Development and characterization of biodiesel from shea nut butter

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A b s t r a c t. Shea nut butter was extracted from shea nut by cold press method and was investigated as feedstock for the production of biodiesel. Biodiesel yield was used to verify the optimization, while density and viscosity were chosen to serve as an indicator for the effectiveness and completeness of the ester conversion process. Based on the amount of shea butter used, the final product yield obtained was 94.55% mass and the percentage conversion of FFA in shea butter to biodiesel was 92.3% using a methanol/oil ratio of 6:1 and 1.0% mass KOH at 60 min and 55°C, respectively. The important properties of the biodiesel (density, kinematic viscosity, cloud point, pour point, cetane number, neutralization number, iodine value, methyl ester content and high heating value) were compared to those of ASTM and EN standards for biodiesel. The comparison shows that the shea butter methyl ester could be used as an alternative to diesel.

K e y w o r d s: shea butter, biodiesel, fuel properties, oil extraction, transesterification

INTRODUCTION

From 1973, the year of the world oil crisis, till 2004 the world primary energy consumption increased from 252 to 463 billion MJ (IEA, 2006). In addition, high emissions of, CO_2, NOx, SO_2, particulate matter, polyaromatic hydrocarbons and hydrocarbon emissions are produced during fossil fuel use, creating environmental problems. These facts have converged in the search for renewable energy sources, such as biodiesel, a non-toxic biodegradable fuel, with a high heating value and high energy oxygen content (Demirbas, 2003).

Among the most promising sources, vegetable oils and animal fats have attracted much attention as a potential resource for production of biodiesel which is quite similar to conventional diesel in its main characteristics and can be blended in any proportion with petroleum diesel to create a stable biodiesel blend (Agarwal and Das, 2001).

The production and use of biodiesel has increased significantly in many countries around the world using numerous feedstock sources. Unfortunately, it is in nascent status in many African countries. Over the past decade, consumption of transport fuels in Sub-Saharan Africa has increased at a rate of about 7% per year in line with increased economic activity (Mulugetta, 2008). This has had a great economic impact on about thirty-five crude oil-importing countries in Africa. With large landmass for farming and abundance of edible and non-edible oils, some of which grow in the wild, Sub-Saharan Africa is a region with a fairly high potential for biodiesel production. One of the promising sources of biodiesel production is the shea tree (*Vitellaria paradoxa*), a deciduous tree which grows naturally in the wild, especially in the savannah belt of Africa. Shea tree produces the shea nut which is processed into shea butter.

Shea butter is classified as oleaginous product. Shea nut contains 37-55% of fats; it is composed mainly of two fatty acids, stearic and oleic, which together account for 85-90% of the total fatty acids (Maranz *et al*., 2004). Soft shea butter has high oleic content (Badifu, 1989). The physicochemical properties of shea butter are comparable with the properties of groundnut oil which has been used in biodiesel production (Ogbonnaya and Adgidzi, 2008).

Also, it has been observed that the properties of biodiesel are largely dependent on the physicochemical properties of the feedstock. According to some researchers (Ramadhas *et al*., 2005), (Sahoo *et al*., 2007), the methyl esters of saturated fatty acids have a higher cloud point, cetane number and better biodiesel stability. Shea butter consists of 41.1% of saturated fatty acids, comprising palmitic and stearic acids. To ensure the quality of biodiesel as an

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alternative fuel, it has been proposed to limit the unsaturated fatty acid in biodiesel species, especially the content of higher unsaturated fatty acid such as linolenic acid which, on heating, polymerises and leads to gum formation (Lang *et al.*, 2001). Unlike many biodiesel fuels, the biodiesel from shea butter may less likely undergo oxidation since shea butter contains natural antioxidants such as tocopherols and some phenolic compounds (Maranz, 2003). Hence, biodiesel from shea butter will make a good alternative fuel.

Several approaches have been used in the production of biodiesel from vegetable oils and animal fats. However, there is a dearth of information on the production of biodiesel from shea butter and where such exists, they are insufficient. Therefore, the production of biodiesel from shea butter has not been fully explored.

