

Production of Neem Oil Methyl Ester by Using Two-Step Esterification Process

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ABSTRACT

The increasing awareness of the depletion of fossil fuel resources and the environmental benefits of biodiesel fuel has made it more attractive in recent times. Its primary advantages deal with it being one of the most renewable fuels currently available and it is also non-toxic and biodegradable. It can also be used directly in most diesel engines without requiring extensive engine modifications. Hence, the recent focus is the use of non-edible plant oil source and waste products of edible oil industry as the feedstock for biodiesel production meeting the international standards. Quality standards are prerequisites for the commercial use of any fuel product. This Research work is about the manufacturing of biodiesel from the non-edible vegetable oil i.e. Neem Oil. This study aims to define the requirements for biodiesel production by the esterification process, testing its quality by determining some parameters such as density, kinematics viscosity, high heating value, cetane number, flash point, cloud pint and pour point and comparing it to Diesel fuel. Two step esterification is used to make the neem oil biodiesel because FFA (free fatty acid) content in neem oil is very high. The recovery of neem oil methyl ester of lowest viscosity(6.11 cst) with approx 80 percent recovery was possible at following parameteric conditions:

First step esterification:

- Catalyst (H_2SO_4) concentration 5 % (w/w_{oil})
- Reaction temperature 45°C
- Ethanol to oil molar ratio 8:1
- Reaction time 60 min
- Settling time 24 h

Second step esterification:

- Catalyst (KOH) concentration 1 % (w/w_{oil})
- Reaction temperature 60°C
- Ethanol to oil molar ratio 8:1
- Reaction time 90 min
- Settling time 36 h

In the first step FFA (free fatty acid) of neem oil was decreased from 20 to 4.2 %. Further reduction takes place during the second step. The relative density of raw neem oil used in the experiment was 10.87 % higher than the diesel and NOME had the relative

density 6.57 % higher than diesel. The kinematic viscosity of raw neem oil used to make neem oil methyl ester (NOME) was about 17 times higher than the diesel and NOME was about 3 times higher than the diesel.

The gross heat of combustion of raw neem oil is found to be 2.75 % higher than the diesel but NOME had the gross heat of combustion 13.45 % lesser than the diesel.

Key words- Biodiesel; Raw neem Oil; Neem Oil Methyl ester NOME ; Transesterification.

1. INTRODUCTION

Energy consumption plays a very important role in the economy of any country. Oil is the major source of the energy for the entire world as it is convenient to store and handle. During the 21st century, an alarming scarcity is supposed to come in the production of crude petroleum oil and they will be costly to produce and at the same time there will likely be an increase in the number of automobile and other internal combustion engines. Although, the fuel economy of an engine has been greatly improved through continued researches across the world and will probably continue to be improved but there will be a great demand for fuel in coming decades due to the rapid pace of industrialization world over. At present, India is the sixth biggest country in the world in terms of energy demands which is 3.5 percent of world commercial energy demand and is expected to grow at the rate of 4.8 percent per annum of its present demand [7]. The petroleum import bill is currently about 30 percent of total import bill and yearly consumption of diesel oil in India is about 40 million tones forming about 40 percent of the total petroleum product consumption.

The advantages of using vegetable oils as fuel for diesel engines include better self ignition characteristics, better compatibility with fuel injection system used in existing CI engine, high energy content and self processing and handling. Above all, these fuels can be readily incorporated into energy pool, should the need arise due to sudden shortage or

disruption in the existing petroleum system [4]. Moreover, vegetable oil fuels produce greater thermal efficiency than diesel fuel [4]. However, the use of vegetable oil in direct injection type diesel fuel engine is limited by at least an important physical property i.e. viscosity. Viscosities of vegetable oils are reported to be 10 to 20 times more than that of diesel fuel and are considered to be lower in total energy and higher in density, carbon residue, and particulate matter [5].

The chemical composition of vegetable oil is directly related to problems with failure of engine lubrication. Some oils are more likely to polymerize or oxidize in the crank case than others, notably those high in unsaturated acids. The problem arises due to the triglyceride composition of the oils. All unsaturated triglycerides have a tendency to polymerize, depending on the degree of saturation.

