SYNTHESIS OF BIODIESEL FROM CRUDE NEEM OIL IN A BATCH REACTOR

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ABSTRACT

Biodiesel production from renewable sources is widely considered to be one of the most sustainable alternatives to petroleum sourced fuels and a viable means for environmental and economic sustainability. Vegetable oils are most widely used for the production of Biodiesel now-a-days .But these cannot be used directly for the production of biodiesel because they have high viscosity, high flame point and high density. In the present study Neem oil is used to convert it into biodiesel because Neem seeds contain 30-40% of the oil. Neem oil is converted to biodiesel by a two-step process. One is by Acid pretreatment and second is base catalyzed Trans esterification reaction to produce biodiesel of various molar ratios and their properties are characterized.

Keywords: *Biodiesel, Tranesterfication, Free fatty acid content, acid pretreatment, Neem Oil.*

1. INTRODUCTION

Sukumaran and Singh reported that the amount of oil removed in a pressing operation was influenced by applied pressure and pressing time. The pressure required to expel the oil is influenced by pre-treatments used.[1]

Chauhan *et al.* Conducted experiments to standardize the jatbopha oil by methyl esterification process parameters. It was observed that raw jatropha oil at 60°C reaction temperature reacted at 6:1 oil to methanol molar ratio. For 1 hour yielded maximum ester recovery.[2]

Production of biodiesel was carried out in 250 litres per day capacity of pilot biodiesel plant that was designed by Tamil Nadu Agricultural University. It was reported by Ramesh and Sampathrajan, that the feed temperature affects the extraction process. The influence of temperature on oil extraction was studied and the per cent oil extracted at different temperatures. It was observed that on an average 0.887 litre of biodiesel and 0.268 kg of glycerol were obtained per litre of raw neem oil, resulting 88.7% biodiesel recovery. [3]

Mustafa Balat and Havva Balat described that the problems with substituting triglycerides for diesel fuels were mostly associated with their high viscosities, low volatilities and polyunsaturated character .[4]

Knothe discussed that the fuel properties of biodiesel are strongly influenced by the properties of the individual fatty esters in biodiesel.[5]

M. Canakci and J. Van Gerpen investigated the use of low–cost, high FFA feedstock to produce fuel–quality biodiesel. It was determined that feedstock with high FFAs could not be transesterified with the traditional alkaline catalysts that have been used with good success for vegetable oils.[6]

M.Mathiyazhagan et al. researched on the non-edible oils as feed stocks for biodiesel production to reduce the cost of biodiesel.[7]
Dhar et al. focused on the development of environmental friendly alternate source of energy, to compensate growing demand of fuel for various purposes. They produced biodiesel with the help of neem oil. The biodiesel yield and quality depends upon the moisture content and the free fatty acid content (FFA).[8]
Ramning et al. examined the impact of various parameters (oil to alcohol molar ratio, reaction time, acid concentration and base catalysts) during the preparation of neem oil methyl ester. They employed oscillatory baffled reactor 1-2% H_2SO_4. The experimentally determined optimum conditions for the production of neem oil methyl ester were 1:9 oil to alcohol molar ratio, reaction time 10 to 15 minutes and temperature was set in the range of 25-300C. It was observed that the viscosity decreases with the increase of molar ratio.[9]
Sathyal and Manivannan used edible oil for the production of biodiesel with the help of methanol and in the presence of alkaline catalyst. The crude neem oil used in this study had large content of free fatty acids (FFA) i.e. 6 %, which could react with the catalyst to form soaps.[10]
Gautam et al.studied physical, chemical and thermal properties biodiesels procured from four different locally available Indian feedstock. Physical properties of biodiesels such as density, viscosity, speed of sound, bulk modulus of compressibility and surface tension are dependent on fuel temperature. Data from previous studies on temperature dependent physical properties was used to determine correlations between fuel temperature and physical properties of the biodiesel.[11]
Tuccar et al. blended citrus sinensis biodiesel with conventional diesel fuel with volumetric ratios of 5%, 10% and 20%. Fuel properties of blends and pure citrus sinensis biodiesel were found out. The performance characteristics and exhaust emissions of the engine fueled with blends were analyzed (CO emissions and NOX emissions). The overall biodiesel production process was more expensive than that of traditional fossil fuels because the raw materials cost usually covers more than 80 % of the total production costs (Haas *et al*., 2006).[12]

