Optimization of Transesterification of *Lophira lanceolata* (False Shea) Seeds Oil to Alkyl Esters using Response Surface Methodology

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ABSTRACT

This research work studied the production and optimization of biodiesel from seeds oil of Lophira lanceolata (False Shea). The esterification reaction was carried out using conc. H_2SO_4 (1% v/v) as acid catalyst with methanol/oil ratio of 4.5:1 at a temperature of 55^oC for 90min to reduce the FFAs contents (< 0.32%).The reaction mixture was transesterified to Lophira lanceolata methyl esters (LLMEs) using NaOH as base catalyst. The biodiesel produced was analyzed for fuel properties using ASTM standard methods. Optimization of LLMEs production from its oil was performed by central composite design and response surface methodology in 30 experimental runs. The optimization result suggested the best combination of process for Lophira l. optimum biodiesel yield of 85.0% variables are as follows: reaction temperature (50^0C); reaction time (120 min); methanol/oil ratio (9:1) and catalyst conc. (0.30 mol/dm^{-3}) respectively. The regression equation obtained by ANOVA showed that the model was adequate to express the actual relationship between the response (biodiesel yield) and significant variables with a satisfactory coefficient of determination R^2 of 96.05 % and adjusted R^2 of 94.64% for Lophira l. and Adjusted R^2 of 98.04% for biodiesel fuels, which can be compared favourably with the prediction model value of (83%). Fuel properties of the biodiesel produced conform to the ASTM specifications, which suggest that; it would make a good alternative fuel for diesel engines.

Key words: *Lophira lanceolata*, Optimization, *LLME* Yield (%), Behnken design, Lower/Upper levels

INTRODUCTION

New and renewable alternative fuels as a substitute for petroleum based fuels have become increasingly important, due to environmental concerns and fossil fuel depletion [1, 2]. This lead to the search for other energy sources such as bioethanol and biodiesel. Biodiesel is a processed fuel derived from renewable sources such as vegetable oils and animal fats [3]. With human population on the increase, more land is required to produce food for human consumption, which poses a challenge to biodiesel production [4]. Researchers focused on different feed stocks of biodiesel and explore non-edible vegetable oil for biodiesel production, such as *Jatropha* and Algae oil [5]. *Lophira lanceolata* seeds oil (LLO) is a plant based oil that could make a good feedstock for biodiesel. However, many parameters affect transterification reaction amongst which are temperature, methanol/oil ratio, catalyst and reaction time amongst others. The steps involved in controlling these factors are labor intensive and time consuming, hence require optimization of the process to minimize the experiments. So

far, studies on transesterification for optimization of reaction parameters were based on changing one separate factor at a time. However, reaction system was influenced simultaneously by more than one factor. Therefore, it is important to investigate the effect of interaction between reaction parameters. Response surface methodology (RSM) is a useful statistical method for the optimization of complex processes and allows the generation of ample data for relevant statistical result [6]. Literature has reported that, recently very few papers are available on the application of Response Surface Method for the optimization of process variables to maximize biodiesel yield [7]. A study by [8] studied the effect of three process variables namely, temperature, catalyst concentration and methanol/oil molar ratio on the methyl esters yield of *Lagenaria vulgaris* seeds oil. Central composite design (CCD) of 20 experiments was applied and a yield of 96.52% biodiesel was achieved. Goyal [9,] also studied effect of four process variables including catalyst concentration, Temperature, methanol oil ratio and reaction time (min) on methyl esters yield of *Jatropha c.* seeds oil. The authors used central composite design based on RSM, employing 54 experimental runs and obtained a biodiesel yield of 98.3%. From the above data, it can be seen that, no work has been reported on the optimization of methyl esters production from LLO using response surface methodology. This work aims at investigating the optimization of methyl esters production from LLO applying the technique of response surface methodology studying four process variables which include: Temperature, Catalyst concentration, Methanol/oil ratio and Reaction time. The paper would report an understanding of how the test variables affect the selected process response. Response surface (Box-Behnken) Statistical experimental design was employed to design the experiments for determining optimal conditions of transesterification of seed oils using sodium hydroxide as catalyst.