Polymerization is accelerated with high temperature, pressure and the presence of certain metal-conditions often found in the crankcase of an internal combustion engine. The same problems of polymerization of crankcase oil in diesel engines occurred with petroleum based fuels in 1950s. The solution was to put additive into motor oil. This problem combined with the viscosity of vegetable oils presents the greatest difficulty in using vegetable oils in diesel engines. Therefore, several techniques are being used to reduce the viscosity. These include heating the vegetable oil to sufficient temperature to lower the viscosity to near

the specification range, diluting the vegetable oil with other less viscous liquid fuels to form blends that have been termed as hybrid fuels, micro emulsifying the vegetable oil and esterification process i.e. chemically converting the vegetable oil to simple ester of methyl, ethyl or butyl alcohols. Esterification process has been preferred because it reduces viscosity and maintains the heat of combustion. Moreover, this process also enhances volatility of the fuel which in turn helps in its better atomization. The esters produced from the esterification process present a very promising alternative to diesel fuel since they are renewable, non-volatile and safer due to increased flash point, biodegradability, contain little or no sulfur and can be produced easily in rural areas where there is an acute need for such form of energy. Moreover, they have been demonstrated to burn in unmodified diesel engines [2]. The various aspects of using vegetable oils as fuel include crop production and development that include selection of high oil processing and storage, filtration, blends and additives, esterification, engine performance, problem with engine deposits and injector coking, use of byproducts, economics of vegetable oil and potential production of oil seeds.

Both edible oils such as Soybean, Rapeseeds, Canola, Sunflower, Cottonseeds, etc. and non edible oils like Jatropha, Karanja, Neem, Mahua etc. have been tried to supplement diesel fuel in various countries. In U.S. biodiesel programme is based on their surplus edible oils like soybean and in Europe from rapeseed and sunflower oils. India has shortage of edible oils so its biodiesel programme is centered around non-edible vegetable oils like Jatropha.

For feedstock diversification and utilization of currently available local resources, non-edible sources like Neem, Karanja, Mahua, Sal etc. should be scientifically investigated for efficient

biodiesel production and engine utilisation. Keeping this background in consideration, production of biodiesel from Neem oil and its utilization as a potential alternative fuel for diesel engine has been investigated.

Neem oil (*Azadirachta indica*) is non-edible oil available in huge surplus quantities in South Asia. Annual production of neem oil in India is estimated to be 30,000 tons. Traditionally; it has been used as fuel in lamps for lighting purpose in rural areas and is used on an industrial scale for manufacturing of soaps, cosmetics, pharmaceuticals and other non-edible products. 'Azardiratchi' is the main biochemical component of the Neem that is used for medicinal purposes.

Neem oil can be used for transesterification after the extraction of 'Azardiratchi'. The seed oil yield is 30–60% of the weight of the kernel.

However this oil suffers from the problem of high FFA therefore transesterification process cannot be used to efficiently convert it to biodiesel. (Ragit et al.) has reported 83% ester yield of base catalyzed transesterification of neem oil with 6:1 alcohol ratio.

In view of the above, a study was carried out with the following objectives:

1. Production of neem oil methyl ester (NOME) or Neem oil biodiesel by two step esterification process.
2. Determination of characteristic fuel properties of neem oil methyl ester (NOME) and comparing with diesel.

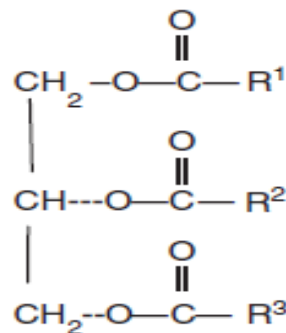


Fig. 1.1 Chemical Structure of Vegetable oil

2. Methodology and Technique used

The process of transesterification yield vegetable oil ester, which has shown promises as alternative diesel fuel as a result of improved viscosity and volatility. Several researchers investigate the different vegetable oil esters and find esters comparable to mineral diesel. The yield of biodiesel in the process of transesterification is affected by several process parameters/variables.

