



REDUCTION OF NO_x EMISSION IN BIODIESEL (SOYABEAN) FUELLED DI DIESEL ENGINE BY CETANE IMPROVER

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ABSTRACT

Biodiesel is explored to be used in standard diesel engines and is thus distinct from the mineral oils. Biodiesel can be used alone, or blended with diesel in any proportions. The number of studies has shown significant increase in nitrogen oxides (NO_x) emissions in biodiesel fuelled diesel engine. The increase in NO_x, HC and CO emissions and solutions to this problem have been the subjects of research for considerable time. It is difficult to control NO_x emissions. In the Internal Combustion Engine, at high temperature, oxidation of nitrogen takes place and a significant amount of NO_x will be formed at the end of combustion. The majority of NO_x formed will however decompose at the low temperatures of exhaust. But due to very low reaction rate at the exhaust temperature, a part of NO_x formed remains in exhaust. An attempt has been made to reduce this emission using cetane improver DEE that helps to reduce the ignition delay thereby reducing the combustion temperature. As the NO_x increases linearly with the amount of blend, in this experiment, DEE is added at 0.01 to 0.05% by volume to the different blends and NO_x emissions are measured with exhaust gas analyser. From the results, it is shown that B30 blend with DEE gives the better results for reduction in NO_x.

Keywords: nitrogen oxides (NO_x), diethylether (DEE), cetane improver, hydrocarbon (HC), carbon monoxide (CO).

1. INTRODUCTION

Biodiesel refers to a vegetable oil - or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, ethyl, or propyl) esters. Biodiesel is typically made by chemically reacting lipids (e.g., vegetable oil, animal fat with an alcohol producing fatty acid esters. Biodiesel can be used alone, or blended with petrodiesel in any proportions. Biodiesel blends can also be used as heating oil. Soya biodiesel is an alternative fuel produced from soybean oil. Soya biodiesel can be used in diesel engines with little or no modifications. Soya biodiesel is made through a chemical process called transesterification whereby the glycerin is separated from the soybean oil. The process gives two products: methyl esters (the chemical name for biodiesel) and glycerin (used to make soap). Soya methyl esters, the predominant type of biodiesel fuel, have higher NO_x emissions, poorer cold flow, and shorter shelf life when compared to petroleum diesel. These shortcomings are partly due to the fatty acid profile of the soybean oil feedstock itself. The fatty acid profile and the alcohol moieties determine the characteristics of the fuel such as cetane number, cold flow, oxidative stability, lubricity, and viscosity (11). This article examines the effects on fuel properties such as Cetane Number, NO_x emissions, and CO & HC emissions.

2. LITERATURE REVIEW

Effect of Longer ignition delay in NO_x Production and introduction of advancement injection timing has been discussed in [1]. Significant decrease in CO and HC and decrease in NO_x due to the usage of anti-oxidants in biodiesel have been discussed in [2]. Decrease of NO_x by the usage of Tri-compound fuels (ethanol-biodiesel-diesel) with the help of additives and retarded

fuel injection timing in EGR accompanied bio-diesel fuelled engine have been discussed in [4]. Implementation of fixed start of injection with the effect of crank angle has been discussed in [10]. Study of Distilled tyre pyrolysis oil diesel blends of different proportion with the result of failure in 100% blend and NO_x reduction of 21% in 80% blends have been taken from [6]. Cetane number estimation and the hydrogenation process in increasing the Cetane number in diesel fuels have been dealt in [7]. Usage of different Cetane number improvers (Aniline Nitrate) which has increased Cetane number significantly with standard pressure resulting in NO_x and SO₂ reduction by 10% [8]. Higher Cetane number by increase in fatty acid compounds (CH₂) with long chain reaction have been discussed in [9]. Blended and fumigated mode of methanol bio-diesel with ultra low-sulphur diesel blend resulting in reduction of CO, HC, NO_x and separate injection type have been discussed in [5]. NO_x reduction due to dual fuel mode (Biogas and Biodiesel) with different load condition and lower exhaust gas temperature has been discussed in [3]. In this research paper, Soyabean oil as Biodiesel fuel and Diethyl ether as a cetane improver are used for reducing the NO_x emission in Diesel engine.

