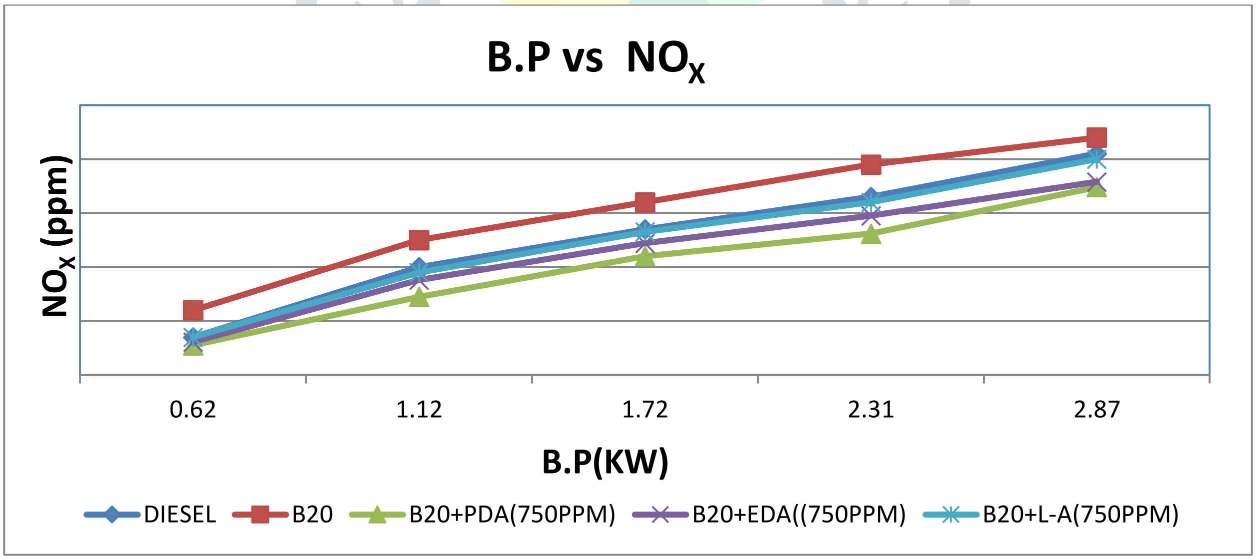

Fig 6.9

Above Fig shows that 750ppm P-PDA additive was found to be most effective antioxidant for reduction of **NO_X** emissions of B20 than other additives .The **NO_X** emissions Blend B20 was reduced by 750 ppm of P-PDA,EDA AND L-A are 36%, 32% and 21% respectively with respect to Blend B20 but nearly equal to diesel .

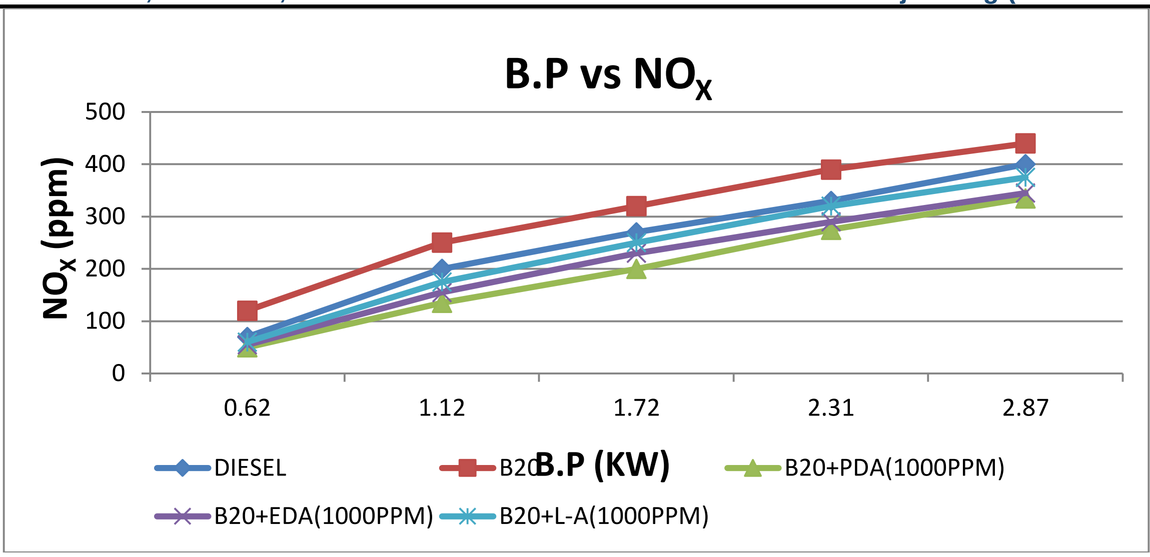

Fig 6.10

Figs 6.8, 6.9 and 6.10 show the variation of NO_x emissions B.P.

