*Advancement in Science and Technology Research*
Vol. 6(1), pp. 8-12, July 2024
ISSN: 2437-1319
*Full Length Research Paper*

# Calorimetric and optimization study for the production of biodiesel from fresh and waste groundnut oil using NaOH as a catalyst

**B. Magaji[1], I. B. Ibrahim[2], S. S. Adamu[2], Z. I. S. G. Adiya[3], M. S. Zubairu[1]* and M. Usman[1]**

[1]Department of Pure and Applied Chemistry, Kebbi State University of Science and Technology, Aliero, P.M.B. 1144, Birnin Kebbi, Kebbi State, Nigeria.
[2]Centre for Advanced Science Research and Analytical Services, Usmanu Danfodiyo University, Sokoto, Sokoto State, Nigeria.
[3]Department of Energy and Applied Chemisry, Usmanu Danfodiyo University, Sokoto, Sokoto State, Nigeria.

Accepted 25 July, 2024

**ABSTRACT**

In this study, an optimization study and calorimetric test for biodiesel production are being investigated. The optimum condition for biodiesel production is 5.68 g/L with 96.59% yield. The WVO biodiesel produced at this condition gave a yield of 98.86%. Methanol gave a yield of 96.59% while ethanol did not give a visible separation; there was a colour change during the reaction but did not lead to a visible separation, it solidified into a gel-like solid mass. As the percent of ethanol increases in the blend from 20, 50, and then to 80, the yield decreases from 97.05 to 86.36% and then to no visible separation at high percent ethanol. Based on the results of the calorimetric test, the amount of energy released by biodiesel is greater than that released by conventional diesel and the three blends. Hence, it can be seen that it has a much greater energy density than diesel fuel. Glycerol was seen to be soluble in water while biodiesel was insoluble. The insolubility of biodiesel in water allows for proper washing of biodiesel with warm or hot water where soap, excess catalyst and alcohol are all removed from the biodiesel into the aqueous layer.

**Keywords:** Biodiesel, calorimetry, methanol, ethanol.

*Corresponding author. E-mail: mszubair2015@gmail.com.

## INTRODUCTION

Biodiesel, the most promising alternative diesel fuel, has received considerable attention in recent years due to its following merits: biodegradable, renewable, non-toxic, less emission of gaseous and particulate pollutants with higher cetane number than normal diesel. In addition, it meets the currently increasing demands of world energy that, to a large degree, is dependent on petroleum-based fuel resources, which will be depleted in the foreseeable future if the present pattern of energy consumption continues (Alcantara et al., 2000).

Biodiesel is derived from vegetable oils or animal fats through transesterification. Transesterification is also called alcoholysis, which uses alcohols in the presence of a catalyst (e.g., base, acid or enzyme depending on the free fatty acid content of the raw material) that chemically breaks the molecules of triglycerides into alkyl esters as biodiesel fuels and glycerol as a by-product. The commonly used alcohols for transesterification include methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are adopted most frequently, particularly the former due to their low cost (Fukuda et al., 2001).

Commonly used feedstocks (vegetable oil) for transesterification include soybean oil, rapeseed oil, etc. In recent years, there exists active research on biodiesel production from cottonseed oil (Demirbas, 2008; Cui et al., 2007; Plentz et al., 2006; Yücesu and Ilkiliç, 2006; Karabektas et al., 2008; Köse et al., 2002), of which the conversion between 72% and 94% was obtained by enzyme-catalyzed transesterification when the refined cottonseed oil reacted with short-chain primary and secondary alcohols. The application of solid acid catalysts on cottonseed oil transesterification was investigated by He et al. (nd). The results showed that the yield of methyl ester was above 90% after 8 hours of reaction (Chen et al., 2007). In contrast, transesterifying cottonseed oil by microwave irradiation could produce a biodiesel yield in the range of 89.5 to 92.7% (Azcan and Danisman, 2007). No matter what kind of catalysts or approaches were applied, all those studies aimed to produce a high yield of biodiesel by optimized reaction conditions based on optimized parameters in terms of alcohol/oil molar ratio, catalyst concentration, reaction temperature, and time. However, nearly in all studied cases, there existed complex interactions among the variables that remarkably affected the biodiesel yield. Moreover, it seems unrealistic to optimize the process by the traditional 1-factor at-a-time approach, which is time-consuming and nearly impossible to achieve the true optimal condition. Alternatively, response surface methodology (RSM), an experimental strategy described first by Box and Wilson for seeking an optimal condition for a multivariable system, is an efficient technique for processing optimization (Kong et al., 2004). However, the traditional method of optimization still gives an idea or insight into the optimal conditions for production processes despite its shortcomings or disadvantages. Hence it can still be applied in optimization research works or studies.