2.1 Effect of catalysts

Catalysts are classified as alkali, acid, or enzymes. Alkali-catalyzed transesterification is much faster than acid-catalyzed reaction. However, if a vegetable oil has high free fatty acid and water content, acid catalyzed transesterification reaction is suitable. Partly due to faster esterification and partly because alkaline catalysts are less corrosive to industrial equipment than acidic catalysts, most commercial transesterification reactions are conducted with alkaline catalysts. Sodium methoxide was found to be more effective than sodium hydroxide. Sodium alkoxides are among the most efficient catalysts used for this purpose, although NaOH, due to its low cost, has attracted its wide use in large scale transesterification. The alkaline catalyst concentrations in the range of 0.5–1% by weight yield 94–99% conversion of vegetable oils into esters. Further increase in catalyst concentration does not increase the conversion and it adds to extra costs because it is necessary to remove the catalyst from the reaction products at the end. Methanol can quickly react with triglycerides and NaOH is easily dissolved in it. The reaction can be catalyzed by alkalis, acids, or enzymes. The alkalis include NaOH, KOH, carbonates and corresponding sodium and potassium

alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Sulfuric acid, sulfonic acids and hydrochloric acid are usually used as acid catalysts. Lipases also can be used as biocatalysts.

2.2 Effect of molar ratio

Another important variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The stoichiometry of the transesterification reaction requires 3mole of alcohol per mole of triglyceride to yield 3 moles of fatty esters and 1 mole of glycerol.

To shift the transesterification reaction to the right, it is necessary to use either a large excess of alcohol or remove one of the products from the reaction mixture continuously.

The second option is preferred wherever feasible, since in this way, the reaction can be driven towards completion. When 100% excess methanol is used, the reaction rate is at its highest. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% by weight. **Freedman *etal.*** studied the effect of molar ratio (from 1:1 to 6:1) on ester conversion with vegetable oils. Soybean, sunflower, peanut and cottonseed oils behaved similarly and achieved highest conversions (93–98%) at a 6:1 molar ratio. Ratios greater than 6:1 do not increase yield (already 98–99%), however, these interfere with separation of glycerol.

2.3 Effect of reaction temperature

The rate of reaction is strongly influenced by the reaction temperature. However, given enough time, the reaction will proceed to near completion even at room temperature. Generally, the reaction is conducted close to the boiling point of methanol (60–70 °C) at atmospheric pressure. The maximum yield of esters occurs at temperatures ranging from 60 to 70 °C at a molar ratio (alcohol to oil) of 6:1. Several researchers have studied the effect of temperature on conversion of oils

and fats into biodiesel. **Freedman et al.** studied the transesterification of refined soybean oil with methanol (6:1), 1% NaOH catalyst, at three different temperatures 60, 45 and 32 °C. After 0.1 h, ester yields were 94%, 87% and 64% for 60, 45 and 32 °C, respectively. After 1 h, ester formation was identical for 60 and 45 °C reaction temperature runs and only slightly lower for 32 °C. It shows that temperature clearly influenced the reaction rate and yield of esters and transesterification can proceed satisfactorily at ambient temperatures, if given enough time, in the case of alkaline catalyst.

2.4 Effect of reaction time

The conversion rate increases with reaction time. **Freedman et al.** transesterified peanut, cottonseed, sunflower and soybean oils under the condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst and 60 °C. An approximate yield of 80% was observed after 1 hour for soybean and sunflower oils. After 1 h, the conversions were almost the same for all four oils (93–98%). **Ma and Hanna** studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to the mixing and dispersion of methanol into beef tallow. From 1 to 5 min, the reaction proceeded very fast. The apparent yield of beef tallow methyl esters surged from 1% to 38%.

2.5 Effect of moisture and FFA

For an alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap. The soap lowers the yield of esters and renders the separation of ester and glycerol and water washing difficult. The glycerol is then removed by gravity separation and remaining ester is mixed with hot water for separation of catalyst. Moisture can be removed using silica gel.

Ester formation eliminates almost all the problems associated with vegetable oils. Saponification reaction also takes place simultaneously along with transesterification process but soap formation is not a major problem if presence of water is less than 1%.

The glyceride should have an acid value less than 2.5% and all reactants should be substantially anhydrous. If the acid value was greater than 2.5%, more KOH is required to neutralize the FFA.

Freedman et al. found that ester yields were significantly reduced if the reactants did not meet these requirements. Sodium hydroxide or sodium methoxide reacted with moisture and carbon dioxide in the air, which diminished their effectiveness.

The effects of FFA and water on transesterification of beef tallow with methanol were investigated by **Ma and Hanna**. The results showed that the water content of beef tallow should be kept below 0.06% w/w and free fatty acid content of beef tallow should be kept below 0.5%, w/w in order to get the best conversion. Water content was a more critical variable in the transesterification process than FFA.