Above graph shows that 1000ppm P-PDA additive was found to be most effective antioxidant for reduction of **NO_X** emissions of B20 than other additives .The **NO_X** emissions Blend B20 was reduced by 1000 ppm of P-PDA,EDA AND L-Aare 37%, 34% and 22% respectively with respect to Blend B20 but nearly equal to diesel .

Temperature plays a predominant role in NOX formation. High temperature produces which causes nitrogen from air will disassociate and combine with oxygen and causes high formation of NO_x in case of biodiesel combustion because high oxygen concentration in biodiesel causes somewhat complete combustion and increases the temperature Results indicate the significant reduction in NO_x is observed while using antioxidant with biodiesel because additives reduces the temperature which causes more formation of NO_x. The general trend of the figs show that as load increases NO_x formation also increases.

B) **CO EMISSIONS**:

The results show the variation of CO with respect to various B.P of the engine.

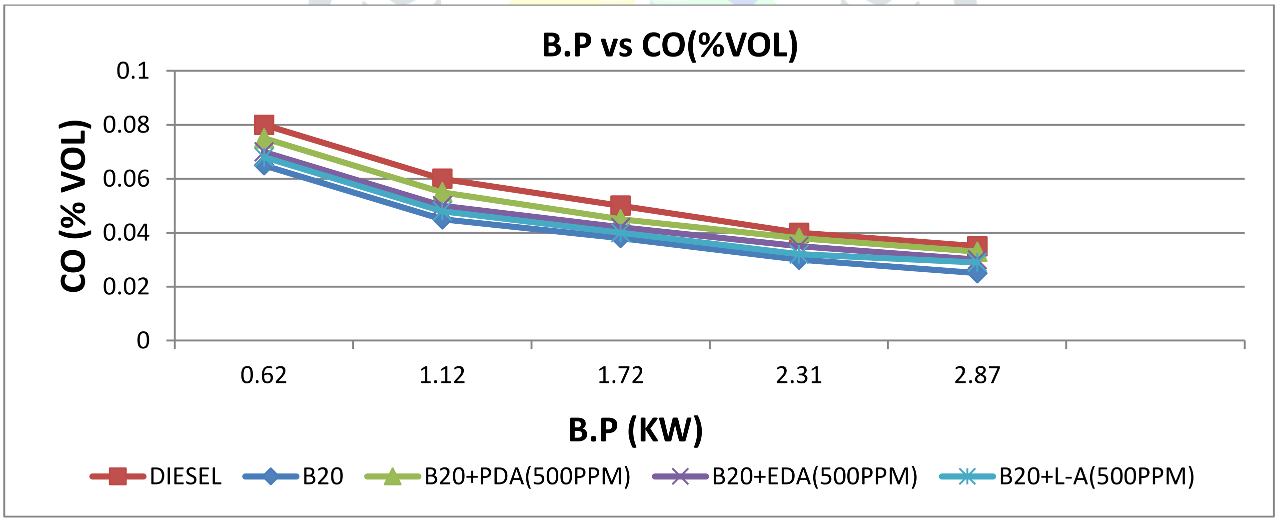

Fig 6.11

Above Fig shows that 500ppm P-PDA additive was highly increased **CO** emissions of B20 than other additives .The CO emissions of Blend B20 was increased by 500 ppm of P-PDA,EDA and L-A are 20%, 14% and 6% respectively with respect to Blend B20 but nearly equal to diesel .