During the production of Biodiesel, reaction variables play an important role to get high yield.[13]A fuel whose energy is derived from biological carbon fixation is termed biofuels. Biofuels comprise fuels derived from biomass conversion, as well as solid biomass, liquid fuels and various biogases.[14]

Alkaline-catalyzed transesterifications proceed at considerably higher rates than acid catalyzed transesterifications. Due to this fact and also because alkaline catalysts are less corrosive to industrial equipment, most commercial transesterifications are conducted with alkaline catalysts.[15-16]

The present study is based on biodiesel production where an ester reacts with alcohol to form ester and alcohol. Ester is the vegetable oil (Neem oil) which consist triglyceride.[16-18]

Schuchardta *et al*. investigated the process of transesterification of vegetable oils with methanol and the main uses of the fatty acid methyl esters. The general aspects of this process and the applicability of different types of catalysts (acids, alkaline metal hydroxides, alkoxides and carbonates, enzymes and non-ionic bases, such as amines, amidines, guanidine's and triamino (imino) phosphoranes) were described.[19]

Sathya and Manivannan used edible oil for the production of biodiesel with the help of methanol in the presence of alkaline catalyst. The crude neem oil used in this study had large content of free fatty acids (FFA) i.e. 6 %, which could react with the catalyst to form soaps.[20]

Hansen et al. discussed the properties and specifications of ethanol blended with diesel fuel. The factors included blend properties such as stability, viscosity and lubricity, safety and materials compatibility. The effect of the fuel on engine performance, durability and emissions was also considered.[21]

Gautam et al. studied physical, chemical and thermal properties. Physical properties of biodiesels such as density, viscosity, speed of sound, bulk modulus of compressibility and surface tension are dependent on fuel temperature. Data from previous studies on temperature dependent physical properties was used to determine correlations between fuel temperature and physical properties of the biodiesel.[22]

Tuccar et al. blended citrus sinensis biodiesel with conventional diesel fuel with volumetric ratios of 5%, 10% and 20%. Fuel properties of blends and pure citrus sinensis biodiesel were found out and performance characteristics and exhaust emissions of the engine fueled with blends were analysed (CO emissions and NO_X emissions) .[23]

Conventional manufacturing of biodiesel was by means of the transesterification of oils with methanol in the presence of catalyst, such as alkali (KOH, NaOH) .[24]

The synthesis of Biodiesel was done by using used oil that can be reused for the production of Biodiesel. [25]

Biodiesel was proven to be one of the best available sources to fulfill the energy demand and to meet the emission standards.[26]Direct use, blending, micro emulsions, thermal cracking and transesterification are the various methods for the production of Biodiesel. In the process explained that how it is going to effect the reaction. [27]

Production of different types of Biodiesel oil was produced by different raw materials that are feasibly obtained from nature and environmental friendly.[28-29]The fossil fuels are degrading and availability of natural resources are becoming less due to the environmental disturbances. Hence, alternate fuels like production of biodiesel is very important that can obtain from available resources with less economy.[30]

2. EXPERIMENTAL

2.1. Production of Biodiesel

Two liters of crude neem oil was purchased from the local store located in the old town market Ananthapuramu, Andhra Pradesh and stored in a container. Chemicals were purchased from Sl Scientific, ananthapuramu. Demonized water was used for all the experimental analysis.

The biodiesel is produced in two ways.

1. Acid pretreatment

2. Base catalysed trans esterification

2.2. Acid Pretreatment:

The crude neem oil was measured (40g) and heated to 60^{o}C for about 10 minutes then mixed with 55.8ml of methanol of 60% w/w of oil. To the mixture 1.2% w/w of concentrated H_2SO_4 was added. The resultant mixture was then stirred on magnetic hot plate for 1h at 50^{o}c .Then it was allowed to settle for 2h by transferring it to separating funnel. The pretreated oil was separated from the methanol water phase with oil at the bottom of the separating funnel and the methanol water phase at the top as shown in **Figure1**. The oil was collected and used to carry out the next step in the process.

2.3. Base catalyzed transesterification:

The experiments were carried out in a batch wise manner in 250ml conical flask containing 40g of the acid pretreated of the oil. The pre-treated oil was heated to 60^{o}c on a magnetic hot plate. The oil to alcohol ratios was maintained at 1:4, 1:5, 1:6, and 1:7. The catalyst KOH percentage was maintained 1 wt %. A solution of KOH was dissolved in the methanol as that of the respective weight percentages.The reaction time maintained was 1h. The procedure was carried out for different runs. The oil and methanol mixture obtained was transferred to a separating funnel and allowed to settle down for the separation of the biodiesel as shown in **Figure2**.after 24h the mixture was separated in two layers. The biodiesel formed was top layer and the glycerin was obtained as bottom layer. The volume of the biodiesel collected for different ratios was measured and noted down.