2.1. Research objectives of the project

- It is proposed to use Bio diesel in the diesel engine (CI engine).
- The emissions like CO, HC, NO_x in the exhaust gases are also proposed to be reduced by adding of Cetane Improver (DEE).
- To study the emission characteristics when using Bio fuel as fuel in the diesel engine by measurement and analysis of the exhaust emissions



2.2. Properties of soyabean bio-diesel

Kinematic viscosity AT CSE 40°C	= 4.78
Specific Gravity	= 865
Flash point	= 163°C
Total sulphur % by mass	= Nil
Distillation % volume/Vol	= 90 to 335°C
Cetane number	= 51
Ash % by mass	= Nil
Oil Ester Methyl Ester %	= 95.69

Soya biodiesel is better for the environment because it is made from renewable resources and has lower emissions compared to petroleum diesel. The use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and soot. The use of biodiesel does not increase the CO₂ level in the atmosphere, since growing soybeans consumes also CO₂. Biodiesel is also more biodegradable than conventional diesel. Studies at the University of Idaho have illustrated biodiesel degraded for 95 percent after 28 days compared to 40 percent for diesel fuel.

Origins of soyabean are in Southeast Asia with first domestication reported in the 11th century BC in China. First planted in the U.S. in 1765, soybeans spread to the Cornmunist Belt by the mid 1800s with major acreage not seen until the 1920s when it was used mainly as a forage crop. Major U.S. expansion as an oilseed crop began in the 1940s (Gibson and Benson 2005). Soybeans contain approximately 18 to 20% oil compared to other oilseed crops such as canola (40%) and sunflower (43%) (National Sunflower Association 2009)

Soybean oil is currently a major feedstock for production of biodiesel by National Biodiesel Board (NBB). The most common method of biodiesel production is a reaction of vegetable oils or animal fats with methanol or ethanol in the presence of sodium hydroxide (which acts as a catalyst). The transesterification reaction yields methyl or ethyl esters (biodiesel) and a byproduct of glycerin. Numerous studies between 1980 and 2000 have shown the use of straight vegetable oil including soybean oil to cause carbon deposits and shorten engine life (Jones and Peterson 2002). Biodiesel use in diesel engines does not have similar negative effects.

3. NOX FORMATION AND CONTROL METHODS

Generally it is accepted that emissions of nitrogen oxides (NO_x) increase as the volume fraction of biodiesel increases in blends with conventional diesel fuel. While many mechanisms based on biodiesel effects on in-cylinder processes have been proposed to explain this observation, a clear understanding of the relative importance of each has explained below.

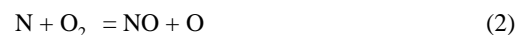
In order to present a clear background to the continuously developing range of Nitrogen Oxides (NO_x) control techniques and equipment, it is essential to

understand NO_x formation chemistry. There are a number of nitrogen oxides, but only three of these are of interest for combustion processes:

1. Nitrogen monoxide, or nitric oxide, NO.
2. Nitrogen dioxide, NO₂.
3. Di-nitrogen oxide, or nitrous oxide, or "laughing gas", N₂O. The first two, NO and NO₂ are collectively referred to as NO_x and they are essential contributors to the acid rain or smog problems. The NO_x content in the combustion gases from conventional power plant boilers and many industrial heating processes contains some 90 % NO with the remainder NO₂. The third oxide, N₂O, is found in flue gases from, among others, Fluidised bed combustors, and from engine exhaust gases after the catalytic converting system. N₂O is not an acidic oxide, and is normally not included in the abbreviation NO_x. However, N₂O is a gas, which contributes to the destruction of the stratospheric ozone. There are basically three recognized mechanism on NO_x formation – Thermal, Fuel and Prompt. These are outlined below.

