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Optimization of a two stage process for biodiesel production from shea butter using response surface methodology ☆

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ABSTRACT

The challenges of biodiesel production from high free fatty acid (FFA) shea butter (SB) necessitated this study. The reduction of %FFA of SB by esterification and its subsequent utilization by transesterification for biodiesel production in a two stage process for optimization studies was investigated using response surface methodology based on a central composite design (CCD). Four operating conditions were investigated to reduce the %FFA of SB and increase the %yield of shea biodiesel (SBD). The operating conditions were temperature (40–60°C), agitation speed (200–1400 rpm), methanol (MeOH): oil mole ratio: 2:1–6:1 (w/w) for esterification and 4:1–8:1 (w/w) for transesterification and catalyst loading: 1–2% (H_2SO_4, (v/v) for esterification and KOH, (w/w) for transesterification. The significance of the parameters obtained in linear and non-linear form from the models were determined using analysis of variance (ANOVA). The optimal operating conditions that gave minimum FFA of 0.26% were 52.19°C, 200 rpm, 2:1 (w/w) and 1.5% (v/v), while those that gave maximum yield of 92.16% SBD were 40°C, 800 rpm, 7:1 (w/w) and 1% (w/w). The *p*-value of <0.0001 for each of the stages showed that the models were significant with R^2 of 0.96 each. These results indicate the reproducibility of the models and showed that the RSM is suitable to optimize the esterification and transesterification of SB for SBD production. Therefore, RSM is a useful tool that can be employed in industrial scale production of SBD from high FFA SB.

1. Introduction

Global energy demand is increasing due to economic and technological development, as well as, population growth [1–4]. Meanwhile, the major source of energy currently is fossil fuel with its attendant challenges such as global warming [3,5]. Biodiesel has been found as an alternative to fossil fuel. However, availability of sufficient feedstock for its production is a drawback. Biodiesel is produced from transesterification of refined vegetable oils such as Soybean, Rapeseed, Sunflower, and Palm oils, which are more costly than fossil diesel [4,6]. More so that the biodiesel production from these refined and edible vegetable oils can lead to food oil crisis [1]. Therefore, biodiesel derived from refined and edible oil are not sustainable, but using cheap and non-edible feedstock such as Jatropha, animal fats, and waste cooking oil as well as unrefined crude edible oil like shea butter have been suggested as an alternative feedstock [7,8]. Biodiesel made from these feedstocks were predicted to be economically viable than that of the refined oil [9].

The SB generally consists of more than 90% triglycerides, of which 41.1% is saturated fatty acids which are a good property for biodiesel production [10]. The saturated fatty acids make a high cloud point, high cetane number, good stability, and quality biodiesel. Another advantage of SB for biodiesel production is that it undergoes less oxidation reaction since it contains tocopherols and phenolic compounds which are natural anti-oxidant [11]. Hence, SB for biodiesel production can make a good alternative fuel in compression ignition engines. However, high consumption of catalyst and formation of soap with a low yield of biodiesel due to high FFA (>1%) and moisture content (>0.5%) in SB are the challenges for its use for biodiesel production [9,12,13]. This is due to

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unwanted saponification reaction that takes place as side reaction and makes the purification of biodiesel difficult, thereby increases the overall cost of biodiesel production [6,8,13,14]. Nevertheless, SB is a suitable alternative to the refined oil due to its abundant availability and aforementioned composition which make a quality biodiesel.

Successful SBD production can be achieved by reducing the percentage content of FFA in SB to <1%. This can be done in an esterification process with the aid of an acid catalyst by a reversible reaction between carboxylic acid and alcohol to give at least one ester product and water [15]. Thereafter, the transesterification process of the SB with FFA < 1% (also known as esterified shea butter, ESB) follows, in the presence of a base catalyst using excess alcohol to shift the equilibrium to favor production of SBD. Therefore, to attain greater yield and quality SBD from high FFA SB, an appropriate quantity of alcohol (methanol) in mole ratio with oil is required. Adequate catalyst loading, proper agitation speed and moderate temperature are also required to obtain a higher yield of SBD through esterification and transesterification reactions. However, excess methanol, higher temperature, and too much agitation speed can lead to wastage of resources. Despite the aforementioned, insufficient catalyst can cause incomplete conversion of SB and lower the yield of SBD while excess catalyst can lead to soap formation, thereby hampering the yield of SBD [4], hence the need for optimization study using response surface methodology (RSM).

