ISSN (Online) : 2319 - 8753
ISSN (Print) : 2347 - 6710

International Journal of Innovative Research in Science, Engineering and Technology

*An ISO 3297: 2007 Certified Organization* *Volume 4, Special Issue 2, February 2015*

5th International Conference in Magna on Emerging Engineering Trends 2015 [ICMEET 2015]

On 27th & 28th February, 2015

Organized by

Department of Mechanical Engineering, Magna College of Engineering, Chennai-600055, India.

# Effect of Antioxidant Additives on Reducing $NO_x$ Emissions

Velmurugan.K [1], Sathiyagnanam A.P[2].

Research Scholar, Department of Mechanical Engineering, Annamalai University, Chidambaram, India

Assistant Professor, Department of Mechanical Engineering, Annamalai University, Chidambaram, India

**ABSTRACT:** Scarcity of conventional petroleum fuels has promoted research in alternative fuels for internal combustion engines. Worldwide energy demand has been growing steadily during the past 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 sources, offers cleaner combustion over conventional diesel fuel. However, several authors report to increase in $NO_x$ emissions (about 13%) for biodiesel compared with conventional diesel fuel. In this paper, the effect of antioxidant additive L-ascorbic acid on $NO_x$ emissions in a Mango Seed methyl ester fuelled direct injection diesel engine have been examined experimentally and compared. The antioxidant additive is mixed in various proportions (100-400mg) with Mango Seed methyl ester is tested on a kirloskar make 4-stroke water cooled single cylinder diesel engine of 5.2 KW rated power. Results show that the antioxidant additive is effective in controlling the $NO_x$ and HC emissions of Mango Seed methyl ester fuelled diesel engines.