3.1. Thermal NO_x formation

Thermal NO_x is produced by the reaction of atmospheric oxygen and nitrogen at elevated temperatures, and is reputed to contribute about 20% of the total NO_x emission in pulverised coal firing, but is the dominant mechanism when the fuel contains little or no inherent nitrogen (i.e. gas firing). Where high air preheat temperatures are employed, for example in cement kilns, thermal NO_x can also contribute considerably to the overall NO_x emission. The reactions are described by the Zeldovich mechanism as follows:



The first step is rate limiting, and due to its high activation energy (314 KJ/mol) requires high temperatures to proceed. Reaction (3) is only significant under reducing conditions. In practice the control/minimisation of thermal NO_x is accomplished primarily by measures, which reduce temperature, but dilution of the available oxygen is also beneficial.

3.2. Fuel NO_x formation

Fuel NO_x arises from the reaction of the organically bound nitrogen in the fuel with oxygen. The process is complex (reaction schemes typically consider of the order of 50 intermediate species and several hundred separate reversible reactions, and there is still considerable uncertainty as to the true value of the various rate constants, etc.), but can be simply expressed as follows:

- i) Volatile fuel nitrogen is evolved mainly as HC



and NH_3 during the processes.

ii) The HCN reacts with various free radical species (O, OH) to form intermediates such as CN, NCO, HCNCO and ultimately with reaction with H to produce NH, NH_2 . Fuel NO_x can be most effectively minimised by burning the fuel by staged combustion, which implies delayed mixing between the fuel gas and air.

3.3. Prompt NO_x formation

Prompt NO_x is formed by the reaction of hydrocarbon radicals with atmospheric nitrogen to produce HCN and hence NO_x via a complex series of gas phase reactions. Measures, which are effective in minimising thermal and fuel NO_x , are also effective in minimising prompt NO_x .

4. CETANE IMPROVERS & SELECTION OF CETANE IMPROVERS

Cetane number is an inverse function of a fuel's ignition delay, and the time period between the start of injection and the first identifiable pressure increase during combustion of the fuel. In a particular diesel engine, higher Cetane number fuels will have shorter ignition delay periods than lower Cetane number fuels. In short, the higher the Cetane numbers the more easily the fuel will combust in a compression setting (such as a diesel engine). The characteristic diesel "knock" occurs when fuel that has been injected into the cylinder ignites after a delay causing a late shock wave. Minimizing this delay results in less unburned fuel in the cylinder and less intense knock. Therefore higher-cetane number fuel usually causes an engine to run more smoothly and quietly. This does not necessarily translate into greater efficiency, although it may be reduce the engine emissions.

A higher cetane number fuel will have a higher initial pressure rate rise in the cylinder than a lower cetane number fuel. They will generally give rise to lower NO_x and noise than lower cetane number fuels. Fuel consumption is likely to be higher as a result of the lower heating values of higher cetane number fuels. cetane improver is an additive that raises cetane number and reduces ignition delay (It is the time between the start of injection and when combustion begins) during combustion and hence improves diesel engine ignition. Delayed ignition is a primary cause of high emissions and poor engine performance. There is a direct relationship between the cetane number of a diesel fuel and its ignition point. The lower the number, the longer the wait. Many low cetane fuels increase engine deposits resulting in more smoke, increased exhaust emissions and greater engine wear.

Diethyl ether, also known as ethoxyethane, ethyl ether, sulfuric ether, or simply ether, is an organic compound in the ether class with the formula $\text{C}_2\text{H}_5\text{O}$. It is a colorless, highly volatile flammable liquid. Diethylether might prove advantageous as future diesel oil

because it incorporates a high cetane rating. Diethyl ether has a high cetane number of 85-96 and is used as a starting fluid, in combination with petroleum distillates for gasoline and diesel engines because of its high volatility and low flash point. For the same reason it is also used as a component of the fuel mixture for biodiesel fuelled compression ignition engines.

5. EXPERIMENTAL PROCEDURE

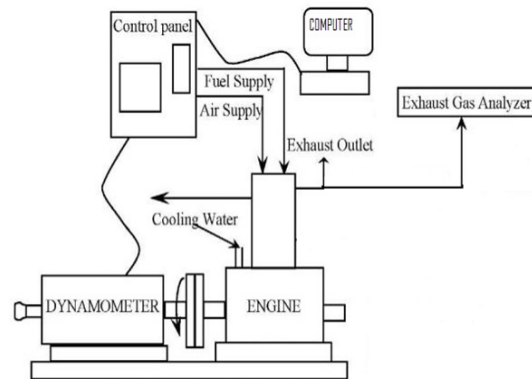


Figure-1.