The primary aim of this research work is to optimize and carry out a calorimetric study for the production of biodiesel from fresh and waste groundnut oil using sodium hydroxide catalysts.

## MATERIALS AND METHODS

### Sample collection and treatment

Two gallons of fresh groundnut oil (5 litres each) were purchased from the market in Aliero town, Kebbi State. One of the fresh 5 litre gallons was given to the fish sellers in the town near the onion market where it was used for fish frying until it turned black indicating that it is a waste vegetable oil and therefore no longer needed for its intended use. This black waste groundnut oil was considered a waste vegetable oil sample while the other unused gallon was considered a fresh groundnut oil sample. Both oil samples were heated to about 120°C for 30 to 45 min to remove moisture and then filtered to remove the non-oil components before being used for further analysis (Sharma et al., 2013).

### Determination of free fatty acid (FFA) by titration

In order to determine the percent of FFA in the oil, a process called titration is used. The vegetable oil is first mixed with isopropyl alcohol. Next, a mixture of Sodium Hydroxide (NaOH) and water is added until all of the FFA has been reacted. This is confirmed by checking the pH of the mixture. A pH of about 9 signifies all of the FFA has been reacted. One gram of NaOH was dissolved in 1 litre of distilled water (0.1%NaOH solution). A phenolphthalein solution was used to get the endpoint. In a smaller beaker, 1 ml of WCO oil is dissolved in 10 ml of isopropyl alcohol. The mixture was stirred gently until all the oil dissolved in the alcohol and the mixture turned clear. Two to three drops of phenolphthalein solution were added. Using a burette, 0.1% NaOH solution was added drop by drop to the oil alcohol phenolphthalein solution, stirring all the time, until the solution stayed pink. The number of ml of 0.1% NaOH solution gives the amount of NaOH to be used per liter of oil and FFA percentage (Sharma et al., 2013).

### Biodiesel production

For safety measures, goggles and gloves were used as personal protective equipment. A known amount of pre-treated oil is heated to about 130 to 135°F (54.44 to 57.22°C). Using a molar ratio of oil to alcohol of 1:6, about 20% of the amount of oil is chosen for the alcohol i.e. Amount of Oil × 0.20 = Required amount of Methanol. The amount of catalyst needed is determined by titration as explained in 2.2 above. The Methanol and Strong Base are mixed until fully dissolved, this forms the methoxide. The methoxide is added to the heated oil and mixed thoroughly for some time. The mixture is allowed to sit for 24 hr to settle. The by-product glycerin is drained off and excess contaminants are washed out using hot water. The biodiesel is dried by removing water using heat (Thirumarimurugan et al., 2012; Blair, 2021). The yield of biodiesel is determined according to Equation 1.

$$\text{Yield (\%)} = \frac{\text{Amount of biodiesel produced}}{\text{Amount of oil used}} \times 100 \quad (1)$$

### Characterization of biodiesel

Some of the tests conducted during the biodiesel production are explained as follows:

#### *Solubility test*

About 5 ml of distilled water is added into two separate test tubes. 1 ml of glycerol is added to one of the test tubes and 1 ml of biodiesel is added to the other test tube. Each test tube is hand shaken and observation is recorded.

### *Calorimetry test*

About 1 ml of biodiesel is measured and then added into a crucible or evaporating dish. A match stick is lit and gently placed into the crucible with the biodiesel in it. A wire guaze is placed on top of the crucible. 15 ml of distilled water is measured into a beaker with a thermometer in it and then placed on the wire guaze. The initial temperature of the water is taken and recorded. The biodiesel will burn up gradually with the lighted match stick. The time taken for the biodiesel to burn up completely is recorded. The final temperature of the water is also taken and recorded. The entire procedure is repeated for petroleum diesel, B20, B50, B80 and waste vegetable oil under ventilated conditions.