2.6 Properties of Selected Vegetable Oil Ester or Biodiesel

The properties of some of the biodiesel fuels are compared in Table 2.4. The characteristics of biodiesel are close to mineral diesel, and, therefore, biodiesel becomes a strong candidate to replace the mineral diesel if the need arises. The conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one-thirds that of the triglycerides, the viscosity by a factor of about eight and increases the volatility marginally. Biodiesel has viscosity close to mineral diesel. These vegetable oil esters contain 10–11%

oxygen by weight, which may encourage combustion than hydrocarbon-based diesel in an engine. The cetane number of biodiesel is around 50. Biodiesel has lower volumetric heating values (about 10%) than mineral diesel but has a high cetane number and flash point. The esters have cloud point and pour points that are 15–25 °C higher than those of mineral diesel.

Table-2.1 Properties of Selected Vegetable Oil Ester or Biodiesel

Prop erties	Biodiesel (vegetable oil methyl ester)					
	Pea nut	Soy abe an	P a l m	Sunfl ower	Li ns eed	Tall ow
Kine matic visco sity*	4.9	4.5	5 . 7	4.6	3.5 9	-
Ceta ne num ber	54	45	6 2	49	52	-
Low e r heati ng value (MJ/l)	33. 6	33.5	3 3 . 5	33.5	35. 3	-
Clou d point (°C)	5	1	1 3	1	-	12
Pour point (°C)	-	-7	-	-	- 15	9
Flash point	176	178	1 6 4	183	17 2	96
Densi ty (g/ml)	0.8 83	0.88 5	0 . 8	0.86	0.8 74	-

)			8			
Carb on resid ue (wt %)	-	1.74	-	-	1.8 3	-

2.7 Preparation of neem oil biodiesel or neem oil methyl ester (NOME)

Transesterification (alcoholysis) is a chemical reaction between triglycerides present in the vegetable oils and primary alcohols in the presence of a catalyst to produce mono-esters (biodiesel) and glycerol.

Nevertheless, transesterification is not always possible. Oils, which have high free fatty acid (FFA) content can't be transesterified by this reaction. The process rather leads to saponification i.e. formation of soap. Formation of soap makes it very difficult to separate the layers of biodiesel and glycerol. Many different thresholds of FFA contents are proposed in literature, but commonly, it is accepted that above 5% FFA level in the vegetable oils, it becomes very difficult to produce biodiesel by transesterification process. The FFA content of the oil influences the yield of biodiesel from this oil. Lower FFA results into easier production and higher yield of biodiesel. FFA content of vegetable oils is very sensitive to different parameters. From one single batch of oil seeds, oils with different FFA content could be produced depending on the process used to produce the oil, conditions of storage, moisture content and quality of the initial feedstock. For producing low cost biodiesel, methods for utilization of low cost feedstock which generally have high FFA needs to be investigated.

The FFA content of the vegetable oils increases with duration of storage of seeds/oils and leads to degeneration of the quality of vegetable oils. For such oils, one of the most frequently used pre-treatment

step is to lower FFA content of the vegetable oils is 'esterification'. In the present study, FFA of neem oil was reduced (from 20.3%) by esterification reaction. This reaction is traditionally catalyzed by acids such as sulphuric acid (fig.2.1).

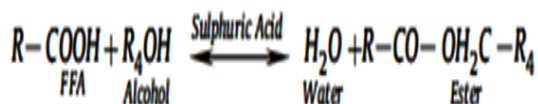


Figure-2.1 Acid catalized esterification reaction

Main parameters ruling esterification are amount of catalyst (W/Woil), molar ratio of alcohol to oil, temperature of reaction, time of reaction .

For our experiment, optimized process parameters for esterification reaction are: 5% catalyst, 8:1 alcohol to oil molar ratio, 90 min reaction time and 50°C temperature. FFA content of the oil decreased from 20.0% to 4.2 % in this esterification step. Further reduction in FFA takes place during the transesterification reaction. This is because of neutralization of FFA by the basic catalyst (KOH).

For this reason, a slightly higher amount of basic catalyst was taken for the transesterification in order to ensure presence of enough catalyst to catalyze the transesterification reaction even after this neutralization reaction for the FFA. Biodiesel was thus produced by transesterification step on this low FFA neem oil from esterification.

