

Production of Biodiesel from Shea Butter Oil using Homogeneous Catalysts

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Abstract

An investigation into the production of biodiesel from shea butter oil using homogenous catalyst was carried out. The properties of the oil obtained were first determined, having an FFA value of 2.279 amongst other properties. Thus, the direct base-catalysis method was used, with potassium hydroxide as the catalyst. In a 1 hour batch run, biodiesel was produced with a conversion of 92%, FAME content of 97.1%, cetane number of 46.84 and kinematic viscosity of 4.30mm²/s, conforming to ASTM D6751 and EN 14214 international standards. As such, it was established that shea butter biodiesel could be produced by the direct base catalysis, over a shorter time with low cost chemicals.

Keywords

Shea Butter Biodiesel; Homogenous Catalyst; Biofuel; Transesterification; Base Transesterification

Introduction

Over the years, there has been a growing demand for energy in all parts of the world. Petroleum fuels have been the topmost source for use in power generation, industrial machine

operation and transportation. But with growing global warming concerns, environmental pollution, all associated with petroleum fuels, there is a great need for alternative, and renewable energy sources in particular [1, 2].

The search for available, sustainable and preferably renewable energy source led to the renewed interest in biofuels (bioethanol and biodiesel). First generation biofuels were produced primarily from agricultural crops grown for food and animal feed purposes and led to unhealthy competition [3]. The second generation biofuels addressed the problem of competition with edible food crops by employing non-edible oils such Castor seed oil, jathropa oil, neem oil, as source material for fuel production [2, 3].

A biodiesel is a mono-alkyl ester of long chain fatty acids derived from vegetable oils or animal fats which conforms to the ASTM D6751 specifications for use in diesel engines [4]. It is a non-petroleum-based fuel that is made up of alkyl esters derived either from the transesterification of triglycerides (TGs) which is found in vegetable oils, animal fats or waste greases, or the esterification of free fatty acids (FFA) with low molecular weight alcohols – methanol or ethanol [5]. Such triglycerides consist of a glycerol (a triol) and three fatty acids (long chain alky carboxylic acids).

Reactions used for biodiesel production primarily reduce the high viscosity of the vegetable oils and animal fats for their use as diesel fuel [6], of which three methods are generally recognized: *Pyrolysis* (also referred to as cracking), which is the application of thermal energy in the absence of air or nitrogen [7]; *micro-emulsification* – formation of a hybrid mixture of vegetable oils, an ester, dispersant, a low molecular weight alcohol, a surfactant and cetane improver; and *transesterification*. The most popular of the methods (that is, transesterification) involves reaction of a triglyceride with a short-chain alcohol in the presence of a catalyst to yield fatty acid methyl esters and glycerol [8].

The transesterification method is further classified based on the type of catalyst used: *Base-catalysed transesterification*, *acid-catalysed transesterification*, and a combination of both.

Amidst a host of available oil sources – coconut, citrus, palm kernel, linseed, rapeseed, sunflower, olive, soyabean, etc. – shea butter obtained from shea tree (*Vitellaria paradoxa*) available in the wooded savannah of West Africa (of which Nigeria is inclusive) was used for this research. It is cheap oil, mostly used for skin treatment owing to a great amount of unsaponifiables, with a relatively low FFA value, which are suitable properties for biodiesel

production [7].

Quite a few researches have been undertaken to investigate biodiesel production from shea butter oil. Galadima and Garba [9] used sodium hydroxide as catalyst with ethanol to produce FAEE from shea butter oil. With an alcohol to oil ratio of 6:1, reaction of time of 2 hours and temperature of 40°C, FAEE Biodiesel was produced with a yield of 92.8%.

Enweremadu and Alamu [10] used the two-step acid-alkali catalysed method to produce biodiesel from shea butter using methanol, sulphuric acid and potassium hydroxide at 55°C for an hour (for each step). Biodiesel produced had a FAME content of 95.21% and conversion of 92.3%. Investigations also showed that ester yield increased with increase in alcohol-oil ratio up to a 6:1. Optimum catalyst concentration was found to be 1.0%wt and optimum temperature at about 62°C.

