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Abstract:

As the fossil fuels are depleting day by day, there is a need to find out an alternative fuel to fulfil the energy demand of the world. Biodiesel is one of the best available sources to fulfil the energy demand of the world. More than 350 oil-bearing crops identified, among which some only considered as potential alternative fuels for diesel engines. The scientists and researchers conducted tests by using different oils and their blends with diesel. They concluded that vegetable oils, either chemically altered or blended with diesel to prevent the engine failure. It was reported that the combustion characteristics of biodiesel are similar as diesel and blends were found shorter ignition delay, higher ignition temperature, higher ignition pressure and peak heat release. The engine power output was found to be equivalent to that of diesel fuel. In addition, it observed that the base catalysts are more effective than acid catalysts and enzymes

1. Introduction:

1.1 Neem - Oil:

Neem oil is a vegetable oil pressed from the fruits and seeds of neem (*Azadirachta indica*), an evergreen tree which is endemic to the Indian subcontinent and has been introduced to many other areas in the tropics. It is perhaps the most important of the commercially available products of neem for organic farming and medicines. Neem oil is generally light to dark brown, bitter and has a rather strong odour that is said to combine the odours of peanut and garlic. It comprises mainly triglycerides and large amounts of triterpenoid compounds, which are responsible for the bitter taste. It is hydrophobic in nature and in order to emulsify it in water for application purposes, it must be formulated with appropriate surfactants.

1.2 Bio - Diesel:

In heavy-duty automotive applications, diesel engines are established as the most fully developed and proven approach for improved fuel economy and reduced exhaust emissions. As the use of C.I. engines grows, concern about exhaust emissions is also growing, particularly emissions of NO_x, Smoke and particulate matter. In this work three different oxygenated compounds were blended along with diesel and using these blends combustion, performance and emission levels were experimentally assessed in a single cylinder diesel engine. The observations were found to be quite practical and satisfactory. Many of the methods for the reduction of diesel exhaust pollutants have included with modern diesel engine management technologies.

The most effective methods such as exhaust gas recirculation (EGR), sophisticated fuel injection systems (e.g. Common Rail Systems), electronic controls and fuel properties modification. EGR has been applied to light-duty diesel engines and has mostly been effective in reducing tail-pipe NO_x emissions. However, the reduction of NO_x is at the expense of an increase in other emissions from the engine, increased engine wear and an increase in fuel consumption. Newly developed common rail injection systems allow for high injection pressures and pilot injections, which helps to reduce pollutant emissions and engine noise. Modern electronic controls have been used to optimize engine the performance and to lower all the exhaust emissions evenly.

Despite promising new diesel after treatment developments, the task to maintain stringent regulations appears to be great. This fact has encouraged automotive researchers to look for the other options to help control diesel emissions. One such option is to control diesel exhaust emissions through fuel modification because it would affect both new and old engines. Modification of diesel fuel to reduce exhaust can be performed by reducing aromatic content (higher cetane number), reducing fuel sulphur, increasing fuel volatility and decreasing the fuel density. While such changes can clearly provide some emissions benefits, the shortfall in NO_x and particulate emissions control in diesel engines is so great that much more drastic fuel changes will be needed for a compromise.

1.3 Oxygenates:

To have the compromise between engine performance and engine out emissions, one such change has been the possibility of using oxygenated blending compounds along with diesel fuels. These blends enhance the combustion efficiency burning, faster burn rates, and the ability to burn more fuel can occur and to increase in the oxygen concentration. Further these blends of a fuel-air mixture, often beneficially increasing the efficiency and power output of an engine and reducing the emissions to an appreciable level. To achieve better performance and emission level the oxygen concentration in the fuel air mixture should be enhanced. Oxygen enhancement can be performed in two ways: intake air enrichment or via

oxygenated fuels. Oxygen enhancement has typically been achieved through oxygenated compound blending proved to be more efficient in achieving better performance and emission level.

Various types of oxygen containing compounds including ethers, alcohols, carbonates, acetates, glycols and esters have been tested in engine to determine the effects of oxygenates on engine combustion performance and exhaust emissions. The fuel blending properties that were used in the screening process of oxygenate selection included: additive solubility, the flash point of blend, the viscosity of blend, the solubility of water in the resultant blend, the water partitioning of the additive and the cost. Based on the above blending properties three oxygenate blending compounds were chosen for the testing purpose: two maleate compounds diethyl and dibutyl maleate, and, diethylene glycol dimethyl ether, also known as diglyme. The maleate compounds have the structure $(R-(O)2C-C=C-C(O)2-R$, where for diethyl maleate R is an ethyl group and for dibutyl maleate R is a butyl group.