Preparation of neem oil methyl ester (NOME) is done by mixing methanol and sulphuric acid for the esterification process step. Catalyst used for the process of esterification and transesterification steps are sulphuric acid (Merck 98% purity), and potassium hydroxide (RFCL, 97% Purity) respectively. Methanol used in both of these process steps was having density 0.789 kg/l with a purity of 99%. For the esterification process step, 8:1 molar ratio of alcohol to oil

and 5% catalyst (w/w oil) was used. The reactants are heated in the flask to 50 °C for 90 min. After the completion of the reaction, the products are kept in a separating funnel for 24 h for gravity separation. The lower layer formed is dark brown, which mostly contains water while the upper layer contains reduced FFA neem oil.

Lower layer is removed and upper layer is used for transesterification process step for conversion into biodiesel. For this, 8:1 molar ratio of alcohol to oil with 1% (w/w oil) KOH is mixed with reduced FFA neem oil. The reactants in the flask are heated at 60 °C. After the completion of the reaction, products are again poured in a separating funnel for gravity separation of the products for 36 h. The lower layer formed is deep dark brown and mainly contains glycerol while the upper layer is biodiesel, which also contains traces of catalyst .

Traces of the catalyst are removed by water washing the biodiesel. However before washing the biodiesel, it is necessary to remove the ethanol content in biodiesel in order to avoid soap formation. Since the boiling point temperature of methanol is 78.3 °C, it can be easily removed by heating biodiesel up to 85 °C. Biodiesel is heated and kept at this temperature for 5 min and then the biodiesel is mixed with warm water and kept in separating funnel for few hours. The lower layer contains water with traced of catalyst and this layer is removed. The upper layer is biodiesel, which is again heated at 70°C for 5–10min so as to remove the traces of moisture before final storage.



Figure – 2.2 A flask filled with Neem Oil



Figure – 2.5 Separation of NOME and Glycerol



Figure – 2.3 Heating of Neem oil by Magnetic Stirrer Heater



Figure –2.4 Washing of NOME in a separating funnel

2.8 Determination of Characteristic Fuel Properties

2.8.1 Kinematic viscosity

The viscosity of a liquid is a measure of internal friction of the liquid in motion. It plays an important role in the performance of an engine fuel system operating through a wide range of temperature. Kinematic viscosity affects the injection system. Low viscosity can result in an excessive wear in the injection pumps and power loss due to pump leakage whereas high viscosity may result in excessive pump resistance, filter blockage, high pressure and coarse atomization affecting the atomization and fuel delivery rates.

An Ostwald Viscometer was used for measurement of kinematic viscosity of selected fuel samples. The instrument measures the time of gravity flow in seconds of a fixed volume of the fluid (50 ml) through specified orifice made as per **IS: 1448 [P : 25] 1976**.

The time taken for a liquid to flow between the two marks in an Ostwald viscometer is a function both of dynamic viscosity and density. The relationship between dynamic viscosity and density is called the kinematic viscosity and is defined as

$$\text{Kinematic Viscosity} = \frac{\text{Dynamic Viscosity}}{\text{Density}}$$

The Ostwald viscometer, therefore, measures kinematic viscosity. However, if the fluid is Newtonian, the dynamic viscosity can be determined from the relationship above. In practice, sucrose solutions are Newtonian over normally encountered range of shear rates.

An Ostwald viscometer is normally supplied with a viscometer constant which can be used to calculate viscosity.

However if one is not available, the viscosity of the test fluid can be compared with one whose viscosity is known (eg. water) and the viscosity of the test fluid can be in this way.

Thus. The viscosity of any liquid (say sucrose) solution may be calculated from:

$$\eta_s = \eta_w \frac{t_s \rho_s}{t_w \rho_w}$$

where ρ = density (kg/m^3)

η = Kinematic viscosity (Pa s)

T = time (s)

Subscripts s and w represent sucrose and water respectively.

2.8.2 Relative density and API gravity

The relative density of the selected fuels as mentioned above at 35°C was determined as per **IS: 1448 [P: 32]: 1992**. The empty pycnometers were weighed on an Adair Dutt make, MJ 500 series electronic balance of range 0 - 500g, having readability of 0.001 g. The pycnometers were then filled with fuel samples and weighed.