5.1. Schematic arrangement of experimental setup

The engine was allowed to run with diesel fuel at various loads for nearly ten minutes to attain the steady state and constant speed conditions. First, the constant flow of water was maintained with the help of Rotameter and indicators of load, speed and temperature were switched on. The engine was started by cranking after ensuring there was no load. The engine was allowed to run at the rated speed of 1500 rev/rpm for a period of 15 minutes to reach the steady state. The fuel consumption was measured at different time intervals with the help of stop watch. The amounts of NO_x , HC and CO were measured using exhaust gas analyser. The exhaust temperature was measured by using a sensor. Then the load was gradually applied for 25, 50, 75 and 100% respectively. First, engine was operated with Mineral diesel and readings were measured for Biodiesel fuel (without cetane improver), in different blends of diesel with biodiesel like B10, B20 and B30 (soya) and readings of NO_x , HC, CO were taken for every loads. Then the engine was run with B10, B20 and B30 with addition of 1ml, 3ml and 5ml of Cetane Improver, the DEE, and the readings of NO_x emissions, HC and CO emissions were taken. The readings of exhaust gas analyser for mineral oil, biodiesel blends with added DEE and, without DEE for the various specified loads are noted, tabulated for analysis, and graph was plotted based on the tabulated readings.

6. RESULTS AND DISCUSSIONS



6.1. Impact of DEE added to biodiesel in reducing NOx emissions

6.1.1. NOx emission compared with B10, B20 & B30 blends

From the Figure-2 given below, the variations in NOx emission with sole Mineral diesel for the different percentages of load can be seen. It can be seen that as load increases NOx level increases gradually up to 2200ppm.

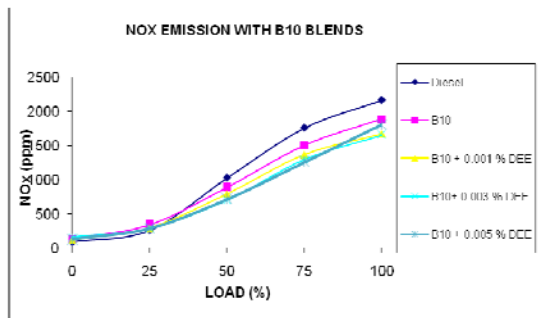


Figure-2. NOx emissions from B10 blends.

For the above, the variation in NOx emission for sole diesel, Blended (B10) fuel and blends with additive of 0.001%, 0.003% and 0.005% DEE for the mentioned percentages of loads can be seen. When compared with the results for NOx emissions for Mineral diesel, there is evidently lowered level less than 2000 ppm in all the other four cases. Further more, we can see a lowered level of NOx emission in all the three cases of blends with added DEE with maximum result for DEE added at 0.005%. An increase in the cetane number helps in the reduction in the ignition delay and hence leads to reduction of premixed combustion, that leads to lower peak cylinder gas temperatures, resulting in the active control of combustion and lower NOx formation rates thereafter. With start of combustion at TDC, as there is moderation in the combustion temperature here also, though there is usually greater exhaust NOx level, even this is lowered than that with the sole blend even for higher loads with the use of the cetane improver. So the cetane improvers show tremendous help in reducing NOx emissions when using in optimum amount, neither lesser, nor in greater amounts for the specified fuel.

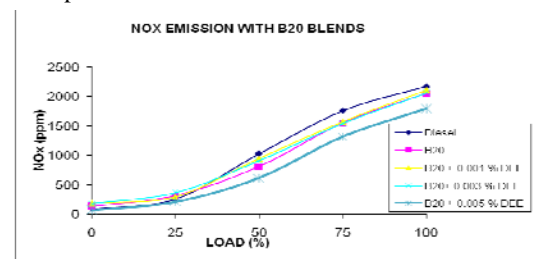


Figure-3. NOx emissions from B20 blends.

