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# NOX REDUCTION STRATEGIES IN BIO-FUELLED COMPRESSION IGNITION ENGINES

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## ABSTRACT

*Rapid Industrialization, increasing demand of the transport and depleting fossil fuel resources has forced the world to get a alternative solution on fuel front, and researchers around the world has shown that bio-fuels like alcohol and biodiesel can provide the alternative solution which is not only a green fuel it is a cheap, and renewable in nature, with a biggest limitation of producing high level of $NO_X$ production which is confirmed in most of the studies, a considerable effort are required in this direction in order to make it acceptable in order to make it popular alternate for fossil fuel. The present study targets on the advantages and disadvantages of the bio-fuels specially $NO_X$ emission from diesel engine and various techniques have been discussed for reducing $NO_X$ emission from a diesel engine.*

## INTRODUCTION

The world today is facing multiple faced crises on the fuel front. On one side rapid escalation of fossil fuel prices due to the shortage and continuous depletion of conventional petroleum fuels and on the other side continuously degrading environmental conditions and global warming which has forced to impose stagnant legislative emission norms by regulating authorities. All these limitation has forced world to look for a new fuel which is renewable in nature and could produce minimum pollution. This need become extremely important in Indian context; India being agriculture based economy which has to import large quantity of oil to meet the demand of stationery power generation and transportation. Diesel engines are mainly used for power generation and transportation because of its durability, low cost of running and high energy efficiency. For the partial replacement of diesel fuel in the recent years Bio-fuels (biodiesel and Alcohols) have gained a lot of popularity because of its renewable characteristic and environmental friendly nature. This becomes more convincing seeing the large waste land bank available which is still uncultivated in India.

## BIO-FUELS

Biodiesel and Alcohols because of having considerable quantity of oxygen are also known as oxygenated fuels. Bio-fuels are generally considered as offering many priorities, including sustainability, reduction of green house gas emission, regional development, social structure and agriculture, security of supply **Rejinders et al [1].** Bio-fuels because of its comparative characteristics with that of fossil diesel can be used in various proportions, with no or very little modification of the engine.

**Biodiesel:** The American Society for testing and Materials (ASTM) defines Biodiesel fuel as mono alkyl esters of long chain fatty acids derived from renewable lipid feed stocks, such as vegetable oils or animal fats for use in diesel engines **Roska R et al,[ 2].** The main commodity source in India can be non-edible oils obtained from plants. Most commonly used species are Jatropha curcus (Ratan Jot), Pongamia Pirinala (Karanjia), Calophyllum inophyllum (Nag champa), Heveca brasiliensis (Rubber) etc. Biodiesel contain no Petroleum product.