The weights of the empty pycnometers were subtracted from the weights of the filled ones to get the weight of the fuel samples. Three replicates were taken for each sample and their mean was

calculated. This value when divided by the volume of the fuel sample gave the density (ρ) of the fuel sample. The density of distilled water at 35°C was also determined.

The following equation was used to calculate the relative density.

$$\text{Relative density} = \frac{\text{Density of the fuel at } 35^\circ\text{C}}{\text{Density of the water at } 35^\circ\text{C}}$$

Density of water at 35°C = 0.1g/cc

The API (American Petroleum Institute) gravity, which is an indicator of heat content and lightness of a fuel, was also calculated.

The higher the API gravity, the lighter is the fuel. The following relationship was used to determine the API gravity of diesel, neem oil and their blends with diesel.

$$\text{API Gravity} = \frac{141.5}{\text{Relative density at } 35^\circ\text{C}} - 131.5$$

2.8.3 Gross heat of combustion

The heat of combustion or calorific value of a fuel is an important measure since it is the heat produced by the fuel within the engine that enables the engine to do the useful work. The gross heat of combustion of fuel samples was determined as per **IS: 1448 [P: 6]: 1984** with the help of a Widson Scientific Works make isothermal bomb calorimeter. A 1 ml fuel sample was burnt in the bomb of calorimeter in the presence of pure oxygen. The sample was ignited electrically. As the heat was produced, the rise in temperature was measured. The water equivalent (effective heat capacity of the calorimeter) was also determined using pure and dry benzoic acid as test fuel. Each sample was replicated three times.

The heat of combustion of the fuel samples was calculated using the equation given below:

$$H_c = \frac{W_c \times \Delta T}{M_s}$$

Where,

H_c = Heat of combustion of the fuel sample, Cal / g

W_c = Water equivalent of the calorimeter, Cal / $^{\circ}\text{C}$ (2883.32 Cal/ $^{\circ}\text{C}$)

ΔT = Rise in temperature, $^{\circ}\text{C}$

M_s = Mass of sample burnt, g

2.8.4 Cloud and pour point

The Cloud and Pour point are the measure which indicates that the fuel is sufficiently fluid to be pumped or transferred. Hence, it holds significance to engines operating in cold climate. The Cloud Point is defined as the temperature at which a cloud or haze of wax crystal appears at the bottom of a test jar when chilled under prescribed conditions. The Pour Point is defined as the temperature at which the fuel ceases to flow. Both properties may indicate the tendency towards filter plugging and flow problems in the fuel line.

The Cloud and Pour point of fuel samples were determined as per **IS: 1448 [P: 10]: 1970** using the Cloud and Pour point apparatus. The apparatus mainly consists of 12 cm high glass tubes of 3 cm diameter. These tubes are enclosed in an air jacket which is filled with a freezing mixture of crushed ice and sodium chloride crystals. The glass tube containing fuel sample is taken out from the jacket at every 1°C interval as the temperature falls and is inspected for cloud formation. The point at which a haze was first seen at the bottom of the sample was taken as the Cloud Point.

The apparatus and the procedure for the Pour Point was same as for Cloud Point, only the sample was pre-heated to 48°C and then cooled to 35°C in air before

it was filled in the glass tube. Thereafter, the cooled samples were placed in the apparatus and withdrawn from the cooling bath at 1°C interval for checking its flow ability. The Pour Point was taken to be the temperature 1°C above the temperature at which no motion of fuel was observed for five seconds on tilting the tube to a horizontal position. Three replications were made for each fuel type.

2.8.5 Flash and fire point

Flash Point measures the tendency of a fuel to form a flammability mixture with air under controlled laboratory conditions. This is the property that must be considered in assessing the overall flammability and hazard of material.

Flash Point can indicate the possible presence of highly volatile and flammable material in relatively non volatile material. It is defined as the lowest temperature at which the fuel gives off enough vapors and ignites for a moment. The Fire Point is an extension of Flash Point in a way that it reflects the condition at which vapor burns continuously for five seconds. The Fire Point is always higher than flash point by 5 to 8°C .

