

Optimization of the Chemical Interesterification of Allanblackia (*Allanblackia floribunda*), African Walnut (*Tetracarpidium conophorum*) and Fluted Pumpkin (*Telfairia occidentalis*) Seed Oil Blend for use in Bakery Shortening Production, a Response Surface Approach

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Abstract

The objective of this work was to optimize the interesterification temperature (X_1), time (X_2) and catalyst concentration (X_3) of *Allanblackia*, African walnut and fluted pumpkin seed oil blend for bakery shortening production, using a rotatable central composite design (RCCD) in response surface methodology (RSM). The extracted seed oils were interesterified using sodium methoxide as catalyst. Solid fat content, smoke point, melting point, density, viscosity, Iodine value and free fatty acid were evaluated as responses. Regression models were generated and adequacy tested with lack of fit test and coefficient of determination (R^2). The results showed that interesterification temperature, interesterification time and catalyst concentration of the oil blend had significant ($p < 0.05$) effects on responses, with R^2 value of 96.8, 95.3, 94.2, 90.1, 99.5, 93.2 and 75.7 % and C.V of 0.266, 0.146, 0.502, 0.499, 0.602, 0.448 and 7.830 %, respectively for solid fat content, smoke point, melting point, density, viscosity, Iodine value and free fatty acid. Model lack-of-fit in all cases were desirably not significant ($p > 0.05$). Adequate precision values were 16.2006, 13.328, 11.758, 10.054, 46.69, 10.024 and 14.182 for solid fat content, smoke point, melting point, density, viscosity, Iodine value and free fatty acid. Predicted optimum condition and desirability index of 0.907 was obtained at 74.57 °C, 46.0 min and 0.278 % interesterification temperature, time and catalyst concentration respectively, while optimum solid fat content, smoke point, melting point, density, viscosity, Iodine value and free fatty acid were 5.15 %, 221.91 °C, 32.49 °C, 0.911, 25.06 cSt, 76.42 g/100g and 0.08 % respectively. The experimental results obtained validate the predicted model within the acceptable range of the responses. The results also suggest that the obtained model is acceptable and recommended for the optimization of interesterification temperature, time and catalyst concentration for improved bakery fat quality and consistency. Melting point and FFA of the oil blend were reduced significantly ($p < 0.05$) after interesterification, while smoke point and Iodine value increased significantly ($p < 0.05$).

Introduction

Majority of the Bakery shortenings in Nigeria are produced from fractionated and partially hydrogenated palm stearin, with relatively high trans-fat content. Interesterification of a blend of hard fat and high poly-unsaturated fatty acids will produce shortenings with appreciable low trans-fat content, and this is heart friendly. Interesterification process is performed in the food industry, using a chemical catalyst (Sodium methoxide) or enzyme (lipases) (Marangoni and Ghazani 2012). Interesterification, hydrogenation, blending, fractionation and genetic modification are five processes available to food manufacturers to tailor the physical, functional and chemical properties of food Lipids (Dijkstra 2015). At present, roughly one-third of all edible fats and oils in the world are hydrogenated, whereas 90% are either fractionated or interesterified. Each operation relies on different principles to attain its goal. Fractionation is a physical separation process based on triacylglycerol crystallization behaviour (Deffense 1993). Hydrogenation, on the other hand, is a chemical process leading to the saturation of double bonds present in unsaturated fatty acids to harden fats for use as margarine and shortening base stocks (Nawar 1996). Interesterification causes a fatty acid redistribution within and among triacylglycerol molecules which can lead to substantial changes in Lipid functionality (Marangoni and Ghazani 2012). Two types of interesterification are presently in use - chemical and enzymatic. Enzymatic modifications rely on the use of random or regiospecific (1,3- or 2-specific) and fatty acid specific lipases as catalysts, while for chemical modifications, usually metal alcoholate catalysts are employed.

Response Surface Methodology (RSM) has been used by different authors for optimization of processes. RSM relates product properties by using regression equations that describe interrelations between input variables and product properties. RSM can be used to reduce the number of experimental runs without affecting the accuracy of results while determining the interactive effect of different variables on the responses. It is different from the procedure that involves the isolation of test variables and changing one parameter at a time (Montgomery 2005). RSM is an essential tool for designing, formulating, developing, and analyzing new scientific studies and product models. These models can then be used to calculate all combinations of variables and their effects within the test range. RSM has been widely applied in food processing. Some reported cases include, optimization of oil extraction from neem (Awolu et al. 2013) and groundnut kernel (Olajide et al. 2014), production of cookies from cassava-groundnut- corn starch blend (Agiriga and Iwe, 2015), fortification of soymilk with micronutrients (Okwunodulu et al. 2017), extrusion cooking of blends of soy flour and sweet potato flour (Iwe et al., 2001), extrusion of African breadfruit mixtures (Nwabueze and Iwe, 2010), to mention a few.

Allanblackia oil is an edible vegetable oil derived from the seeds from the fruits of vegetable tallow tree. *Allanblackia floribunda* (vegetable tallow tree) is a tree species that is commonly distributed in the moist tropical forest zone that extends from Nigeria east to the Central African Republic and the eastern Democratic Republic of the Congo, then south to northern Angola and eastward to Uganda (Crockett 2015). An early study of *A. floribunda* seed oil reported that the fatty acid constituents were made up of primarily Stearic acid (56.8%) and Oleic acid (39.4%), followed by minor amounts of Palmitic acid (3.2%), Linoleic acid (0.4%), and Eicosanoic acid (0.2%). Triglyceride components consisted mostly of 2-oleostearin (76.2%), 1-stearo-diolein (15.5%), and 2-oleopalmitostearin (5%) (Crockett 2015).

Fluted pumpkin (*Telfairia occidentalis* Hook F) belongs to the family Cucurbitaceae. It is grown in West Africa basically for the consumption of its leafy vegetable and its seeds. Fluted pumpkin seeds are potential sources of industrial and domestic oil, with high nutritional value (Horsefall and Spiff, 2005; Akang et al. 2010). Its Iodine value is high (123.83g/100g) as reported by Nwabanne (2012).