**KEYWORDS** :Biodiesel, mango seed oil, antioxidants, L-ascorbic acid, fuel additives, engine emissions

## I. INTRODUCTION

Biodiesel refers to mono-alkyl esters of long-chain fatty acids prepared from plant oils, animal fats (or) other lipids. The production of biodiesel has been growing worldwide and will continue to do so because of the rising price of petro diesel [1,2]. $NO_{x\ is}$ a major cause of Smog, ground level ozone also a cause of acid rain. The fuel $NO_x$ is considered as negligible, it does not contain fuel bound nitrogen. Among the all radical formations during combustion, hydroperoxyl (-OOH), hydroxyl (HO-), alkoxyl (RO-) and peroxyl (ROO-) radicals have significant impact on $NO_x$ formation. These radicals react with $N_2$ and $N_2O$ to form nitrogen oxides. Furthermore, antioxidants can reduce free radical formation by four routes; chelating the metal catalysts, chain breaking reactions, reducing the concentration of reactive radicals and scavenging the initiating radicals. The objective of this research is to investigate the effect of antioxidants on $NO_x$ formation of a mango seed derived biodiesel fuelled direct injection diesel engine [3, 4]. In spite of its lower heating value, biodiesel also has a lower stoichiometric air- fuel ratio. Thermodynamically, adiabatic flame temperature is a function of heating value and stoichiometric air/fuel ratio. Benajes et al [5] show significant effects of adiabatic flame temperature, heat release rate and stoichiometric burning on $NO_x$ formation in diesel engines. The adiabatic flame temperature of biodiesel is reported to have slightly higher than petro –diesel due to complete combustion resulting from fuel bound oxygen[6].Szibist et al.[7], however, observe a lower rate of heat release for the biodiesel fuel at full loads. The reduced soot formation of biodiesel leads to decreased radiative heat transfer which results in increased combustion temperature and $NO_x$. Yuan and Hansen [8] conducted computational study using Zeldovich $NO_x$ formation model together with a Kelvine Helmholtz Rayleighe Taylor (KH-RT) spray break-up model and conducted that decreased spray cone angle and advanced start of injection of biodiesel influences $NO_x$ formation. Biodiesel requires longer pulse-width than diesel in electronic controlled engines due to its lower calorific value causing more quantity of fuel entry into the cylinder which results in high temperature and $NO_x$ [9]. Varuvel et al.[10] concluded that the increased premixed combustion of biodiesel fuel is one of the reasons for biodiesel NOx effect. Since biodiesel contains oxygen, it premixes more fully during the ignition delay, and a larger fraction of its heat release occurs during the premixed –burn phase of combustion at ignition. Combustion that is more premixed has higher oxygen concentrations and therefore produces more NOx. Allen and Watts [11] stated that the sauter mean diameter of the methyl ester biodiesel varies from 5 to 40% higher than petroleum diesel fuel. An increase in the sauter mean diameter reduces the premix phase of combustion , causing an increase in the diffusion phase of combustion and $NO_x$. CH and OH radicals are continuously formed during combustion reactions. The formation of CH-radicals is an indicator of low temperature pre- combustion reactions, which is the first step for the combustion process, once fuel is evaporated. OH radicals are formed during high pressure reactions and are located in the flame front, where vaporized fuel reaches the highest temperatures [12]. Brezinsky et al.[13] claimed that the high rate of acetylene production from the unsaturated fatty acids of biodiesel is the major cause of increased $NO_x$ formation. The acetylene is , responsible for hydrocarbon CH radical generation and prompt $NO_x$. Many researchers have found that the higher $NO_x$ emissions produced in biodiesel combustion is influenced by factors such as the physic chemical properties, molecular structure of the biodiesel, adiabatic flame temperature, injection timing and ignition delay time and so on[14]. Higher biodiesel $NO_x$ emissions occur mainly due to the increase in the formation of prompt $NO_x$ in biodiesel combustion in diesel engines [15]. $NO_x$ is generated during combustion by three main 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 hydrocarbon flames and it is considered as moderately significant compared to total $NO_x$ formation. Thermal and prompt are the dominant mechanisms for the $NO_x$ generation during combustion, thermal mechanism is largely unaffected by fuel chemistry, where as the prompt mechanism is sensitive to free radical concentration within the reaction zone. The free radicals formation during combustion determines the rate of reaction and prompt $NO_x$ production [16]. Free radical is a highly reactive molecule with one or more unpaired electrons. Antioxidants inhibit oxidative processes by donating an electron or hydrogen atom to a radical derivative. The mixture of antioxidant and biodiesel fuel suppresses the peroxyl free radical formations by reaction with aromatic amines. These peroxyl free radicals are the main cause of the higher biodiesel $NO_x$ emission [17]. In this study, L-ascorbic acid is chosen as the antioxidant test additive to reduce $NO_x$ emissions based on cost, effectiveness and availability. The L-ascorbic acid antioxidant is purchased from Sd-fine chem. Ltd, India.

Table 1.Comparison of diesel, mango seed oil and MEMSO

| ***properties*** | ***Standard method*** | ***Diesel*** | ***Mango seed oil*** | ***MEMSO*** |
|---|---|---|---|---|
| ***Density(g/cm$^3$)*** | ***ASTM D941*** | ***0.8359*** | ***0.9711*** | ***0.882*** |
| ***Net calorific value(kJ/Kg)*** | ***ASTM D240*** | ***44519*** | ***39812*** | ***40453*** |
| ***Kinematic viscosity(Cst)*** | ***ASTM D613*** | ***2-3*** | ***34.5*** | ***4.73*** |
| ***Flash point(°C)*** | ***ASTM D445*** | ***76*** | ***226*** | ***135*** |
| ***Cetane number*** | ***ASTM D93*** | ***51*** | ***50*** | ***54*** |

Table 2. Specifications of the test engine

| | |
|---|---|
| Make | Kirloskar TV- 1 Engine |
| Type | 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 kgf/cm$^2$ |
| Loading Device | Eddy current dynamometer |

