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RESPONSE SURFACE METHODOLOGY (RSM) A GOOD OPTIMIZER FOR TRANSESTERIFICATION REACTION OF *CHRYSOPHYLLUM ALBIDIUM* SEED OIL TO *CHRYSOPHYLLUM ALBIDIUM* OIL BIODIESEL

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ABSTRACT

In an effort to optimize the reaction conditions of biodiesel production from Chrysophyllum albidium seed oil, Response Surface Methodology (RSM) was applied and the effects of reaction temperature (X_1), catalyst amount (X_2), reaction time (X_3) and methanol/oil molar ratio (X_4), and their reciprocal interactions were examined. A total of 30 experimental runs were generated based on Central Composite Design (CCD) and carried out. A quadratic polynomial was obtained for predicting the transesterification process and the ANOVA test showed the model to be significant ($p<0.05$). The validity of the predicted yield (82.7323 % w/w) was confirmed by carrying out three independent replicates experiments at the following optimized conditions, $X_1 = 41.63$ °C, $X_2 = 0.59$ (wt %), $X_3 = 62.32$ min and $X_4 = 3.00$. The optimal biodiesel yield was validated to be 82. 6702% (w/w), which was well within the range predicted by the model. The fuel properties of Chrysophyllum albidium biodiesel produced were found to be within the ASTM D6751 and DIN EN 14214 biodiesel standards. The fatty acid profile of the biodiesel revealed that the dominant fatty acids were oleic (60.101%), arachidic (2.0145%), palmitic (18.403%) and linoleic (18.942%).

Keywords: *Chrysophyllum albidium* seed oil, Biodiesel, Trans esterification, Optimization, Response surface methodology.

Contribution/ Originality

This study contributes in the existing literature to knowledge. This study uses new estimation methodology for conversion of seed oil to biodiesel. This study originates new formula to improve the yield of biodiesel. This study is one of very few studies which have investigated the use of biomass waste to produced biodiesel. The paper contributes the first logical analysis in optimization of transesterification process. The paper's primary contribution is finding that a

renewable energy can be obtained from biomass waste. This study documents economic impact of using biomass waste to produce biodiesel.

1. INTRODUCTION

The increasing in energy demand around the globe, the depletion of fossil fuels, and the fluctuation of crude oil price in the international market as well as the greater recognition of the unfavorable environmental consequences of fossil fuels has made renewable biofuels an attractive alternative to conventional fuels. Fatty acid methyl esters known as biodiesel which is considered as a substitute of convectional diesel is gaining ground as a biodegradable, environmental friendly, readily available, energy conservation and management [1]. Biodiesel is produced through a chemical process known as "transesterification or alcoholysis" in which there is displacement of alcohol from an ester under acidic or basic catalytic conditions producing free glycerol and fatty acid esters of the respective alcohol [2]. Other process includes hydrotreatment and oleaginous microorganisms [3].

Biodiesel is derived from renewable feedstock like vegetable oils or animal fats. Both edible and non-edible oils have been successfully employed in biodiesel production [4]. In developing nation like Nigeria, crude oil is used mainly to produce conventional diesel. However, there are alternative oil producing crops which can be utilized as feedstocks, such as Moringa oil, Palm oil Sorrel seed oil, Coconut oil, Beniseed oil, Sunflower oil, Melon seed oil, Jatropha oil and Groundnut oil. *Chrysophyllum albidium* seed oil, a new competitor is emerging as a promising feedstock.The *Chrysophyllum albidium* seed oil is rich in both linoleic (36.0%) and oleic (37.6 %) fatty acids [5]. Ugboge and Akukwe [6] reported that there is a potential to use oils from non-utilized oil seeds in management of wounds. Numerous methods exist in oil separation from oilseeds such as mechanical pressing, pressurized solvent extraction, Soxhlet extraction, and ultra-sonic extraction, Aqueous Enzymatic Oil Extraction (AEOE), among others. However, in commercial sense, this oil is not in current widespread use hereby having relatively few competing medicinal and food uses.