**Performance and Emissions from biodiesel fueled engine:**

Mukul Goel, ( M. Tech, "Thesis" IIT, Delhi, 2005) performed experiment with Biodiesel Jatropha Oil Methyl Ester (JOME) in the various ratio with a fossil diesel[3] Experiments were performed on various operation load on the engine. The performance and the emission charactestics for the various blends were evaluated the result showed the JOME is found to burn more efficiently then diesel**.** The emission of carbon monoxide, hydrocarbon, and smoke were decreased by 51.42% 13.8 % and 1% respectively. It was observed that brake thermal efficiency of JOME was increased to 32.03 % for pure JOME as compared to 28.39% for pure diesel at maximum Load. Smoke value of JOME was comparable with diesel values. Exhaust gas temperature and noise level were also comparable. There was an increase in $NO_x$ formation from 329 ppm to 1100 ppm for pure biodiesel at full load. Value of BSFC for JOME was found to be comparable at various loads. **N Usta .[4]** Investigated on the performance and exhaust emissions of the turbocharged Indirect Injection diesel engine fuelled with Tobacco seed methyl ester on full and partial loads. The result showed that the addition of tobacco seed methyl ester to the diesel fuel reduced CO and $SO_2$ emission while slight higher $NO_x$ emission but the power and the efficiency increased slightly. **Magin Lapverta et al. [5]** Investigated methyl ester of Sunflower and cynara caduculus as pure and in the blend of 25% with fossil Diesel. Result showed vegetable ester provides a significant reduction in particulate matter emission no reduction in particle size was found also no increase in $NO_X$. **A.S.Ramodos. [6] :** Biodiesel of unrefined rubber seed oil was produced and various blends of biodiesel-diesel were used as fuel in the C I engine and its performance and emission characteristics were analyzed. The lower concentration of biodiesel blend found to improve the thermal efficiency. B10 biodiesel blend gives a good improvement in the BTE of the diesel engine by 3% at the rated load condition also reduced emissions and BSFC. Higher the concentration of biodiesel blend, higher is the reduction of smoke density in exhaust gas. The exhaust gas temp increased as a function of concentration of biodiesel in the blend. Since the NOx emission formation is a highly temp dependent phenomenon, with the increase in biodiesel blends, $NO_X$ emission is also increased. **Sharp et al. [7]** performed experiment with soy biodiesel B100 and reported 10% increase in $NO_X$, a 77% reduction in PM, and 25% reduction in CO. **Grimaldi CN et al. [8]** Tested Diesel engine with 100% Soybeen methyl ester and reported with slight reduction in power as compared with that on pure mineral diesel. CO, HC, PM and smoke exhaust emission reduced while $NO_X$ emission increased when fuelled on biodiesel. **Schumacher et al. [9]** tested a 200kW 6-cylinder at 1200 and 2100 rpm and 50% and 100% load with 10%, 20%, 30% and 40% soybean-oil biodiesel blends. The $NO_X$ emissions increased up to 15% in the case of the 40% blend. **Marshall et al. [10]** tested a Cummins L10E engine under transient conditions with diesel fuel and 20% and 30% biodiesel blends. They observed an increase in $NO_X$ emissions of 3.7% with the 20% blend while only a 1.2% with the 30% blend. They also tested the engine with pure biodiesel under steady conditions $NO_X$ emission increased 16% with respect to diesel fuel. **Serdari et al. [11]** measured on-road emissions from three different vehicles using high sulfur diesel fuel (1800 ppm) and 10% sunflower-oil biodiesel blends. They found both increases and decreases in $NO_X$ emissions, and attributed such differences to the different engine technology and maintenance conditions. **Hamasaki et al. [12]** tested a single-cylinder engine at 2000 rpm and different loads with three waste-oil biodiesel fuels. They measured slight decreases in $NO_X$ emissions at low loads but increases at high loads. **Staat and Gateau [13]** tested a 6-cylinder engine following the ECE R49 test cycle and an urban transient cycle named AQA F21 established by the French Agency of Air Quality. They observed a 9.5% increase in $NO_X$ emissions in the ECE R49 test cycle, while a 6.5% reduction in the transient urban cycle. **Krahl et al. [14]** collected different European experiments with rapeseed-oil biodiesel and obtained an average increase of 15% in $NO_X$ emissions. However, they recorded some cases, mainly those testing indirect injection diesel engines under transient cycles, where the $NO_X$ emissions were similar with diesel and biodiesel fuels. **Murayama et al. [15]** reported that vegetable oils and methyl ester of rapeseed oil offered lower smoke and oxides of nitrogen ($NO_X$) emissions **Babu et al [16]** Experimented with blends of soya bean methyl ester and diesel and reported reduction of 16.7% in THC 20.2% in CO 6.1% in in PM emission and increase in 4.5% in $NO_X$ emission. **Munoz et al [17]** performed experiment taking Sunflower methyl ester and reported reduction in HC and CO emission and High $NO_X$. **Nagaraja et al [18]** conducted experiment on single cylinder, four stroke, Direct Injection, diesel engine using Rice bran oil Methyl ester and report showed less smoke, High level of $NO_X$ and HC emission. Biodiesel is an oxygenated fuel and after combustion gives higher NOx emissions. The reason behind this is higher boiling point, higher bulk modulus, and inherent oxygen content. However this presence of oxygen reduces CO and HC emission. Bulk modulus is another important property, which results in a dynamic advance of injection timing in bio-diesel fuelled engine. Bulk modulus of biodiesel is higher than the diesel fuel, which leads to a more rapid transfer of the pressure waves from fuel pump to lift the needle of the injector much earlier. This advance results in more fuel accumulation before the start of combustion leading to higher peak temperature and pressure in premixed phase and subsequently higher $NO_X$. The performance of Biodiesel fueled engine in most the cases is found to close to the mineral diesel because of witch researchers support the use of biodiesel as a viable alternative to the diesel oil for use in the internal combustion engines. In India, non-edible type oil yielding trees such as linseed, castor, karanji, neem, rubber, jatropha are available in large number. Based on the work of various researchers the advantages and limitations are listed below.

**Advantages of Biodiesel:**

1) It is Renewable, biodegradable, non toxic and has close properties with that of Mineral Diesel **[19-23 ]**
2) Complete combustion possible due to high oxygen content. **Garboski et al. [24]**
3) Less combustible in nature with greater flash point which make storage and transportation.
4) Reduced CO, HC, PM emission when used in diesel engine **[24].**
5) Low smoke emission.
6) Good lubricating properties because of high viscosity **Tate RE [25].**
7) Biodiesel requires very small amount of modification in the engine for its use.
8) Biodiesel contains very small amount Phosphorous and sulfur, therefore SOx emission are almost negligible **C. Carraretto et al [26**].
9) Temperature of the flue gases is reduces.
10) Biodiesel has high density and higher Cetane number that reduces the ignition delay of air fuel mixture.
11) Biodiesel is completely miscible with diesel oil thus allowing the use of blending of diesel and biodiesel in any percentage .
12) Because of higher density and viscosity it gives higher torque and power and gives higher thermal efficiency.
13) Because of good lubrication properties there is reduced wear in the engine and the injection system. **Graboski et al [21]**
14) When burned, biodiesel produces pollutants that are less detrimental to human health **[27,28].**
15) Biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content and biodegradability **[29]**
16) Cetane number of biodiesel is higher than those of vegetable oil and diesel fuel and hence produce less THC emission.

