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Standardization of Process Parameters for Neem Oil & Determination of Properties for Using as a Fuel

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ABSTRACT: Studies on the exploration of alternate fuels obtained from renewable sources of energy to supplement conventional fossil fuels are being carried out throughout the world. The edible and non edible oils are being tried to either supplement or to replace diesel as fuel in CI engines. India is the net importer of edible oils and, therefore, emphasis is being laid to explore the possibility of using non-edible oils or their esters to be used in diesel engines alone or blended with diesel.

A study was, therefore, undertaken to standardize ethyl esterification process parameters of raw Neem oil, comparing characteristic fuel properties of different blends of Neem oil ester with ethanol and use of the blends as a constant speed CI engine fuel. Raw Neem oil was esterified with methyl alcohol to obtain Neem methyl ester having lowest possible kinematic viscosity. The process parameters such as alcohol, catalyst concentration and reaction temperature were standardized to obtain higher recovery of esters. The characteristic fuel properties such as kinematic viscosity, relative density, gross heat of combustion, cloud and pour point, flash and fire point, carbon and ash content and total acidity of diesel, raw Neem oil, its methyl and ethyl ester and blends methyl ester with ethanol were compared.

The recovery of Neem methyl ester of lowest kinematic viscosity (6.65 cS) with 84 percent recovery was possible at the following standardized parametric conditions: Main Transesterification Process: Molar Ratio (6:1),Type of Catalyst (KOH) ,Concentration of Catalyst (2%), Reaction Temperature (65^0c),Reaction Time (60min), Setting time (24h). The relative density of the Neem oil used in the experiment was 6.07 percent higher than that of diesel, whereas the Neem methyl ester of 6.65 cS viscosity has the relative density 2.57 percent higher than the diesel. The cloud and pour point of diesel used in the experiment were 4.2^0C and 1.5^0C respectively and raw Neem oil had the cloud and pour point of 19^0C and 3^0C respectively. The cloud point was observed 4,18,20,21,22 and 23^0C and the pour point as 6.0,7.0,8.0,9.0,10.0 and 5.0 for NME90E10, NME80E20,NME70E30,NME60E400,NME50E50 and NME100 respectively. The flash and fire point of diesel used in the experiment were observed as 54.3 and 59.4^0C respectively where as for Neem oil these values were 152 and 159^0 respectively. The blends of Neem methyl ester-ethanol were blends found to have lower flash and fire point than diesel.

Key words- Neem Oil, Biofuels, Diesel, Flash Point, Methyl Ester

INTRODUCTION

The tremendous increase in number of automobiles in recent years have resulted in greater demand of petroleum products.The depletion of crude oil reserves are estimated for few decades, therefore, effort are on way to research now alternatives to diesel.**Ganguli, S. (2002) [1]**There are different kinds of vegetable oils and biodiesel have been tested in diesel engines its reducing characteristic for green house gas emissions. Its help on reducing a country's reliance on crude oil imports its supportive characteristic on agriculture by providing a new market for domestic crops, its effective lubricating property that eliminates the need of any lubricate additive and its wide acceptance by vehicle manufacturers can be listed as the most important advantages of biodiesel fuel. There are more than 350 oil bearing crops identified, among which only Jatropha, ongamia, sunflower, Soyabean, cottonseed, rapeseed, palm oil and peanut oil are considered as potential alternative fuels for diesel engines. The present study aims to investigate the use of neem oil blend with ethanol as an alternate fuel for compression ignition engine. Ethanol has some detergent properties that reduce buildup of carbon deposits on injectors due to which engines run smoothly and fuel injection systems remain clean for better performance**.** Use of vegetable oil and ethanol blend gave satisfactory results (Goering *et al.*, 1983). But ester of vegetable oil and ethanol has never been used before as fuel in CI engines. The concept of employing alcohol, especially ethanol with ester of vegetable oils as a fuel in engines is totally new and revolutionary. Since there is no use of diesel, there is 100 per cent replacement of diesel. In view of the above, a study was carried out with the objectives Standardization of methyl esterification process parameters for neem oil by single stage

Acid-Base catalyst process & Determination of characteristic fuel properties of different blends of methyl ester of neem oil with ethanol.