MATERIALS AND METHODS.

All chemicals used for this work were of Analytical Reagent grade. These include methanol (99%), sulphuric acid (98%) petroleum ether (99%) and sodium hydroxide pellet (95%) was used as a base catalyst.

Table 1.0: Fuel properties of LLO and its Yield

S/no.	Properties	Yield
1.	Crude Oil Yield (%)	34.00±0.41
2.	FFA (%)	2.46±0.14
3.	SV(mgKOH)	223.0±1.45
4.	IV (I_2g/100g)	61.00±1.33
5.	MW (g/mol)	652.62

IV= Iodine Value, SV=Saponification value, FFA= Free Fatty Acid content, MW= Molecular Weight

Fresh fruits of false Shea were obtained from Adamawa North-Eastern part of Nigeria. The seeds were manually separated from the kernels, dried and grounded into powder. Oil was extracted from the seeds using Soxhlet apparatus and experimental runs were performed. The extracted *Lophira lanceolata* seed oil was analyzed for fuel properties in accordance with [10] methods and reported in Table 1.0.

Acid-Base Catalyzed Esterification of FFAs in LLO

Fresh LLO was warmed and filtered to remove impurities. The oil was heated at 100ºC for 15min to remove moisture. LLO had FFA value of 2.46±0.14 which is not suitable for base catalyzed transesterification. The FFAs were converted to esters in a pretreatment process for the production of *Lophira lanceolata* methyl esters (LLME). The esterification reaction was carried out using conc. H_2SO_4 (1% v/v) as acid catalyst with methanol/oil ratio of 4.5:1 at a temperature of 55ºC for 90min. Thereafter, the FFAs were reduced to < 0.32%. The reaction mixture was transesterified to LLME using NaOH as base catalyst. The derived LLME was separated washed with warm water and dried over anhydrous Na_2SO_4 followed by filtration to remove residual water as reported by [11] and [12]. The process of LLME production was optimized using response surface method for maximization of product. The yield (%) of LLME was estimated using the following equation,

$$\text{Biodiesel yield (\%)} = \frac{weight\ of\ the\ biodiesel}{weight\ of\ the\ oil\ used}\ X\ 100 \qquad (1)$$

Table 2.0: Fuel Properties of LLME Produced from *Lophira l.* Seeds Oil

Parameters	**LLME**	**ASTM D6751 limits**
Acid Value ($mgKOHg^{-1}$)	0.53±0.01	0.80 Max
Kin. Viscosity @ 40 ºC (cSt)	5.30±0.12	1.9-----6.0
Cloud point (ºC)	6.0±1.10	NS
Sulphur content (wt. %)	0.04±0.00	0.050
Flash Point (ºC)	150.0±5.01	Min 130

The fuel properties of derived Lophira lanceolata methyl esters (LLMEs) is reported in Table 2.0 and compared favourably with the standard specifications of ASTM methods.

Experimental Design for Optimization of LLMEs Production from Lophira lanceolata Seeds Oil

Response surface (Box-Behnken) statistical experimental design was employed in the experiments for determining optimal conditions of transesterification of seeds oil using sodium hydroxide as catalyst. Four independent variables, including reaction time, temperature, methanol/oil ratio and catalyst concentration were chosen. Table 3.0 shows the lower and upper levels (range) of the variables studied in the design. The process was carried out based on literature as reported by [13] and [14]. Each run was set twice and all the runs were completely randomized to obtain a total of 30 runs. The design and analysis, as well as optimization of the results were conducted using MINITAB 16 statistical software platform.