**Figure 1.** Experimental setup for biodiesel production.

**Figure 2.** Experimental setup for the calorimetry test.

The energy released by the biodiesel is calculated according to Equation 2:

$$Q_{biodiesel} = m \times C \times (T_f - T_i) \quad (2)$$

Where; m is mass of water = 15.00 g, C is the specific heat capacity of water = 4.18 $Jg^{-1}K^{-1}$, and $T_f$ and $T_i$ are the final and initial temperatures of water respectively.

Also, $Q_b/V$ and $Q_b/g$ are determined for the biodiesel where $Q_b$ is the quantity of the energy released by the biodiesel, V is the volume of biodiesel (1.00 $cm^3$), and g is obtained by multiplying density with volume i.e. 1.00 × 0.883.

## RESULTS AND DISCUSSION

In Table 1, the results of the optimization study for biodiesel yield at different grams of NaOH catalyst with methanol as alcohol are given. GO1, GO2, GO3, GO4, and GO5 stand for groundnut oil samples 1 to 5 having the mass of NaOH catalyst of 1.14 g/L, 3.41 g/L, 5.68 g/L, 7.95 g/L, and 10.23 g/L respectively. The optimum condition from the table is 5.68 g/L since it had a high-quality combustion of biodiesel with 96.59% yield. The WVO biodiesel is produced considering the optimum 5.68 g/L catalyst amount plus the additional amount from titration giving a yield of 98.86%.

**Table 1.** Optimization study for biodiesel yield at different grams of NaOH catalyst with methanol as alcohol.

| Sample | %Yield | Separation | Combustion quality |
|---|---|---|---|
| GO1 | 94.77 | VS | Low |
| GO2 | 93.44 | VS | Low |
| GO3 | 96.59 | VS | High |
| GO4 | 92.05 | VS | High |
| GO5 | 67.95 | VS | High |
| WVO | 98.86 | VS | High |

GO: Groundnut oil, VS: Visible separation, WVO: Waste vegetable oil.

In Table 2, the effect of alcohol type and blend ratio on the yield of biodiesel using sodium hydroxide as a catalyst within 10 to 15 mins time and a fresh groundnut oil sample is shown. Methanol gave a yield of 96.59% while ethanol did not give a visible separation; there was a colour change during the reaction but did not lead to a visible separation, it solidified into a gel-like solid mass. As the percent of ethanol increases in the blend from 20, 50, and then to 80, the yield decreases from 97.05% to 86.36% and then to no visible separation at high percent ethanol. This shows that methanol is better than ethanol. For the M20/E80 blend, there was a colour change during the reaction but did not lead to a visible separation. However, it did not solidify but remained in liquid state. Ethanol seems to have a problem with glycerol separation as in the case of 100% ethanol and 80% ethanol.

In Table 3, the results of the calorimetry test for the fuel samples are shown. We can see from the table that the amount of energy released by biodiesel, diesel and their blends is shown in various units as obtained from the calorimetry test. Based on the results of the test, the amount of energy released by biodiesel is greater than that released by conventional diesel. Hence, it can be seen that it has a much greater energy density than diesel fuel. Though some other factors determine which fuel is better, the high energy density in biodiesel shows that it is better than diesel fuel in this aspect. The B20 and B80 had energy densities greater than the conventional diesel fuel while the B50 had less than diesel. All the blends had energy content less than B100. Hence, due to the fact that biodiesel is a cleaner fuel and more environmentally friendly than diesel, blending diesel fuel with biodiesel has the double advantages of energy content and environmentally friendly better than just pure diesel. Blending biodiesel with diesel reduces the amount of harmful chemicals emitted into the environment by using pure diesel fuel.