Response surface methodology (RSM) is a useful optimization tool, which has been applied in research for optimizing various processes including transesterification reaction of vegetable oils: Beniseed oil [4], *Moringa oleifera* [7], Sorrel oil [8], *Jatropha* oil [9] and cottonseed oil [10] to mention a few. The main advantage of RSM is the ability to reduce the number of experimental runs needed to arrive at optimized and statistically acceptable results. Thus, it saves time and less difficult compared with full-factorial design [11]. In this present study, an effort was made to optimize the process conditions for the transesterification step of

Chrysophyllum albidium seed oil. Fatty acid composition and physicochemical analysis of the produced biodiesel was also carried out with a view to determine it suitability as renewable fuel.

2. METHODOLOGY

2.1. Extraction of *Chrysophyllum Albidium* Seed Oil

The method employed by Betiku, et al. [4] was used for this study. The seed of *Chrysophyllum albidium* were collected from Omu-Aran market, Kwara State, Nigeria. The chaffs were winnowed from the oilseeds and the clean seed was sun dried and then milled into powder. 1-liter Soxhlet apparatus and n-hexane as solvent were used for the oil extraction.

2.2. Experimental Design of *Chrysophyllum Albidium* Biodiesel Production

In this study, central composite rotatable design (CCRD) was employed to optimize the *Chrysophyllum albidium* biodiesel production. Five-level-four factors design was employed, which generated 30 experimental runs. This included 16 factorial points, 8 axial points, and 6 central points to provide information regarding the interior of the experimental region, making it possible to evaluate the curvature effect. Selected factors for transesterification process are reaction time (min); X_1, reaction temperature (°C); X_2, catalyst amount (% wt); X_3, and methanol/oil molar ratio (v/v); X_4. The coded levels of the independent factors are given in Table 1. However, the experiments were randomizes to minimize the effects of unexplained variability in the observed response due to extraneous factors.

Table-1. Factors and their levels for composite central rotatable design

Variable	Symbol	Coded factor levels				
		-2	-1	0	1	2
Reaction temperature (°C)	X_1	40	45	50	55	60
Catalyst amount (wt %)	X_2	0.5	0.6	0.7	0.8	0.9
Reaction time (min)	X_3	40	45	50	55	60
Methanol/oil ratio	X_4	3	4	5	6	7

Source: Response surface methodology (Design-Expert software version 8.0.3.1)

2.3. *Chrysophyllum Albidium* Biodiesel Production Procedure

Alkalis catalyst transesterification reaction was applied for the biodiesel production, due to the low FFA value of the seed oil. A known weight of NaOH pellet was dissolved in a known volume of anhydrous methanol and was quickly transferred into the *Chrysophyllum albidium* oil in the reactor placed on the hot plate magnetic stirrer, the reaction was monitored according to the design variables from CCRD. At the reaction completion, the product was transferred to a separating funnel for glycerol and biodiesel separation. Glycerol was tapped off and the biodiesel left in the separating funnel was washed with ionized water to remove residual catalyst, untapped glycerol, methanol and soap. The washed biodiesel was further dried over heated calcium chloride ($CaCl_2$) powder. The final biodiesel yield was determined using Eqn. 1

$$Biodiesel\ yield\ \%(w/w) = \frac{Weight\ of\ Chrysophyllum\ albidium\ \ oil\ used}{Weight\ of\ biodiesel\ produced} \qquad (1)$$

2.4. Statistical Data Analysis

Chrysophyllum albidium biodiesel production data were analyzed statistically using RSM, so as to fit the quadratic polynomial equation generated by the Design-Expert software version 8.0.3.1 (State-Ease Inc., Minneapolis, USA). To correlate the response variable (Y) to the independent factors, multiple regressions was used to fit the coefficient of the polynomial model. The quality of the fit model was evaluated using test of significance and variance analysis (ANOVA). The fitted quadratic response model is given by Eqn. 2

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i<j}^{k} b_{ij} X_i X_j + e \qquad (2)$$

Where, *Y* is response factor (*Chrysophyllum albidium* biodiesel), b_o is the intercept value, b_i (i = 1, 2, k) is the first order model coefficient, b_{ij} is the interaction effect, and b_{ii} represents the quadratic coefficients of X_i, and *e* is the random error.