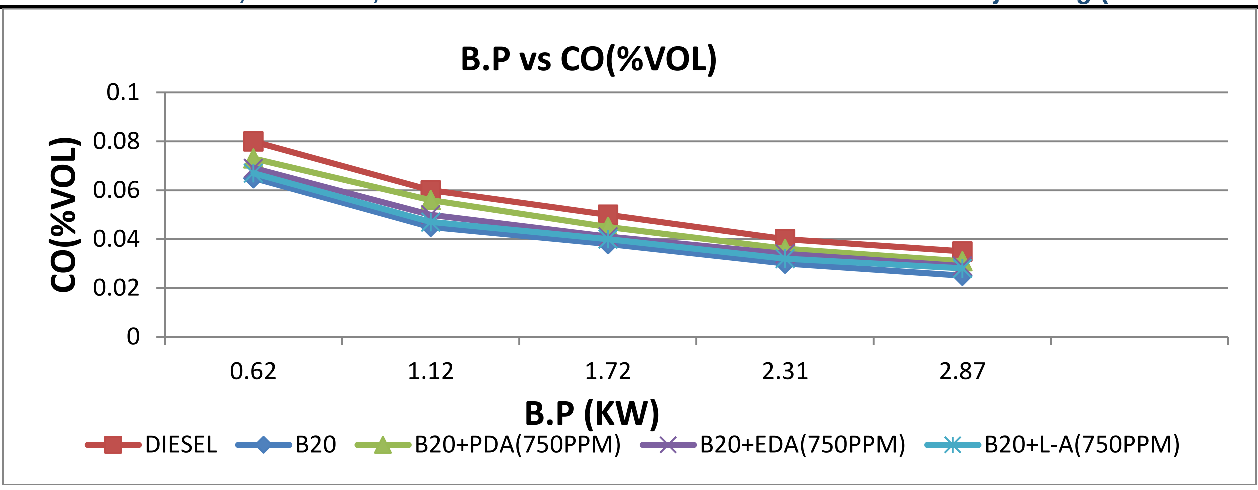

Fig 6.12

Above Fig shows that 750ppm P-PDA additive was highly increased **CO** emissions of B20 than other additives .The CO emissions of Blend B20 was increased by 750 ppm of P-PDA,EDA and L-A are 16%,11% and 6% respectively with respect to Blend B20 but nearly equal to diesel.

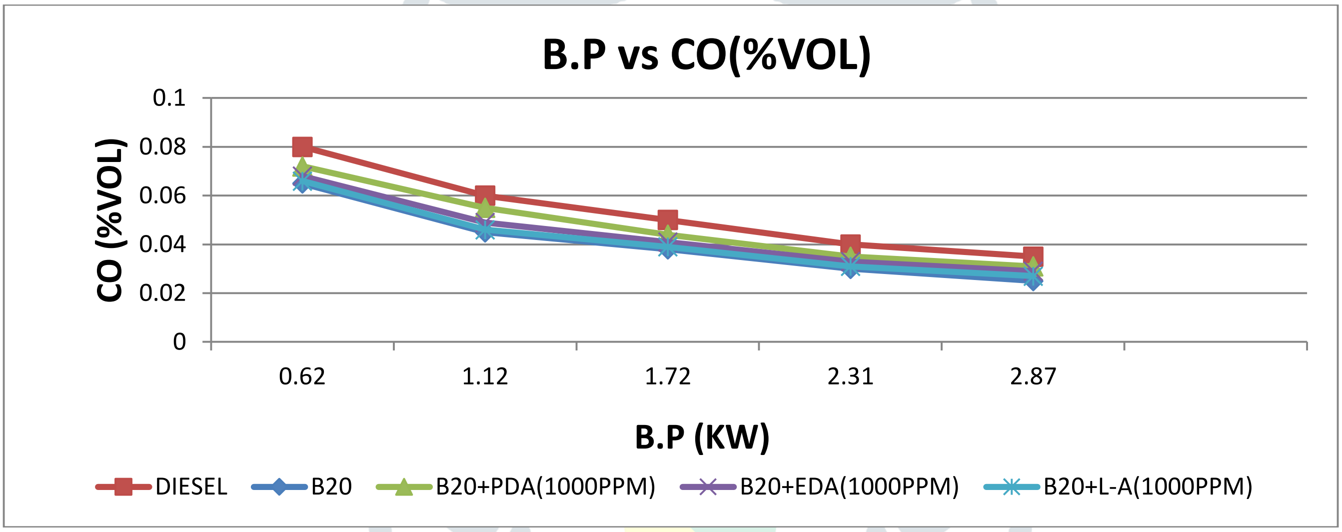

Fig 6.13

Figs 6.11, 6.12 and 6.13 shows variation of CO emissions with B.P.

Above fig shows that 1000ppm P-PDA additive was highly increased **CO** emissions of B20 than other additives .The CO emissions of Blend B20 was increased by 1000 ppm of P-PDA,EDA and L-A are 14.2%, 8% and 3% respectively with respect to Blend B20 but nearly equal to diesel.