The aim of the present work was to synthesise and characterise biodiesel from shea nut butter and compare it with existing standards. The effects of different parameters were also investigated.

MATERIALS AND METHODS

The different physical and chemical properties of the shea butter were determined (Tables 1 and 2):
– fatty acid composition by a Varian GC (model No. CP3400);
– acid value (as oleic acid), by standard titrimetry (ISO 660, 1996);
– viscosity at 40°C;
– density at 15°C;
– iodine value, using Wijs reagent (ISO 3961, 1996);
– saponification value (ISO 36557, 2002);
– peroxide value (ISO 3961, 1998);
– water content (ISO 662, 1998).

The shea butter was heated to 100°C to eliminate residual water and speed up the reaction. An estimate for the heating time (h) needed to heat the shea butter is given in Eq. (1):

$$\text{Heating time (h)} = \frac{\text{Oil (dm}^3\text{) DT}(°C)\,2.342\left[\dfrac{Wh}{dm^3 \circ C}\right]}{\text{Heaterpower (W)}}. \tag{1}$$

where: Wh is watt-hour.

As there was no adequate information on biodiesel synthesis from shea butter, the alkali transesterification and the "foolproof" (Kac, 2001) methods were tested. The foolproof method, which is basically a two-stage acid-base transesterification method found online, was modified by the authors, as the alkali transesterification method was not successful due to the free fatty acid content.

During the acid-catalysed stage, the amount of methanol used is 20% of the volume of oil plus 60% excess methanol. One litre of crude shea butter and 40% of the required volume of methanol was measured and added to the heated shea butter at 55°C. The mixture was stirred gently for 5 min using a magnetic stirrer until it became murky. 1 ml of 95%

T a b l e 1. Properties of crude shea nut butter

Properties	Values
Density(kg m^{-3}) at 25°C	0.91
Viscosity (mm^2 s^{-1}) at 38°C	39.98
Acid value (mg KOH g^{-1})	3.62
Iodine value (I$_2$ g 100 g^{-1})	59.5
Saponification value (mg KOH g^{-1})	190
Peroxide value (meqO$_2$ kg^{-1})	12.15
Water content (% w.b.)	0.037
Fatty acid composition (%)	
Palmitic (C16:0)	5.4
Stearic (C18:0)	35.7
Oleic (C18:1)	49.6
Linoleic (C18:2)	7.8
Arachidic (C20:0)	1.3

T a b l e 2. Properties of shea butter biodiesel

Properties	Values	Standards		
		ASTM D6751	*EN14214*	*No.2 diesel*
Density at 15°C (kg m^{-3})	877		860-900	820-860
Kinematic viscosity at 40°C (mm^2 s^{-1})	4.42	1.9-6.00	3.5-5.0	2.5-3.5
Flash point (°C)	171	130 min	>101	>55
Pour point (°C)	3			-33
Cloud point (°C)	6			-16
Heating value (MJ kg^{-1})	37.93			42
Cetane number	58	47 min	51 min	49-55
Acid value (mg KOH g^{-1})	0.28	0.5 max	0.5 max	–
Iodine value (I$_2$ g 100 g^{-1})	36.44		120 max	–
Water content (mg kg^{-1})	Trace	500 max	500 max	–
Methyl ester content (% w.b.)	95.21		96.5 min	–

sulfuric acid was added to the mixture. Holding the temperature at 55°C, the mixture was stirred gently for 1 h at 500-600 r.p.m. The heat was removed and stirring continued for another hour after which the mixture was allowed to settle for 2 h. To the remaining 60% of the methanol 4.9 g potassium hydroxide (KOH) was added to form potassium methoxide solution. 50% of this solution was added to the acid-treated mixture and stirred gently for 5 min and allowed to settle for 6-12 h after which the glycerine was drained off. During the alkali-catalysed stage, the mixture was heated to 55°C and the second half of the methoxide solution was slowly stirred in, mixing at the same speed for 1 h. On completion of the reaction, the product was poured into a separating funnel and allowed to settle for 18-24 h. After separation of the biodiesel and glycerol, the fatty acid methyl ester was washed with 2 ml of 10% phosphoric acid added to warm distilled water and dried with anhydrous sodium sulphate.