Table 3. Technical Specifications of the exhaust gas analyser

| *Measured quality* | *Measuring range* | *Resolution* | *Accuracy* |
|---|---|---|---|
| ***CO*** | ***0...10% vol*** | ***0.01% vol*** | ***<0.6%vol:±0.03% vol*** <br> ***≥0.6% vol:±5% of ind.value*** |
| ***$CO_2$*** | ***0...20% vol*** | ***0.1% vol*** | ***<10% vol:±0.5% vol*** <br> ***≥10% vol:±0.5% of vol*** |
| ***HC*** | ***0...20,000 ppm vol*** | ***≤2000:1 ppm vol,*** <br> ***>2000:10ppm vol*** | ***<200 ppm vol:±10 ppm val*** |
| ***$O_2$*** | ***0...22% vol*** | ***0.01% vol*** | ***<2% vol:±0.1% vol*** |
| ***NO*** | ***0...5000 ppm vol*** | ***1 ppm vol*** | ***<500 ppm vol:±50 ppm vol*** |

Model: AVL DiGas 444

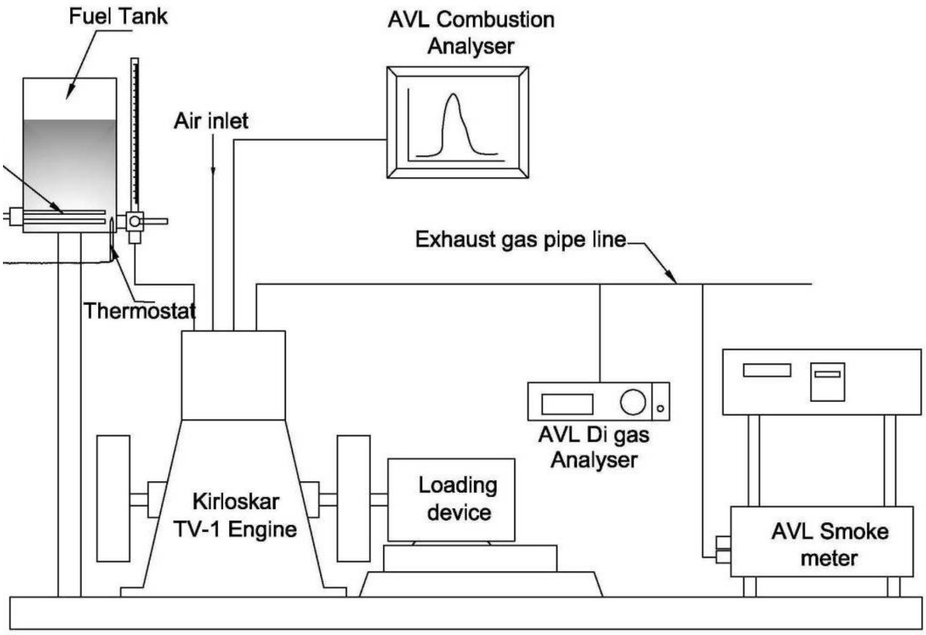

Fig 1.schematic of the experimental setup

## II. 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 DiGas 444 gas analyser. The analyser provided a CO measurement range of 0 to 20% by volume with a resolution of 0.01%, $NO_x$ 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 1 ppm. L-ascorbic acid is accurately weighed using a high-precision electronic weighing balance and added to measure quantity of mango seed biodiesel. To make 100 ppm of antioxidant mixture 100mg of the antioxidant is added to 1 kg of the biodiesel. A 3000 rpm speed mixer is used to prepare a homogenous mixture of the antioxidant and fuel.

## III. RESULTS AND DISCUSSION

The effect of antioxidant additives on $NO_x$, HC, $CO_2$, CO and smoke intensity with mango seed methyl ester is investigated in this study. The $NO_x$ measurements are repeatable within each engine run, with replicate measurements varying by 3-8 ppm. As per the specifications of the analyser the maximum possible error in the measurement of $NO_x$, CO and HC emissions are ±5%.

### 3.1Comparison of $NO_x$ emissions:

Fig.2 shows the variation of $NO_x$ with brake power. Results indicate that significant reductions in $NO_x$ is observed while using antioxidants and the reduction is not linearly correlated with the amount of antioxidants present in the biodiesel. L-ascorbic acid is a radical-trapping antioxidant that scavenges reactive nitrogen oxide species such as NO, $NO_2$ and $N_2$ to prevent nitrosation of target molecules [18]. The main reason for the NO increase with the use of mango seed methyl ester is discussed by Fennimore [19] mechanism and it is proposed that NO formation is initiated by reactions of hydrocarbon radicals (CH,$CH_2$, $C_2$,C and $C_2H$) with molecular nitrogen. The production rates of HCN, N and NO increase with the concentration of CH radicals.

