INVESTIGATION AND COMPARISON OF THE OPTIMAL CONDITION FOR THE PRODUCTION OF BIODIESEL FROM SHEA BUTTER OIL AND GROUNDNUT OIL USING HOMOGENEOUS CATALYSIS

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ABSTRACT
Due to the depletion of world petroleum reserves and increased environmental concerns, recent interest in alternative source for petroleum-based fuels has been developed. Biodiesel arose as the potential candidate for a diesel substitute due to the similarities it has with petroleum-based diesel. Chemically biodiesel is monoalkyl esters of long chain fatty acids derived from renewable feedstock like vegetable oils and animal fats. It is produced largely by transesterification in which oil or fat is reacted with a monohydric alcohol in the presence of a catalyst. In this research, biodiesel was produced from groundnut oil and shea butter oil using homogeneous catalyst under varying operating conditions such as temperature, concentration of $NaOH_{(s)}$ *and time of reaction, and the conditions which gave the optimum biodiesel yield were obtained. The best operating temperature and catalyst concentration for the transesterification of both oils were found to be 70℃ and 1% catalyst (NaOH) respectively. While the optimum reaction time was found to be 75 and 60 min for shea butter and groundnut oils respectively. The study showed that both shea butter and groundnut oils are viable for the production of biodiesel as alternative to petrodiesel.*

Key words: *Biodiesel, Transesterification, Reaction conditions and Petrodiesel.*

1.0 Introduction

Energy is central to sustenance of livelihoods, the discovery of fossil energy resources in the last centuries contributed immensely to industrial revolution and human development, creating huge wealth (Chandrashekhar, 2017). However, as a result of the hazardous greenhouse gases emissions from the consumption of fossil fuels and exploration of crude oil, the very sustainability of its entire discovery is now threatened. With the price of crude oil that continuously fluctuates, coupled with the rising environmental concerns over its consumption, a renewable and environmentally friendly alternative is imperative to be sought after. Biodiesel is generally defined as the monoalkyl esters of long-chain fatty acids, and has attracted considerable amount of research interests as a renewable substitute to fossil diesel. Countries like United States of America, Brazil, Indonesia, Malaysia, France and Germany use more and more biodiesel.

Biodiesel has comparable physical and chemical characteristics with the petrol-diesel and several other advantages such as non-toxicity, high lubricity, and absence of sulphur, ultra-low greenhouse gases emissions, biodegradability and presence of oxygen in its structure which produces efficient and complete combustion (Helwani *et al.,* 2009). More precisely, biodiesel cuts down on the amount of carbon dioxide, hydrocarbons and particulate matter released into the environment. Biodiesel is conventionally produced via transesterification of vegetable oils and animal fats with methanol in presence of homogeneous alkali (Enciner *et al.,* 2002), and enzyme catalysts (Ali and Kaur, 2011). Moreover, vegetable oils (edible and non-edible) are readily available from various sources. The subsequent research found that triglycerides present in the vegetable oil could be converted into simple alkyl fatty acid esters (biodiesel) which has similar properties to biodiesel BTCE, (1994).

Groundnut is grown in nearly 100 countries. Major groundnut producers in the world are: China, India, Nigeria, USA, Indonesia and Sudan. Developing countries account for 96% of the global groundnut area and 92% of the global production. Asia accounts for 58% of the global groundnut area and 67% of the groundnut production with an annual growth rate of 1.28% for area, 2.00% for production and 0.71% for productivity (Fukuda, 2001). Nigeria, is blessed with much agricultural materials, among which is the shea butter oil which is also known as *vitellaria pardoxa.* Shea butter is largely produced in the southern parts of Nigeria. The facts that these plant oils are readily available in Nigeria, there is the need to investigate the production process to know the operating conditions that will give the optimum biodiesel yield. Table 1 gives the analytical properties of groundnut and shea butter oil relevant in biodiesel production.

Table 1: Analytical properties of Shea butter and Groundnut oil

Properties	Groundnut oil	Shea butter oil
% of oil in seed or kernel	45-55	11 - 30
Specific Gravity at 25℃	0.910-0.915	0.910 – 0.917
Saponification Value	188-195	237 - 261
Iodine Value	84-100	81 - 85
Melting Point ℃	26-32	34 - 38

Source: Olaniyan A.M (2007) and Chinyere (2005)

1.1 Biodiesel Properties and Description: Biodiesel is a light to dark yellow liquid, it is practically immiscible with water, has a high boiling point and low vapour pressure. The flash point of a typical methyl ester biodiesel can be as high as150℃ (300 °F), making it rather non-flammable. Biodiesel has a density of 0.88 g/cm³. Biodiesel uncontaminated with starting material can be regarded as non-toxic (Ma, 1998).