The tropical African walnut, known as *Tetracarpidium conophorum* or *Plukenetia conophora* (Oyekale et al. 2015), belongs to the family Euphorbiaceae (Edem et al. 2009). Walnuts have plasma cholesterol-lowering properties (Saxena et al. 2009). The major fatty acids (FA) found in walnut oil are oleic (C18:1), linoleic (C18:2) and linolenic (C18:3) acids. (Dogan and Akgui, 2005). Higher levels of polyunsaturated fatty acids are more desirable because of their potential health benefits (Saxena et al. 2009). Blending and interesterification of *Allanblackia* seed fat, which is stable at room temperature with African walnut and fluted pumpkin seed oils, liquid at room temperature and rich in essential polyunsaturated fatty acids will produce margarine and bakery shortenings with improved functional properties, and enhanced nutrition and health values. There is the Need to develop a suitable model that will optimize the interesterification process variables and the physicochemical properties of oils for use in margarine and bakery shortening production. The objective of this study was thus, to optimize the interesterification temperature (X_1), time (X_2) and catalyst concentration (X_3) of *Allanblackia*, African walnut and fluted pumpkin seed oil blend, to obtain a suitable fat for bakery shortening production, using a rotatable central composite design (RCCD).

Material And Methods

Raw materials

Mature fruits of *Allanblackia floribunda* were obtained from the Rivers State *Allanblackia* Project farm, Mgbu-Azuogu in Oyigbo Local Government Area of Rivers State, Nigeria. Fresh fruits were stored in a covered bag for five days to allow the fruit pulp to disintegrate and enhance seed extraction. Seeds were cleaned and, sundried to 10% moisture content before storing in an air tight polythene bag for further analysis. Mature and good quality African Walnut seeds were procured from Oil mill market in Port Harcourt, Rivers State, Nigeria. Freshly harvested fluted pumpkin fruits were procured from Bori market in Rivers State, Nigeria.

Oil Extraction (Hot Water Flotation Method)

Allanblackia, African walnut and fluted pumpkin seeds were dehulled and cleaned separately, then oven dried at 60°C for 24h (Giami et al. 1999) in a hot air oven (model QUB 305010G, Gallenkamp, UK), milled using a laboratory mill (model MXAC2105, Panasonic, Japan). Oil extraction was done using hot water floatation method as described by Rosenthal et al. (1996), with slight modification. Here, the milled seeds were made into paste by adding warm and cold water intermittently. The paste was placed in boiling water and allowed to boil for 6 hours. Oil floated to the surface and kept to stand overnight in the refrigerator. This allowed the oil to crystallize out, making it easier to be skimmed from the mixture and washed after which the oil was heated to 100 °C to remove any trace of moisture before storing in air tight plastic containers. Oils extracted through the hot water floatation method was used for the modification process.

Experimental Design

A Central Composite Design (CCD) of Response Surface Methodology (RSM) was used to optimize the interesterification variables and to study the interaction of process variables. There are 3 independent variables; interesterification temperature (X_1), interesterification time (X_2) and catalyst concentration (X_3) for chemical interesterification. Each variable is given 5 different coded levels, as shown in the design Matrix (Table 1) from low (-1), to medium (0) and high (+ 1) as well as star points ($\pm a$) for efficient determination of curvature and quadratic term. Dependent variables such as solid fat content (SFC), melting point (MP), smoke point (SP), viscosity (VS), density (Dn), free fatty acid (FFA) and Iodine value (IV) of the interesterified fat blend were evaluated as responses for the factors studied (Table 2). All experiments were performed in triplicates. Statistical analyses for the interesterified fat blends were performed using Design Expert (Stat-Ease Inc., Minneapolis, MN, USA) software version 11.0.

Table 1
Experimental Range and Levels of the Independent Variables for
Chemical Interesterification

Independent Variables	Levels				
	-a	-1	0	+ 1	+a
Temp. (°C), X_1	32.96	50	75	100	117.05
Time (m), X_2	19.77	30	45	60	70.23
Catalyst Conc. (%), X_3	0.03	0.15	0.33	0.50	0.62
$\pm a$ = star points, -1 = low, 0 = medium, + 1 = high					

Table 2
Design Matrix and Experimental Values of the Responses for Chemical Interesterification of *Allanblackia*. African Walnut and Fluted Pumpkin Seed Oil Blend based on Response Surface Methodology

Run	Space Type	X ₁ : Temp.	X ₂ : Time	X ₃ : Catalyst	SFC	SP	MP	Dn	Vs	IV	FFA
		°C	min	Conc. (%)	%	°C	°C	g/ml	cSt	g/100g	%
1	Axial	117.0	45	0.325	5.00	222	31.2	0.8847	20.54	74.03	0.084
2	Center	75	45	0.325	5.15	222.02	32.6	0.9131	25.24	76.22	0.081
3	Factorial	100	60	0.150	5.07	222	31.6	0.8989	21.51	75.00	0.082
4	Factorial	50	30	0.500	5.10	219.35	32.28	0.9060	24.12	74.22	0.055
5	Center	75	45	0.325	5.13	221.99	32.5	0.9095	25.18	76.97	0.080
6	Factorial	50	60	0.150	5.12	221.85	31.6	0.9080	23.55	74.10	0.089
7	Axial	75	45	0.031	5.15	221	32.65	0.9166	23.63	75.31	0.092
8	Center	75	45	0.325	5.15	222	32.53	0.9131	24.98	76.62	0.081
9	Axial	75	45	0.619	5.06	221	32	0.8987	23.54	75.57	0.054
10	Factorial	50	60	0.500	5.00	219.95	31.5	0.8867	23.88	74.54	0.060
11	Center	75	45	0.325	5.13	221.2	32.2	0.9000	24.33	76.11	0.070
12	Factorial	100	60	0.500	5.00	222.01	31.6	0.8865	21.50	76.00	0.069
13	Factorial	100	30	0.150	5.02	221.4	31.61	0.8900	21.62	75.19	0.087
14	Axial	32.9	45	0.325	5.03	219.24	31.6	0.8890	24.46	74.28	0.081
15	Center	75	45	0.325	5.15	222.11	32.6	0.9131	25.00	76.18	0.084
16	Factorial	50	30	0.150	5.08	219	32.22	0.9007	23.91	76.26	0.079
17	Factorial	100	30	0.500	5.05	222.02	31.61	0.8955	21.55	74.23	0.062
18	Center	75	45	0.325	5.14	222.01	32.5	0.9113	25.22	76.51	0.083
19	Axial	75	19.8	0.325	5.09	220.1	32.23	0.9042	23.27	75.23	0.084
20	Axial	75	70.2	0.325	5.02	221.98	31.3	0.8907	23.00	75.79	0.079