The following fuel properties of the biodiesel were evaluated with ASTM standard methods: acid value, by colour indicator titration; iodine value (IV), by volumetric titration using Wijs reagent (ISO 3961, 1996); kinematic viscosity at a temperature of 40°C; density, at 15°C; water content, by coulometric Karl Fischer titration method; pour, cloud and flash points.

The higher heating value (HHV) was calculated from the model developed by Demirbas (1998) using iodine value (IV) and saponification value (SV):

$$HHV = 49.43 - (0.015 \ IV) - (0.041 \ SV). \qquad (2)$$

From the iodine value and the saponification value of the biodiesel, the cetane index (CI) was calculated as per the correlation given by Krisnangkura (1986):

$$CI = 46.3 + 5458/SV - 0.225 \ IV. \qquad (3)$$

Cetane number (CN) has been known not to differ much from cetane index. Therefore the correlation reported by Patel (1999) is used to calculate the cetane number:

$$CN = CI - 1.5 \ to \ 2.6. \qquad (4)$$

The methyl ester content was determined using a Varian GC (model No. CP3400) equipped with an auto sampler (model No. CP3800). Results obtained were compared with the correlation of Felizardo et al., (2006):

$$FAME \ (\%) = -45.055* \ ln\mu + 162.85, \qquad (5)$$

where: μ is kinematic viscosity at 40°C.

Using the following definition, the conversion of FFA in shea butter to methyl ester was calculated (Yong et al., 2007; Marchetti and Errazu, 2008):

$$Conversion \ (\%) = \left(1 - \frac{AV_{bio}}{AV_{oil}}\right), \qquad (6)$$

where: AV_{bio} is the acid value of biodiesel and AV_{oil} is the acid value of the shea nut butter.

RESULTS AND DISCUSSION

In this study, the GC analysis as well as density and kinematic viscosity of the end product as it varied with reaction time were chosen to serve as an indicator for the effectiveness and completeness of the ester conversion process (Al-Widyan and Al-Shyoukh, 2002; Brito et al., 2006, 2007; Canakci and van Gerpen, 1999; Felizardo et al., 2006). Lower values of density are interpreted to indicate a more complete ester conversion. Viscosity is the basic parameter reflecting the extent of the reaction, directly related to the methyl ester content. Where there is an insignificant change in viscosity with reaction time, it is taken to indicate that more of the heavy glycerine was removed, which, in turn, meant more complete reaction.

Stoichiometrically, three moles of alcohol are required for each mole of triglyceride transesterification. However, in practice this is not sufficient to complete the reaction. Higher molar ratio is needed to drive the reaction to completion at a faster rate. To determine the effect of methanol-shea butter ratio on biodiesel yield, the ratio of methanol was varied from 3:1 to 7:1 while keeping all other process parameters fixed (Fig. 1a). For this process, it was observed that the ester yield increases with increase in molar ratio. Although the percent yield increased with increase in molar ratio, among the molar ratios studied, ratio 6:1 gave the best results as there was a significant difference between the yields for ratios 6:1 and 7:1. It has been observed that the incremental gain in biodiesel yield decreases with increase in the molar ratio. When the methanol goes on increasing, the density difference between the two phases obtained after transesterification keeps decreasing and hence leads to separation problems. Also at a higher molar ratio, a large amount of alcohol present in the transesterified products requires large amount of energy for distillation. The change in the density shows that the density of the biodiesel decreased with increasing molar ratio. This was probably due to a decrease in residual triglicerides. On the other hand, there was no notable difference in the viscosity of the biodiesel with increase in molar ratio (Fig. 1b).