**Limitation of Biodiesel:**

1) Increase in $NO_X$ emission due to higher temp because of complete combustion of fuel in presence of excess oxygen present in oxygenated fuel.
2) Filter plugging problem in biodiesel fuelled engine become more sever in cold weather.
3) The solvent like property of biodiesel also dissolve estimators as well as fuel tank deposits and lead to fuel and injection plugging as a consequence of increased viscosity.
4) Biodiesel is known to degrade up to four time faster than diesel fuel. **[30,31]**

**Alcohols:** Mainly ethanol and to a much lesser extent methanol, have been considered as alternative fuels for diesel engines too. Methanol can be produced from coal or petrol based fuels with low cost production, but it has a restrictive solubility in the diesel fuel. On the other hand, ethanol is a biomass based renewable fuel, which can be produced by alcoholic fermentation of sugar from vegetable materials, such as corn, sugar cane, sugar beets, barley, sweet sorghum, cassava, molasses and the like, and agricultural residues, such as straw, feedstock and waste woods by using already improved and demonstrated technologies **Demirbas [32].** Therefore, it has the advantage over methanol of higher miscibility with the diesel fuel and of being of renewable nature (bio-ethanol). The light alcohols are of very low –compression ignition quality and cannot be used alone as fuel for diesel engine without some in cylinder assistance to ensure ignition. The alcohols may be blended or emulsified with diesel fuel to give mixture of acceptable ignition properties. Pure ethanol is completely miscible with diesel fuel at temp in excess of about 30 degree. Another method of introducing alcohol is by fumigation. In this technique, alcohol is introduced in the intake air manifold by a simple carburetor and vaporizing in the intake air stream. Fourth method is by Dual injection (separate Injection system for each fuel)

**Emissions from Alcohols with diesel in blending or fumigation mode: M. Abu Quadais et al. [33]** compared the effect of ethanol fumigation and ethanol diesel blend, result showed the fumigation method was effective than blending. The optimum percentage for ethanol fumigation is 20%. BTE increases by 7.5%, CO emission by 55%, HC emission 36%.reduction of soot mass concentration by 51%.Optimal percentage for ethanol diesel fuel blend is 15%, which increases BTE by 3.6%,CO by 43.3%,HC by 32% . $NO_X$ emissions were not measured.

**Z.H.Zheng et al [34]** conducted experiments on 4 cylinders, DI Diesel engine for performance and emission characteristics By fumigating methanol and ethanol, results shows both alcohols reduce BTE at low engine speed but improves at high engine speed, both alcohols leads to higher fuel consumption with methanol leading to higher fuel consumption than ethanol. HC and CO emission increases with the level of fumigation because of cooling effect of alcohols and poorer combustion associated with very lean air/alcohol mixture.

NOx emission reduced and reduction increases with the level of fumigation which is independent of alcohol being used at low engine load, it is due to cooling effect of alcohols and at high loads, the reason may be the lower oxygen availability with lower air/fuel ratio. Fumigation methanol leads to higher $NO_X$ emission probably due to the presence of unburned methanol which is favorable for NO to $NO_2$ conversion. The particulate mass concentration and total number concentration decreased with the increase in the level of fumigation methanol or ethanol. Fumigation methanol is more effective in reducing PM emission due to simple molecular structure as well as high oxygen content.

**Rokopoulas et al. [35,36 ]** conducted experiment with ethanol blended with diesel, result shows smoke density, $NO_X$ emission, CO emission were slightly reduced with the use of blends and reduction increases with the increase in % of ethanol in diesel. Unburned Hydrocarbon increased, a little higher SFC was observed.

**De –Gang li et al. [37]** The effects of different ethanol–diesel blended fuels on the performance and emissions of diesel engines were evaluated experimentally and compared. The experiments were conducted on a water-cooled single-cylinder Direct Injection (DI) diesel engine using 0% (neat diesel fuel), 5% (E5–D), 10% (E10–D), 15% (E15–D), and 20% (E20–D) ethanol–diesel blended fuels. The results indicate that: the brake specific fuel consumption and brake thermal efficiency increased with an increase of ethanol contents in the blended fuel at overall operating conditions; smoke emissions decreased with ethanol–diesel blended fuel, especially with E10–D and E15–D. CO and $NO_X$ emissions reduced for ethanol–diesel blends, but THC increased significantly when compared to neat diesel fuel.