Table 2: Fatty Acid Composition of Groundnut oil and Shea butter oil

Fatty acid	% Composition	
	Groundnut oil	Shea butter oil
Palmitic acid (Hexadecanoic)	6.0-9.0	2.6 – 8.4
Stearic acid (n-Octadecanoic)	3.0 - 6.0	25.6 – 50.2
Oleic (C18:1)	52.0-60.0	37.1 – 62.1
Linoleic acid (C18:2)	13.0-27.0	0.6 – 10.8
Arachidic acid C20 (Eicosanoic)	2.0-4.0	0.0 – 3.5
Lignoceric acid	1.0 - 3.0	6.18 – 7.79
Behenic acid	1.0 -3.0	0.65 – 0.9

Source: (www.chempro.in, 2007) and Okullo JBL et.al (2010)

1.2 Advantages of Biodiesel over Conventional Diesel: Biodiesel possesses several distinct advantages over petro-diesel in terms of its exhaust emissions qualities (Kegl, 2008). Its primary advantages include the fact that it is 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 (Van, 2004a). it has been found that combustion efficiency remains constant when using either biodiesel or diesel fuel (Dorado, 2003b). Compared to mineral diesel, biodiesel generally decreases unburned HC, CO and increase NOx emission (Tat, 2007). Biodiesel can reduce by as much as 20% the direct (tailpipe) emission of particulates, on vehicles with particulate filters compared with low-sulfur (less than 50 ppm) diesel. Particulate emissions as the result of production are reduced by around 50%, compared with fossil-sourced diesel (Van, 2004b).

Table 3: Comparison of typical properties of diesel and biodiesel

Properties	**Diesel**	**Biodiesel**
Density (kg/L)	0.835	0.88
Gross calorific value (MJ/L)	38.30	33.30
C:H:O (ratio)	3.56	2.38
Sulphur (%)	0.15	<0.01
Viscosity (mm^2/s @37.8°C)	3.86	4.70

Source: BTCE (1994) and from www.afde.doe.gov and www.biodiesel.org/feets/summary.shtml#attributes

2.0 Materials and Methods

Three different sets of experiments were conducted in which different parameters were varied to optimize biodiesel production reaction conditions from shea butter oil and groundnut oil. The parameters are temperature, time of reaction and catalyst concentration. Yusuf and Sirajo (2009) detailed the procedure for the determination of the optimum conditions for biodiesel synthesis. The same procedures were followed in this study.

2.1 Varying Temperature: 40ml of groundnut oil was measured using a measuring cylinder and poured into a conical flask. The oil was then pre-heated to 70℃ (using oil bath with temperature regulator). 0.3595g of sodium hydroxide pellets (1 weight % of oil) was weighed and added to 10.0ml of methanol (6:1 methanol to oil ratio). The mixture was stirred until all the pellets dissolve into solution of sodium methoxide. The sodium methoxide solution was then added to the pre-heated methanol. Mixing/stirring was maintained until homogeneity was achieved. The reaction mixture was maintained at a temperature of 70℃ for 40 min. The product of the reaction was left for 16 hr for proper settling of the glycerine produced. Biodiesel was separated from the glycerine using a separating funnel. The same experimental procedure was repeated for other values of temperature (70℃, 55℃, 40℃ and 32℃) keeping all other parameters constant. The same sets of experiments were repeated using shea butter oil.

2.2 Varying Catalyst Concentration: In these sets of experiments, temperature and time of reaction were kept constant. The alcohol to oil ratio was also maintained at a constant value of 6:1. The same experimental procedure above was repeated, but with varying concentration of catalyst (0.17976g, 0.071904g, 0.53928g and 0.71904g of sodium hydroxide pellets) keeping all other parameters constant (temperature at70℃ and time at 40 min).

2.2 Varying Time of Reaction: The time of reaction was varied keeping the other parameters constant. The catalyst concentration was maintained at 1% (oil weight) and temperature was maintained at 70℃, because in the previous experiments, these reaction conditions were the best in terms of yield (volume of product). Only the reaction time was varied from 15, 20, 60 and 80 min. All other experimental variables were kept constant.