Key SFC = solid fat content, SP = smoke point, MP = melting point, Dn = density, Vs = viscosity, IV = iodine value, FFA = free fatty acid.

The experimental data was fitted to a quadratic model to express the response variables as a function of the independent variables using Eq. (1).

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (1)$$

Where Y is the desired value of response; X₁, X₂, X₃ are independent variables; β₀ is the constant; β₁, β₂, β₃ are coefficients of linear regression; β₁₂, β₁₃, β₂₃ are coefficients of interaction regression and β₁₁, β₂₂ and β₃₃ are coefficients of quadratic regression. The lack of fit of the model was evaluated and the model adequacies was assessed using coefficient of determination (R²), adjusted R², predicted R², adequate precision and coefficient of variation (CV). Analysis of variance (ANOVA) Tables were generated and the effect and regression coefficients of individual linear, quadratic and interaction terms were determined. The significance of all terms in the polynomial were judged statistically at 5% level of probability (p < 0.05).

Chemical Interesterification

The different based stocks of *Allanblackia* seed oil, African walnut seed oil and fluted pumpkin seed oil were blended in the following ratio: 60: 20: 20, in accordance with recommended blend of solid and liquid fats for bakery and all-purpose shortening formulation (Petrauskaite et al. 1998; Chibor et al. 2017). The fat blends were chemically interesterified using the method described by Marangoni and Ghazani (2012). Sodium Methoxide (CH₃ONa) powder was used as catalyst. To each 100g of fat was added (based on experimental design) 0.03 to 0.62 g of CH₃ONa powder, stirred at 32.96 to 117 °C for 19.77 to 70.23min (Table 2). The reaction was stopped with acidic water (4% citric acid), then the blend was washed with dilute basic water (0.1N NaOH) (1:8), three grams (3g) of bleaching earth was added, stirred thoroughly then filtered through Whatman (no 4) filter paper. The product was washed with warm water and dried at 100°C.

Physicochemical Analysis

The physicochemical properties of; smoke point, melting point, density, iodine value and free fatty acids were determined using standard methods of AOAC (2019).

Viscosity

The Kinematic viscosity was measured using the established procedure of the ASTM D445 (2009). It was determined with a calibrated Cannon- Ubbelohde Viscometer: No 2 A149 (Cannon Instrument Co. PA, USA). The viscometer was charged with the oil sample and suspended vertically in a constant temperature bath. The temperature of the system was maintained at 40 °C.

The efflux time of the oil through the capillary bulb was measured and recorded in seconds.

The Kinematic viscosity was calculated using the following formula:

$$V = Kc \times t_f \quad (2)$$

V = Kinematic viscosity (mm²/s)

Kc = Capillary factor/ Viscometer constant (mm²/s²)

t_f = Sample efflux time (s)

note mm²/s = cSt (centistokes)

Solid Fat Content (Sfc)

The solid fat content was determined using the density method, as noted by Onwuka (2018). The glass pycnometer was used to measure density at the following temperatures: 10°C, 20°C, 30°C, 40°C, 50°C, and 60°C. The percentage SFC was calculated using the following equation (Onwuka, 2018):

$$\text{SFC (\%)} = \frac{\rho - \rho^l}{\rho_s - \rho^l} \times \frac{100}{1} \quad (3)$$

ρ = density of fat at the desired temperature

l = density of fat when completely liquid.

s = density of fat when completely solid.

Results And Discussion

Model Fitting

The estimated regression coefficient for solid fat content, smoke point, melting point, density, viscosity and iodine value are presented in Table 3 and Equations 4 to 10. linear effect of interesterification temperature, time, catalyst concentration; interaction effect of interesterification time and catalyst concentration; quadratic effect of interesterification temperature, time and catalyst concentration (X_1 , X_2 , X_3 , X_2X_3 , X_1^2 , X_2^2 and X_3^2) were significant model terms. Only the linear model term (X_3) was significant, for FFA. Model p-value less than 0.01 suggested that the models for the responses were statistically correct and effective with insignificant lack of fit for solid fat content, smoke point, melting point, density, viscosity, iodine value and free fatty acid. Coefficient of variability (CV) ranged from 0.265–7.83%, for all the responses. CV of less than 10% is desirable (Edem and Elijah 2016). Showing that the fitted models of responses were highly reliable and can be considered reasonably reproducible. CV is a measure of deviation from the mean values, which shows the reliability of the experiment. CV describes the extent to which the data were dispersed as well as the reproducibility and repeatability of the model (Firatiligil-Durmus and Evranus 2010). Shishir et al. (2016) reported that a CV < 10% indicates better precision and reliability. The goodness-of-fit of the model was also ascertained by the coefficient of determination (R^2) shown in Table 3. R^2 is a measure of the amount of variation around the mean explained by the model (Stat-Ease 2018). Jusoh et al. (2013) reported that the best R^2 value for a good model fitting was estimated between 0.8 and 1.0. Consequently, R^2 of 0.9699, 0.9528, 0.9418, 0.9000, 0.9952, 0.9322 and 0.7566 given for solid fat content, smoke point, melting point, density, viscosity, iodine value and free fatty acid indicate good fit for the models. The predicted R^2 for all the responses were in reasonable agreement with the Adjusted R^2 , with a difference of less than 0.2. Adjusted R^2 compares model with different numbers of variables, while predicted R^2 can guard against models that are too complicated. Adequate precision for the responses ranged from 10.024 to 16.2006. Adequate precision measures the signal to noise ratio. It compares the range of the predicted values at the design points to the average prediction error. A ratio greater than 4 is desirable (Edem and Elijah 2016). The ratio greater than 10 seen in all the responses indicate adequate signals. The models can be used to navigate the design space.