**Bhupender singh chauhan et al [38]** conducted experiment with fumigation of ethanol with diesel, result shows that fumigation of ethanol exhibit better engine performance with lower $NO_X$, CO, $CO_2$ and exhaust temp. ethanol fumigation has resulted in increase of unburned hydrocarbon (HC) emission in the entire loading range, and found optiumal % of ethanol fumigation is 15%.

**Emission from Alcohols with biodiesel in blending or fumigation mode:**

**Hu Chen et al. [39]** Vegetable methyl ester was added in ethanol–diesel fuel to prevent separation of ethanol from diesel in his study. The ethanol blend proportion can be increased to 30% in volume by adding the vegetable methyl ester. Engine performance and emissions characteristics of the fuel blends were investigated on a diesel engine and compared with those of diesel fuel. Experimental results show that the torque of the engine is decreased by 6%–7% for every 10% (by volume) ethanol added to the diesel fuel without modification on the engine. Brake specific fuel consumption (BSFC) increases with the addition of oxygen from ethanol but equivalent brake specific fuel consumption (EBSFC) of oxygenated fuels is at the same level of that of diesel. Smoke and particulate matter (PM) emissions decrease significantly with the increase of oxygen content in the fuel. However, PM reduction is less significant than smoke reduction. In addition, PM components are affected by the oxygenated fuel. When blended fuels are used, nitrogen oxides ($NO_X$) emissions are almost the same as or slightly higher than the $NO_X$ emissions when diesel fuel is used. Hydrocarbon (HC) is apparently decreased when the engine was fueled with ethanol–ester–diesel blends. Fuelling the engine with oxygenated diesel fuels showed increased carbon monoxide (CO) emissions at low and medium loads, but reduced CO emissions at high and full loads, when compared to pure diesel fuel.

**C H Cheng et al. [40]** Used biodiesel converted from waste cooking oil as based fuel and Methanol was used in fumigation and blending mode on a 4-cylinder naturally aspirated direct injection diesel engine operating on a constant speed of 1800 rpm, result showed reduction of $CO_2$, $NO_X$ and reduction in particulate mass emissions and reduction in mean particle diameter in both the cases compared with the diesel fuel**.** In fumigation there is also an increase in CO, HC, and $NO_2$ and particulate emission in engine exhaust, which is disadvantage compared with the blending mode. Blend mode gives slightly higher BTE efficiency at low engine load while fumigation mode gives slightly higher BTE at medium and high engine loads.

**Lei zhu et al. [41]** Investigated and compared the characteristics of diesel engine operating on biodiesel and biodiesel blend with ethanol and methanol and the result showed the blended fuels could lead to reduction of both $NO_X$ and PM with biodiesel- methanol blend being more effective than biodiesel-ethanol blend. The effectiveness of $NO_X$ and particulate emission reduction is more effective with the increase of alcohols in the blend, the HC,CO, emissions could increase and BTE might slightly reduced but the use of 5% blend could reduce the HC and CO emissions.

**Rambabu Kantipudi et al. [42] :** Investigated performance and emission characteristics of diesel engine fueled with Rice Bran Methyl ester biodiesel and ethanol the result showed higher BTE at the higher replacement of RBME with ethanol at higher load. No change in SFC, HC emissions increased with the increase in ethanol induction. NO emission in the exhaust is decreased with the increase of ethanol content. CO increased with increase in ethanol content, $CO_2$ emission decreased with the increase in ethanol flow rate. Exhaust gas tem is decreased with the increasing ethanol flow rate at any load.

**K Anand et al. [43]** The experiment was carried out on a turbocharged, direct injection, multi-cylinder truck diesel engine fitted with mechanical distributor type fuel injection pump using biodiesel-methanol blend and neat karanji oil derived biodiesel under constant speed and varying load conditions without altering injection timings. The results of the experimental investigation indicate that the ignition delay for biodiesel-methanol blend is slightly higher as compared to neat biodiesel and the maximum increase is limited to 1 deg. CA. Themaximum rate of pressure rise follow a trend of the ignition delay variations at these operating conditions. However, the peak cylinder pressure and peak energy release rate decreases for biodiesel-methanol blend. In general, a delayed start of combustion and lower combustion duration are observed for biodiesel-methanol blend compared to neat biodiesel fuel. A maximum thermal efficiency increase of 4.2% due to 10% methanol addition in the biodiesel is seen at 80% load and 16.67 s_1 engine speed. The unburnt hydrocarbon and carbon monoxide emissions are slightly higher for the methanol blend compared to neat biodiesel at low load conditions whereas at higher load conditions unburnt hydrocarbon emissions are comparable for the two fuels and carbon monoxide emissions decrease significantly for the methanol blend. A significant reduction in nitric oxide and smoke emissions are observed with the biodiesel-methanol blend investigated.