MATERIAL & METHOD

The methodology used for standardization of ethyl esterification process parameters for Neem oil, preparation of fuel blends,characteristic fuel properties. The experiments were conducted in the Bio Energy Technology Laboratory, Department of Farm Machinery and Power Engineering.

Selection of Fuel Constituents

The experiments were carried out using high speed diesel as reference fuel and methyl esters of neem oil and their blends with ethanol in various proportions used as the engine fuel.

Neem oil

Neem oil used in the present investigation was taken from the local market of pantnagar.

Reference fuel

High speed diesel marketed by Indian Oil Corporation in accordance with IS: 1460-1974 was taken as reference fuel for comparison.

Ethanol

Anhydrous ethanol was used as one of the constituent of blended fuel for the experiment. The experiment was conducted using Changsu Yangyuan Chemical, China make anhydrous ethanol procured from the local market. Ethanol, chemically named ethyl alcohol (CH_3CH_2OH) is a colourless liquid with a sweet alcohol odour.

Neem methyl ester

Neem methyl ester was used as another constituent of the blended fuel. Better self ignition characteristics, compatibility with fuel injection system of existing CI engines. The sample which gave the highest yield and had its viscosity in the permissible range was used for the main transesterification process. The main transesterification process was carried out with methanol to oil ratio of 6:1 and 2% KOH concentration as an alkaline catalyst. The reaction was carried out at 65ºC for an hour which gave a methyl ester yield of 85%(v/v).

Esterification Process Standardization of methyl esterification process parameters and preparation of Neem ethyl ester

Fukuda, H (2001) [2]Esterification process is defined as the chemically reacting triglycerides such as one of the vegetable oil with an alcohol in presence of an alkaline or acidic catalyst to produce glycerol and fatty acids ester. Barnwal (2005) [3] In this process the ester is produced when vegetable oil combines with a simple alcohol in presence of a catalyst. The fatty acids of vegetable oil exchange places with the (OH) groups of the alcohol producing glycerol and methyl, ethyl or butyl fatty acids ester depending on the type of alcohol used. The four distinct stages in the preparation of an ester are namely:

- Heating oil at a desired temperature.
- Stirring and heating of alcohol-oil mixture with an alkaline or acidic catalyst.
- Separation of glycerol and washing of ester with water.
- Evaporating traces of water from ester recovered.

The following parameters affect the level of ester recovery:

- Molar ratio of vegetable oil- alcohol mixture
- Preheating time
- Preheating temperature
- Reaction time
- Reaction temperature
- Type of catalyst
- Concentration of catalyst
- Degree of proof of alcohol used
- Settling time
- Method of removal of traces of water from washed ester either by heating or absorbing using a suitable chemical.

The main transesterification reaction of raw neem oil was carried out as per the steps described in Fig. 3.1. Since the recovery of ester from esterification process is affected by the parameters described above, the process was carried out as per steps described in Fig.

3.1. The effect of process parameters shown in Table 3.1 was studied to standardize the esterification process for estimating recovery of ester as well as recovering ester of lowest possible viscosity.

In order to standardize the process parameters, three levels of molar ratios (6:1,8:1 and 10:1), four levels of catalyst (KOH) concentration (1.0%, 1.5%, 2.0% and 2.5%) and two levels of reaction temperature (60^0C and 65^0C) was set. The esterification was done at 6:1, 8:1 and 10:1 molar ratios in order to obtain maximum recovery of ester with lowest possible kinematic viscosity by preliminary experiments. Esterification was carried out at selected molar ratio at different levels of catalyst concentration for 60 minutes at different reaction temperature in shaking water bath and then allowed to settle for 24 h for separation of lighter ester layer at the top and heavy glycerol layer at the bottom. Total 24 ester samples were prepared to study the effect of the catalyst concentration, preheating time and reaction temperature on ester recovery and subsequent measure of their kinematic viscosity.

Determination of Characteristic Fuel Properties

Relative density and API gravity

The relative density of the selected fuels at 15^0C was determined as per **IS: 1448 [P: 32]: 1992**.