The effect of KOH concentration was studied in the range of 0.5-1.5% (mass of KOH/mass of oil), while keeping other process parameters constant. It was observed that the catalyst concentration influenced the biodiesel yield in a positive manner only up to a certain concentration. Beyond this concentration, the biodiesel yield decreased with increase in potassium hydroxide concentration. A plot of the biodiesel yield against KOH concentration showed a peak ester yield at KOH concentration of 1.0% (Fig. 2a). The influence of the catalyst amount on the density of the methyl ester shows a decrease as the catalyst amount increased. On the other hand, viscosity decreased up to 1.0% KOH concentration for the biodiesel and after that it was almost constant as shown in Fig. 2b.
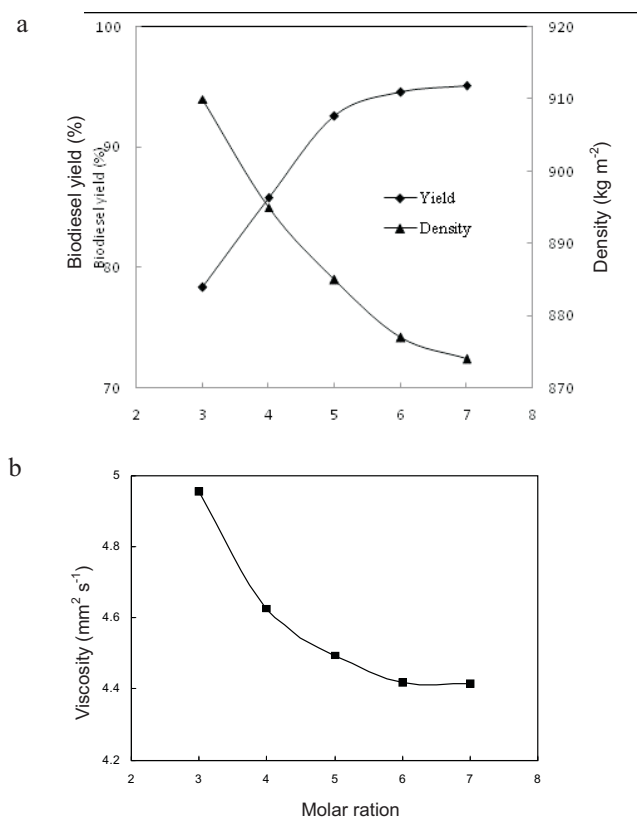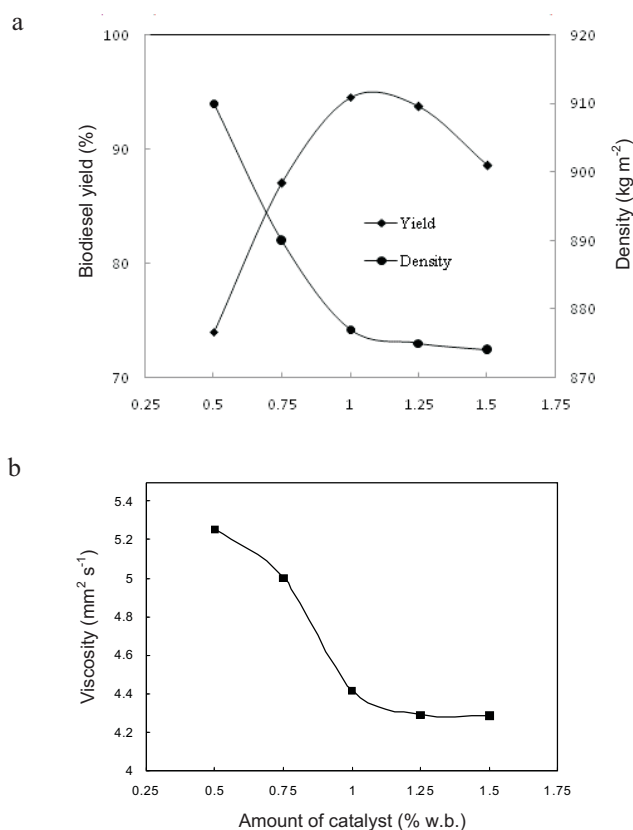
Fig. 1. Variation of: a – biodiesel yield and density, b – viscosity with molar ratio.

Fig. 2. Variation of: a – biodiesel yield and density, b – viscosity with catalyst concentration.