The RSM is an effective and important tool for statistical analysis to find the optimal conditions for different complex processes, which has been applied in the optimization of multiple variables with a minimum number of experiments [16,17]. Meanwhile, the central composite design (CCD) of RSM has been applied in the optimization of several chemical and technological processes. The benefit of the CCD of RSM is in the reduction of experimental runs that would provide sufficient data to generate enough information for a statistically acceptable result. RSM has been successfully used for the optimization of esterification and transesterification of beauty leaf (*Calophyllum inophyllum*) and jatropha caucus for biodiesel production [4,18].

The present study, therefore, investigates the effect of temperature, MeOH: oil mole ratio, catalyst loading and agitation speed on optimization studies using RSM for esterification and transesterification reactions in a two stage process to reduce the %FFA of SB and improve the %yield of SBD respectively.

2. Materials and methods

2.1. Materials

Shea butter with FFA of 6.86% was purchased from Ilorin South of Kwara State, Nigeria. The chemicals used were of analytical grades. A 4.5 L reactor developed at the Engineering Workshop of the University of Ilorin was used for the study. The reactor was made of stainless steel and had heater band with a temperature and electric motor speed controllers.

2.2. Experimental design for the esterification and transesterification of SB

A three-level-four-factor CCD of RSM with design expert (version 8.06 Stat-Ease Inc., Minneapolis, MN) was used for both esterification and transesterification process. A total number of 30 experiments were designed for each of the stages to determine the %FFA and %yield of SBD using ranges of variables as reaction temperature (A) (40–60°C), agitation speed (B) (200–800 rpm), MeOH: oil mole ratio (C) (2:1–6.1 (w/w)) for esterification and 4:1–8:1 (w/w) for transesterification, and catalyst loading (D) (0.5–1.5 (%)) of H_2SO_4 (v/v) for esterification and KOH (w/w) for transesterification. The ranges for each of the variables were chosen based on the preliminary studies.

2.3. Esterification process

The SB was filtered after melting, to remove impurities and heated to 100°C for 10 min to eliminate moisture and obtained

Table 2
GC–MS Quantitative Analysis of FAME Composition of SBD.

S/N	Retention time (min)	FAMEs	Molecular formula	% Composition
1	24.5	Methyl palmitate	C16:0	25.6
2	27.6	Methyl linoleate	C18:2	7.53*
3	28.0	Methyl oleate	C18:1	–
4	28.5	Methyl stearate	C18:0	46.32
5	31.3	Methyl gondoate	C20:1	4.55*
6	31.7	Methyl arachidate	C20:0	14.04
7	34.9	Methyl behenate	C24:0	1.95

* Monosaturated Fatty Acid Methyl Esters.
Source: Ajala et al. [19].

Table 1
Physico-chemical Properties of SBD as Compared with Diesel and the ASTM Specifications.

Property	SBD	Diesel	ASTM method	Limits
Density kg/m^3@15 °C	883.0	860.4	4052-11	860–900
Specific gravity kg/m^3@15 °C	883.4	860.8	4052-11	
Kinematic viscosity mm^2/s@40 °C	5.93	2.6	445-12	1.9–6.0
Flash point (°C)	130.0	73.0	93-02a	130 min
Cloud point (°C)	12	2.4	2500-11	−3 to 12
Pour point (°C)	10	−9	97-12	−15 to 10
Cetane	47	49	976-11	47–60
Total sulfur (% mass)	0.001	0.300	4294-10	0.005 max
Water content (% vol.)	<0.05	<0.05	95-13	0.05 max
Color	L0.5	L2.0	1500-12	L2.0
Total acid value (mg KOH/g)	0.16		974-12	0.80 max
Distillation IBP	220.0	176.0	86-12	
Distillation 90% recovery °C	342.0	341.0	–	360 max
Distillation FBP	352.0	365.0	–	
Recovery (%)	98.5	98.5	–	90 min
Residue	1.0	1.0	–	
Loss	0.5	0.5	–	
Diesel index	30	28	IP21	
Aniline point (°F)	104.0	86	611-12	

Source: Ajala et al. [19].