**Emissions from Tri compound fuels(alcohols, biodiesel and diesel)**

**Xiasbing Pang. [44]** Investigated Biodiesel ethanol and Diesel (BE diesel) and compared with those from fossil diesel, it was found that total carbonyl emission from BE diesel were 1-22% Higher than from diesel and was in positive correlation with engine speed. BE diesel significantly reduced PM and increase slightly $NO_X$ emission.

**Xioayan Shi et al. [45]** studied three compound oxygenated diesel fuel blend (BE Diesel) which consist of biodiesel of Methyl Soyate, ethanol and mineral diesel. The blend ratio of 5:20:75 ( E B diesel). The result showed a significant reduction in PM emission and 2%-14% increase in $NO_X$ emission, CO emission was not conclusive and depand on operating condition, THC from BE diesel was lower than that of diesel fuel.

**Istvan et al. [46]** Investigated Diesel biodiesel ethanol blend and compared with diesel fuel. Biodiesel used in the study was rapeseed oil methyl ester and result showed that BSF increased especially at lower engine loads, with max. 32.4%, reducing engine BTE with max. 21.7% CO emission decreased at high load with max. 59%, $NO_X$ emission slightly increased especially at partial and high loads, HC and smoke emission decreased in all engine load.

**Promes kuanchrean.[47]** used diesel-biodiesel-ethanol blend in the fuel tank and found that CO and HC reduced significantly at the engine load, where as the $NO_X$ increased, when compared with that of diesel, a blend of 80% diesel, 15% biodiesel and 5% ethanol was most suitable ratio for diesohal production.

**Chen et al. [48]** Investigated engine performance and emission characteristics of soy methyl ester – ethanol-diesel blend in diesel engine. The result showed that 30% smoke reduction with (ethanol-10%; biodiesel-5%; diesel-85%), 55% with (ethanol-20%; biodiesel-5%; diesel-75%), and 85% with (ethanol-30%; biodiesel-5%; diesel-65%), compared to diesel. $NO_X$ produced were higher in all the three samples.

**Shi et al. [49]** studied the emission characteristics of a tri-compound oxygenated diesel fuel blend with a ratio 5:20:75 (ethanol: methyl soyate: diesel fuel ) by volume. The result showed reduction of 30% PM emission and 5.6-11.4% increase in $NO_X$ emission. **Advantage of Alcohols:**

1) Ethanol is cheaper and simple to produce than biodiesel. **[50,51]**
2) Ethanol oxygen concentration is higher and thus its potential for particulate emissions reduction is also higher. **[52-55]**
3) Ethanol can be blended with diesel with no engine modification required. **Prommes Kwanchareon [47]**
4) The Auto-ignition temp of ethanol is higher than that of diesel fuel, which make it safer for transportation and storage**. [56,57]**
5) Alcohol-biodiesel-diesel hybrid fuel blends are stable well below the sub-zero temp and have equal or superior fuel properties to regular diesel fuel. **Shi X2006 [49]**
6) Exhaust gas temperature are lower

**Limitation of alcohols:**

1) Ethanol-diesel blend has lower viscosity and lubricity. **Hansen AC [58]**

2) Reduce ignibility and cetane number and higher volatility. **Satge de Caro P [59]**
3) Higher unburned hydrocarbon emission. **Merritt PM [60]**
4) Lower miscibility which may cause phase separation with catastrophic consequences.
5) Diesel engine cannot operate normally on ethanol diesel blend without special additives .**[ 61,62 ]**
6) More alcohols fuel than diesel fuel is required by mass and volume. **Doann H-A [63]**
7) Alcohols used in diesel engine will emit more volatile hydrocarbons. **Chao et al 2000.[64]**

In comparison with the blending mode, the fumigation method of alcohol addition seems to be more flexible despite extra fuel injection system required. **Z.H. Zhang 2011[65]**

1) It allows the amount of alcohol to be injected to vary, Depending on actual requirement.
2) Since alcohols is not premixed with the diesel fuel an Emulsion additive to ensure proper mixing of alcohol And the diesel is not required.
3) Large quantity of alcohols can be added by way of fumigation as compared to blending. Up to 50% of fuel energy can be derived from alcohols by fumigation. **Eugene EE [66]**

It can be concluded from the work of above mentioned researchers that there is need to curb the $NO_X$ emission for making the alternative fuel more acceptable for replacement of fossil fuel.