2.4 Washing of biodiesel product: The products of the transesterification reaction Fatty Acid Methyl Esters (FAME) usually contain some impurities like unreacted methanol, sodium methoxide and possibly sodium alkylate (soap), and therefore it needs some forms of purification before it can be used in diesel engines. Since all the impurities are polar groups, water is a suitable solvent for dissolving them.

The following procedure was used in washing the biodiesel: 20ml of water was measured using a measuring cylinder and poured gently on the product sample. The mixture was gently stirred to avoid foam formation. Shaking rigorously is not advised (Van, 2004b). The mixture of water and biodiesel was left for 16 hrs to settle into two phases viz; water-impurities phase and biodiesel phase. The two phase mixture was then separated using a separating funnel. The biodiesel layer was then heated to about 100℃ for 1hr to evaporate the remaining water molecules in it.

2.5 Determination of Specific Gravity (IP 59/72): A clean dry empty 50ml density bottle was weighed and the mass was recorded as M_g, it was then filled up with distilled water and subsequently with the samples. The mass of the bottle and water were recorded as M_{1g} and M_{2g} respectively. Hence, the specific gravity was evaluated. This procedure was used to determine the specific gravity of all the samples.

2.6 Viscosity Measurement: Brookfield viscometer measures viscosity in the speed range of 0.1rpm to 100rpm (1rpm = 1.703s) with spindle size numbered from 1 to 7. The smaller the quantity of the sample the larger the spindle number to be used. For this study, since the quantity was small (except for the raw sample), spindle number 7 was used throughout and the angular speed selected was 50rpm. The following procedure was used to determine the viscosities of the samples. The viscometer spindle No 7 was inserted into the shaft of the instrument. The oil sample at room temperature of 25℃ was poured into a 10ml beaker and placed on the bench; the viscometer spindle was lowered into the sample up to the marked level so that the spindle head was completely immersed. The spindle rotated clock-wisely inside the oil sample. The pointer of the dial deflected and stabilized on a given dial value. The reading was then taken.

2.7 Determination of Flash Point Using ASTM D97-73: The oil sample was placed in the Pensky-Martin's cup in such quantity as to just touch the prescribed mark on the interior of the cup. The cover was then fitted onto the position on the cup and Bunsen burner used to supply heat to the apparatus at a rate of about 5℃ per min. During heating, the oil was constantly stirred. As the oil approaches its flashing, the injector burner was lighted and injected into the oil container after every 12 sec intervals until a distinct flash was observed within the container. The temperature at which the flash occurred was then recorded. The test was duplicated for each of the oil samples and the average value of the flash point recorded.

2.8 Gross Calorific Value (GCV) Determination: The calorific value was determined using Perr 6100 bomb calorimeter. The gelatine capsule used in placing the sample in the calorimeter was weighed; 0.1 g of the biodiesel sample was then added into the lower part of the capsule. The bomb calorimeter was closed and connected to an oxygen cylinder for filling. The calorimeter was properly placed in a water bucket that contains about one litre of water. The calorimeter was switched on and it gave automatic readings of the bucket temperature and energy equivalent value. After about 15 min, the calorimeter reading of the jacket temperature was then recorded. The experiment was then repeated for the other biodiesel samples, though some of them using different masses. The calorific values are then determined using the formular below.

$$\text{Calorific value} = \frac{(Energy\ equivalent)(Temp.of\ jacket - Temp.of\ bucket)}{sample\ weight} \quad ......1$$

3.0 Results and Discussions

Biodiesel was produced from groundnut and shea butter oil under different operating conditions (catalyst concentration, time of reaction and operating temperature), and the product analysed in order to ascertain the best operating conditions and the quality of the biodiesel. The results of the experiments conducted are presented below.

The volumes of biodiesel obtained in the transesterification reaction before and after washing are given in Tables 4 to 6. While Vol_1 and Vol_2 represent volume before and after washing respectively.

Table 4: Transesterification results when catalyst concentration was varied at constant temperature of 70°C and constant time of 30 min.