Table 3.0: Experimental Variables and Their Levels for Box-Behnken Design

S/n	Independent variable	Code	Lower level	Upper level
1.	Reaction Time (minute)	A	40	120
4.	Methanol volume (cm^3)	B	20	40
3.	Catalyst concentration (w/w %)	C	0.3	0.65
2.	Temperature (^oC)	D	40	60

Analysis of LLMEs profile using GC-MS

The LLME was prepared in the laboratory under the prescribed conditions of operation, optimized by the RSM and analyzed for fatty acid composition using GC-MS (Model-6890N), Agilent machine; as described by **[15]** and **[16]** in quantifying fatty acids.

Statistical Analysis of Response (Yield)

The response Y (% methyl ester yield) was fitted with a full quadratic polynomial regression model (equation 2) in order to correlate the yield to the operating variables.

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 + \sum_{i=1}^{4} \sum_{j=i+1}^{4} \beta_{ij} x_i x_j \quad \ldots\ldots\ldots\ldots\ldots (2)$$

Where β_o β_i, β_{ii}, β_{ij} are intercept, linear, quadratic and interaction coefficients respectively, and x_i, x_j are the encoded independent variables. MINITAB 16 Statistical Software Package was used for the regression analysis of the experimental data. The quality of the model fit was evaluated using the coefficient of determination (R^2) and effect of terms was evaluated using ANOVA at $\alpha = 0.05$. 3k Surface plots were developed using the fitted quadratic polynomial equation obtained from regression analysis, holding two of independent variables at a constant value corresponding to the stationary points and changing the other variables. Optimization of the results was carried out using Minitab Response Optimizer facility. Results of Analysis of variance (Table 5.0) on the data in Table 4.0 reveals that the linear, quadratic and interaction terms of the model are all significant ($p < 0.05$) at $\alpha = 0.05$, although with significant lack of fit ($p = 0.001$) which may be due to the unusual observations for the yield.

RESULTS AND DISCUSSION

Thirty (30) experimental runs were conducted to generate the values of LLME yield. The experimental values obtained for LLME yield responses at designated points are presented in Table 4.0. Table 5.0; shows the analysis of variance for the response surface model for the optimization of LLMEs yield from Lophira seeds oil. From the results shown, Model F-value of 68.08 was recorded; which implies that, the probability value (P) for the model is significant since it is lower than 0.0001. Values of "Prob > F" less than 0.050 indicate that, the model terms are significant. Value of regression coefficient R^2 for the model is 0.960, showing the fitness of the model. The values of adjusted coefficient of determination (R^2adj) and predicted R^2 are 0.946 and 0.911 respectively. A low value of coefficient of variation (C.V. = 2.79%) was recorded. These are indication of precision of fitted model **[9]** and **[18]**. In this study, A (reaction time) B (methanol/oil ratio) C (catalyst concentration), interaction effect of

(methanol/oil ratio with catalyst concentration) BC, (methanol/oil ratio with reaction temperature) BD, (catalyst concentration with reaction temperature) CD, (quadratic effect of methanol/oil ratio) B^2 all have significant effect on the LLMEs yield. However, AC and AD are not significant model terms for they have values > 0.0500. Values greater than 0.100 indicate that model terms are not significant. There are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The "Pred R^2" of 0.911 is in reasonable agreement with the "Adj R^2" of 0.946."Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 32.819 indicates an adequate signal, this model can be used to navigate the design space.

Table 4.0: Design Matrix of the Experiment and Its Result for LLME Fuel.

Run	Parameter 1 D:Temp(°C)	Parameter 2 A:Time (min)	Parameter 3 C:Catal.(%w/w)	Parameter 4 B:Methanol/Oil (w/w)	*LLME Yield (%).*
1	40	40	0.65	30	47
2	60	40	0.65	30	63
3	40	120	0.65	30	72
4	60	120	0.65	30	81
5	50	80	0.30	20	73
6	50	80	0.47	20	54
7	50	80	0.30	40	76
8	50	80	0.47	40	58
9	40	80	0.65	20	58
10	60	80	0.65	20	70
11	40	80	0.65	40	61
12	60	80	0.65	40	69
13	50	40	0.30	30	56
14	50	120	0.30	30	85
15	50	40	0.47	30	48
16	50	120	0.47	30	70
17	40	80	0.30	30	65
18	60	80	0.30	30	75
19	40	80	0.47	30	53
20	60	80	0.47	30	62
21	50	40	0.65	20	50
22	50	120	0.65	20	81
23	50	40	0.65	40	50
24	50	120	0.65	40	79
25	50	80	0.65	30	64
26	50	80	0.65	30	64
27	50	80	0.65	30	64
28	50	80	0.65	30	64
29	50	80	0.65	30	64
30	40	40	0.65	30	61