## MECHANISM OF NOX FORMATION

The increase in $NO_X$ emission serves as biodiesel's major impediment to widespread use. A major hurdle in understanding the mechanism of formation and controlling $NO_X$ emission is that combustion is highly heterogeneous and transient in diesel engines. While NO and $NO_2$ are lumped together as $NO_X$, there are some distinctive differences between these two pollutants. NO is a colourless and odourless gas, while $NO_2$ is a reddish- brown gas with pungent odour. Both gases are considered toxic, but $NO_2$ has a level of toxicity 5 times greater than that of NO. Although $NO_2$ is largely formed from oxidation of NO, attention has been given on how NO can be controlled before and after combustion **Avinash Kumar Agrawal [67].** NO is formed during the post flame combustion process in a high temperature region. The most widely accepted mechanism was suggested by Zeldovich. **J.B. Heywood[ 68].** The principal source of NO formation is the oxidation of the nitrogen present in atmospheric air. The nitric oxide formation chain reactions are initiated by atomic oxygen, which forms from the dissociation of oxygen molecules at the high temperatures reached during the combustion process. The principal reactions governing the formation of NO from molecular nitrogen are, Chemical equilibrium consideration indicates that for burnt gases at typical flame temperatures, $NO_2$ /NO ratios should be negligibly small. While experimental data show that this is true for spark ignition engines, in diesels, $NO_2$ can be 10 to 30% of total exhaust emissions of oxides of nitrogen. A plausible mechanism for the persistence of $NO_2$ is as follows. NO formed in the flame zone can be rapidly converted to $NO_2$ via reactions such as Subsequently, conversion of this $NO_2$ to NO occurs via unless the $NO_2$ formed in the flame is quenched by mixing with cooler fluid. This explanation is consistent with the highest $NO_2$ /NO ratio occurring at high load in diesels, when cooler regions which could quench the conversion back to NO are widespread**. J.B. Heywood [68].** The local atomic oxygen concentration depends on molecular oxygen concentration as well as local temperatures. Formation of $NO_X$ is almost absent at temperatures below 2000 K. Hence any technique, that can keep the instantaneous local temperature in the combustion chamber below 2000 K, will be able to reduce $NO_X$ formation **Avinash Kumar Agrawal [67]**. Canakci has also suggested that the $NO_X$ increase is not driven by the Zeldovich mechanism, but instead by the fact that during combustion the double bonded molecules cause higher levels of certain hydrocarbon radicals in the fuel-rich zone of the diesel spray **M. Canakci [69].**

## NOX REDUCTION TECHNIQUES

By Modifying biodiesel James P Szybist.[70] used reformulated soy-derived biodiesel in yonmer L 70 EE air cooled, four stroke single cylinder Direct Ignition diesel engine at 3600 rpm by reducing the iodine value through increasing the ethyl oleate (Methyl ester of oleic acid) by using a B20 blend with reformulated biodiesel containing 76% methyl oleate, the biodiesel $NO_X$ effect was eliminated and a $NO_X$ neutral blend was produced as compared to conventional B20 Biodiesel.

**Use of additive:** James P Szybist et al. [70] Experimented with Cetane improver 2 ethyl hexy nitrate 1000ppm to B20 and derived cetane number was improved they found EHN is not effective for reducing $NO_X$ emission at the early injection timing but decrease $NO_X$ emission to the ULSD level at the mid and late injection timing. McCormick RL et al. [71] studied the effect of cetane improver (EHN) on two different samples by varying the portion of EHN, with new DCN increased by 8 units and 10 units respectively. In both cases adding cetane improver

Injection timing is another mechanism for controlling $NO_X$ emission. Biodiesel advances injection timing due to its higher bulk modulus of compressibility. Advancing injection timing causing higher $NO_X$ emission because of early starting of combustion which increases the duration of fuel mixture residence time inside the cylinder.

Monjem et al. [72] observed a retardation in $NO_X$ emission of 35% to 45% for a six degree retardation injection timing although retarding injection timing is an effective method , however this method leads to increase the fuel consumption , smoke emission, increased hydrocarbon emission.

**SCR Technique:** Selective catalytic reduction technique is most versatile technique for $NO_X$ control in diesel engines. Catalysts used in SCR are manufactured from various ceramic materials used as a carrier, such as titanium oxide, and active catalytic components are usually oxides of base metals (such as vanadium and tungsten), zeolites, and various precious metals. The two most common designs of SCR catalyst geometry used today are honeycomb and plate. The honeycomb form usually is an extruded ceramic applied homogeneously throughout the ceramic carrier or coated on the substrate.

Like the various types of catalysts, their configuration also has advantages and disadvantages. Plate type catalysts have lower pressure drops and are less susceptible to plugging and fouling than the honeycomb types, however plate type configurations are significantly larger and more expensive. Honeycomb configurations are significantly smaller than plate types, but have higher pressure drops and plug much more easily.

**Biodiesel emulsified with water:**

Water emulsification although leads to corrosion in various part of engine, however this technique reduces $NO_X$ emission to a considerable level.