$CH + N_2 \longleftrightarrow HCN + N$
$N + O_2 \longleftrightarrow NO + O$
$HCN + OH \longleftrightarrow CN + H_2O$
$CN + O_2 \longleftrightarrow NO + CO$

The $NO_x$ concentration decreases up to LA 300 mixture with the increase in antioxidant fraction, then it increases. It is important to note that LA 300 reduces NOx emission by 8.12% compared with pure biodiesel at full load. LA 300 concentration with B20 blend gives the maximum decrease in $NO_x$ emission is due to the reduction in the formation of free radicals by the antioxidant L-ascorbic acid[20].

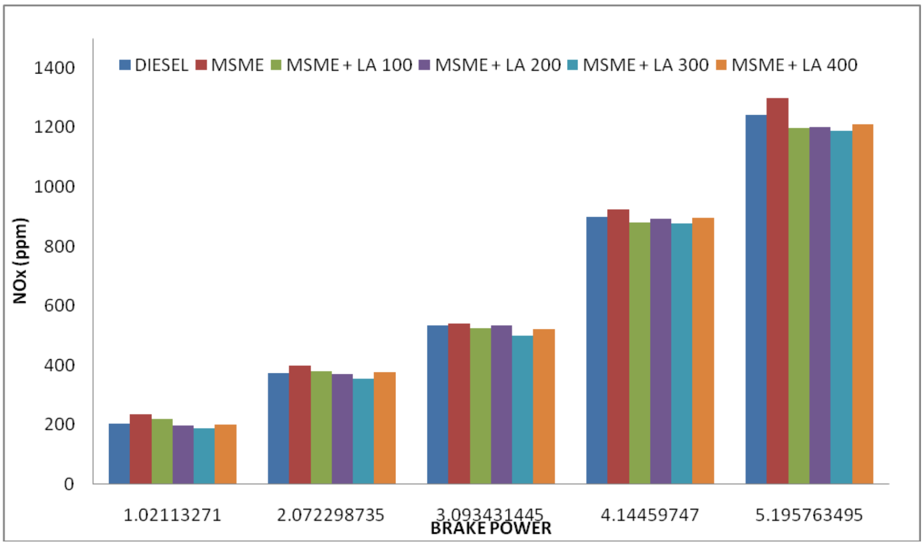

Fig.2. Variation of $NO_x$ emission with brake power

### 3.2Comparison of HC emissions:

Fig. indicates the variation of HC emission with brake power. Generally unburned hydrocarbons come under different forms such as drops of fuel, vapour and products of fuel after thermal degradation. The HC emission is found to be lower when the antioxidant traction in the biodiesel is increased. LA 300 concentration with B20 blend reduces the HC emission by 22.8% at full load condition. Generally, all antioxidant mixtures reduce HC compared with pure mango seed methyl ester. L-ascorbic acid reduces the functional groups present in the Mango seed methyl ester and basically it's a reducing agent. Having high oxygen content in the Mango seed methyl ester leads to prolonging complete combustion and results in lower HC emission.

### 3.3Comparison of CO emissions:

Fig. shows the variation of carbon monoxide with brake power. It is observed that biodiesel blends reduce CO emissions significantly compared to diesel. CO emission is formed due to incomplete combustion. Too rich fuel -air ratio and low flame temperature are the major causes of CO emissions from engine. The oxidation of CO is related to the amount of OH radicals present in the reaction. The antioxidant concentration is the Mango seed methyl ester slightly reduces CO emission then it increases.