Table 3
Estimated Regression Coefficient for Solid Fat Content (SFC), Smoke point (SP), Melting point (MP), Density (Dn), Viscosity (Vs), Iodine value (IV) and free fatty acid (FFA) for Interesterified Allantoin, African Walnut and Fluted Pumpkin Seed Oils based on Response Surface Methodology (RSM).

	SFC (%)		SP (°C)		MP (°C)		Dn (g/cm ³)		Vs (cSt)		IV (g/100g)	
Factor	Coefficient	p-Value	Coefficient	p-Value	Coefficient	p-Value	Coefficient	p-Value	Coefficient	p-Value	Coefficient	p-Value
	Estimate.		Estimate.		Estimate.		Estimate.		Estimate.		Estimate.	
Model Const. β_0	5.14	0.0001	221.88	0.0001	32.49	0.0001	0.91	0.0006	25.11	0.0001	76.44	0.000
Linear												
Temp. (°C) X_1	-0.0161	0.0013	0.8729	0.0001	-0.136	0.0109	-0.003	0.0466	-1.16	0.0001	0.0644	0.496
Time (min) X_2	-0.0137	0.0037	0.5273	0.0001	-0.219	0.0005	-0.003	0.0627	-0.0889	0.0429	0.0499	0.596
Cat. Conc. (%) X_3	-0.0221	0.0001	-0.0674	0.4583	-0.083	0.0854	-0.004	0.0097	0.0546	0.1848	-0.082	0.389
Interaction												
X_1X_2	0.0087	0.0967	-0.3575	0.0106	0.1725	0.0125	0.0015	0.3716	0.055	0.298	0.4275	0.005
X_1X_3	0.0087	0.0967	0.2725	0.0381	0.005	0.9316	0.0011	0.4908	-0.0775	0.1529	0.205	0.116
X_2X_3	-0.0288	0.0001	-0.3575	0.0106	-0.02	0.7321	-0.006	0.0057	0.0225	0.6629	0.555	0.000
Quadratic												
X_1^2	-0.0442	0.0001	-0.4228	0.0006	-0.392	0.0001	-0.008	0.0001	-0.963	0.0001	-0.808	0.000
X_2^2	-0.03	0.0001	-0.2743	0.0091	-0.263	0.0001	-0.004	0.0038	-0.7385	0.0001	-0.329	0.004
X_3^2	-0.0123	0.006	-0.2884	0.0069	-0.065	0.1582	-8.00E-04	0.4952	-0.6254	0.0003	-0.353	0.002
R ²	0.9699		0.9528		0.9418		0.9007		0.9952		0.9322	
Adj. R ²	0.9428		0.9103		0.8894		0.8113		0.9908		0.8712	
Pred. R ²	0.8177		0.7788		0.6925		0.6336		0.9742		0.6806	
CV (%)	0.2656		0.1459		0.5021		0.4993		0.6024		0.4476	
Adeq. Prec.	16.2006		13.3282		11.758		10.054		46.69		10.024	
Lack of Fit		0.1439		0.5928		0.3001		0.7381		0.275		0.46
p < 0.05 (significant)												
p > 0.05 (not significant)												

The fitted regression model in terms of coded factors, excluding insignificant terms:

Solid Fat Content = + 5.14 – 0.0161 X_1 – 0.0137 X_2 – 0.0221 X_3 – 0.0288 X_2X_3

– 0.0442 X_1^2 – 0.030 X_2^2 – 0.0123 X_3^2 (4)

Smoke Point = + 221.88 + 0.873 X_1 + 0.527 X_2 – 0.358 X_1X_2 + 0.273 X_1X_3 –

0.358 X_2X_3 – 0.423 X_1^2 – 0.274 X_2^2 – 0.288 X_3^2 (5)

Melting Point = + 32.49 – 0.136 X_1 – 0.219 X_2 + 0.173 X_1X_2 – 0.392 X_1^2 – 0.263 X_2^2 (6)

Density = + 0.91 – 0.003 X_1 – 0.004 X_3 – 0.006 X_2X_3 – 0.008 X_1^2 – 0.004 X_2^2 (7)

Viscosity = + 25.11 – 1.16 X_1 – 0.0889 X_2 – 0.963 X_1^2 – 0.739 X_2^2 – 0.625 X_3^2 (8)

$$\text{Iodine Value} = +76.44 + 0.428X_1X_2 + 0.555X_2X_3 - 0.808X_1^2 - 0.329X_2^2$$

$$- 0.353X_3^2 \quad (9)$$

$$\text{Free fatty acid} = +0.077 - 0.011X_3 \quad (10)$$

Effect of Interesterification Temperature (X_1), Time (X_2) and Catalyst Concentration (X_3) on the Solid Fat Content of *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oils Based on Response Surface Methodology.

The interaction effect of time and catalyst concentration on the solid fat content of *Allanblackia*, African walnut and fluted pumpkin seed oils, during interesterification by Response Surface Methodology, is presented in the 3D surface plot of Fig. 1. Increase in the interaction effect of interesterification time and catalyst concentration, is shown to reduce the solid fat content of the oil blend. Solid fat content (SFC) was reported to be a function of linear, interactions and quadratic effects of the independent variables (Eq. 4). Result showed that X_1 , X_2 , X_3 , X_2X_3 , X_1^2 , X_2^2 , X_3^2 had significant ($p < 0.05$) effects on the Solid fat content of the interesterified fats. A negative coefficient of the independent variables in the model represents antagonistic effects. The mean effect of temperature indicated that decrease in temperature results in increased SFC, as observed also by earlier researchers (Nazaruddin 2013). This is probably because increase in temperature increases the melting and diffusion of solid fats while decreasing the viscosity (Meziane 2013). Decrease in interesterification time and catalyst concentration also increases Solid fat content. Increase in interaction effect of interesterification time and catalyst concentration (X_2X_3) as shown in Fig. 1, decreased the solid fat content of the fats.