Hamasaki et al [74] Experimented on waste vegetable oil Methyl ester with emulsified with 15% water, a 18% reduction in $NO_X$ was reported and also better combustion with lower smoke emission.

Chrng –yoanlin et al [75] Emulsified biodiesel derived from soybean oil, the biodiesel product was than emulsified with distilled water to produce a three phase oil-droplets in water-droplet in oil (I.e. O/W/O) Biodiesel emulsion. four stoke diesel engine was used to investigate performance and emission characteristics O/W/O biodiesel emulsion appears to have the largest fuel consumption ratio, BSFC but the lower heat value, CO2 emission and exhaust gas temperature and slight $NO_X$ reduction were reported.

B.Sachurthan et al [76] Water /oil emulsion was prepared by mixing neat biodiesel fuel and a constant 1% surfactant [TWEEN 80] with 30 % double distilled water by volume the neat biodiesel fuel and surfactant were first mitted together for 15 minute using a mechanical mixer. The water was than added and the blend was stirred mechanically for another period of 30 minutes and this way a emulsion for 30 % W/O was obtained. Biodiesel emulsified fuel gave simultaneous improvement in $NO_X$ concentration, smoke density and BSFC

**Exhaust Gas Recirculation in Bio fueled engine**

Exhaust gas recirculation is an effective method for $NO_X$ control. The exhaust gases mainly consist of inert carbon dioxide, nitrogen and possess high specific heat. When recirculated to engine inlet, it can reduce oxygen concentration and act as a heat sink. This process reduces oxygen concentration and peak combustion temperature, which results in reduced $NO_X$ EGR is one of the most effective techniques currently available for reducing $NO_X$ emissions in internal combustion engines. However, the application of EGR also incurs penalties. It can significantly increase fuel consumption and reduce thermal efficiency unless suitably optimized. The higher $NO_X$ emission can be effectively controlled by employing EGR. Deepak Agarwal[ 77]

Deepak Aggarwal et al. [77] performed experimental work using Rice Bran Oil Methyl Ester (ROME) and EGR result showed Smoke opacity Increases with EGR rate, $NO_X$ is decreased with EGR rate, reduction in $NO_X$ is higher at higher load, temperature is found to be lower compared to engine operating on diesel, thermal efficiency increased with EGR at low engine load BSFC with EGR is lower at low engine load.

V. pradeep [78] Used biodiesel from jatropha oil and HOT EGR and found Hot EGR of 15% effectively reduced NO emission without much adverse effect on performance, smoke and other emission.

A. Tsolakis et al. [79] investigated use of EGR on Rape seed methyl ester and ULSD blend and reported that the $NO_X$ emission were reduced at the level similar to those of ULSD with the use of similar volumetric percentage of EGR while the smoke was kept low.

H E SALEH et al. [80] experimented on 2 cylinder, naturally aspirated four stroke engine direct injection diesel engine and JaJoba Methyl Ester (JME) was used as fuel with hot and cold EGR engine speed of 1600 rpm and result showed that EGR is an effective technique for reducing $NO_X$ emission with JME fuel specially in the light duty diesel engine with the application of EGR method. The CO and HC concentration in the engine out emission increased for all operating condition a better trade off between HC,CO and $NO_X$ emission can be obtained with in a limited EGR rate of 5-15% with very little economic penalty. Use of EGR cooler at full load has a positive effect on improving the engine economy and decreasing the exhaust emissions.

Md. Nurun Nabi et al[ 81] used Biodiesel from non edible neem oil (NOME) for blend of diesel and biodiesel. A 4-stroke, NA, DI Diesel engine for 15% NOME with the increasing EGR rate and emission speed set at 1000 rpm. $NO_X$ emissions increased and become slightly lower than level of neat diesel and for same level of 15% NOME CO emission is almost identical or slightly lower than that neat diesel for every EGR rate, same is for smoke emission.

Donghui Qi et al. [82] Studied, the effect of EGR rate on the combustion and emissions of a Ford Lion V6 split injection strategy direct injection diesel engine by using neat biodiesel produced from soybean oil. The results showed that, with the increasing of EGR rate,
the brake specific fuel combustion (BSFC) and soot emission were slightly increased, and nitrogen oxide ($NO_X$) emission was evidently decreased.