3.0. Characterization of biodiesel produced from neem oil

The characterization of biodiesel was carried out by various methods

3.1 Density:

The density of the biodiesel was measured by using the specific gravity bottle of 25ml.The dry specific gravity bottle was weighed and was noted then it was filled with distilled water and the weight of the bottle with water was noted down. Then specific gravity bottle was filled with the sample and the weight was noted down and the respective densities of the samples were calculated.

3.2 Acid Value:

5g of oil was weighed and taken into the dried conical flask. Added 25 ml of absolute ethanol alcohol and 2-3 drops of phenolphthalein indicator. The solution was heated in water bath for 10 minute, then cooled for few minutes and titrated against 0.1 N KOH solution until pink color appeared as an end point. The values obtained were noted down as shown in **table5**. The acid value and free fatty acid values were calculated using the equation1 and equation2.

AV= ml of KOH x Nx56/ wt of sample-- (1)

% Free Fatty Acid (FFA) = AV x 0.503…………………….. (2)

Approximately 2 g of the oil was weighed and taken into a 250 ml conical flask. 25 ml of potassium hydroxide solution (0.5 N) was added. The solution was taken in a conical flask with a reflux condenser connected on to a heating mantle. During the period 2-3 drops of phenolphthalein indicator was added and titrated the excess potassium hydroxide with the 0.5 N hydrochloric acid.

Saponification number was calculated by using the equation3.

$$\text{Saponification number} = \frac{56.1*(B-S)*N}{\text{Gram of sample}} \quad \ldots (3)$$

S-ml of HCL required by sample

B-ml of HCL required by the Blank

3.4. Ester Value:

The saponification Value (SV) and the acid Value (AV) was calculated and obtained by the equation4.

Ester Value (EV) = Saponification Value (SV) – Acid Value (AV) --------------- (4)

4.0. RESULTS

The variation in the volume of biodiesel collected by varying the molar ratios of oil to methanol was determined. The resultant variation in the respective acid values of different molar ratios of biodiesel and the saponification number and the ester values were determined.

4.1. Amount of the methanol and KOH required for different molar ratios of oil to methanol:

The amount of the oil and the catalyst KOH (1%) needed to carry out the transesterification reaction after the acid pretreatment is shown in **table3**.

4.2. Volume of the Biodiesel collected for different ratios

The graph obtained in **Figure3** between the ratio of oil to methanol and the volume of biodiesel is increasing with the increase in the molar ratio of the oil to methanol. Thus it can be concluded from the graph that volume of the biodiesel collected will be increasing with the increase in the molar ratio of oil to methanol.

4.3 Density variation of biodiesel collected:

The density of the biodiesel was calculated and the value of biodiesel obtained is shown in graph was plotted between the density of biodiesel and the ratio of oil to methanol volume. From the **figure4** obtained it can be inferred that the density will be decreasing slightly as the ratio of the oil to methanol was increasing and this shows that the density of biodiesel decreases which is desired to get biodiesel of required quality.

4.4. Acid value variation:

The graph obtained for the mg of KOH required to neutralise the free fatty acids and the ratio of oil to methanol was shown in **Figure5**and hence it can be inferred that the acid value decreases with increase in ratio of oil to methanol. This implies that the free fatty acid content which is undesirable in the biodiesel is decreased with the increased use of methanol.

4.5. Saponification value:

The values of the saponification number obtained for different ratios are shown in **table6**.The graph obtained by plotting the saponification number and their respective percentages are shown in **Figure6**.The ratio of the oil to methanol and the saponification number variation were shown in the graph. There is a decrease in the saponification value which shows that the ester content and the free fatty acid content will be low in value. Thus the low acid value and the fatty acid content reflect its efficiency.

4.6. Ester value:

The ester value is the amount of the methyl esters present in the biodiesel produced. The ester value was calculated and the ester values of different ratios of biodiesel obtained is tabulated in **table 7.**The graph obtained for the ester value and the different ratios of oil to methanol is shown in **Figure7**and defines that the ester value decreases with the increase in the ratio of oil to methanol .

4.7. Comparative graph for acid value and free fatty acid content

The values for the comparison between the acid value and the free fatty acid content tabulated in **table8**.The graph obtained for the free fatty acids and the acid values shown in **Figure8**.The free fatty acid value and the acid values decrease with the values of acid values of different ratios of oil to methanol. The decrease in the free fatty acid content was desirable for a good biodiesel.