2.8.6 Acid value

Free fatty acid present in vegetable oil may be corrosive to some engine parts. At elevated temperatures, free fatty acid may react with many metals producing fatty acid metal salts thus increasing wear. Acid value is, therefore, an important characteristic to be measured. The acid value or number defined as the mg KOH required to neutralize the free fatty acid present in one gram of sample. However, free fatty acid content is expressed as oleic acid equivalents. The procedure described below was followed in order to determine total acidity of various fuels selected for the study:

- Dissolve 1 to 10 g of oil 50 ml of neutral solvent (neutral solvent is the mixture of 25 ml ether, 25 ml alcohol

and 1 ml of 1% phenolphthalein solution and neutralize with N/10 alkali) in a 250 ml conical flask.

- Add a few drops of phenolphthalein.
- Titrate the contents against 0.1N KOH
- Shake constantly until a pink colour which persists for 15 seconds is obtained.

During the course of study, each sample was replicated three times. The total acidity of a fuel sample was then calculated using equation given below:

$$A_v = \frac{56.1N \times T_v}{W_s}$$

Where,

A_v = Acid value, mg of KOH/g
 T_v = Titrate value, ml
 N = Normality of the potassium hydroxide solution
 W_s = Weight of the sample, g

3. Case Study

3.1 Use of edible vegetable oil as engine fuel

Worgetten(1981) carried out a series of tests using a tractor fuelled with a blend of 50 percent food grade quality rapeseed oil and diesel prepared on volume basis. The test showed a power loss after 100 hours.

After 350 hours of test, the injection nozzle was found to have carbon residues which however, were deemed suitable for continued use of the manufactures.

Singh (2009) carried out the feasibility of supplementing rice bran oil in a CI engine.

A 3.73 kW Kirloskar make, single cylinder water cooled compression ignition engine having a displacement volume 552.92 cc and compression ratio 16.5:1 was tested. The fuel types used were blends of diesel-rice bran oil in 90:1, 80:20, and 70:30 and diesel methyl ester of rice bran oil blended in 90:10, 80:20, 70:30, 60:40, 50:50 ratio. The characteristic fuel properties of all the above fuel blends were reported to be comparable with diesel fuel.

It was observed that there was an increase in the ash and carbon residue content in the blend with increase in concentration of rice bran oil in the fuel blend. All fuel types found to be stable and homogeneous at normal room temperature. All the fuel types showed similar power producing capabilities at rated load. The fuel consumption of the engine was found to be lower on all the fuel blends compared to diesel at rated load. The brake thermal efficiency of the engine on diesel-methyl ester rice bran oil was comparable with diesel. The emission of CO, HC and NOx from the engine on above fuel blends was within the limits. However, the exhaust gas temperature of the engine on blends of rice bran oil and diesel and methyl ester of rice bran oil and diesel was reported to be lower than that observed on diesel at rated load condition.

3.2 Use of non-edible vegetable oils as engine fuel

Rao et al. (1991) used karanja oil, soybean oil, sunflower oil, neem oil and their methyl ester to determine the diesel engine performance of a kirlosker make model-AV1, single cylinder compression ignition engine. The ignition delay of 1 and 2° was observed on all the vegetable oils the highest ignition delay occurred with neem oil. The ignition delay was reported to be shorter for the methyl esters than that of raw vegetable oils. The brake thermal efficiency of the engine was reported to be less on vegetable oils as well as on their methyl esters.

3.3 Use of Neem oil as CI Engine Fuel

Ragitet al.(2010) conducted experiments on standardization of transesterification process parameters for the production of methyl ester of filtered neem oil and fuel characterization for engine performance. The effect of process parameters such as molar ratio, preheating temperature, catalyst concentration and reaction time was studied to standardize the transesterification process for estimating the highest recovery of ester with lowest possible viscosity.

It was observed that filtered neem oil at 6:1 M ratio (methanol to oil) preheated at 55°C temperature and maintaining 60°C reaction temperature for 60 min in the presence of 2 percent KOH and then allowed to settle for 24 h in order to get lowest kinematic viscosity (2.7 cS) with ester recovery (83.36%). Different fuel properties of the neem methyl ester and neem oil were also measured.

4. Result and Discussion

4.1 Relative density and API gravity

The relative density and API gravity of diesel used in the experiments were found to be 0.812 and 34.65 respectively. The relative density of the neem oil used in the experiments was observed to be 0.956, which is 10.87 percent higher than that of diesel. After Transesterification relative density was 0.888.

The result also indicate that the two step esterification of raw neem oil resulted in reduced relative density of the ester and was able to bring the relative density of ester closer to that of diesel.