2.5. Quality and Fuel Properties of *Chrysophyllum albidium* Biodiesel

Fuel properties namely, moisture content, specific gravity, kinematic viscosity at 40 ^oC, acid value, saponification value, higher heating value, flash point, cloud point and cetane number of *Chrysophyllum albidium* biodiesel were determined following standard methods and compared with American and European standards (ASTM and DIN EN 14214).

3. RESULTS AND DISCUSSION

3.1. Optimization of the Transesterification Step

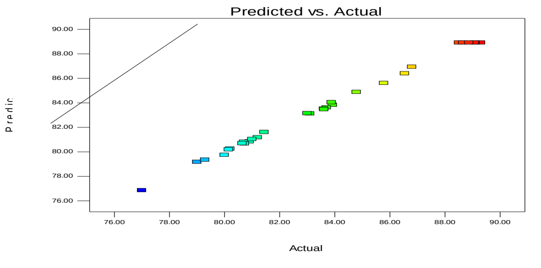
Table 2 depicts the coded factors considered in this study with experimental values, predicted values as well as the residual values obtained. Figure 1 shows the predicted against the actual values. Design Expert 8.0.3.1 software was employed to evaluate and determine the coefficients of the full regression model equation and their statistical significance. Table 3 shows the significance results for every regression coefficient. The results showed that the p-value of the model terms were significant, i.e. $p < 0.05$. In this case, the four linear terms (X_1, X_2, X_3, X_4), four cross-products (X_1X_3, X_1X_4, X_2X_3, X_3X_4) and the four quadratic terms (X_1^2, X_2^2, X_3^2 and X_4^2) were all remarkably significant model terms at 95% confidence level except X_1X_2 and X_2X_4. However, all other model terms were more significant than X_4. In order to minimize error, all the coefficients were considered in the design. Table 4 shows the variance of analysis (ANOVA) of the regression equation. The model F-value of 364.20 implied a high significant for the regression model [12]. The goodness of the fit of a model was checked by the determination coefficient (R^2). R^2 should be at least 0.80 for the good fit of a model [13]. The R^2 of 0.9978 in this case indicated that the sample variation of 99.78% for *Chrysophyllum albidium* biodiesel yield was attributed to the independent factors and only 0.32% of the total variation are not explained by the model. The value of adjusted determination coefficient (Adj. R^2 = 0.9958) was also very high, supporting a high significant of the model [14] and all p-value coefficients were less than 0.0001, which implied that the model proved suitable for the adequate representation of the actual relationship among the selected variables. The lack-of-fit term of 0.9138 was not significant relative to the pure error.

Table-2. Central Composite Design (CCD), Experimental, Predicted and Residual Values for Five – Level-Four Factors Response Surface Analysis

Std order	**X_1 (°C)**	**X_2 (wt %)**	**X_3 (min)**	**X_4**	**Experimental value % (w/w)**	**Predicted value % (w/w)**	**Residual values % (w/w)%**
1	-1	-1	-1	-1	79.00	79.17	-0.17
2	1	-1	-1	-1	80.00	79.75	0.2525
3	-1	1	-1	-1	83.92	83.83	0.093
4	1	1	-1	-1	84.79	84.88	-0.090
5	-1	-1	1	-1	80.90	80.84	0.065
6	1	-1	1	-1	80.20	80.25	-0.054
7	-1	1	1	-1	83.70	80.62	0.081
8	1	1	1	-1	83.60	83.52	0.085
9	-1	-1	-1	1	77.00	76.86	0.14
10	1	-1	-1	1	80.70	80.81	-0.11
11	-1	1	-1	1	81.20	81.18	0.021
12	1	1	-1	1	85.78	85.62	0.16
13	-1	-1	1	1	80.73	80.67	0.058
14	1	-1	1	1	83.61	83.47	0.14
15	-1	1	1	1	83.10	83.12	-0.023
16	1	1	1	1	86.54	86.40	0.14
17	-2	0	0	0	80.15	80.19	-0.036
18	2	0	0	0	83.88	84.04	-0.16
19	0	-2	0	0	79.29	79.35	-0.061
20	0	2	0	0	86.80	86.94	-0.14
21	0	0	-2	0	80.64	80.69	-0.053
22	0	0	2	0	83.00	83.14	-0.14
23	0	0	0	-2	81.00	81.03	-0.033
24	0	0	0	2	81.44	81.60	-0. 61
25	0	0	0	0	88.50	88.92	-0.42
26	0	0	0	0	89.30	88.92	0.38
27	0	0	0	0	89.10	88.92	0.18
28	0	0	0	0	88.65	88.92	-0.27
29	0	0	0	0	89.07	88.92	0.15
30	0	0	0	0	88.87	88.92	-0.045