The general trend of the figs show that CO emissions of diesel and blend B20 with and without additives decrease with increase of load. Generally , oxygen availability in biodiesel blends is high , so at high temperatures carbon easily combines with oxygen and reduces CO emissions. But the addition of additives with biodiesel increases the CO emissions because additives reduces the temperature and oxygen availability which are main responsible for the oxidation of CO.

C) HC EMISSIONS:

The result shows the variation of HC with respect to various B.P of the engine.

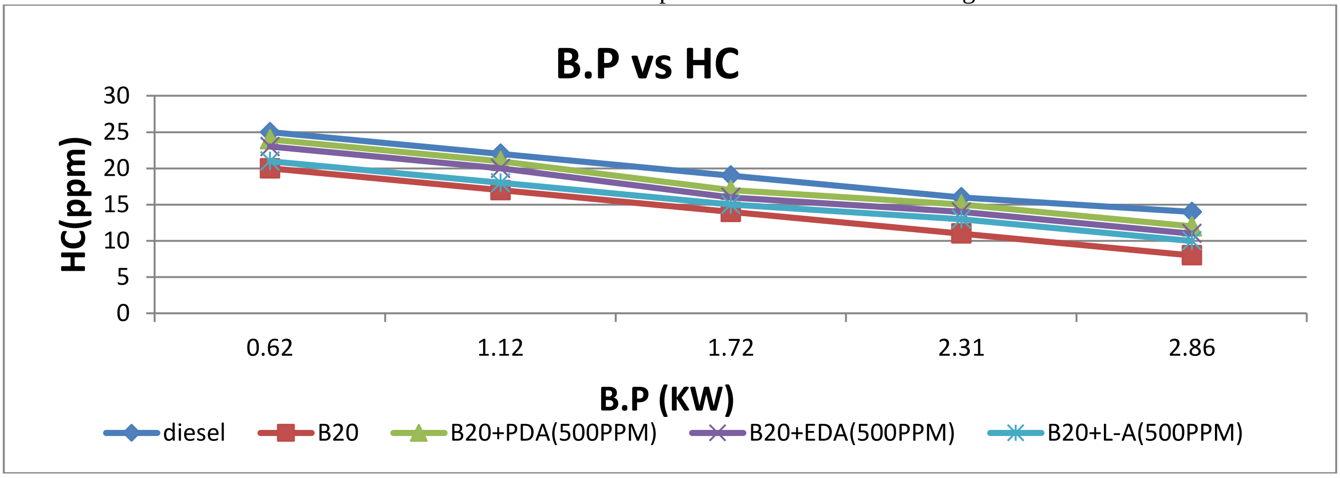

Fig 6.14

Above Fig shows that 500ppm P-PDA additive was highly increased **HC** emissions of B20 than other additives .The HC emissions of Blend B20 was increased by 500 ppm of P-PDA,EDA and L-A are 25%, 21% and 15.3% respectively with respect to Blend B20 but nearly equal to diesel