The purpose of this research was to synthesize and characterize biodiesel from shea butter oil, by the direct base catalyzed transesterification, using a low molecular weight alcohol, in order to realize a faster and cheaper production method than realized from previous researchers.

Material and Method

Shea butter oil was obtained from Ilorin, Kwara State in Nigeria. The oil was first melted and pre-treatment procedures were carried out to remove solid impurities and determine the basic properties of the oil.

Oil Pre-Treatment

- Sieving

In order to remove undissolved solid impurities from the shea butter, after heating to a temperature of about 40°C, the oil was passed through a sieve cloth, removing all unwanted solid substances contained in the parent shea butter.

- Water Removal

Water present in the parent oil was removed by heating. This was done by heating the oil to about 120°C until constant weight was achieved at this temperature.

The water content of the oil was then calculated from the equation given by Belewu *et al.* [11]:

$$\% \text{moisture} = [(\text{Initial weight of oil} - \text{Final weight of oil}) / \text{Initial weight of oil}] * 100 \quad (1)$$

- Free Fatty Acid (FFA) Determination

In order to determine the FFA content of the oil, a standard solution of 0.1M KOH was prepared as the titrant. About 1.5g of the oil sample was weighed and transferred to a conical flask (with the exact weight measure being recorded, W) to which 50cm³ of Propan-2-ol was added with stirring until dissolution. 4-5 drops of Phenolphthalein indicator was then added to the mixture. The potassium hydroxide solution was titrated against the mixture in the conical flask to the first permanent purple colour and the volume of the titrant (v) read and recorded.

The acid value (AV) of the sample was then calculated as follows:

$$AV = (M * v * 56.1) / W \quad (2)$$

where M is the concentration of KOH, v is the volume of titrant used; W is the weight of oil sample.

The free fatty acid (FFA) content was determined as [12]:

$$FFA = AV/2 \quad (3)$$

Biodiesel Production

Based on the FFA value obtained for the shea butter oil, the direct base-catalysed method was employed. Direct base-catalysed method is only recommended for oils with a FFA value of less than 5.0% [10].

- Base-catalysed Method

The exact FFA value for the reacting batch of oil was first determined and 400cm³ of oil was measured out. The oil sample was transferred to a conical flask and pre-heated to 60°C with stirring with the help of a magnetic stirrer. The amount of KOH was determined according to:

$$KOH = \{ [\%FFA](0.197) \} / 0.86 + 1\% \quad (4)$$

and found to be 5.3745g to which 120cm³ (9:1) of methanol was added in a separate vessel until complete dissolution. The resulting KOH-methanol mixture was added to the oil sample with stirring and allowed to run at 60°C for 1 hour.

On completion of the reaction, the mixture was then transferred to a separating funnel and allowed to stand for about 24 hours and post production procedures were carried out.

Post Production Procedure

- Washing of Biodiesel

The biodiesel was washed with 10% v/v distilled water to remove catalysts present, glycerol and water soluble impurities. This was done three times. After washing, the biodiesel was heated to remove water present due to washing and production.

- Density Measurement

The density of the biodiesel was measured with the help of a density bottle. The weight and volume of the oil were recorded and the density calculated.

- Viscosity Measurement

The viscosity of the biodiesel was measured using a viscometer. A 250 ml of the biodiesel was measured out and tested, noting the temperature and viscosity value.

- Cloud Point Test

The cloud point refers the temperature at which the biodiesel begins to solidify and cannot pour. About 10 ml of the biodiesel was put in a test tube and into an ice bath noting the temperature at which solidification began with the help of a thermometer.

- Flash Point Measurement

To determine the flash point of the biodiesel, 100 ml was put in a flash point pot and fired. A flame source was passed across the heated samples and the temperature at which a flash of light was observed was recorded.