From the Figure-3, given above, the NOx emission for sole mineral diesel, Blended (B20) fuel, and

for blends with additive of 0.001%, 0.003% and 0.005% DEE for various percentages of loads can be compared. When compared with the results for NOx emissions for Mineral diesel, there is higher level of NOx up to about 2200 ppm in sole biodiesel blend, when we can see a lowered level of NOx emission in all the three cases of blends with added DEE with maximum marked decrease in emission result for DEE at 0.005% up to 500ppm. An appropriate cetane value helps in the reduction in the ignition delay and hence leads to reduction of premixed combustion, that leads to lower peak cylinder gas temperatures and lower NOx formation rates. Then with start of combustion at TDC, as there is moderation in the combustion temperature here also, the exhaust NOx level is lowered than that with the sole blend even for higher loads when with the use of the cetane improver. Cetane improvers are used to improve the quality of diesel fuel, and to enhance the performance of diesel engine, allowing: quicker cold start up. These active combustion control measures seek to find an optimum combustion efficiency and to control combustion (and hence emissions) at that efficiency.

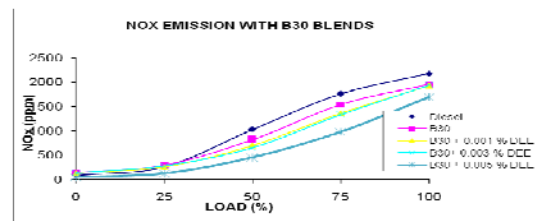


Figure-4. NOx emissions from B30 blends.

From the Figure-4, given above, we can examine and analyse the variation in NOx emission for sole Mineral Diesel, Blended (B30) fuel, and for blends with additives of 0.001%, 0.003% and 0.005% DEE for various percentages of loads. When compared with the results for NOx emissions for Mineral diesel, there is a markedly lowered level of NOx, only less than 2200 ppm in all the cases, even without additives. Further we notice a very low level of NOx emission in all the three cases of blends with added DEE for up to less than 1500ppm only. At 75% of load efficiency there is maximum result for DEE added at 0.005% with emissions up to less than 1000 ppm only. At maximum loads also there is a remarkably lowered level of NOx up to a maximum of 1500 ppm. An increase in the cetane number helps in the reduction in the ignition delay and hence leads to reduction of premixed combustion that leads to lower peak cylinder gas temperatures and lower NOx formation rates. Cetane improvers are not only used to improve the quality of diesel fuel, but also to enhance the performance of diesel engine and quicker cold start up.

6.2. Impact of DEE added to biodiesel in reducing CO emissions



6.2.1. CO emission compared with B10,B20 &B30 blends

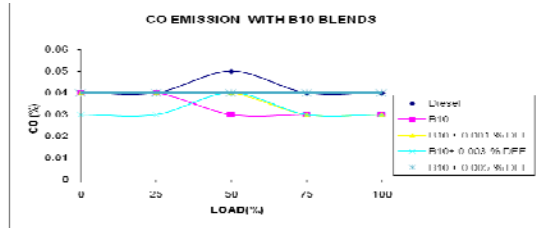


Figure-5. CO emissions from B10 blends.

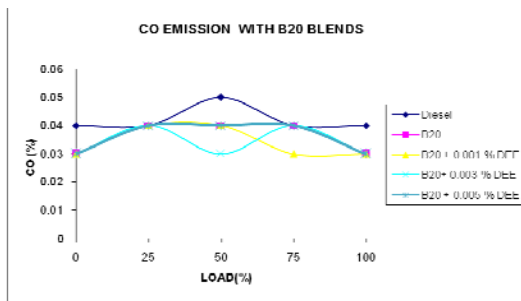


Figure-6. CO emissions from B20 blends.

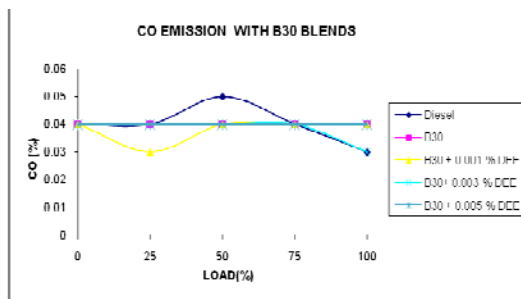


Figure-7. CO emissions from B30 blends.