Source: Response surface methodology-CCD- (Design-Expert software version 8.0.3.1)

Figure-1. Plot of predicted yield against the experimental yield



Source: Design-Expert software version 8.0.3.1

Table-3. Test of Significance for Every Regression Coefficient of CCD

Source	Sum of Squares	df	Mean Square	F-Value	p-value
X_1	22.90	1	22.90	425.01	< 0.0001
X_2	86.30	1	86.30	1645.36	< 0.0001
X_3	9.02	1	9.02	171.90	< 0.0001
X_4	0.49	1	0.49	9.35	0.0080
X_1X_2	0.23	1	0.23	4.35	0.0546
X_1X_3	1.34	1	1.34	25.54	<0.0001
X_1X_4	11.44	1	11.44	218.14	< 0.0001
X_2X_3	3.51	1	3.51	66.85	< 0.0001
X_2X_4	0.11	1	0.11	2.11	0.1671
X_3X_4	4.63	1	4.63	88.34	< 0.0001
X_1^2	79.30	1	79.30	1511.89	< 0.0001
X_2^2	57.10	1	57.10	1088.63	< 0.0001
X_3^2	83.91	1	83.91	1599.83	< 0.0001
X_4^2	98.92	1	98.92	1886.00	< 0.0001

Source: Response surface methodology-CCD- (Design-Expert software version 8.0.3.1)

Table-4. Analysis of Variance (ANOVA) of Regression Equation

Source	**Sum of squares**	**df**	**Mean Square**	**F-value**	**p-value**
Model	364.20	14	26.01	495.98	< 0.0001
Residual	0.79	15	0.052		
Lack of Fit	0.34	10	0.084	0.37	0.9138
Pure Error	0.45	5	0.090		
Cor Total	364.98	29			
			R-Sq = 99.78%,		R-Sq(adj) = 99.58%

Source: Response surface methodology-CCD- (Design-Expert software version 8.0.3.1)

Table-5. ANOVA for Response Surface Quadratic Model for Intercept.

Factors	**Coefficient Estimate**	**df**	**Standard Error**	**95%CI Low**	**95%CI High**	**VIF**
Intercept	88.92	1	0.093	88.72	89.11	-
X_1	0.96	1	0.047	0.86	1.06	1.00
X_2	1.90	1	0.047	1.80	2.00	1.00
X_3	0.61	1	0.047	0.51	0.71	1.00
X_4	0.14	1	0.047	0.043	0.24	1.00
X_1X_2	0.12	1	0.057	-0.00266	0.24	1.00
X_1X_3	-0.29	1	0.057	-0.41	-0.17	1.00
X_1X_4	0.85	1	0.057	0.72	0.97	1.00
X_2X_3	-0.47	1	0.057	-0.59	-0.35	1.00
X_2X_4	-0.083	1	0.057	-0.21	0.039	1.00
X_3X_4	0.54	1	0.057	0.42	0.66	1.00
X_1^2	-1.70	1	0.044	-1.79	-1.61	1.05
X_2^2	-1.44	1	0.044	-1.54	-1.35	1.05
X_3^2	-1.75	1	0.044	-1.84	-1.66	1.05
X_4^2	-1.90	1	0.044	-1.99	-1.81	1.05

Source: Response surface methodology-CCD- (Design-Expert software version 8.0.3.1)

The final equation in terms of coded factors for the response surface quadratic model is expressed in Eqn. (3).