Equation 3.1 was used to calculate the relative density.

$$\text{Relative density} = \frac{\text{Density of the fuel at } 15^0\text{C}}{\text{Density of the water at } 15^0\text{C}} \quad \text{..... (3.1)}$$

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 ethanol.

$$\text{API Gravity} = \frac{141.5}{\text{Relative density at } 15^0\text{C}} - 131.5 \quad \text{..... (3.2)}$$

Kinematic viscosity

A Redwood Viscometer No.1 of WISWO make as shown in 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 (50ml) through specified orifice made in an agate piece as per **IS : 1448 [P : 25] 1976** Kinematic viscosity in centistokes was then calculated from time units by using the relationships given by **Guthrie (1960)**.

$$\nu_k = 0.26\,t - \frac{179}{t} \quad \text{..... (3.3)}$$

When 34 < t < 100 and

$$\nu_k = 0.24\,t - \frac{50}{t} \quad \text{..... (3.4)} \quad \text{When } t > 100$$

where, ν_k = Kinematic viscosity in centistokes, cS

t = Time for flow of 50 ml sample, s

Gross heat of combustion

The heat of combustion or calorific value of a fuel 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. The gross heat of combustion of the fuel samples was calculated using the equation given below:

$$H_c = \frac{W_C \times \Delta T}{M_S} \quad \text{..... (3.5)}$$

where,

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

W_c = Water equivalent of the calorimeter, Cal / ^{0}C

ΔT = Rise in temperature, ^{0}C

M_s = Mass of sample burnt, g

Cloud and pour points

The Cloud and Pour point is 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 and Pour point of fuel samples were determined as per **IS: 1448 [P: 10]: 1970** using the Cloud and Pour point apparatus.

Three replications were made for each fuel type.

Flash and fire point

Flash point measures the tendency of the sample to form a flammability mixture with air under controlled laboratory conditions. The flash and fire point of the fuel samples was determined as per **IS: 1448 [P: 32]: 1992**.

RESULT AND DISCUSSION

Studies were conducted for standardizing transesterification process parameters for Neem oil, determination of compatible fuel properties of the oil, its methyl ester and their blends with ethanol. The fuel properties such as kinematic viscosity, relative density, gross heat of combustion, cloud and pour point, flash and fire point, of Neem oil, its methyl ester as well as their blends with ethanol were compared.

Standardization of Esterification Process Parameters

The effect of selected level of parameters as mentioned in table 3.1 to standardize the methyl esterification process for Neem oil & Table 3.2 gives Esterification Process Parameters Selected to Produce Neem Methyl Ester of 6.65 cS Kinematic Viscosity. It is, therefore, seen that highest recovery of 84 percent of methyl ester was obtained at 6:1 molar ratio when the raw Neem oil was reacted with ethanol at 65^{0}C reaction temperature for 60 minute in presence of 2.00 percent KOH and then allowed to settle for 24h. Based on the observation of percent recovery of methyl ester from esterification of raw Neem oil at 6:1 molar ration may be reacted with ethanol at 65^{0}C reaction temperature for 60 minute in presence of 2.00 percent KOH and then allowed to settle for 24h due to availability of more polarity to dissolve KOH concentration.

Effect of process parameters on kinematic viscosity of recovered esters

Table 4.1 show the kinematic viscosity of Neem methyl esters obtained by esterification of raw Neem oil at the selected process condition. Anjana Srivastava(2007) [6] It is evident from the table that the methyl esters obtained from the estrerificatin of raw Neem oil at different process conditions ranged between 6.65 to 11.99 cs. It is evident from the table that kinematic viscosity was found at different selected process parameters which varied between 9.12 to 13.02 and 10.15 to 1`3.98 cS for the molar ratio of 6:1 and 8:1 respectively. Based on the observations on the recovery and kinematic viscosity, it may be concluded that raw Neem oil at 6:1 molar ratio may be reacted with ethanol at 65^{0}C reaction temperature for 60 minute in presence of 2 percent KHO and then allowed to settle for 24hin order to get maximum ester recovery with lowest possible kinematic viscosity.

Fuel properties of Neem oil, methyl esters of Neem oil and their blends with ethanol

The characteristic fuel properties such as kinematic viscosity, relative density, gross heat of combustion, cloud and pour point, flash and fire point, were measured for different fuels to assess their compatibility with diesel fuel.

Relative density and API gravity

The relative density at 15^0c and API gravity of diesel, raw Neem oil and different blends are shown in Table 4.2 the relative density and API gravity of diesel used in the experiments were found to be 0.839 and 37.15 respectively. The relative density of NME90E10, N30, NME60E400, NME50E50 and NME 100 were found to be 0.85, 084, 083, 082, 0.82 and 0.86. The results obtained during the experiments indicate that the relative density of all the ester blends was almost closer to that of diesel.