Catalyst conc. (%)	Groundnut oil		Shear butter oil	
	Vol_1 (cm^3)	Vol_2 (cm^3)	Vol_1 (cm^3)	Vol_2 (cm^3)
0.2	3.5	20.4	24.2	22.5
0.5	29.2	26.0	23.6	21.8
1.0	32.4	28.8	25.8	23.8
1.5	26.4	24.8	20.2	19.0
2.0	15.0	13.2	20.2	18.8

From the above experiment, it can be seen that $1\%\ w/w\ or\ 0.27g$ of NaOH gave the highest volume of biodiesel produced for both oils. Hence, $0.27g$ of NaOH was considered to be the best NaOH concentration, and therefore used as the optimum NaOH concentration for the other experiments. This is in agreement with the work of Salahudeen et. al (2012), who investigated the optimum condition for the production of biodiesel from *Canarium Schumfurteii*, they found the optimum catalyst concentration to be 1% w/w. Keeping the weight of the NaOH constant at $0.27g$ and varying the time of reaction, the volume of biodiesel obtained for the respective time used are show in Table 5

Table 5: Transesterification results when temperature is varied at constant time of 30 min and catalyst conc. of 1%

Time (min)	Groundnut oil		Shear butter oil	
	Vol_1 (cm^3)	Vol_2 (cm^3)	Vol_1 (cm^3)	Vol_2 (cm^3)
15	26.9	24.2	22.4	20.5
20	27.5	25.4	25.8	23.8
40	32.4	28.8	26.0	24.5
60	33.1	30.6	27.0	25.5
75	33.9	30.8	27.20	26.0

Table 6: Transesterification results when temperature is varied at constant time of 60 min and catalyst conc. of 1%.

Temperature (°C)	Groundnut oil		Shear butter oil	
	Vol_1 (cm^3)	Vol_2 (cm^3)	Vol_1 (cm^3)	Vol_2 (cm^3)
30.0	2.0	20.0	2.4	22.7
40.0	23.4	20.8	25.4	22.9
50.0	28.0	25.4	25.3	23.3
60.0	32.4	28.8	24.7	23.8
70.0	31.7	29.0	26.5	25.5

The results given above were used to determine the yield of the reactions based on the volume of oils consumed. The yield was determined in the following way;

$$Yield = volume\ of\ biodiesel\ produced\ x\ 100\ \% \div volume\ of\ oil\ use \quad ....2$$

A constant oil volume of $40cm^3$ was used in the whole experiment; therefore the yields will then be evaluated using the volume of biodiesel after washing (vol_2), since it is the volume of the pure product.

The following figures employ the use of Equation 1 in the computation of the fractional yields and consequently the percentage yield taking note of

$$Yield\ (\%w/w) = \frac{mass\ of\ biodiesel}{mass\ of\ oil} = \frac{m_i}{m_0} \text{..........3}$$

$$Mass\ of\ pure\ biodiesel = volume\ of\ pure\ biodiesel \times density \text{............... 4}$$

Average densities of the biodiesel produced from both oils were determined and were used to calculate the yield of biodiesel obtained for all the runs. Density of biodiesel produced from shea butter oil was found to be 0.8551 and that from groundnut oil was 0.9010. The yield would be best explained by plotting the graphs of the respective yields against the varying parameters in the respective experiment. These are shown in Figures 1 to 3.

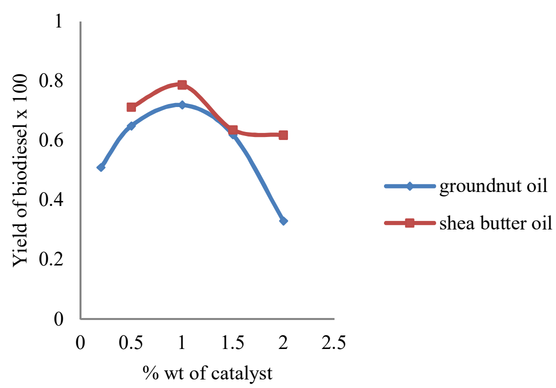

Figure 1: Change in yield of biodiesel with change in NaOH weight (g).

3.1 Varying Catalyst Concentration: For the biodiesel produced from shea butter oil, the yield increased with increasing catalyst concentration from 0.5% (0.14g NaOH) to 1% (w/w) (0.24g NaOH), and then decreased as the concentration was further increased from 1%. This shows that the yield has a maximum value of $0.787\ at\ 1\%\ (w/w)$ catalyst concentration. While for biodiesel produced from groundnut oil, 1 % (wt of oil) concentration of catalyst was found to give the highest yield (0.700). The yields behaviour under varying catalyst concentration is shown in Figure 1. At a catalyst concentration of 2.0%, soap was produced in an excess amount making the biodiesel more viscous than that of $1\%\ w/w$ concentration.