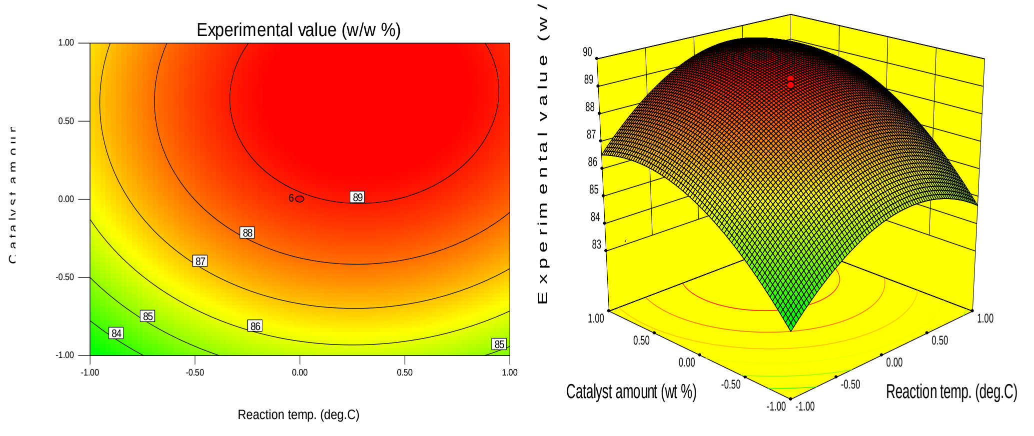
$$Y(w/w\ \%) = 88.92 + 0.96X_1 + 1.90X_2 + 0.61X_3 + 0.14X_4 + 0.12X_1X_2 - 0.29X_1X_3 + 0.85X_1X_4 - 0.457X_3 - 0.083X_2X_4 + 0.54X_3X_4 - 1.70X_1^2 - 1.44X_2^2 - 1.75X_3^2 - 1.90X_4^2 \quad (3)$$

All the X_1, X_2, X_3, X_4, X_1X_2, X_1X_4 and X_3X_4 had positive effect on the *Chrysophyllum albidium* biodiesel yield while the rest had negative influence on the yield (Table 4).

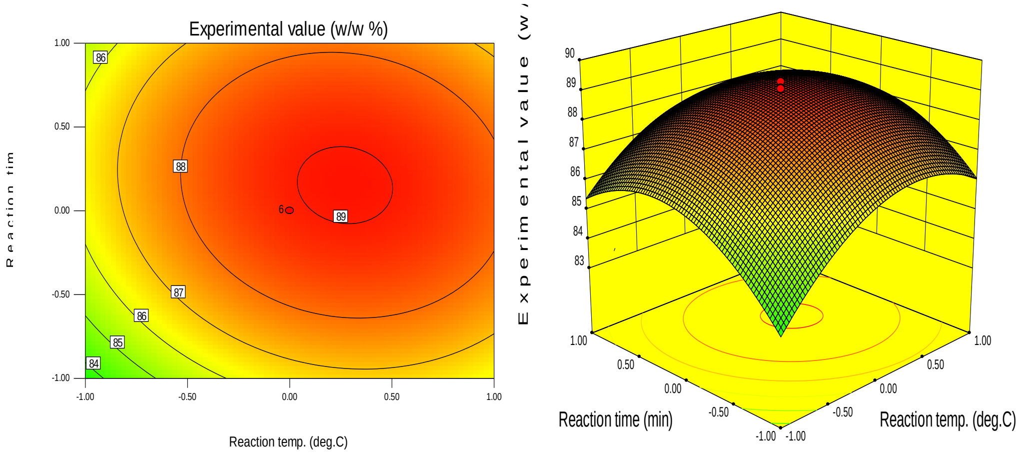
In general, the contour and 3D response surface plot is a graphical representation of the regression equation for the optimization of the reaction variables. Figure 2(a-f) described the contours and 3D surfaces linked to the effect of two variables on the yield of *Chrysophyllum albidium* biodiesel. The curvatures nature of 3D surfaces in Fig. 2b, c, e and f indicated the mutual interaction of the reaction time with reaction temperature, methanol/oil molar ratio with reaction temperature, methanol/oil molar ratio with catalyst amount and methanol/oil molar ratio