4.7. Comparison between Ester value and Glycerin percentage:

The glycerin percentage present in the biodiesel produced is calculated. The glycerin percentage and the ester value for different ratios are tabulated in the **Table9**.The graph obtained by plotting the values in order obtain a comparison between the glycerin percentage and ester value shown in **Figure9.**By the study of **Figure9** obtained, the glycerine percentage and the ester value decreases with the increase in the ratio of oil to methanol. This was the desired pattern of the biodiesel low glycerin percent will yield a good quality of biodiesel.

5. CONCLUSION

Biodiesel was prepared from the neem oil using transesterification process which includes a two stage process first stage is acid catalyzed stage and the second stage is base catalyzed stage.

The acid value and the saponification number are decreasing with increase in the molar ratio of oil to methanol. A good biodiesel should have low acid value and saponification number and the acid value. According to the literature is less than 0.8 according to the standards of U.S. (ASTM D6751) which was satisfied by the biodiesel from oil to methanol ratio of 1:7 which has 0.3696 acid values. The saponification number should be less than 188.5 according to U.S.(ASTM D6751) standards. This was also satisfied by the produced biodiesel with the saponification number of 182.1 for 1:7. The ester value is 181.704 and the glycerol percentage is 9.934 for the ratio of 1:7 which were also satisfactory.

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Figure1. Pretreated oil on magnetic stirrer with heating

Figure2. Oil after base catalyzed transesterification transferred to separating funnel

Figure3: Graph between volume of biodiesel collected versus ratio of the oil to methanol

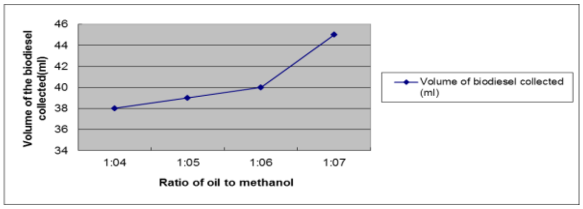


Figure4: Graph obtained between Density of biodiesel and ratios of oil to methanol

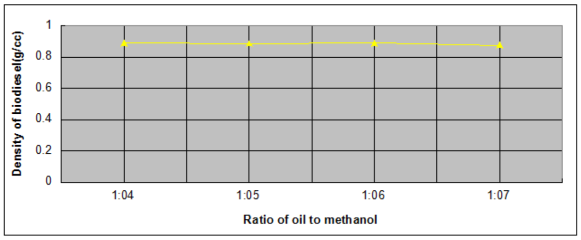


Figure5: Acid value versus ratio of oil to methanol

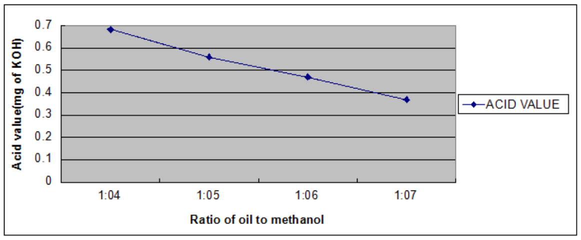


Figure6: Saponification value versus the ratio of oil to methanol

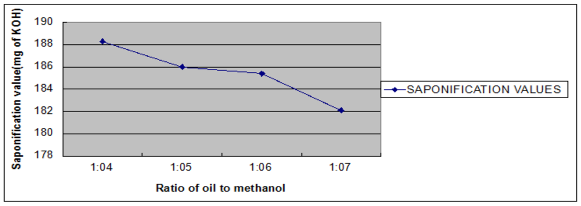


Figure7: The graph between the ester value and the ratio of oil to methanol

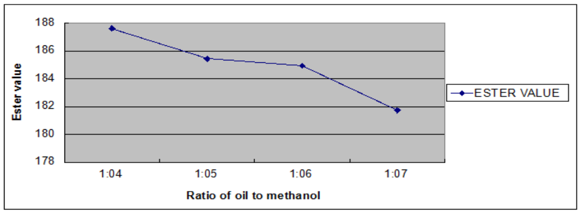


Figure8: The comparitive graph between the freefatty acid value and the ratio of oil to methanol