The API gravity of NME90E10, NME80E20, NME70E30, NME60E400, NME50E50 and NME 100were found to be 34.64, 36.95, 38.98, 41.06, 41.06 and 32.71.

Kinematic viscosity

Table 4.3 shows the kinematic viscosity of diesel, raw Neem oil and different blends at 38^0C. The kinematic viscosity if diesel was found to be 3.21 cS. The kinematic viscosity of diesel at 38^0C may range between 2.0 to 7.5 cS. (IS: 1460-1974). The Neem oil had the kinematic viscosity of 48.32 cS at 38^0C. The kinematic viscosity of NME 100, NME0D10, NME80D20, NME70D30, NME60D40 and NME50D50 were found to have kinematic viscosity of 6.47, 4.33, 3.46, 2.82, 2.38 and 1.82cS respectively.

The kinematic viscosity od diesel as reported by Sandun Fernando **(2007) [4]**is 3.41, 3.24 and cS respectively. On the basis of above it was seen that the observed kinemetic viscosity of selected fuels are in line with the findings reported earlier.

Gross heat of combustion

The gross heat of combustion of diesel, Neem oil and the blends of Neem ester with ester with ethanol mixed in various proportions are shown in Table 4.4. The table indicates that gross heat of combustion of diesel was found to be 47.80MJ/Kg.The gross heat of combustion of Neem oil was observed as 32.02 MJ/kg, which is 33.0 percent less than that of diesel. The gross heat of combustion was observed as 36.34,35,90,34.56,33.40,32.89 and 37.12 for NME90E10, NME80E20, NME70E30,NME60E400,NME50E50 and NME 100 respectively.The gross heat of combustion of diesel reported by Sandun Fernando (2007) [4]was 49.05 ,47.8 and 48.46MJ/Kg respectively. On the basis of above it was seen that the observed gross heat of combustion of selected fuels are in line with the findings reported earlier.

Cloud and pour point

The could and pour point of diesel, Neem oil and Neem ester blends with ethanol are shown in Table 4.5. The table indicates that the cloud and pour point of diesel was 2.6^0C and -2^0C respectively. The Neem oil had the cloud and pour pint as 19 and 3^0C respectively. The cloud point was observed as 4,18,20,21,22 and 23^0C and pour point as 6.0,7.0,8.0,9.0,10.0 and 5.0 for NME90E10, NME80E20, NME70E30 NME60E400,NME50E50 and NME100 respectively.

Flash and fire point

The flash and fire point of diesel, Neem oil and Neem ester blends with ethanol are shown In Table 4.6. The flash and fire point of diesel was 54.3^0C and 59.4^0C respectively. The flash and fire point of Neem oil wa found to be 152^0C and 159^0C respectively. The table also reveals that NME90E10, NME80E20, NME70E30, NME60E400, NME50E50 and NME 100were having the flash point of 39.0,38.0,36.0, 35.0,33.0 and 58^0C and fire point of 45.0,43.0, 40.0,40.0,39.0,37.0 and 66.0^0C respectively. The flash and fire point of methyl ester of Neem oil was having value as compared to diesel. The blends of Neem methyl ester-ethanol were found to have lower flash and fire point than diesel.

The observed results on flash and fire point are in accordance with the findings of flash point of Neem oil as 152^0C. The reduced flash and fire point of Neem methyl esterethanol blends reflects that greater care may be required in handling these fuels during high ambient temperature conditions. On the basis of above it was seen that the observed flash and fire point of selected fuels are in line with the findings reported earlier.

CARBON RESIDUE

The observed carbon residue content of diesel, Neem oil and Neem ester blends with ethanol are shown in Table 4.7. The carbon residue content in diesel was found as 0.16 percent. The maximum recommended carbon residue level in diesel fuel as per IS: 1460-1974 is 0.2 percent. The observed carbon residue content in diesel falls is in line with the findings of Nurun nabi (2007) [5] who reported it as 0.1 percent. The Neem oil was found to have the carbon residue content of 3.561 perent. The carbon residue content of 0.822, 0.789, 0.793,0689, 0.689, 0.630 and 0.933 percent was found in NME90E10 NME80E20, NME70E30,NME60E400,NME50E50 and NME100 were respectively.