Effect of Interesterification Temperature (X_1), Time (X_2) and Catalyst Concentration (X_3) on the Smoke Point of Interesterified *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oils. Based on Response Surface Methodology.

The interaction effect of temperature and time (X_1X_2), temperature and catalyst concentration (X_1X_3) and time and catalyst concentration (X_2X_3) on the smoke point of *Allanblackia*, African walnut and fluted pumpkin seed oil blends, based on Response Surface Methodology are presented in the 3D surface of plots of Figs. 2, 3 and 4, respectively. Increase in interaction effect of temperature and time (X_1X_2), time and catalyst concentration (X_2X_3) are shown to be antagonistic to the smoke point, while increase in interaction effect of temperature and catalyst concentration (X_1X_3) showed synergistic effect on smoke point of the interesterified *Allanblackia*, African walnut and fluted pumpkin seed oil blend.

Smoke point was a function of linear, interactions and quadratic effects of the independent variables (Eq. 5). Results showed that X_1 , X_2 , X_1X_2 , X_1X_3 , X_2X_3 , X_1^2 , X_2^2 and X_3^2 had significant ($p < 0.05$) effects on the smoke point of the interesterified fats. A positive and negative coefficient of the independent variables in the model represents synergistic and antagonistic effects. The linear effect of temperature and time indicated that increase in temperature and time result in increased smoke point. This is probably because increase in temperature dried the oils further and reduced moisture impurities and volatile matters, which could have affected smoke point negatively if present. Increase in smoke point of vegetable oil heated initially to 180°C for 50 min had earlier been reported (Idum-Acquah et al. 2016). The interaction effect of temperature and time (X_1X_2), was however shown to reduce the smoke point (Fig. 2). Interaction effect of temperature and catalyst concentration (X_1X_3) increased the smoke point of interesterified fats, as shown in Fig. 3. Interaction effects of interesterification time and catalyst concentration (X_2X_3) reduced the smoke point as seen in Fig. 4, this was probably due to break down of triglycerides to free fatty acids, which affects smoke point of fats negatively. Dijkstra (2015) also reported reduction in smoke of interesterified fat due to increase in Sodium Methoxide catalyst concentration and interesterification time, resulting in increased formation of fatty acid methyl esters (FAME) and yield lost. Quadratic effects of temperature, time and catalyst concentration were also seen to be antagonistic on smoke point.

Effect of Interesterification Temperature (X_1), Time (X_2) and Catalyst Concentration (X_3) on The Melting Point of Interesterified *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oils. Based on Response Surface Methodology.

The interaction effect of temperature and time (X_1X_2) on the melting point of *Allanblackia*, African walnut and fluted pumpkin seed oil blend during interesterification, evaluated through Response Surface Methodology is presented in the 3D surface plot of Fig. 5. Increased interaction effect of temperature and time increased the melting point of the interesterified seed oils. Melting point was reported to be a function of linear, interactions and quadratic effects of the independent variables (Eq. 6). Results showed that X_1 , X_2 , X_1X_2 , X_1^2 , and X_2^2 had significant ($p < 0.05$) effects on the melting point of the interesterified fats. A positive and negative coefficient of the independent variables in the model represents synergistic and antagonistic effects. The linear effect of temperature and time indicated that increase in temperature and time had a negative effect on melting point of fats, as corroborated by the reports of Klinkesorn et al. (2004), Rodriguez et al. (2001) and Norizzah et al. (2004). The interaction effect of interesterification temperature and time (X_1X_2) was however shown to increase the melting point of the fat samples (Fig. 5). Quadratic effects of temperature and time affects the melting point negatively.

Effect of Interesterification Temperature (X_1), Time (X_2) and Catalyst Concentration (X_3) on the Density of Interesterified *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oils. Based on Response Surface Methodology.

The interaction effect of time and catalyst concentration (X_2X_3) on the density of interesterified *Allanblackia*, African walnut and fluted pumpkin seed oils is presented in the 3D surface plot of Fig. 6. The interaction effect of the time and catalyst concentration is shown to be antagonistic to the density of the oil blends during interesterification. Density was reported to be a function of linear, interactions and quadratic effects of the independent variables (Eq. 7). A negative coefficient of the independent variables in the model represents antagonistic effects. The linear effect of temperature and catalyst concentration indicated that increase in temperature and catalyst concentration had a negative effect on density of fats. The interaction effect of interesterification time and catalyst concentration (X_2X_3) was also shown to decrease the density of the fat samples (Fig. 6). Quadratic effects of temperature and time affect the density negatively.

Effect of Interesterification Temperature (X_1), Time (X_2) and Catalyst Concentration (X_3) on the Viscosity of Interesterified *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oils. Based on Response Surface Methodology.

Viscosity was observed to be a function of linear and quadratic effects of the independent variables (Eq. 8). Results showed that linear effect of interesterification temperature and time, quadratic effects of interesterification temperature, time and catalyst concentration had significant ($p < 0.05$) effects on the viscosity of the interesterified fats. A negative coefficient of the independent variables in the model represents antagonistic effects. The linear effect of temperature and time indicated that increase in temperature and time result in decreased viscosity. This is probably because increase in temperature increases the melting and diffusion of solid fats while decreasing the viscosity (Meziane 2013). The interaction effect of temperature, time and catalyst concentration were not significant ($p > 0.05$). Quadratic effects of temperature, time and catalyst concentration were also seen to be antagonistic on interesterified fat viscosity.

Effect of Interesterification Temperature (X_1), Time (X_2) and Catalyst Concentration (X_3) on the Iodine Value of Interesterified *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oils. Based on Response Surface Methodology.