B Sachuthurthern et al. [76] The EGR system was tested for different settings of 10%, 15% and 20%. They found that hot EGR keeps the temp of the re-circulated exhaust gases at a very high level not only keeps the $NO_X$ low but also contributes to achieve lower smoke and particulate matter emissions. Zheng et al. [83] Compare engine performance and emission between the use of soy, Canola and yellow grease derived B100 biodiesel fuels and an ultra-low sulphur diesel fuel in the high load engine operating conditions. Compared to the diesel fuel engine-out emissions of nitrogen oxides ($NO_X$), a high-cetane number (CN) biodiesel fuel produced comparable $NO_X$ while the biodiesel with a CN similar to the diesel fuel produced relatively higher $NO_X$ at a fixed start of injection. The soot, carbon monoxide and unburnt hydrocarbon emissions were generally lower for the biodiesel-fuelled engine. Exhaust gas recirculation (EGR) was then extensively applied to initiate low temperature combustion (LTC) mode at medium and low load conditions. An intake throttling valve was implemented to increase the differential pressure between the intake and exhaust in order to increase and enhance the EGR. Simultaneous reduction of $NO_X$ and soot was achieved when the ignition delay was prolonged by more than 50% from the case with 0% EGR at low load conditions. The research intends to achieve simultaneous reductions of $NO_X$ and soot emissions in modern production diesel engines when biodiesel is applied. Hountalas et al. [84] investigate the performance and emissions of diesel engine with EGR system. The method is based on the reduction of gas temperature level and O2 availability inside the combustion chamber, but unfortunately it has usually an adverse effect on soot emissions and brake specific fuel consumption (BSFC). The use of high EGR rates creates the need for EGR gas cooling in order to minimize its negative impact on soot emissions especially at high engine load were the EGR flow rate and exhaust temperature are high. it is examined, using a multi-zone combustion model, the effect of cooled EGR gas temperature level for various EGR percentages on performance and emissions of a turbocharged DI heavy duty diesel engine operating at full load. Results reveal that the decrease of EGR gas temperature has a positive effect on BSFC, soot (lower values) while it has only a small positive effect on NO. As revealed, the effect of low EGR temperature is stronger at high EGR rates. Maiboom et al. [85] investigated performance of cooled exhaust gas recirculation to control $NO_X$ in diesel engine. Cooled exhaust gas recirculation (EGR) is a common way to control in-cylinder $NO_X$ production and is used on most modern high speed direct injection (HSDI) diesel engines. The increase of inlet temperature with EGR has contrary effects on combustion and emissions, thus sometimes giving opposite tendencies as traditionally observed, as, for example, the reduction of $NO_X$ emissions with increased inlet temperature. At low-load conditions, use of high EGR rates at constant boost pressure is a way to drastically reduce $NO_X$ and PM emissions but with an increase of brake-specific fuel consumption (BSFC) and other emissions (CO and hydrocarbon), whereas EGR at constant AFR may drastically reduce $NO_X$ emissions without important penalty on BSFC and soot emissions but is limited by the turbo-charging system. Saleh et al. [86] Have studied to quantify the efficiency of exhaust gas recirculation (EGR) when using Jojoba methyl ester (JME) fuel in a fully instrumented, two-cylinder, naturally aspirated, four-stroke direct injection diesel engine. The tests were carried out in three sections. Firstly, the measured performance and exhaust emissions of the diesel engine operating with diesel fuel and JME at various speeds under full load are determined and compared. Secondly, tests were performed at constant speed with two loads to investigate the EGR effect on engine performance and exhaust emissions including nitrogenous oxides ($NO_X$), carbon monoxide (CO), unburned hydrocarbons (HC) and exhaust gas temperatures. Thirdly, the effect of cooled EGR with high ratio at full load on engine performance and emissions was examined. The results showed that EGR is an effective technique for reducing $NO_X$ emissions with JME fuel especially in light-duty diesel engines. With the application of the EGR method, the CO and HC concentration in the engine-out emissions increased. For all operating conditions, a better trade-off between HC, CO and $NO_X$ emissions can be attained within a limited EGR rate of 5–15% with very little economy penalty. Rajasekar E. et al. [87] conducted experiment using Jatropha methyl ester, ethanol and diesel in the ratio of (ethanol -15%;biodiesel-20%; diesel-65%) and compared with using Methanol instead of ethanol in same ratio with the use of EGR on engine performance and emission characteristics. The result showed the EGR addition reduced the BTE. And increase in fuel consumption ,it also increased HC emission due to low oxygen available in incoming charge because of dilution due to Exhaust gases.15% EGR reduced 65.9% $NO_X$ and 5.4% smoke . In the case of tri-compound oxygenated diesel fuel blend lower $NO_X$ emitted due to lower combustion temperature. Compared to B20 and B100 the $NO_X$ emission reduction obtained for E15B20 and M15B20 are only marginal with the increased EGR rate.

## CONCLUSION

Most of the researchers have reported higher level of $NO_X$ emission using biodiesel compared with diesel. Using Alcohols especially Ethanol in fumigation mode reduces $NO_X$ emission. Water emulsification technique reduces $NO_X$ emission to a considerable level although it leads to corrosion in various part of engine. Among the various techniques discussed the hot EGR technique is found to be most effective technique without much adverse effect to reduce $NO_X$ level, it also reduces the Smoke and PM emission.

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