Experiments to study the effects of oxygenated fuels on emissions and combustion were performed in a single cylinder direct-injection (DI) diesel engine. A matrix of oxygen containing fuels assessed the impact of weight percent oxygen content, oxygenate chemical structure, and oxygenate volatility on emissions. Several oxygenated chemicals were blended with an ultra-low sulphur diesel fuel and evaluated at an equivalent energy release and combustion phasing. Additional experiments investigated the effectiveness of oxygenated fuels at a different engine load, a matched fuel/air equivalence ratio, and blended with a diesel fuel from the Fischer- Tropsh process. Interactions between emissions and critical engine operating parameters were also quantified.

The main objective of the investigation is to analyse the combustion and performance diesel engine with DGL blended biodiesel. Various parameters, as follows:

- Effect of pressure
- Maximum pressure
- Rate of pressure rise
- Heat release
- Cumulative heat release
- Ignition delay
- Combustion duration
- Specific fuel consumption
- Brake thermal efficiency
- Volumetric efficiency, are computed at full load and no load conditions are computed and expressed in the form of graph. Combustion and performance of biodiesel is to be analysed in this investigation.

2. Neem Oil and Its Properties:

Neem oil is a vegetable oil pressed from the fruits and seeds of neem (*Azadirachta indica*), an evergreen tree which is endemic to the Indian subcontinent and has been introduced to many other areas in the tropics. It is perhaps the most important of the commercially available products of neem for organic farming and medicines.

2.1 Characteristics:

Neem oil is generally light to dark brown, bitter and has a rather strong odour that is said to combine the odours of peanut and garlic. It comprises mainly triglycerides and large amounts of triterpenoid compounds, which are responsible for the bitter taste. It is hydrophobic in nature and in order to emulsify it in water for application purposes, it must be formulated with appropriate surfactants.

Neem oil also contains steroids (campesterol, beta-sitosterol, stigmasterol) and a plethora of triterpenoids of which azadirachtin is the most well-known and studied. The azadirachtin content of neem oil varies from 300ppm to over 2500ppm depending on the extraction technology and quality of the neem seeds crushed.

The method of processing is likely to affect the composition of the oil, since the methods used, such as pressing (expelling) or solvent extraction are unlikely to remove exactly the same mix of components in the same proportions. The neem oil yield that can be obtained from neem seed kernels also varies widely in literature from 25% to 45%. The oil can be obtained through pressing (crushing) of the seed kernel either through cold pressing or through a process incorporating temperature controls.

Neem seed oil can also be obtained by solvent extraction of the neem seed, fruit, oil, cake or kernel. A large industry in India extracts the oil remaining in the seed cake using hexane. This solvent-extracted oil is of a lower quality as compared to the cold pressed oil and is mostly used for soap manufacturing. Neem cake is a by-product obtained in the solvent extraction process for neem oil.

Table 1: Average composition of neem oil fatty acids

Average composition of neem oil fatty acids		
Common Name	Acid Name	Composition Range
Omega-6	Linoleic acid	6-16%
Omega-9	Oleic acid	25-54%
Palmitic acid	Hexadecanoic acid	16-33%
Stearic acid	Octadecanoic acid	9-24%

3. Bio - Diesel:

An enormous increase in the number of automobiles in recent years has resulted in greater demand for petroleum products. With crude oil reserves estimated to last only for a few decades, therefore, effort are on way to research now alternatives to diesel. Depletion of crude oil would cause a major impact on the transportation sector. Of the various alternate fuels under consideration, biodiesel, derived from esterified vegetable oils, appears to be the most promising alternative fuel to diesel due to the following reasons.

- Biodiesel can be used in the existing engines without any modifications.
- Biodiesel obtained from vegetable sources does not contain any slur, aromatic hydrocarbons, metals or crude oil residues.
- Biodiesel is an oxygenated fuel; emissions of carbon monoxide and soot tend to reduce.
- Unlike fossil fuels, use of Biodiesel does not contribute to global warming as the CO₂ so produced absorbed by the plants. Thus in nature CO₂ is balanced.
- The Occupational Safety and Health Administration classify biodiesel as a non-flammable liquid.
- The use of biodiesel can extend the life span of diesel engines because it is more lubricating than petroleum diesel fuel.
- Biodiesel is mostly obtained from renewable vegetable oils/animal fats and hence it may improve the fuel or energy security and thus leading to economy independence.