3.2 Varying Time of Reaction: The yield of biodiesel increased as the time of reaction was increased from 15 min to 75 min. The maximum yield obtained at 75 min of reaction was 0.809 for the shea butter oil experiment. While for the groundnut oil experiment, reaction times were varied from 15 min to 80 min. As shown in Figure 3, the optimum reaction time is 60 min. However, for the shea butter oil there was a more rapid increase in yield from 15 to 30 min before a steady increase was observed between 40 to 60 min.

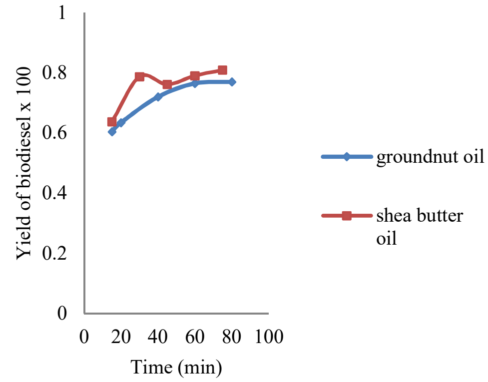

Figure 2: Change in yield of biodiesel with change in time of reaction (min).

3.3 Varying Temperature:
The yield of biodiesel increased as the temperature increased. At 70℃, the yield obtained was 0.808, which was the maximum yield obtained for the shea butter oil. While for the groundnut oil, there was a steady increase in the yield of biodiesel up to 70℃ then a gentle increase from 70℃ to 80℃ as can be seen in figure 3. However, since the boiling point of the sodium methoxide solution is less than 80℃, the yield of the biodiesel is expected to reduce at temperatures greater than 80℃. Hence, 70℃ was considered to be the optimum temperature.

Combining the results obtained for the three variables, it can be reasonably inferred that at catalyst concentration of 1% $(0.27g)$ and reaction temperature of 70℃ are the optimum conditions for the production of biodiesel from the two oils. While reaction time of 75 and 60 min are the optimum time for the shea butter and ground oil reactions respectively.

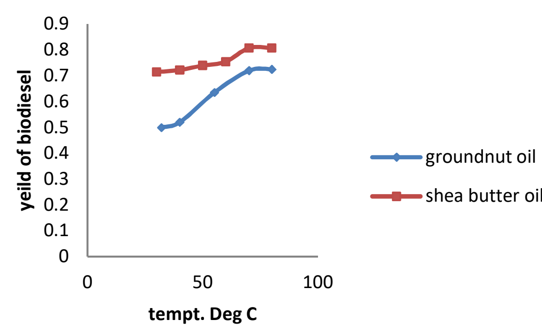

Figure 3: Change in the yield of biodiesel with change in temperature.

3.4 Results of Calorific Value, Specific Gravity, Viscosity and Flash Point Analysis: Table 7 summarises the values obtained for calorific value, specific gravity, viscosity and flash point of the biodiesels produced from groundnut and shea botter oil. It also compared these values with those of standard biodiesel and Automotive Gas Oil (petrodiesel).

Table 7: Comparison of the physical properties of biodiesel produced with standards

Property	Biodiesel produced from groundnut oil	Biodiesel produced from shea butter oil.	Biodiesel's Standards.	AGO Standards.
Viscosity, cP	3.0 – 6.8	3.6 – 0.60	1.17 – 5.83	1.25 – 4.30
Density, $g/cm3$	0.85 – 0.97	0.85-0.94	0.88	0.81
Flash point, ℃	98.0	102℃	93 minimum	50 – 58
GCV, kJ/kg	30137 - 48608	34067- 47856	-	41830

From Table 7 it can be seen that the properties of the produced biodiesels are in close range with those of automotive gas oil (petrodiesel) and Biodiesel's standards.

4.0 Conclusion

This study has been able to establish that catalyst concentration of 1 % (weight of oil), was found to be the optimum concentration for the production of biodiesel from shea butter oil and groundnut oil. With biodiesel yield of 0.78 and 0.70 respectively. Also, the optimum temperature for biodiesel production from shea butter oil and groundnut oil was found to be 70℃ for both oils, with maximum yield of 0.8 and 0.72 for shea butter oil and groundnut oil respectively. While the optimum reaction time was found to be 60 min for groundnut and 75 min for shea butter oil and the viscosities, specific gravity, calorific value and flash point were found to meet the international standards.

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