The interaction effect of temperature and time (X_1X_2) on the iodine value of *Allanblackia*, African walnut and fluted pumpkin seed oil blends during interesterification using a rotatable Central Composite Design based on Response Surface Methodology is presented in the 3D surface plot of Fig. 7. Increase in the interaction effect of temperature and time is shown to increase the iodine value of the fat blend. The interaction effect of time and catalyst concentration on the iodine value of the oil blend is shown to be synergistic (Fig. 8). Iodine value was found to be a function of interactions and quadratic effects of the independent variables (Eq. 9). A positive and negative coefficient of the independent variables in the model represents synergistic and antagonistic effects. Quadratic effects of interesterification temperature, time and catalyst concentration affect the iodine value negatively.

Free fatty acid was found to be a function of linear effects of the independent variables (Eq. 10). Result showed that linear effect of catalyst concentration (X_3) affects the percentage free fatty acid of the interesterified fats negatively. A negative coefficient of the independent variables in the model represents antagonistic effects.

Set Goals, Constraints and Desirability Function for Numerical Optimization of The Interesterification Variables and Responses, Based on Response Surface Methodology.

For the independent variable; temperature was minimized, time and catalyst concentration were set in range. Minimal temperature was desirable for energy economy and to minimize destruction of fat's compositional properties. Increased temperature had been reported to increase the free fatty acid content of palm kernel oil from 1.49 to 1.81% and reduced iodine value from 23.52 to 22.52 g/100g as temperature increased from 25 to 100°C (Dawodu et al. 2015). Solid fat content and smoke point were set at maximum to allow for sufficient solid fats in the final product, for dough proving efficiency (dos Santos et al. 2014) and for use of fat products in wider cooking applications. Density was set at maximum to enhance the solid fat content. Density is reported to correlate positively with the solid fat content of vegetable oils (Nazaruddin 2013). Iodine value was set at maximum as maximum polyunsaturated fatty acid (PUFA) is desirable for enhanced nutritional quality of the product (O'Brien 2009). Free fatty acid (FFA) was set at minimum for product storage stability.

The desirability function was generated after limiting the preferred goal of interesterification variables and responses. The desirability function approach is one of the most frequently used multi-response optimization techniques in practice. The desirability lies between 0 and 1 and it represents the closeness of a response to its ideal value (Nwabueze 2010). The more closely the response approaches the ideal intervals or ideal values, the closer the desirability is to 1 (Raissi and Farsani 2009). As shown in Table 4, the selected optimum process condition was; temperature (74.59 °C), time (45.99 min) and catalyst concentration (0.279%), these gave optimum responses of 5.146%, 221.909°C, 32.49°C, 0.911, 25.06 cSt, 76.424 g/100g and 0.08% for Solid fat content, Smoke point, Melting point, Density, Viscosity, Iodine value and Free fatty acid, respectively. With desirability index of 0.907.

Validation of Optimization for The Interesterification of *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oils Based on Response Surface Methodology.

The predicted and experimental values are presented in Table 4. The result showed that there was no significant difference ($p > 0.05$) on the corresponding experimental values between the predicted (simulated) and actual properties of interesterified oils. Significant difference ($p < 0.05$) in response was only noticed in smoke point (SP) 221.91 and 222.00°C for Predicted and Experimental values, respectively. This result attests to the effectiveness of this design for optimum and effective interesterification of *Allanblackia*, African walnut and fluted pumpkin seed oils. In general, the optimized values of process variables (interesterification temperature of 74.6°C, interesterification time of 46.0 and catalyst concentration of 0.28%) obtained from the predicted optimum condition and desirability index were different from data on CCD report for predicted and actual value Table (Table 4). This is because the optimization has been carried out by software and the variable in range has been selected to obtain the optimum response, as supported by report from earlier researchers (Edem and Elijah 2016).

Table 4
Validation of Optimization for the Interesterification of
Allanblackia, African Walnut and Fluted Pumpkin Seed Oils
based on Response Surface Methodology

Responses	Values	
	Predicted	Experimental
Solid Fat Content (%)	5.15	5.11 ± 0.035
Smoke Point (°C)	221.91	222.00*±0.058
Melting Point (°C)	32.49	32.42 ± 0.161
Density (g/ml)	0.911	0.911 ± 0.002
Viscosity (Cst)	25.06	24.99 ± 0.125
Iodine (g/100g)	76.42	76.47 ± 0.416
Free Fatty Acid (%)	0.080	0.081 ± 0.012
*Significant (p < 0.05): using independent samples T-test		

Conclusion

The fitted regression model for the response variables from RSM were significant ($p < 0.05$) with coefficient of variation (CV) value ranging from 0.146–0.602% and coefficient of determination (R^2) of 96.8, 95.3, 94.2, 90.1, 99.5, 93.2 and 75.7%, respectively for solid fat content, smoke point, melting point, density, viscosity, iodine value and free fatty acid. Lack-of-fit for the models were not significant ($p > 0.05$). Predicted optimum condition and desirability index of 0.907 was obtained at 74.57 °C, 46.0 min and 0.278% interesterification temperature, time and catalyst concentration, respectively with optimum solid fat content, smoke point, melting point, density, viscosity, iodine value and free fatty acids of 5.14%, 221.91°C, 32.49°C, 0.9110 g/ml, 24.97 cSt, 76.42 g/100g and 0.08%, respectively. Fat obtained from the optimum interesterification process is suitable for bakery shortening, as seen in the result for the optimum responses. Interesterification reduced the solid fat content and melting point to desirable range for shortenings. Smoke point of interesterified oils increased significantly, making it suitable for a wide range of baking operations. Interesterification process reduced the percentage free fatty acids, which will enhance the shortening storage stability. Production of bakery shortening from the optimum interesterified fat and its baking performance shall be evaluated in the subsequent study.

Declarations

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Ethics approval and consent to participate

Not applicable.

Competing interests

The authors declare that they have no competing interests

Consent for publication

Not applicable.