**Table 2.** Effect of alcohol type and blend ratio on the yield of biodiesel using sodium hydroxide as catalyst within 10 to 15 mins time and fresh groundnut oil sample.

| Methanol Yield % | Ethanol Yield % | 50/50 Blend Yield % | M80/E20 Blend Yield % | M20/E80 Blend Yield % |
|---|---|---|---|---|
| 96.59 | Colour changed but NVS | 86.36 | 97.05 | Colour changed but NVS |

NVS: No visible separation

**Table 3.** Results of the calorimetry test for the fuel samples.

| Fuel | Time (s) | $T_i$ (°C) | $T_f$ (°C) | Q (kJ) | Q/V (kJ/dm$^3$) | Q/g (kJ/g) |
|---|---|---|---|---|---|---|
| Biodiesel | 316 | 34 | 80 | 2.88 | $2.88 \times 10^3$ | 3.26 |
| Diesel | 159 | 34 | 74 | 2.51 | $2.51 \times 10^3$ | 2.84 |
| B50 | 161 | 34 | 72 | 2.38 | $2.38 \times 10^3$ | 2.70 |
| B20 | 163 | 34 | 75 | 2.57 | $2.57 \times 10^3$ | 2.91 |
| B80 | 192 | 34 | 76 | 2.63 | $2.63 \times 10^3$ | 2.98 |

The result of the solubility test is shown in Figure 3 which indicates that biodiesel is insoluble in distilled water while glycerol is soluble in distilled water. The first image in the figure for both biodiesel and glycerol shows 5 ml of distilled water in the test tube while the second image shows the effect of the addition of 1 ml of biodiesel and 1 ml of glycerol to the first test tube. Based on the principle of like dissolves like, the glycerol dissolved in the distilled water due to its similarity in polar nature, while biodiesel as a non-polar compound cannot dissolve in polar water. The separation between the biodiesel and water indicates that water is denser than biodiesel. The insolubility of biodiesel in water allows for proper washing of biodiesel with warm or hot water where soap, excess catalyst and alcohol are all removed from the biodiesel into the aqueous layer. The bottom layer (water) is then removed or drained off using a separatory funnel.

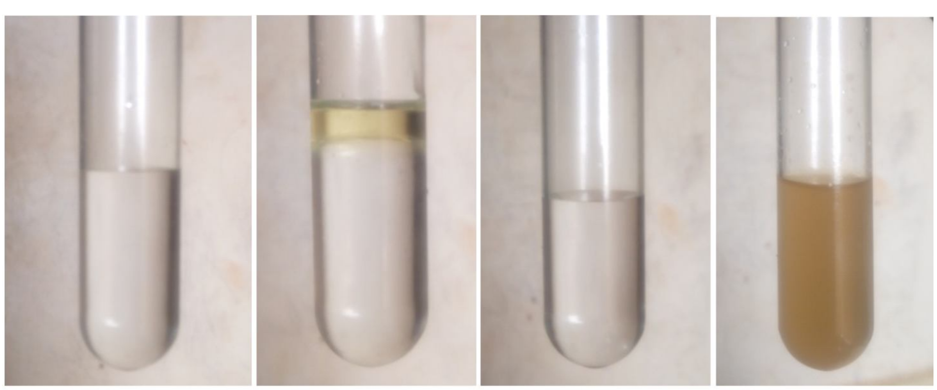


**Figure 3.** Results of the solubility test for the products of transesterification reaction.

## CONCLUSIONS

The optimum condition for biodiesel production is 5.68 g/L since it had a high-quality combustion of biodiesel with a 96.59% yield. The WVO biodiesel produced at this condition gave a yield of 98.86%. Methanol gave a yield of 96.59% while ethanol did not give a visible separation; there was a colour change during the reaction but did not lead to a visible separation, it solidified into a gel-like solid mass. As the percent of ethanol increases in the blend from 20, 50, and then to 80, the yield decreases from 97.05% to 86.36% and then to no visible separation at high percent ethanol. Based on the results of the calorimetric test, the amount of energy released by biodiesel is greater than that released by conventional diesel and the three blends. Hence, it can be seen that it has a much greater energy density than diesel fuel. Glycerol was seen to be soluble in water while biodiesel was insoluble. The insolubility of biodiesel in water allows for proper washing of biodiesel with warm or hot water where soap, excess catalyst and alcohol are all removed from the biodiesel into the aqueous layer.

### Conflicts of interest

The authors declare no conflict of interest.