Several investigations have shown that the conversion rate of biodiesel increases with increase in reaction time. In the present work, the effect of reaction time was monitored and samples were taken every 10 for 60 min, when it was considered that the reaction was complete. The reaction was very fast during the first 10 min. The production of the biodiesel reached the maximum value at about 60 min (Fig. 3a). It is clearly shown that density decreased over the reaction time and eventually reached a fairly constant value. There was no noticeable change in the viscosity of the biodiesel with reaction time (Fig. 3b).

In the biodiesel preparation process used, the shea butter was heated up to 55°C. Studies were conducted also at lower temperatures, to determine the effect of heating of shea butter on the biodiesel yield. In carrying out this test, all other parameters remained constant while the temperature to which the oil was heated was varied. The results showed that biodiesel yield increased with increase in oil temperature (Fig. 4). An explanation of this has been attributed to the fact that a higher initial temperature helps in faster settlement of glycerol (Gupta *et al.*, 2007).

Several researchers have found that temperature increase clearly influences the reaction rate and biodiesel yield in a positive manner. In studying the effect of reaction temperature on shea butter transesterification, the reactions

were carried out at 20, 30, 40, 50, 60 and 70°C while other parameters were kept constant. The temperature increase affected the biodiesel yield in a positive manner till 60°C and after that it decreased (Fig. 5a). The density of the biodiesel decreased with increasing reaction temperature. On the other hand, the viscosity of the biodiesel increased slightly with increase in reaction temperature (Fig. 5b).

Most of the fuel properties of the shea butter methyl ester tested compare well with ASTM D6751 standard. Among the general parameters, kinematic viscosity and density are key fuel properties for diesel engines. According to ASTM standard, for biodiesel to be used in diesel engines the kinematic viscosity must be between 1.9 and 6.0 $mm^2 s^{-1}$. According to EN-14214 standard, the density must fall between 0.86 and 0.90 $g cm^{-3}$. The results obtained showed that for the conditions studied, the biodiesel produced in this study had a kinematic viscosity of 4.42 $mm^2 s^{-1}$ while the density was 0.877 $g cm^{-3}$ as shown in Table 1. Other important properties obtained for the biodiesel sample produced in the work, such as high heating value, cetane number, acid value (number), iodine value, flash point, cloud point, pour point and methyl ester content are presented in Table 1. From the results, the methyl ester determined by GC was 95.21% while that calculated according to Felizardo *et al.* (2006), was 95.9%.

a

b
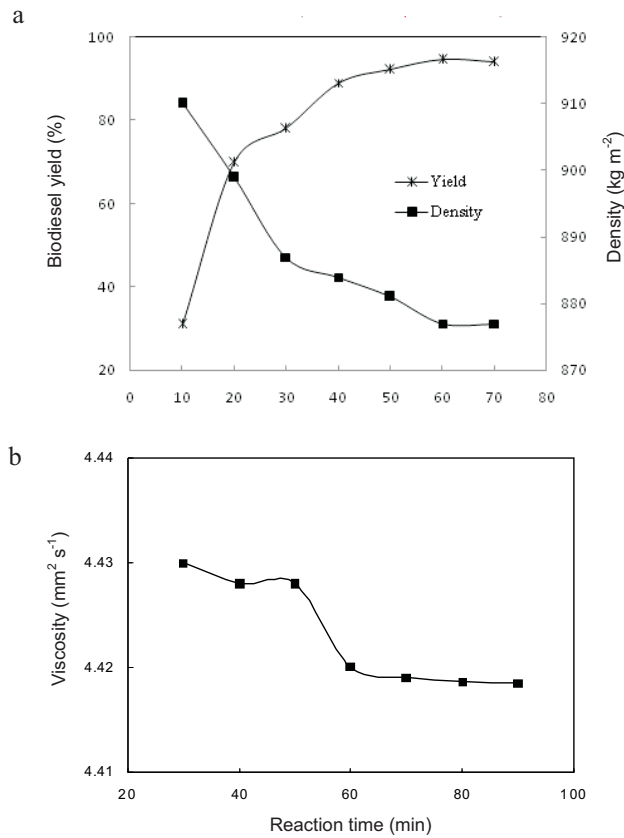
Fig. 3. Variation of: a – biodiesel yield and density, b – viscosity with reaction time.
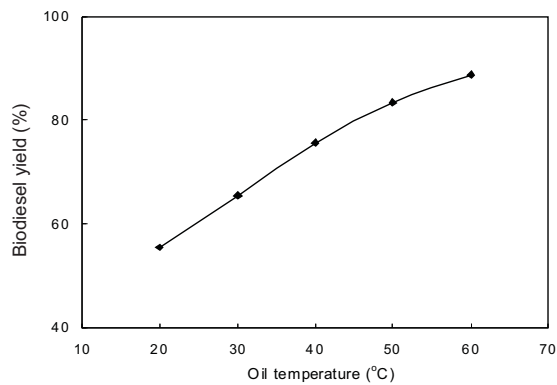
Fig. 4. Variation of biodiesel yield with oil temperature.