Authors' contributions

Bariwere S. Chibor: Conceptualization, Methodology, Resources, Formal Analysis, Investigation, Writing-original draft, Writing-review and editing. Maduebibisi O. Iwe: Supervision, Editing and Project Administration. Nneoma E. Obasi: Supervision, Editing and Project Administration. The author(s) read and approved the final manuscript.

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Figures

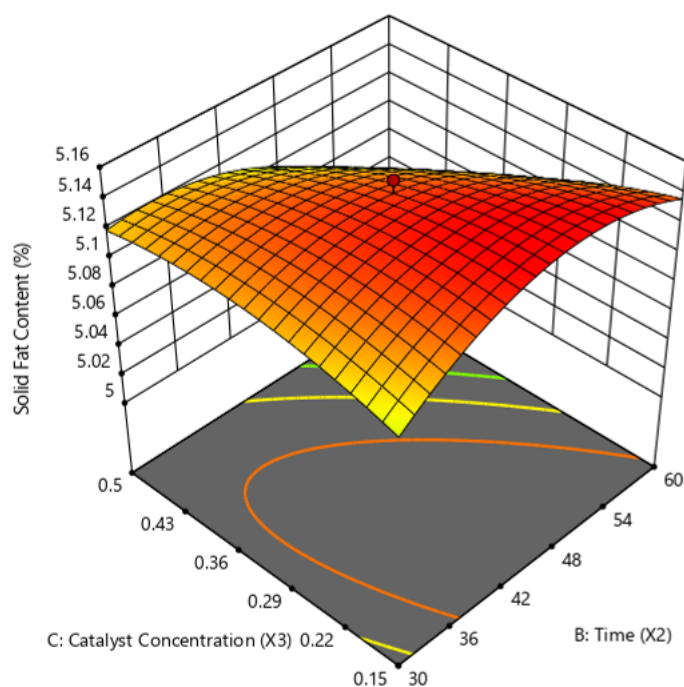


Figure 1

Effect of Interesterification Time (X_2) and Catalyst Concentration (X_3) on Percentage Solid Fat Content (SFC) of *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oil Blend.

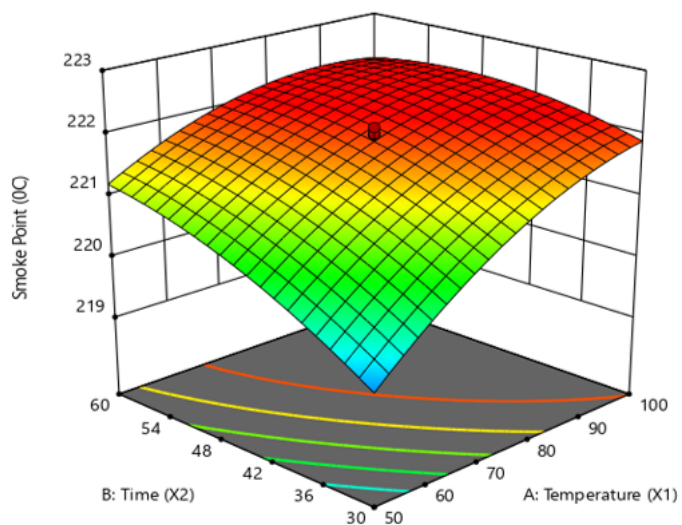


Figure 2
Effect of Interesterification Temperature (X_1) and Time (X_2) on the Smoke Point (SP) of *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oil Blend

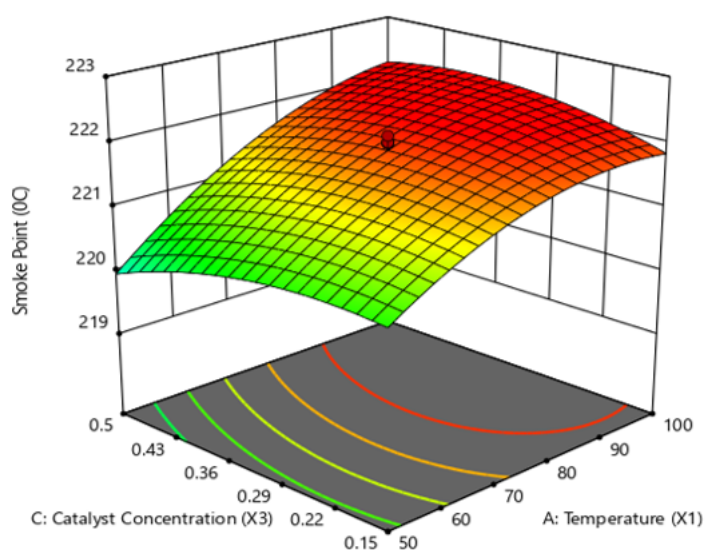


Figure 3
Effect of Interesterification Temperature (X_1) and Catalyst Concentration (X_3) on the Smoke Point (SP) of *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oil Blend

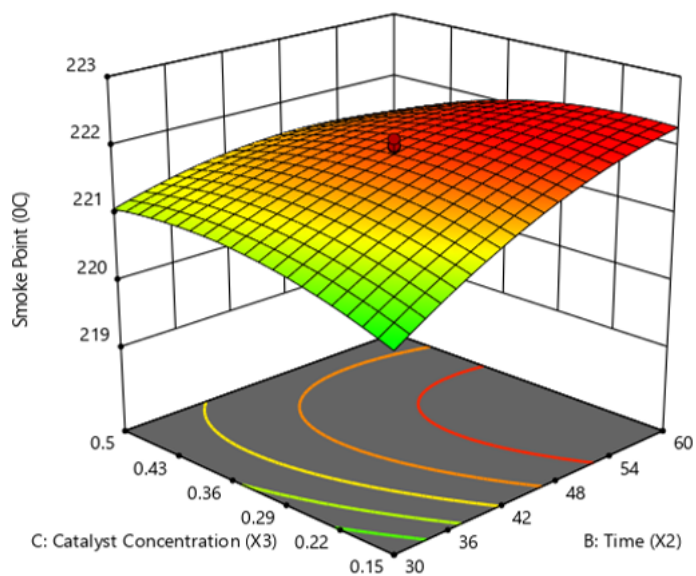


Figure 4
Effect of Interesterification Time (X_2) and Catalyst Concentration (X_3) on the Smoke Point (SP) of *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oil Blend