A lot of research work has already been carried out to use vegetable oil both in its pure form and also in modified form. Studies have shown that the usage of vegetable oils in pure form is possible but not preferable. The high viscosity of vegetable oils and their low volatility affects the atomization and spray pattern of fuel, leading to incomplete combustion and severe carbon deposits, injector choking and piston ring sticking. The methods used to reduce the viscosity are pyrolysis, blending with diesel, transesterification, and emulsification.

Among these, the transesterification is the most commonly used commercial process to produce clean and environmental friendly fuel. Methyl/ethyl/butyl esters of sunflower oil, rice bran oil, palm oil, mahua oil, jatropha oil, karanja oil, soybean oil, and rapeseed oil and rubber seed oil have been successfully tested on C.I. engines and their performance has been studied. Vegetable oils that can be blended with existing petroleum-based fuel have a distinct advantage because they can be used whenever available and the vehicle can also be fuelled with conventional fuels when the alternative fuels are not available.

Biodiesel is environment friendly alternative diesel fuel consisting of alkyl monoesters of fatty acids from vegetable oils and animal fats. One drawback however, of biodiesel is that there is an inverse relationship between biodiesel's oxidative stability and its cold flow properties, which leads to reduction in the performance of engine. Similar to alcohol fuels, biodiesel has lower energy content and different physical properties than diesel fuels and this may require engine-setting adjustments to improve engine performance and emissions.

4. Preparation of Bio - Diesel:



Figure 1: Biodiesel Extraction Apparatus

Bio-diesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. Currently, most of the biodiesel is produced from the refined/edible type oils using methanol and an alkaline catalyst. However, large amount of non-edible type oils and fats are available. The difficulty with alkaline-esterification of these oils is that they often contain large amounts of free fatty acids (FFA).

A two-step transesterification process is developed to convert the high FFA oils to its mono-esters. The first step, acid catalyzed esterification reduces the FFA content of the oil to less than 2%. The second step, alkaline catalyzed transesterification process converts the products of the first step to its mono-

esters and glycerol. The growing concern due to environmental pollution caused by the conventional fossil fuels and the realization that they are non-renewable have led to search for more environment friendly and renewable fuels. Among various options investigated for diesel fuel, biodiesel obtained from vegetable oils has been recognized world over as one of the strong contenders for reductions in exhaust emissions. Worldwide biodiesel production is mainly from edible oils such as soybean, sunflower and canola oils.

Since, India is not self sufficient in edible oil production, hence, some non-edible oil seeds available in the country are required to be tapped for biodiesel production. With abundance of forest and plant based non-edible oils being available in our country such as *Pongamia pinnata* (karanja), *Jatropha curcas* (jatropha), *Madhuca indica* (mahua), *Shorea robusta* (Sal), *Azadirachta indica* A Juss (neem) and *Hevea brasiliensis* (rubber), no much attempt has been made to use esters of these non-edible oils as substitute for diesel except jatropha. Moreover, there are plenty of wastelands available in India, which can be utilized for growing such oil seed crops.

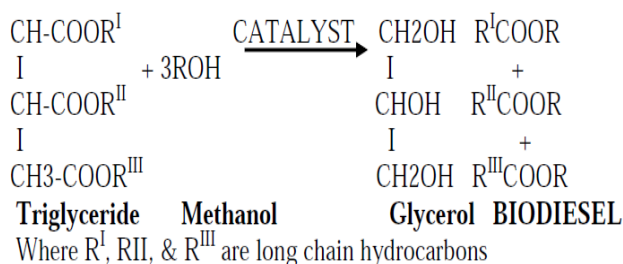
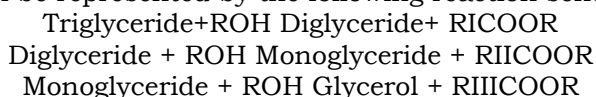
In the recent years, systematic efforts have been made by several researchers and to use the various vegetable oils as fuel in compression ignition engines. The calorific value of vegetable oil is comparable to that of diesel. However, their use in direct injection diesel engines is restricted by some unfavourable physical properties, particularly their viscosity. The viscosity of vegetable oil is about ten times higher than that of diesel. Therefore, the vegetable oil cause poor fuel atomization, incomplete combustion and carbon deposition on the injector and valve seats resulting in serious engine fouling. This necessitates the reduction in viscosity of the vegetable oils for use as fuel in CI engines. Many standardized procedures are available for production of bio diesel. The commonly used methods are:

- Blending
- Micro Emulsification
- Thermal Cracking
- Transesterification

Among these, transesterification of vegetable oils appears to be more suitable because the by product (glycerol) has commercial value.