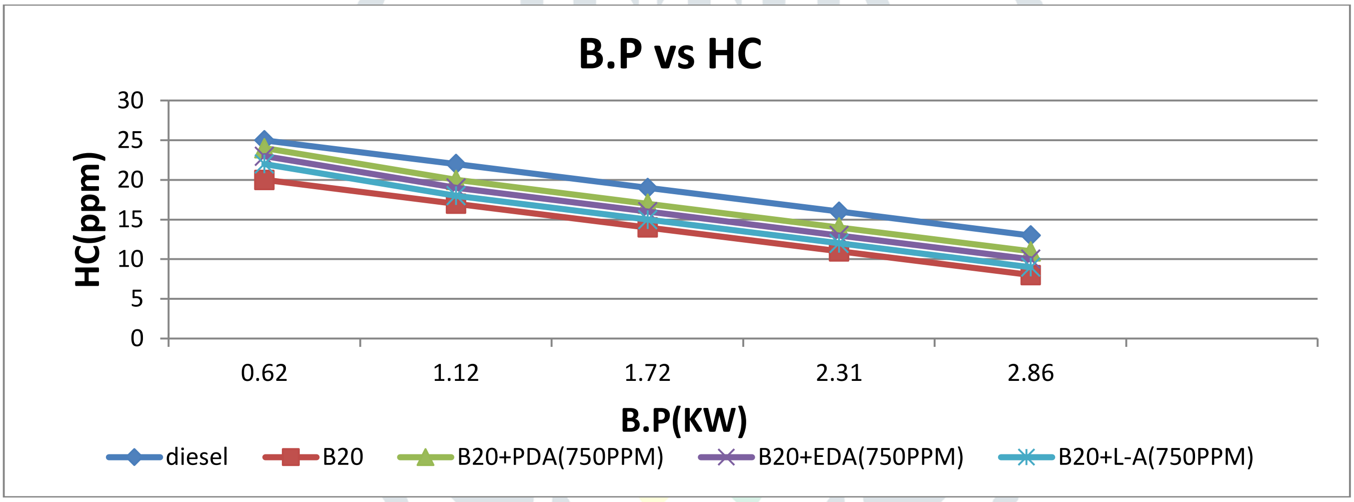

Fig 6.15

Above Fig shows that 750ppm P-PDA additive was highly increased **HC** emissions of B20 than other additives .The HC emissions of Blend B20 was increased by 750 ppm of P-PDA,EDA and L-A are 21.4%, 15.3% and 8.33% respectively with respect to Blend B20 but nearly equal to diesel

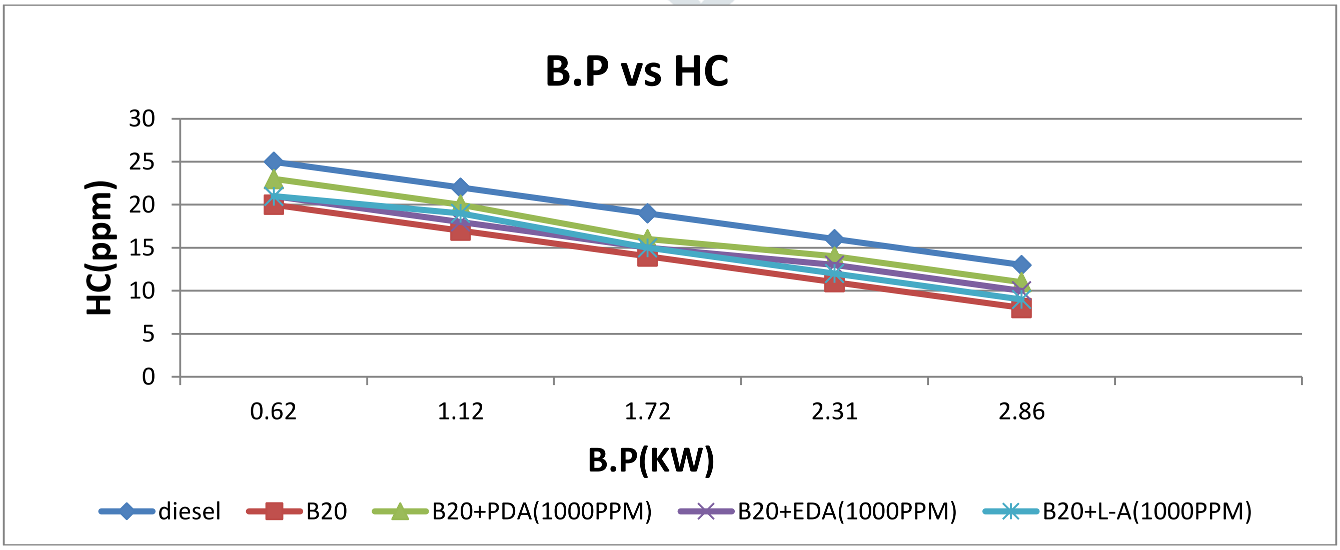

Fig 6.16

Figs 6.14, 6.15 and 6.16 shows the variation of HC emissions with B.P.

Above Fig shows that 1000ppm P-PDA additive was highly increased **HC** emissions of B20 than other additives .The HC emissions of Blend B20 was increased by 1000 ppm of P-PDA,EDA and L-A are 21%, 15% and 8% respectively with respect to Blend B20 but nearly equal to diesel

It is clearly seen in the figs that the HC emissions of diesel and blend B20 with and without additives decrease with increase of B.P. Generally, oxygen availability in biodiesel blends is high, so at high temperatures HC easily combines with oxygen and reduces HC emissions. But the addition of additives with biodiesel increases the HC emissions because additives reduces the temperature and oxygen availability which are main responsible for the oxidation of HC.

VII. FINAL CONCLUSION:

Finally, the blend B20 with 1000ppm of P-PDA additive is suitable for the better Performance i.e increases brake thermal efficiency and decreases brake specific fuel consumption and reduced NO_x emissions than other concentrations with other additives.

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