From the Figures-5, 6, 7 given above, we can compare the variations of CO emission for sole diesel, Blended (B10) fuel, blends with additive of 0.001%, 0.003% and 0.005% DEE for various percentages of loads. When compared with the results for CO emissions for Mineral diesel, there is evidently lowered level in all or most of the cases. Furthermore, we can see a lowered level of CO emission in all the three cases of blends with added DEE. So, here also, when biodiesel with increase in the cetane number which helps in the reduction in the ignition delay is used, leads to reduction of premixed combustion, that leads to lower peak cylinder gas temperatures and lower CO formation rates. At half the full load limit, though there is usually increase in the exhaust CO level, this does not increase linearly whereas get reduced thereafter. Cetane improves helps in reduction in engine knock and wear, production of lower pressures resulting in smoother performance, decrease or elimination of carbon

build-up on injector nozzles and hence a decreased CO emissions level.

6.3. Impact of DEE added to biodiesel in reducing HC emissions

6.3.1 HC emission compared with B10, B20 &B30 blends

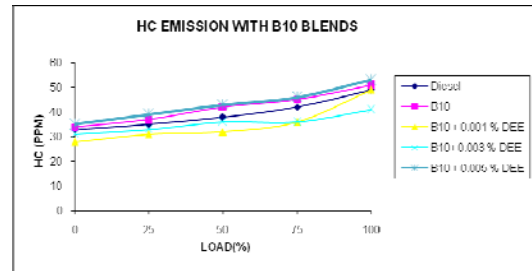


Figure-8. HC emissions from B10 blends.

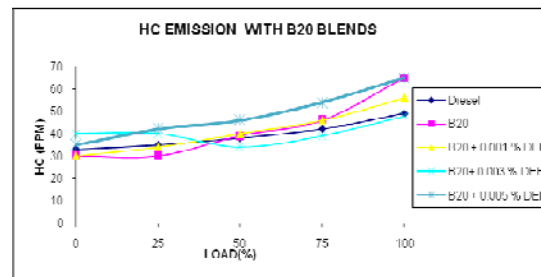


Figure-9. HC emissions from B20 blends.

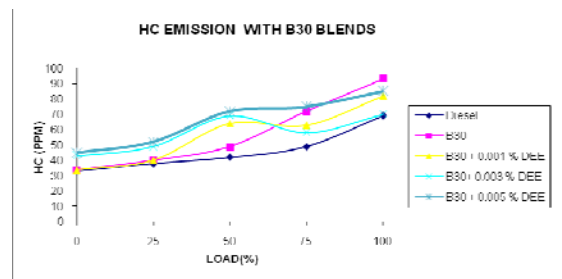


Figure-10. HC emissions from B30 blends.

From the Figures-8, 9 and 10 given above, we can see the variations in HC emission for sole diesel, Blended (B10) fuel, and blends with additive of 0.001%, 0.003% and 0.005% DEE for various percentages of loads. When compared with the results for HC emissions for Mineral diesel, HC emission in all the three cases of B30 blends with added DEE with maximum emissions for DEE at 0.005%. An increase in the cetane number though helps in the reduction in the ignition delay and accumulation of fuel particles (Improper air-fuel ratio) leads to significant increase in HC emissions. Hence there is an increase noted.

7. CONCLUSIONS



Thus the variation in the exhaust emissions of a diesel engine using sole mineral diesel, soya bean biodiesel fuel at various blends were investigated and compared as also the blends were added with cetane improvers and the emission results were compared. Using soya bean biodiesel fuel blends of B10, B20 and B30 in the engine even without DEE as an additive produces significant reduction in NO_x emission than sole diesel. Based on the emissions of soya bean Biodiesel (B30) along with 0.005% of DEE, is concluded that the biodiesel represents a good alternative fuel with better emission characteristics to that of a mineral diesel. From the above analysis the soya bean biodiesel shows decrease in the emission parameters like, NO_x and CO but HC is little higher. Hence the biodiesel along with 0.005% of DEE can be used for reduction of NO_x emission in soya bean biodiesel. If as strategic method is evolved to reduce HC emission also. This soya bean biodiesel can be an ideal choice as an alternative fuel.

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