4.1 Transesterification:

Transesterification (alcoholysis) is the chemical reaction between triglycerides and alcohol in the presence of catalyst to produce mono-esters. The long and branched chain triglyceride molecules are transformed to mono-esters and glycerine. Transesterification process consists of a sequence of three consecutive reversible reactions. That is, conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. The glycerides are converted into glycerol and yielding one ester molecule in each step. The properties of these esters are comparable to that of diesel. The overall transesterification reaction can be represented by the following reaction scheme.



4.2 Processing of Biodiesel from Non Edible Oil (Neem Oil):

Free fatty acid (FFA) percentage in neem oil is very high. There are many methods to find out the free fatty acid percentage content in oil. Simple titration with the KOH is a simple method. For titration first 0.1 to 10 g of oil was weighed and dissolved in about 50 ml of a suitable solvent. Methanol, ethanol and ether are some normally used solvents; in this case methanol was used as the solvent. It was heated gently for some time. A small drop of indicator was added. Phenolphthalein was used as indicator. Then the solution was titrated with KOH. The amount of KOH required, in milligram (mg) to neutralizing the free fatty acid in one gram of oil expressed as a number is known as acid number. From acid number the free fatty acid present in the oil can be calculated.

4.3 Acid Number Calculation for the Selected Sample:

$$\text{Acid value} = 56.1 \times N \times V / M$$

Where,

V is the number of ml of KOH,

N is the normality of KOH,

M is the mass (in g) of sample

Acid number for neem oil is 52. generally FFA value is half of the acid value so percentage of free fatty acid (FFA) in neem oil is 26% it is very high so we cannot use directly alkaline esterification before that we do acid pre-treatment method 'acid-base' process Acid pre-treatment followed by main base

transesterification reaction; using methanol as reagent and H₂SO₄ and KOH as catalysts for acid and base reactions, respectively, was followed to produce biodiesel from crude neem oil.

5. Esterification Procedure:

5.1 Methodology:

The objective of this study is to develop a process for producing biodiesel from non-edible neem oil. The process consists of two steps namely, acid esterification and alkaline esterification.

- **Acid Esterification:** The first step reduces the FFA value of crude neem oil to about 2% using acid catalyst
- **Alkaline Esterification:** After removing the impurities of the product of first step, it is transesterified to mono-esters of fatty acids using alkaline catalyst. The parameters affecting the process such as alcohol to oil molar ratio, catalyst amount, reaction temperature and duration are analyzed.

5.2 Esterification Setup:

A round bottom flask is used as laboratory scale reactor for these experimental purposes. A hot plate with magnetic stirrer arrangement is used for heating the mixture in the flask. The mixture is stirred at the same speed for all test runs. The temperature range of 50–60 °C is maintained during this experiment.

5.2.1 Acid Esterification:

One litre of crude neem oil requires 250 ml of methanol for the acid esterification process. The neem oil is poured into the flask and heated to about 50 °C. The methanol is added with the preheated neem oil and stirred for a few minutes. 1% of sulphuric acid is also added with the mixture. Heating and stirring is continued for 30 min at atmospheric pressure. On completion of this reaction, the product is poured into a separating funnel for separating the excess alcohol. The excess alcohol, with sulphuric acid and impurities moves to the top surface and is removed. The lower layer is separated for further processing (alkaline esterification).

5.2.2 Effect of Reaction Temperature:

At room temperature the conversion efficiency is noted to be very low, even after 2 hrs of stirring. With increase in temperature the conversion takes place at a faster rate. The optimum temperature for this reaction is found to be in the range of 50±5 °C. At higher reaction temperatures, there is a chance of loss of methanol and increase in darkness of the product. High reaction temperature increase the production cost of biodiesel also. The maximum yield of ester is obtained at the temperatures of 50±5 °C. The decrease in yield is observed when the reaction temperature goes above 55 °C. The reaction temperatures greater than 60 °C should be avoided, in the case of neem oil, because they tend to accelerate saponification of the glycerides by the alkaline catalyst before completion of the alcoholysis.