SUMMARY AND CONCLUSION

On the basis of the results obtained from the whole experiment the following conclusions were drawn:

(i) The recovery of Neem methyl ester of lowest kinematic viscosity (6.65 cS) with 84 percent recovery was possible at the following standardized parametric conditions:

Main Transesterification Process:

1.	Molar Ratio	6:1
2.	Type of Catalyst	KOH
3.	Concentration of Catalyst	2%
4.	Reaction Temperature	65^0c
5.	Reaction Time	60min
6.	Setting time	24h

The recovery of Neem methyl ester was 84 percent with kinematic viscosity of 6.65cS.

(ii) The relative density of the Neem oil used in the experiment was 6.07 percent higher than that of diesel, whereas the Neem methyl ester of 6.65 cS viscosity has the relative density 2.57 percent higher than the diesel. The relative density of Neem methyl ester-ethanol blends decreased with increase in level of ethanol in the blend

(iii) The cloud and pour point of diesel used in the experiment were 4.2^0C and 1.5^0C respectively and raw Neem oil had the cloud and pour point of 19^0C and 3^0C respectively. The cloud point was observed 4,18,20,21,22 and 23^0C and the pour point as 6.0,7.0,8.0,9.0,10.0 and 5.0 for NME90E10, NME80E20,NME70E30,NME60E400,NME50E50 and NME100 respectively.

(iv) The flash and fire point of diesel used in the experiment were observed as 54.3 and 59.4^0C respectively where as for Neem oil these values were 152 and 159^0 respectively. The blends of Neem methyl ester-ethanol were blends found to have lower flash and fire point than diesel.

(v) The carbon residue content of diesel (0.16 percent) was observed to be within the permissible level specified by the Bureau of Indian Standards but the raw Neem oil and very high carbon residue content (3.561persent). however, esterification of raw Neem oil reduced the carbon residue content to a great extent.

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Table 3.1 Process Parameters Selected for Standardization of Esterification Process

Sl. No.	Name of Parameter	Levels selected
1.	Molar ratio	6:1, 8:1 and 10:1
2.	Catalyst concentration (%)	1.0,1.5,2.0 and 2.5
3.	Reaction Temperature, (^{0}C)	60and 65^{0}C
4.	Reaction Time, (hr)	1hr
5.	Catalyst	KHO
6.	Settling Time, (hr)	24hr

7.

Table 3.2 Esterification Process Parameters Selected to Produce Neem Methyl Ester of 6.65 cS Kinematic Viscosity

Sl. No.	Name of Parameter	Levels selected
1.	Molar ratio	6:1,
2.	Type of Catalyst	KHO
3.	Concentration of Catalyst	2%
4.	Reaction Temperature, (^{0}C)	65^{0}C
5.	Reaction Time	60min

6.	Settling Time	24hr

Table 4.1 Recovery and Kinematic Viscosity of Neem Methyl Ester under Different Estertification Process Conditions at constant 1h reaction time and 24th settling time.

Sl. No.	Molar ratio	Catalyst Concentration (%)	Reaction temperature (°C)	Ester recovery (%)	Kinematic viscosity (cS)
1.	6:1	1.0	60	Ester not found	-
2.	8:1	1.0	60	Ester not found	-
3.	10:1	1.0	60	Ester not found	-
4.	6:1	1.5	60	62	11.04
5.	8:1	1.5	60	61	11.67
6.	10:1	1.5	60	49	12.30
7.	6:1	2.0	60	78	7.37
8.	8:1	2.0	60	59	7.72
9.	10:1	2.0	60	64	8.06
10	6:1	2.5	60	70	9.42
11.	8:1	2.5	60	68	10.07
12.	10:1	2.5	60	70	10.70
13.	6:1	1:0	65	Ester not found	-
14.	8:1	1:0	65	Ester not found	-
15.	10:1	1:0	65	Ester not found	-
16.	6:1	1:5	65	64	10.72
17.	8:1	1:5	65	63	11.36
18.	10.1	1:5	65	59	11.99
19.	6:1	2.0	65	84	6.65
20.	8:1	2.0	65	73	7.01
21.	10:1	2.0	65	74	7.37
22.	6:1	2.5	65	76	8.75
23.	8:1	2.5	65	76	9.08
24.	10:1	2.5	65	71	9.75