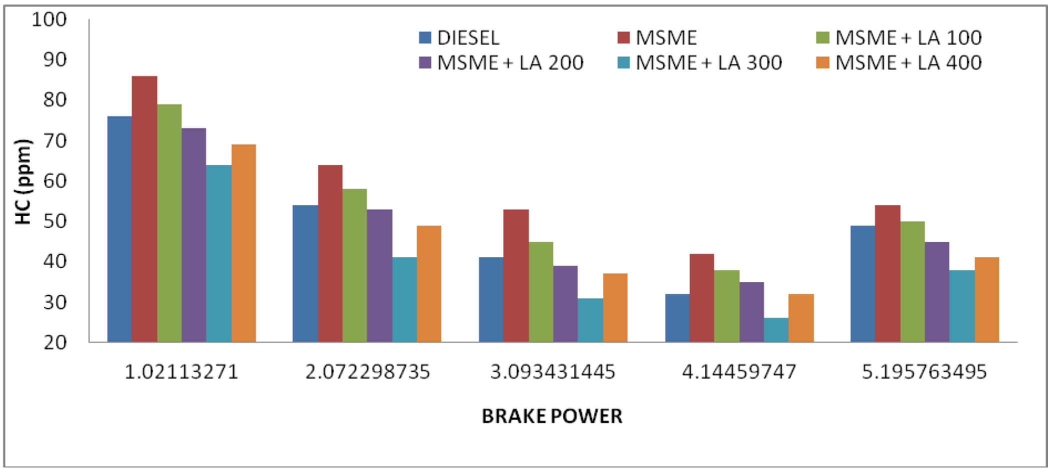

Fig.3. Variation of HC emissions with brake power

### 3.4Comparison of brake specific fuel consumption:

Fig. shows the variation of brake-specific fuel consumption with brakepower. The specific fuel consumption of the L-ascorbic acid is slightly higher when compared with neat biodiesel , it may be by a little more fuel supplied to the engine to compensate the slight power loss due to the incomplete combustion and improper combustion.

### 3.5Comparison of smoke intensity

Fig. shows the variation of smoke intensity with the brake power for diesel and biodiesel-antioxidant mixtures. The results show that smoke intensity increases with the increase in engine load. The smoke intensity is increased at all load conditions when the antioxidant concentration slightly increases and it may be due to improper combustion resulting from antioxidant addition.