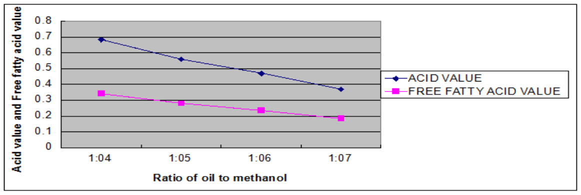


Figure9: The comparitive graph between the glycerine percentage and ester value

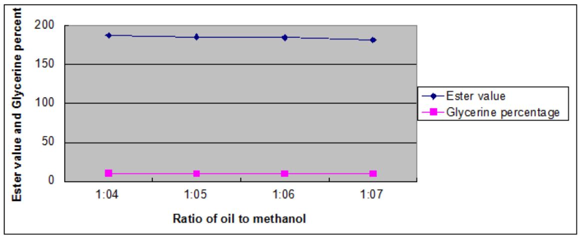
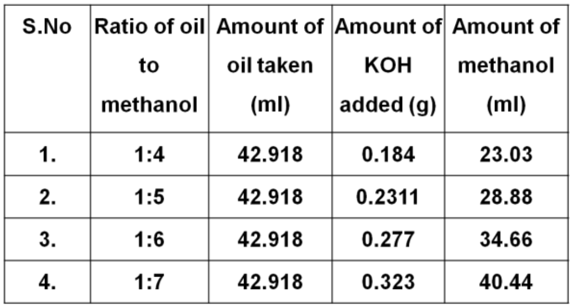


Table1. Neem oil properties

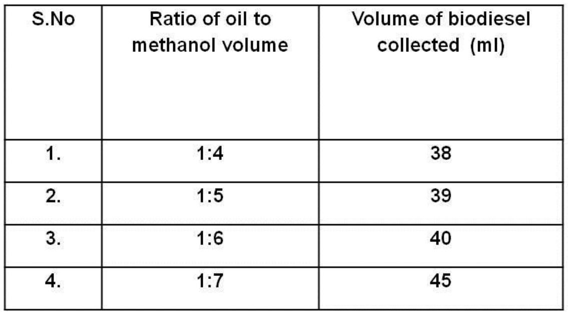
S.No	Fatty acid	Formula	Wt (%)
1	Palmitic	$C_{16}H_{32}O_2$	18.1
2	Stearic	$C_{18}H_{36}O_2$	18.1
3	Oleic	$C_{18}H_{34}O_2$	44.5
4	Linoleic	$C_{18}H_{32}O_2$	18.3
5	Linolenic	$C_{18}H_{30}O_2$	0.2
6	Arachidic	$C_{20}H_{40}O_2$	0.8

Table2.Amount of the methanol and KOH required for different molar ratios of oil to methanol



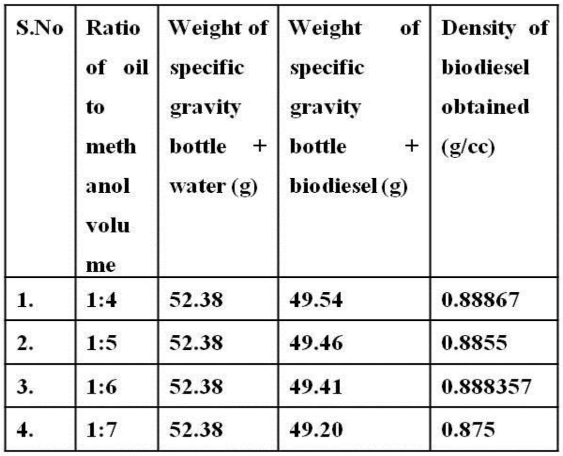
S.No	Ratio of oil to methanol	Amount of oil taken (ml)	Amount of KOH added (g)	Amount of methanol (ml)
1.	1:4	42.918	0.184	23.03
2.	1:5	42.918	0.2311	28.88
3.	1:6	42.918	0.277	34.66
4.	1:7	42.918	0.323	40.44

Table 3: Volume of the Biodiesel collected for different ratios



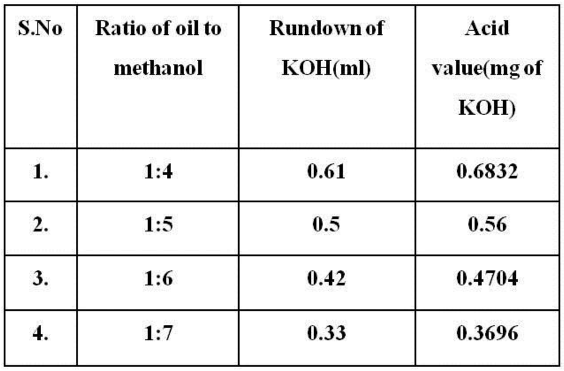
S.No	Ratio of oil to methanol volume	Volume of biodiesel collected (ml)
1.	1:4	38
2.	1:5	39
3.	1:6	40
4.	1:7	45