Table 5.0: Analysis of variance for Response Surface Model for *Lophira Lanceolata* Fuel

Parameters	Sum of Square	DF	Mean Squares	F-Value	Prob > F
Model	5021.80	15	334.79	68.08	< 0.0001
A	316.48	1	316.48	64.35	< 0.0001
B	1593.01	1	1593.01	323.93	< 0.0001
C	383.35	1	383.35	77.95	< 0.0001
D	177.49	1	177.49	94.75	0.1534
AB	0.000	1	0.000	0.000	0.0000
AC	1.13	1	1.13	0.23	0.6349
AD	2.09	1	2.09	0.43	0.5175
BC	98.00	1	98.00	19.93	< 0.0001
BD	138.33	1	138.33	28.13	< 0.0001
CD	60.95	1	60.95	12.39	0.0011
A^2	17.69	1	17.69	14.25	0.0068
B^2	2947.05	1	2947.05	1695.30	< 0.0001
C^2	37.50	1	37.50	12.75	0.1684
D^2	21.57	1	21.57	7.65	0.0242
Residual	138.85	32	4.17		
Lack of Fit	96.97	34	6.07		
Pure Error	3.17	6.65	0.654		
Cor Total	5228.34	57			

Std. dev = 2.02, C.V. = 2.79%, R^2 = 0.9605, Adjusted R^2 = 0.9564, Pred. R^2 = 0.9106

Analysis of acquired LLMEs

The result of analysis of fatty acid composition of LLME using the given parametric variables shown in Table 3.0 and determined by Gas Chromatograph–Mass Spectrophotometer (GC-MS) is presented Table 6.0. The result shows that LLME contained mainly cis-9-Octadecenoic (oleic) and Eicosanoic (arachidic) acids at 72.26 and 13.02% respectively. Others are Hexadecanoic (palmitic) 7.32% and Octadecanoic (stearic) 4.02% acids. Amongst the fatty acids listed oleic acid is highly unsaturated and the most dominant in the composition. Properties of alkyl esters depend on the nature and chemical composition of oil feed stock. Each feedstock has a unique chemical composition that influences the characteristic of fuel produced from different feedstocks [17].

Table 6.0: Fatty Acid Composition of Lophira Lanceolata Oil

S/No.	Fatty acid	Molecular Formula	Approximate (wt. %)
1.	Hexadecanoic acid	$C_{16}H_{32}O_2$ $CH_3(CH_2)_{14}COOH$	7.32
2.	Eicosanoic acid	$C_{20}H_{40}O_2$ $CH_3(CH_2)_{18}COOH$	13.02
3.	Cis-9-Octadecenoic acid	$C_{18}H_{34}O_2$ $CH_3(CH_2)_7$-CH=CH-$(CH_2)_7COOH$	72.26
4.	Docosanoic acid	$C_{22}H_{44}O_2$ $CH_3(CH_2)_{20}COOH$	0.23
5.	Octadecanoic	$C_{18}H_{36}O_2$ $CH_3(CH_2)_{16}COOH$	4.02
6.	Other non-fatty acid detected	-	3.15

Effect of Parameters

Figure 1–3 Present contour plots of LLME yields to show the relationships between the dependent and independent variables of the developed model. Each plot presents the effect of two variables on the LLMEs fuel yield, holding the other variables at constant level.