## ACKNOWLEDGEMENTS

The authors are very grateful to the staff in the Department of Pure and Applied Chemistry, Kebbi State University of Science and Technology, Aliero, as well as those from Advanced Science Laboratory Usmanu Danfodiyo University Sokoto for providing all the chemicals, glassware apparatus and other facilities used in this work. Special thanks go to Dr A. Muhammad, Head of the Department of Chemistry, KSUST, Aliero for his help regarding the chemicals and materials in this work.

### REFERENCES

Alcantara R., Amores J., Canoira L., Fidalgo E., Franco M. J., Navarro A., (2000). Catalytic production of biodiesel from soy-bean oil, used frying oil and tallow. Biomass and Bioenergy, 18(6), 515-527.

Azcan N., Danisman A. (2007). Alkali catalyzed transesterification of cottonseed oil by microwave irradiation. Fuel, 86: 2639-2644.

Blair, G. (2021). How biodiesel is made from. http://biodieseltutorial.utahbiodieselsupply.com/makingbiodiesel/ accessed on 18/02/2021

Cui L.F., Xiao G.M., Xu B., Teng G.Y. (2007). Transesterification of cottonseed oil to biodiesel by using heterogeneous solid basic catalysts. Energy and Fuel, 21: 3740-3743.

Chen H., Peng B. X., Wang D. Z., Wang J. F. (2007). Biodiesel production by the transesterification of cottonseed oil by solid acid catalysts. Frontiers of Chemical Science and Engineering China, 1: 11-15.

Demirbas A. (2008). Studies on cottonseed oil biodiesel prepared in noncatalytic SCF conditions. Bioresource Technology, 99: 1125-1130.

Fukuda H., Kondo A., Noda H. (2001). Biodiesel fuel production by transesterification of oils. Journal of Bioscience and Bioengineering, 92: 405-416.

Karabektas M., Ergen G., Hosoz M. (2008). The effects of preheated cottonseed oil methyl ester on the performance and exhaust emissions of a diesel engine. Applied Thermal Engineering, *28*, 2136-2143.

Köse Ö., Tüter M., Aksoy H. A. (2002). Immobilized *Candida Antarctica* lipase-catalyzed alcoholysis of cotton seed oil in a solvent-free medium. Bioresource Technology, 83: 125-129.

Kong Q., He G. Q., Chen Q. H., Chen F. (2004). Optimization of medium composition for cultivating *Clostridium butyricum* with response surface methodology. Journal of Food Science, 69, M163-M168.

Lam M. K., Tan K. T., Lee K. T., Mohamed A. R. (2009). Malaysian palm oil: Surviving the food versus fuel debate for a sustainable future. Renewable and Sustainable Energy Reviews, 13(6-7), 1456-1464.

Plentz M. S. M., Meneghetti M. R., Wolf C. R., Silva E. C., Lima G. E. S., Coimbra M. A., Soletti J. I., Carvalho S. H. V. (2006). Ethanolysis of castor and cottonseed oil: A systematic study using classical catalysts. Journal of the American Oil Chemists' Society, 83: 819-822.

Sharma R., Pal A., Sharaf J. (2013). Production of bio-diesel from waste cooking oil. International Journal of Engineering Research and Applications, 3(6): 1630-1637.

Thirumarimurugan M., Sivakumar V. M., Merly Xavier A., Prabhakaran D., Kannadasan. T. (2012). Preparation of biodiesel from sunflower oil by transesterification. International Journal of Bioscience, Biochemistry and Bioinformatics, 2(6): 411-414.

van Gerpen J. H. (2005). Biodiesel processing and production. Fuel Process Tech., 86(10): 1097-1107.

Yücesu H. S., Ilkiliç, C. (2006). Effect of cotton seed oil methyl ester on the performance and exhaust emission of a diesel engine. Energy Sources, Part A, *28*: 389-398.

**Citation:** Magaji B., Ibrahim I. B., Adamu S. S., Adiya Z. I. S. G., Zubairu M. S., Usman M. (2024). Calorimetric and optimization study for the production of biodiesel from fresh and waste groundnut oil using NaOH as a catalyst. Advancement in Science and Technology Research, 6(1): 8-12.