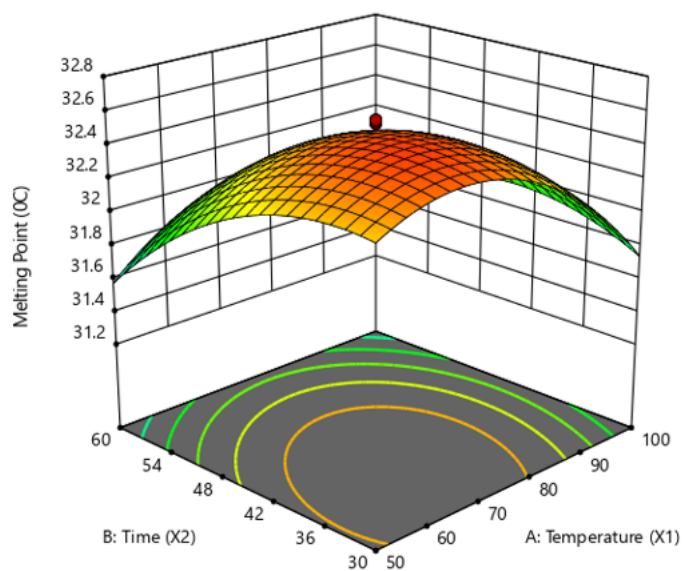


Figure 5
Effect of Interesterification Temperature (X_1) and Time (X_2) on the Melting Point (MP) of *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oil Blend

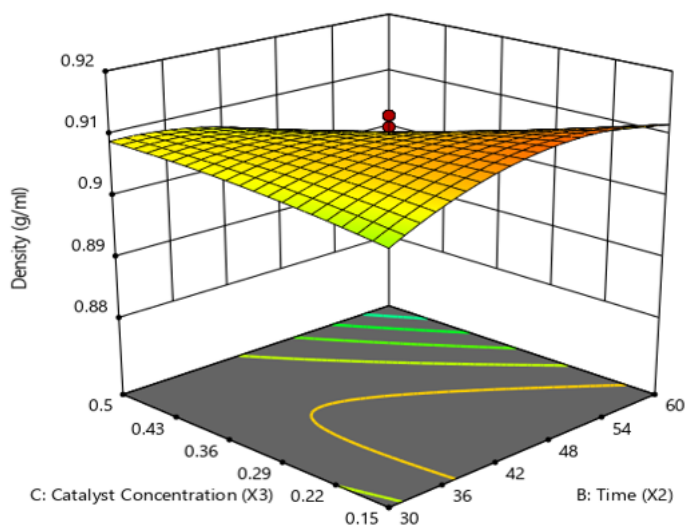


Figure 6

Effect of Interesterification Time (X_2) and Catalyst Concentration (X_3) on the Density (DN) of *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oil Blend

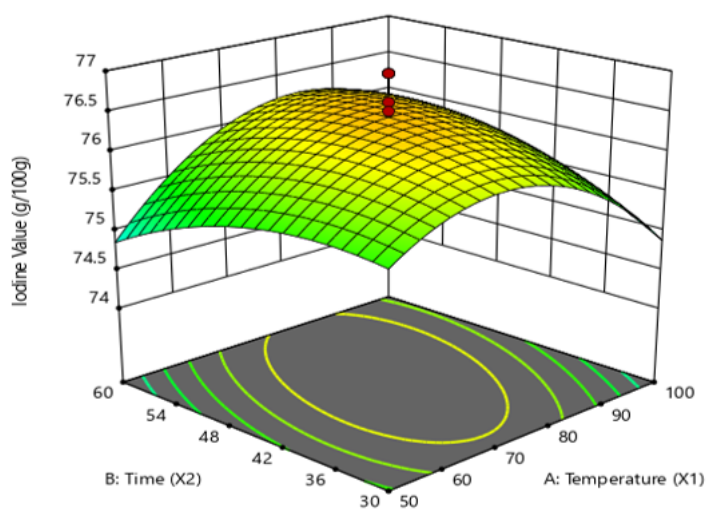


Figure 7

Effect of Interesterification Temperature (X_1) and Time (X_2) on the Iodine Value (IV) of *Allanblackia*, African Walnut and Fluted Pumpkin Seed Oil Blend

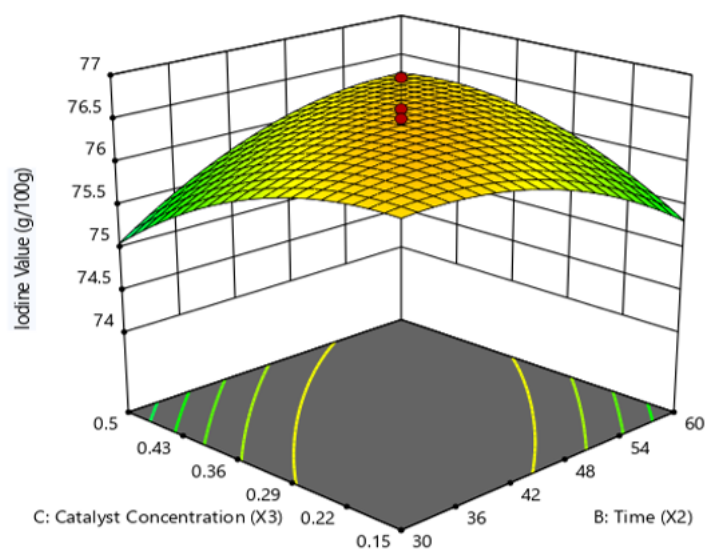


Figure 8

Effect of Interesterification Time (X_2) and Catalyst Concentration (X_3) on the Iodine Value (IV) of *Allnblackia*, African Walnut and Fluted Pumpkin Seed Oil Blend