5.2.3 Alkaline Esterification:

Alkaline catalyzed esterification process uses the experimental setup of acid catalyzed pre-treatment process. The products of first step are preheated to the required reaction temperature of 50±5 °C in the flask. Meanwhile, 5 gm of KOH is dissolved in 250 ml methanol and is poured into the flask. The mixture is heated and stirred for 30 min. The reaction is stopped, and the products are allowed to separate into two layers. Glycerine which is heavier deposits at the bottom and the esterified neem oil is obtained at the top portion. The esterified neem oil is separated from the funnel and now it is ready for blending with diesel.

6. Effects of Oxygenated Fuels on Di Diesel Combustion:

Experiments to study the effects of oxygenated fuels on emissions and combustion were performed in a single cylinder direct-injection (DI) diesel engine. A matrix of oxygen containing fuels assessed the impact of weight percent oxygen content, oxygenate chemical structure and oxygenate volatility on emissions. Several oxygenated chemicals were blended with an ultra-low sulphur diesel fuel and evaluated at an equivalent energy release and combustion phasing. Additional experiments investigated the effectiveness of oxygenated fuels at a different engine load, a matched fuel/air equivalence ratio, and blended with a diesel fuel from the Fischer- Tropsch process.

Interactions between emissions and critical engine operating parameters were also quantified. A scanning mobility particle sizer (SMPS) was used to evaluate particle size distributions, in addition to particulate matter (PM) filter and oxides of nitrogen (NO_x) measurements. The oxygenated diesel fuels were found to decrease the volume fraction of particles, but did not alter the total number of particles emitted.

The reduction was a function of the fuel's weight percent oxygen content and oxygen containing functional group. Agreement was achieved between the relative trends observed with the integrated SMPS particle volume fraction and filter based mass measurement. Preliminary physical and chemical characterization of particulate matter from the reference and oxygenated fuels did not reveal any significant morphological or compositional differences.

6.1 Diglyme Properties:

Table 2: Properties of Diglyme

Properties	Diglyme
Chemical Formula	CH ₃ O(CH ₂) ₂ O(CH ₂) ₂ OCH ₃
Oxygen Content (wt %)	35.8

Density(g/cm ³)	0.943
Boiling point °C	162
Calorific value(MJ/KG)	42

7. Advantages of Biodiesel:

- Bio-diesel is non-toxic.
- Bio-diesel degrades four times faster than diesel.
- Pure bio-diesel degrades 85–88% in water.
- Blending of bio-diesel with diesel fuel increases engine efficiency.
- The higher flash point makes the storage safer.
- Bio-diesel is an oxygenated fuel, thus implying that its oxygen content plays a role in making fatty compounds suitable as diesel fuel by “cleaner” burning.
- 90% reduction in cancer risks, according to Ames mutagenicity tests.
- Provides a domestic, renewable energy supply.
- Bio-diesel does not produce greenhouse effects, because the balance between the amount of CO₂ emissions and the amount of CO₂ absorbed by the plants producing vegetable oil is equal.
- Bio-diesel can be used directly in compression ignition engines with no substantial modifications of the engine.
- Bio-diesel contains no sulphur and is generally suitable to match the future European regulations which limit the sulphur content to 0.2% in weight in 1994 and 0.05% in 1996.
- Chemical characteristics revealed lower levels of some toxic and reactive hydrocarbon species when bio-diesel fuels were used.
- The emissions of PAH and nitro PAH compounds were substantially lower with bio-diesel are compared to conventional diesel fuel.
- The larger reductions in PAH are not unexpected when considering the bio-diesel contains no aromatics and no PAH compounds.

8. Disadvantages of Bio-Diesel:

- Slight decrease in fuel economy on energy basics (about 10% for pure bio-diesel).
- Density is more than diesel fuel in cold weather, but may need to use blends in sub-freezing conditions.
- More expensive due to less production of vegetable oil.

9. Conclusion:

We ensure that our fuel will be the best alternative for conventional diesel fuel. We hope that further studies on this alternative fuel by us will rectify the disadvantages and improves the performance.

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