Table4: Density of Biodiesel obtained for different ratios of oil to methanol



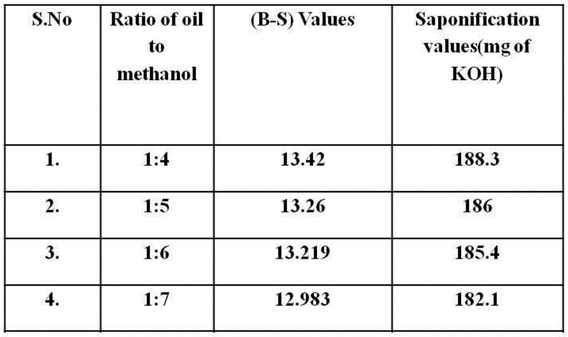
S.No	Ratio of oil to methanol volume	Weight of specific gravity bottle + water (g)	Weight of specific gravity bottle + biodiesel (g)	Density of biodiesel obtained (g/cc)
1.	1:4	52.38	49.54	0.88867
2.	1:5	52.38	49.46	0.8855
3.	1:6	52.38	49.41	0.888357
4.	1:7	52.38	49.20	0.875

Table 5: Acid values for different ratios of oil to methanol



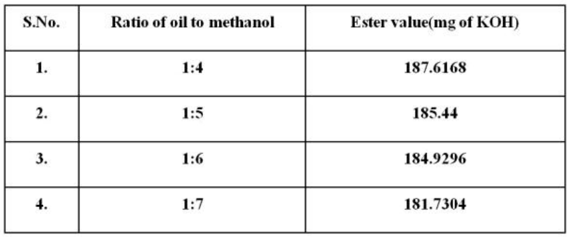
S.No	Ratio of oil to methanol	Rundown of KOH(ml)	Acid value(mg of KOH)
1.	1:4	0.61	0.6832
2.	1:5	0.5	0.56
3.	1:6	0.42	0.4704
4.	1:7	0.33	0.3696

Table 6: The saponification values of various ratios are tabulated:



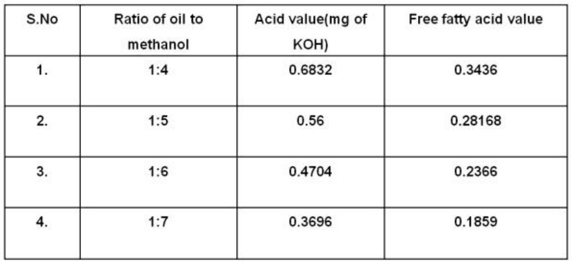
S.No	Ratio of oil to methanol	(B-S) Values	Saponification values(mg of KOH)
1.	1:4	13.42	188.3
2.	1:5	13.26	186
3.	1:6	13.219	185.4
4.	1:7	12.983	182.1

Table7: The ester values with the respective ratio of oil to methanol



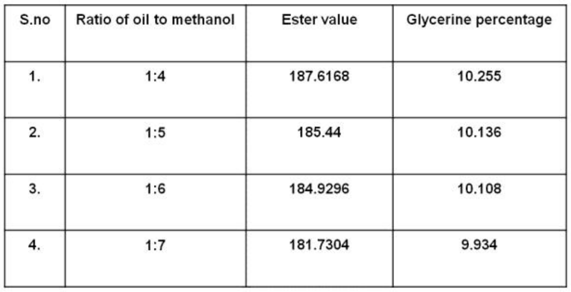
S.No.	Ratio of oil to methanol	Ester value(mg of KOH)
1.	1:4	187.6168
2.	1:5	185.44
3.	1:6	184.9296
4.	1:7	181.7304

Table8: Values of free fatty acid content and the respective acid values



S.No	Ratio of oil to methanol	Acid value(mg of KOH)	Free fatty acid value
1.	1:4	0.6832	0.3436
2.	1:5	0.56	0.28168
3.	1:6	0.4704	0.2366
4.	1:7	0.3696	0.1859

Table 9: Values of glycerin percentage and the ester value of different ratios



S.no	Ratio of oil to methanol	Ester value	Glycerine percentage
1.	1:4	187.6168	10.255
2.	1:5	185.44	10.136
3.	1:6	184.9296	10.108
4.	1:7	181.7304	9.934