- Iodine Value

To 0.3g of the shea butter biodiesel, 10ml of chloroform and 20cm³ of Wij's reagent were added and the mixture kept in the dark for an hour. 15ml of 10% potassium iodide was then added, rinsing the solution with 50ml of distilled water. The resulting mixture was titrated with sodium thioisulphate using starch indicator.

The whole procedure was carried out for a 'blank' and the Iodine value calculated.

- Saponification Value

To 2g of the shea butter biodiesel, 25ml of 0.5M ethanolic KOH was added and heated under reflux for 30 minutes with the final mixture being titrated with 0.5M hydrochloric acid using phenolphthalein indicator. From the values obtained the saponification of the biodiesel was calculated.

The **Cetane index (CI)** was determined from the correlation given by Krisnangkura [10]:

$$CI = 46.3 + (5458/SV) - 0.25 IV \quad (5)$$

where SV – Saponification value; IV – Iodine value.

The **Cetane number (CN)** was then obtained from a correlation reported by Patel (1999) [10]:

$$CN = CI - 2.6 \quad (6)$$

Conversion was calculated by the relation given by Yong et al. (2007) and Marchetti and Errazu [10]:

$$\text{Conversion}(\%) = 1 - (AV_{\text{bio}}/AV_{\text{oil}}) \quad (7)$$

where AV_{bio} – Acid value of biodiesel, AV_{oil} – Acid value of oil

The **Fatty Acid Methyl Ester (FAME)** content was determined using the correlation given by Felizardo et al. [10]:

$$FAME\% = -45.055 \ln \mu + 162.85 \quad (8)$$

where μ - kinematic viscosity

The **Higher Heating value (HHV)** of the biodiesel was also determined according to the model developed by Demibras [10]:

$$HHV = 49.43 - (0.015 IV) - (0.042 SV) \quad (9)$$

Results and Discussion

The properties of shea butter oil were determined according to standard procedure and the results are as shown in Table 1.

Table 1. Properties of shea butter oil

Property	Value (Author)
Colour	Ivory yellow
Melting temperature (°C)	35
Density (kg/m ³)	895.4 (at 32°C)
Specific gravity	0.9001
Free Fatty Acid (FFA) value (%)	2.279
Kinematic Viscosity (mm ² /s)	38.7

As the FFA value of the shea butter oil was < 5.0, the direct base catalysed method was most suitable. Potassium hydroxide was used as the catalyst as it is cheap and most effective in the transesterification process, owing to its higher reactive nature.

Biodiesel production was successful showing separation into two phases: the biodiesel phase and the glycerol phase. This was achieved with a single batch run for an hour. Post production procedures were then carried out on the produced biodiesel (Figure 1),

characterising the biodiesel produced as shown in Table 2.

Table 2. Summary of Results for the Biodiesel Production

Property	Value
Volume of oil used (cm ³)	400
Volume of biodiesel produced (cm ³)	352
Volume of glycerol obtained (cm ³)	130
Conversion (%)	92.03
Density (kg/m ³) at 32 °C	873.05
Specific gravity	0.8815
Free Fatty Acid (FFA) value (%)	0.1968
Saponification value (mg KOH/g oil)	269.28
Iodine Value (mEq/g)	76.14
Pour point (°C)	19
Cloud point (°C)	24
Kinematic Viscosity (mm ² /s)	4.30
Cetane index	49.4374
Cetane number	46.8374
FAME (%)	97.13
Flash point (°C), open cup	96
Fire point (°C)	110
HHV (MJ/kg)	37.247