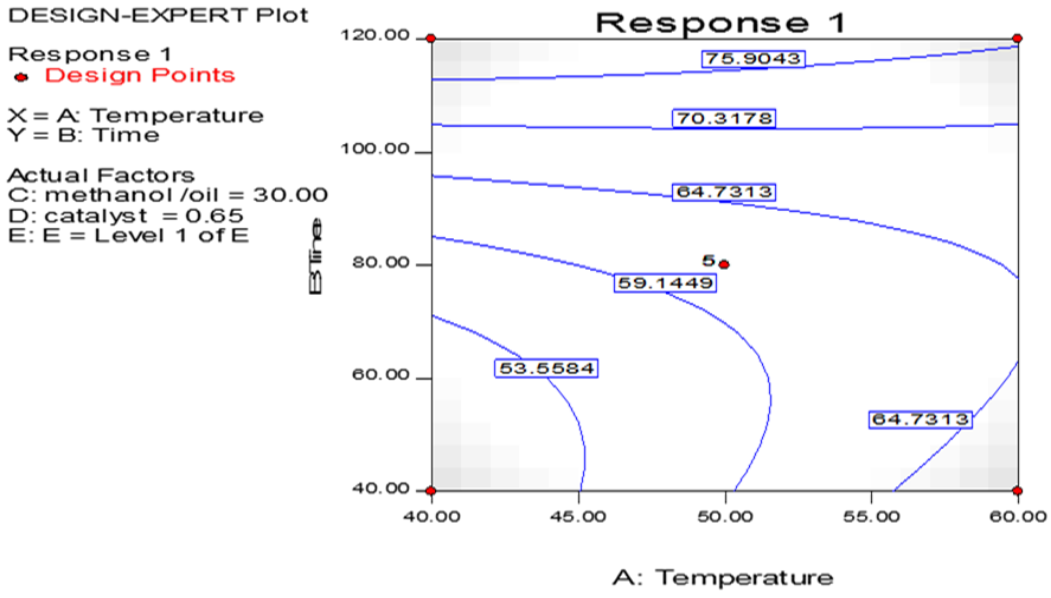

Figure 1.0: Plot of Time versus Temperature for LLME Yield

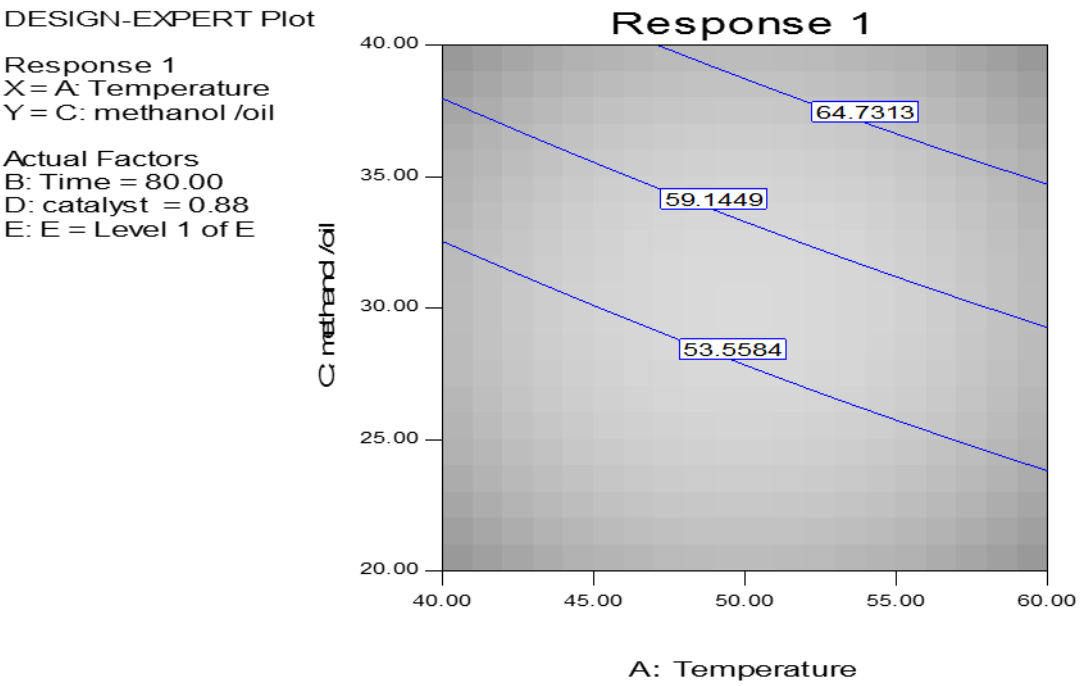

Figure 2.0: Plot of Methanol/Oil versus Temperature for LLME

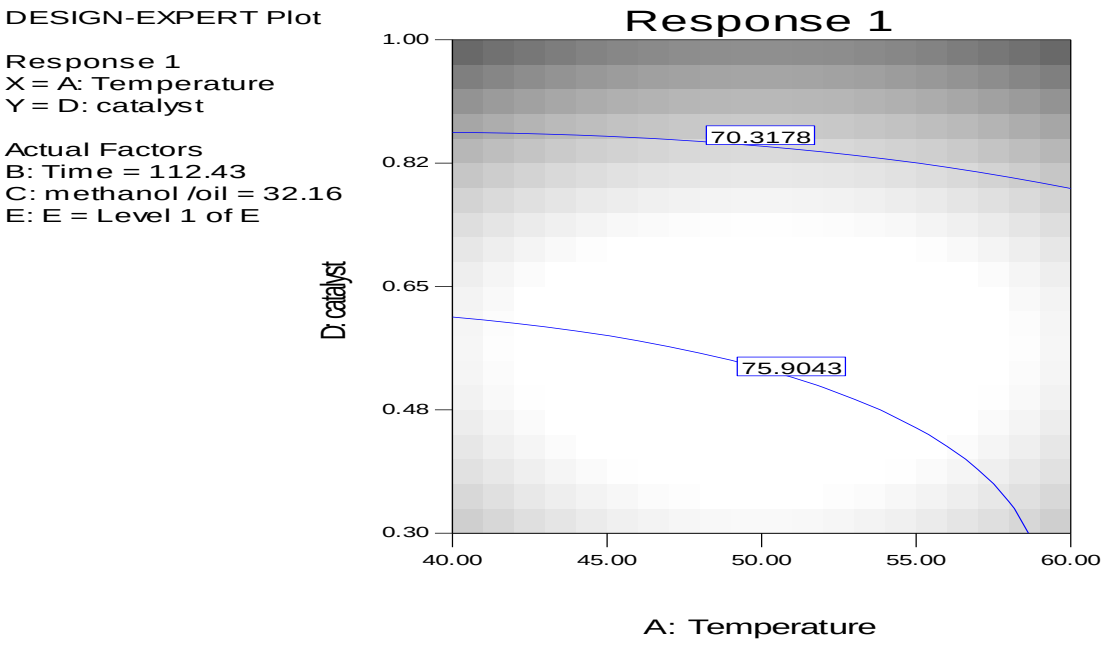

Figure 3: Plot of Catalyst versus Temperature for LLME Yield

CONCLUSION

Seeds oil extracted from Lophira lanceolata was transesterified to fatty acid methyl esters using methanol and sodium hydroxide. The transesterification process was optimized using RSM in 30 experiments. The results indicate that a LLME yield of 85% was achieved with catalyst concentration (0.30mol/dm^3), methanol/oil ratio (9:1) at 50^Oc in 120 min. reaction time. The optimal conditions for *Lophira lanceolata* biodiesel agreed with the prediction model value (83%) by numerical optimization. Physico-chemical parameters of derived LL biodiesel compared favourably with the ASTM standard specifications. Thus, the seeds oil could serve as feedstock for biodiesel production.

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