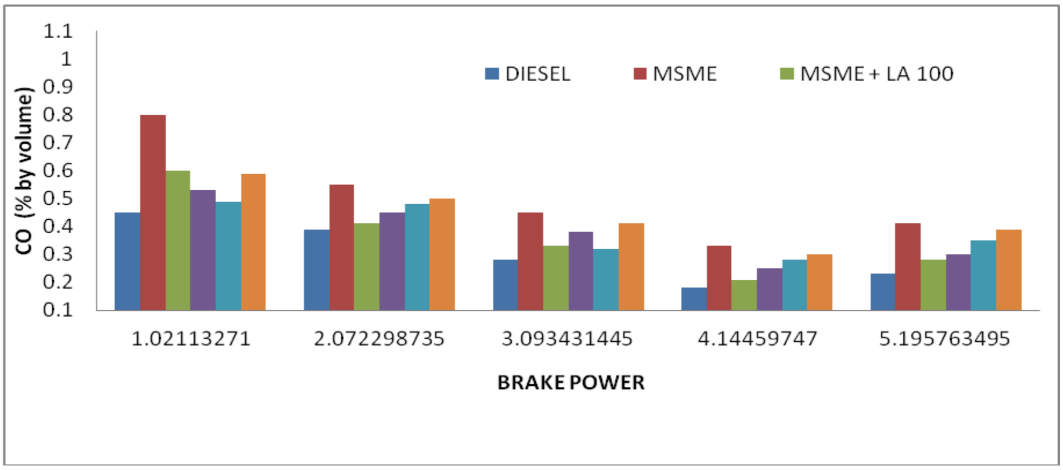

Fig.4. Variation of CO emissions with brake power

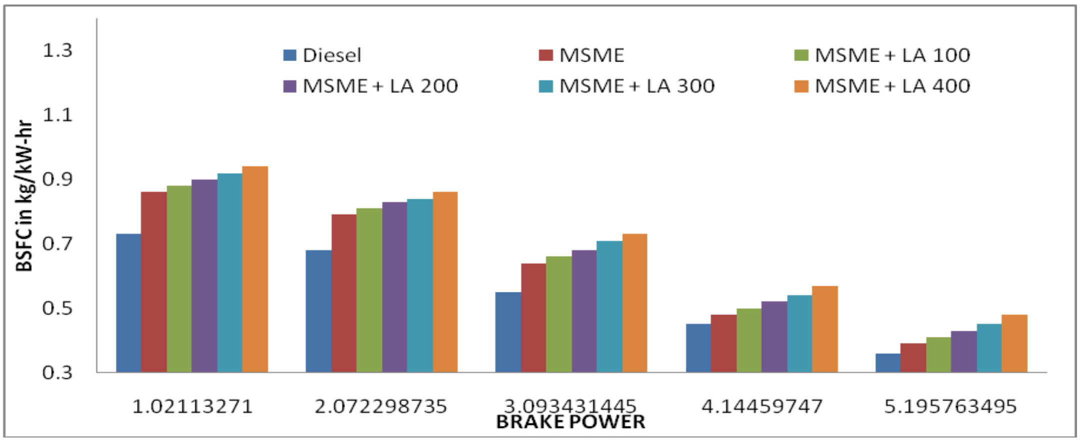

Fig.5. Variation of BSFC with brake power

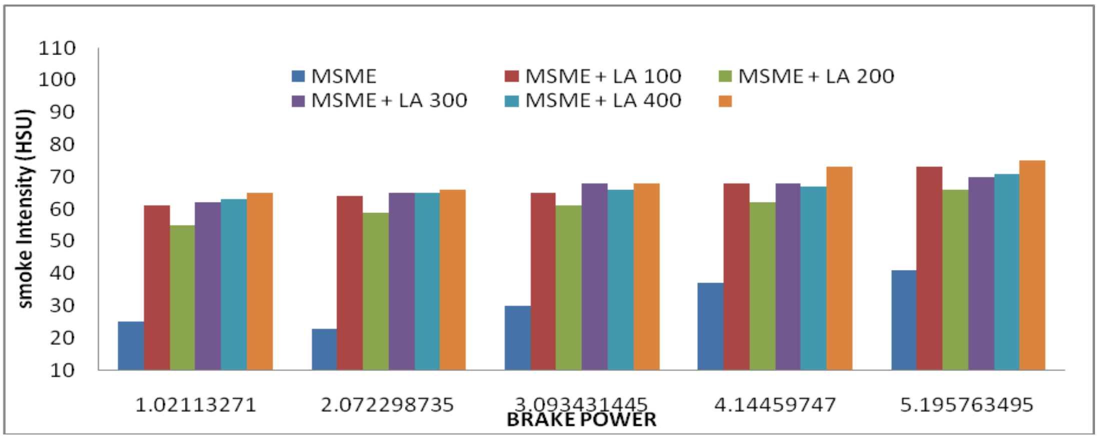

Fig.6 Variation of Smoke Intensity with brake power

## IV.CONCLUSION

The effect of antioxidant L-ascorbic acid addition on $NO_x$, HC,CO and smoke intensity with Mango seed methyl ester fuelled DI diesel engine at different concentrations have been reported in this paper. Results show the benefit antioxidant additives for $NO_x$ reduction in biodiesel fuelled diesel engines. The main conclusions of the study are:

1. L-ascorbic acid is quite effective in controlling $NO_x$ formation. However, it has more CO and HC emissions. Due to the addition of LA 300 with Mango seed methyl ester, the $NO_x$ emission is reduced by 21.33% and also HC emission is reduced by 8.12% at full load condition compared with MSME.
2. The remaining mixtures of LA 100, LA 200, LA 400 with Mango seed methyl ester, the $NO_x$ emissions are reduced by 4.22%,7.57%,6.94% respectively, and further HC emissions are reduced by 5.32%,11.64%,17.23% respectively at full load condition compared to pure biodiesel.
3. Slight increase in CO emission, BSFC is observed with L-ascorbic acid compared to mango seed methyl ester. Smoke intensity for all mixtures found to be increased slightly due to the disturbance during combustion.