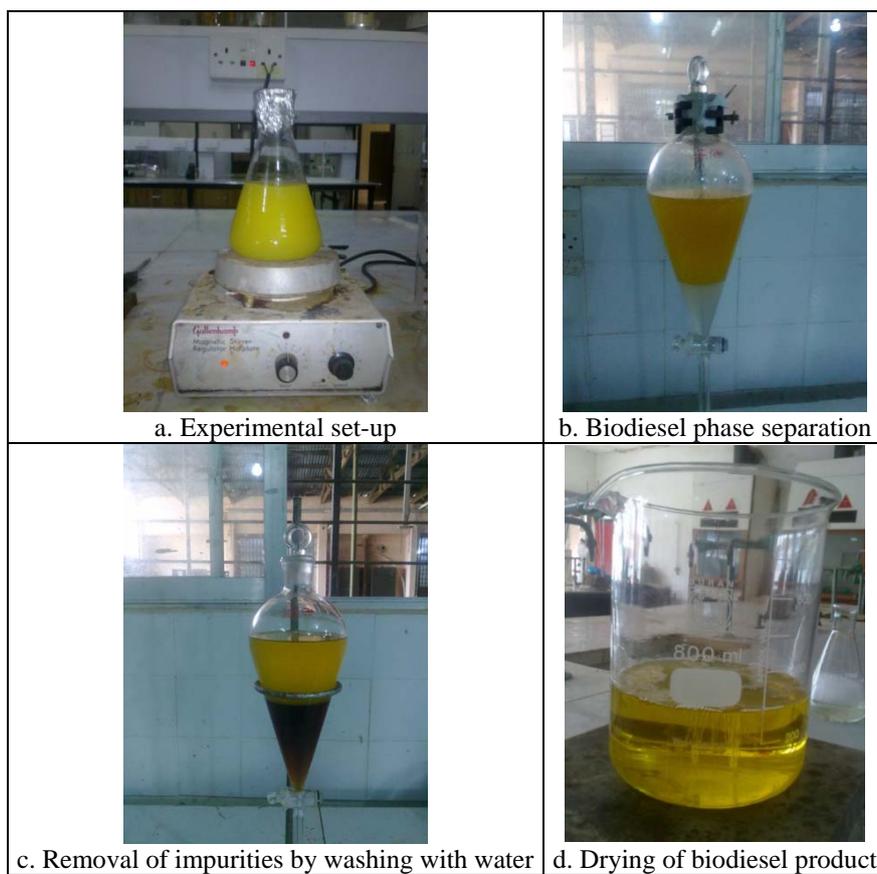


Figure 1. Biodiesel production from shea butter oil

The density of the biodiesel produced was found to be 873.05 kg/m³ which fall within

acceptable biodiesel standard (Table 3). The pour point and cloud point of the biodiesel produced, though, had a high value of 19°C and 24°C respectively. This indicated a poor cold flow property. As such, it may not be suitable for direct use in temperate regions; rather it can be used by blending with petro-based diesel fuels or by the addition of suitable additives to bring such values well below zero.

The kinematic viscosity of the fuel produced also meets acceptable standards both ASTM and EN standards. A viscosity value of 4.30 indicates a good flow, combustion and reduced exhaust smoke and emissions [4].

The biodiesel also shows a good higher heating value (HHV) of 37.247MJ/kg. Biodiesel values range from 33 to 40[4]. Higher heating values indicate the combustibility in combustion engines.

Care needs to be taken in handling the fuel as its flash point value is low, having a value of 96°C. If not handled carefully, rapid ignition could occur leading to fires. This property does not meet ASTM standards (130°C min.) but can be solved by blending it with petro-based diesel.

The iodine value of the biodiesel also met acceptable standards. The iodine value gives a measure of the stability of the biodiesel fuel against oxidation. It measures the amount of double bonds present as iodine absorption occurs at double bonds positions. An acceptable standard thus indicated that the biodiesel produced was stable.

Conclusions

Shea butter biodiesel was produced with acceptable quality in a one hour batch run with KOH catalyst and methanol at 60°C. Shea butter oil was also found to be a viable source material for biodiesel giving a conversion of 92% of oil to biodiesel and a FAME content of 97.1% in a shorter time as compared to some commercial vegetable oil sources now in use, such as jatropha oil. The shea butter biodiesel properties fell within acceptable biodiesel standards.

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