4.2 Kinematic viscosity

The kinematic viscosity of diesel was found to be 3.1 cS. The kinematic viscosity of diesel at 35°C may range between 2 to 7.5 cS (IS: 1460-1974).

The neem oil had the kinematic viscosity of 35cS at 35°C. NOME was found to have kinematic viscosity of 6.11 cS. The results indicate that the neem oil had the kinematic viscosity 13.14 times higher than that of diesel.

The kinematic viscosity of diesel as reported by Singh (2009), and Kundu (2010) is 3.41, 2.94, 2.69 and 3.12 respectively. Hence the observed kinematic viscosity of neem oil and its esters are in accordance with the results reported by the past researchers.

4.3 Gross heat of combustion

The gross heat of combustion of diesel was found to be 43.1 MJ/kg. The gross heat of combustion of neem oil was

observed as 44.32 MJ/kg which is higher than that of diesel.

The gross heat of combustion of NOME was observed as 37.30 MJ/kg

4.4 Flash and fire point

The flash and fire point of diesel used in the experiment was observed as 54 °C and 60 °C respectively. The flash and fire point of neem oil was found to be 104 °C and 113 °C respectively. NOME having the flash point of 140 °C and fire point of 147 °C respectively.

The observed results are in line with the results reported by Ragitet al. (2010) who reported flash point and fire point of neem oil 100 and 109 °C respectively.

4.5 Cloud point and pour point

The cloud point and pour point of diesel used in the experiment was observed as -13 and -17 °C respectively. NOME having the cloud point of 10 °C and pour point of 3 °C respectively.

The observed results are in line with the results reported by Ragitet al. (2010) who reported cloud point and pour point of neem oil methyl ester 9 and 2 °C respectively. They also reported the cloud point and pour point of diesel as -12 and -16 °C respectively.

5. CONCLUSION

A lot of research is being carried out throughout the world to obtain renewable source of energy to supplement conventional fossil fuels.

The edible and non edible oils are being tried to either supplement or to replace diesel as fuel in CI engine. India is one of the largest importers of edible oil and, therefore, emphasis is being laid to explore the possibility of using non-edible oils or their esters to be used in diesel engine alone or blended with diesel. The biodiesel programme of India is centered around non-edible vegetable oil like

jatropha. For feedstock diversification and utilization of currently available local resources like neem, karanja, mahua, saletc. should be scientifically investigated for efficient biodiesel production. Keeping this background in consideration, production of neem oil methyl ester (NOME) and its utilization as a potential alternative fuel for CI engine has been investigated.

The characteristic fuel properties such as relative density, kinematic viscosity, gross heat of combustion, cloud and pour point, flash and fire point of diesel, raw neem oil, its methyl ester (NOME) with diesel were compared.

On the basis of the results obtained from the whole experiment the following conclusion can be drawn:

- 1) Two step esterification is used to make the neem oil biodiesel because FFA (free fatty acid) content in neem oil is very high.
- 2) The recovery of neem oil methyl ester of lowest viscosity(6.11 cst) with approx 80 percent recovery was possible at following prameteric conditions:

First step esterification:

- Catalyst (H_2SO_4) concentration
5 % (w/w_{oil})
- Reaction temperature
45°C
- Ethanol to oil molar ratio
8:1
- Reaction time
60 min
- Settling time
24 h

Second step esterification:

- Catalyst (KOH) concentration
1 % (w/w_{oil})
- Reaction temperature
60°C
- Ethanol to oil molar ratio
8:1

- Reaction time
90 min
- Settling time
36 h

In the first step FFA (free fatty acid) of neem oil was decreased from 20 to 4.2 %. Further reduction takes place during the second step.

- 3) The relative density of raw neem oil used in the experiment was 10.87 % higher than the diesel and NOME had the relative density 6.57 % higher than diesel.
- 4) The kinematic viscosity of raw neem oil used to make neem oil methyl ester (NOME) was about 17 times higher than the diesel and NOME was about 3 times higher than the diesel.
- 5) The gross heat of combustion of raw neem oil is found to be 2.75 % higher than the diesel but NOME had the gross heat of combustion 13.45 % lesser than the diesel.

The above discussion indicate thatneem oil ethyl ester (NOME) may be recommended as CI engine fuel due to its properties which are comparable with diesel.Further, the engine performance characteristics and emissions ofneem oil ethyl ester(NOME) may be investigated.

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