## REFERENCES

1. A. Karmakar, S. Karmakar, S. Mukherjee:Properties of various plants and animals feedstock for biodiesel production. Bioresource Technology 101(19) 7201 – 7210(2010).

2. M.A.Hess, M.J. Haas, T.A. Foglia, W.N. Marmer:The effect of antioxidant addition on $NO_x$ emissions from biodiesel. Energy and fuels 191749-1754(2005).

3. E. Denisov, I. Afanas'ev:Oxidation and Antioxidants in Organic chemistry and biology, Taylor & Francis , Boca Raton(2005).

4. A. Monyem, J. Van Gerpen, M. Canakci.The effect of timing and oxidation on emissions from biodiesel- fuelled engines.Transactions of the ASAE 44 35-42(2001).

5. Benajes, J., Molina, S., Gonzalez, C., and Donde, R.The role of nozzle convergence in diesel combustion.Fuel 87 pp.1849-1858(2008).

6. Yuan, W., Hansen, A., Tat, M., Gerpen, J., and Tan, Z:Spray, ignition, and combustion modelling of biodiesel fuels for investigating $NO_x$ emissions. TASAE. 48, pp. 933-39, (2005).

7. Szybist, J., Kirby. S., and Boehman A: $NO_x$ emissions of alternative diesel fuels: a comparative analysis of biodiesel and FT diesel. Fuel 19 pp. 1484-92, (2005).

8. Eckerle, W., Lyfordpike. E., Stanton. D., LaPointe. L., Whitacre. S., and Wall. J:Effects of Methyl Ester Biodiesel Blends on $NO_x$ Emissions.SAE Paper No. 2008-01-0078(2008).

9. Varuvel, E., Mrad, N., Tazerout, M., and Aloui, F:Experimental analysis of biofuel as an alternative fuel for diesel engines. Appl. Energy, 94, pp.224-231, (2012).

10. Allen, C., and Watts, K:Comparative analysis of the atomization characteristics of fifteen biodiesel fuel types.TASAE, 43(2), pp.207-11, (2000).

11. Salvador. F., Gimeno, J., and Morena . J:Effects of Nozzle Geometry on Direct Injection Diesel Engine Combustion Process. Appl. Them. Eng., 29, pp.2051-2060, (2009).

12. Garner, S., Sivaramakrishnan, R., and Brezinsky, K:The high-pressure pyrolysis of saturated and unsaturated C7 hydrocarbons. Proc. Combust. Inst. 32, pp. 464-67,(2009).

13. K.Varatharajan, M. Cheralathan and R.Velraj:Mitigation of $NO_x$ emissions from a jatropha biodiesel fuelled DI diesel engine using Antioxidant Additives. Fuel 90 2721-2725(2011):.

14. K.Varatharajan, M. Cheralathan: Influence of fuel properties and Composition on $NO_x$ emissions from biodiesel powered diesel engines.Renewable and Sustainable Energy Reviews 16 3702-3710(2013):.

15. C. Mueller, A. Boehman, G. Martin :An experimental investigation of the origin of increased $NO_x$ emissions when fuelling a heavy –duty compression- ignition engine with soy biodiesel. SAE International Journal of Fuels and Lubricants 2 (1) 789-816 (2009-01-1792) (2009).

16. Tannenbaum SR, Wishnok JS, Leaf CD: Inhibition of nitrosamine formation by ascorbic acid . Am J Clin Nutr. 53:247-50(1991).

17.C.Fenimore:Formation of nitric oxide in premixed hydrocarbon flames,in:13th Symp.on combustion ,13. The combustion Institute, ,pp.373-380(1975).

18. S.M. Palash, H.H. Masjuki, M.A. Kalam, B.M. Masum, A. Sanjid, M.J. Abedin:State of the art of NOx mitigation technologies and their effect on the performance and emission characteristics of biodiesel-fuelled Compression ignition engines. Energy Conversion and Management, 76 400-420(2013).

19. T.T. kivevele, L. Kristof, A. Bereczky, M.M. Mbarawa: Engine performance, exhaust emissions and combustion characteristics of Jatropha curcas methyl ester with antioxidant.Fuel, 90(2011) 2782-2789(2011).