The results showed that transesterification improved the important fuel properties tested. As expected, the methyl ester of shea butter has relatively closer fuel properties to petroleum diesel than the shea nut butter.

The present study has enabled us to confirm that shea nut butter may be used as a resource to obtain biodiesel, which could offer more opportunities for generation of rural employment and increasing income. However, further re-

a

b
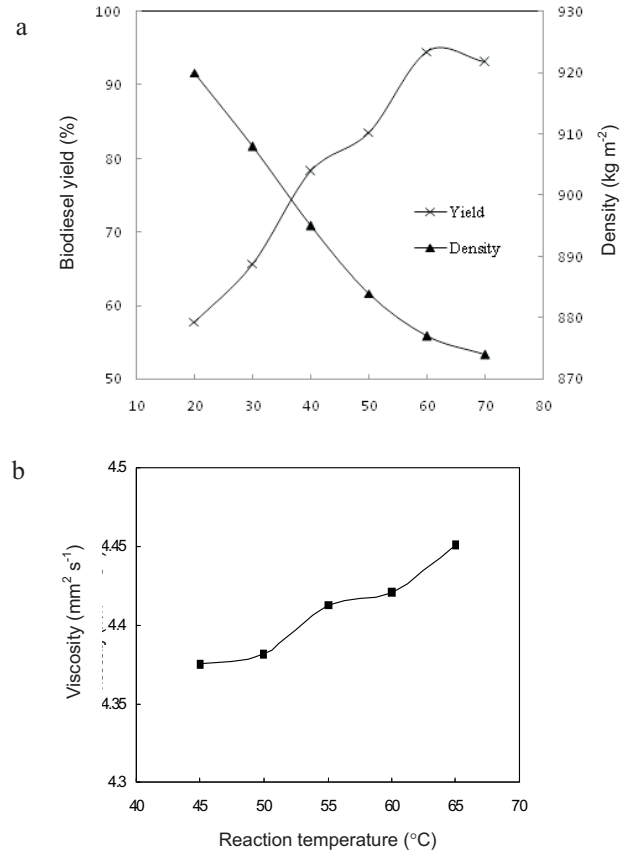
Fig. 5. Variation of: a – biodiesel yield and density, b – viscosity with reaction temperature.

search and development on additional fuel property measrements, engine performance and emission tests and techno-economic analysis are necessary.

CONCLUSIONS

1. A two-step acid-alkali catalysed method was used in the synthesis of biodiesel from shea nut butter.

2. The variables affecting ester yield, such as molar ratio, catalyst concentration, reaction temperature and reaction time, were investigated to determine the best strategy for producing biodiesel from shea butter.

3. It was observed that the ester yield increases with increase in molar ratio, with the ratio of 6:1 giving the best result. The best result was obtained at a catalyst concentration of 1.0% w.b. and temperature of 55°C, respectively, while the reaction was complete at about 60 min.

4. The density and viscosity were adopted as measures of the extent of ester conversion.

5. The fuel properties tested are within the ASTM and EN norms and were found to be very close to those of petroleum diesel. The calorific value of the shea butter biodiesel is slightly lower than that of diesel by about 11% but has a higher calculated cetane number.

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