Figure-2. Contour and 3D response surface plots

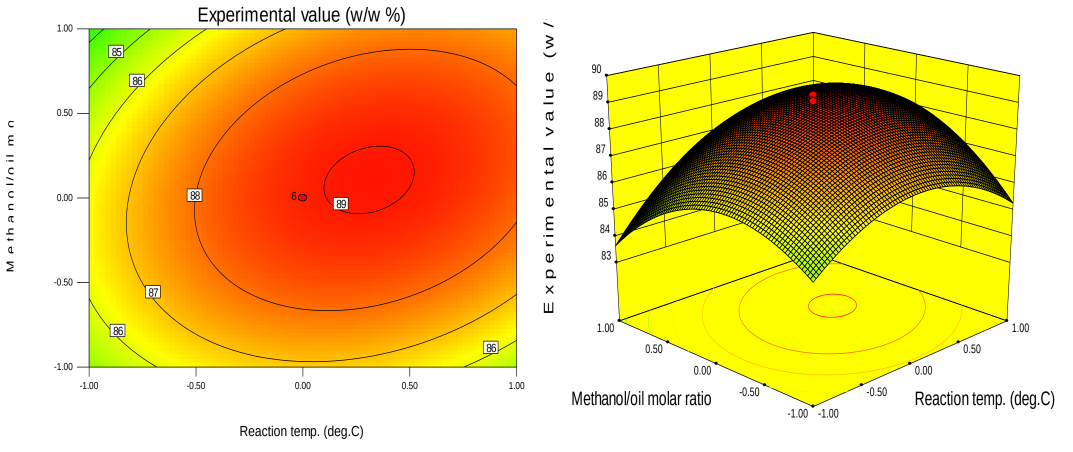
(a)



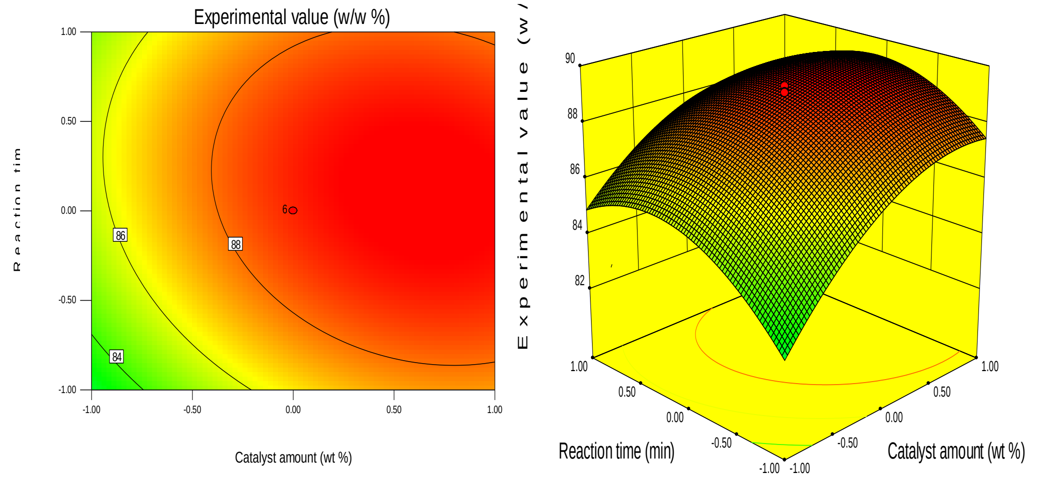
(b)



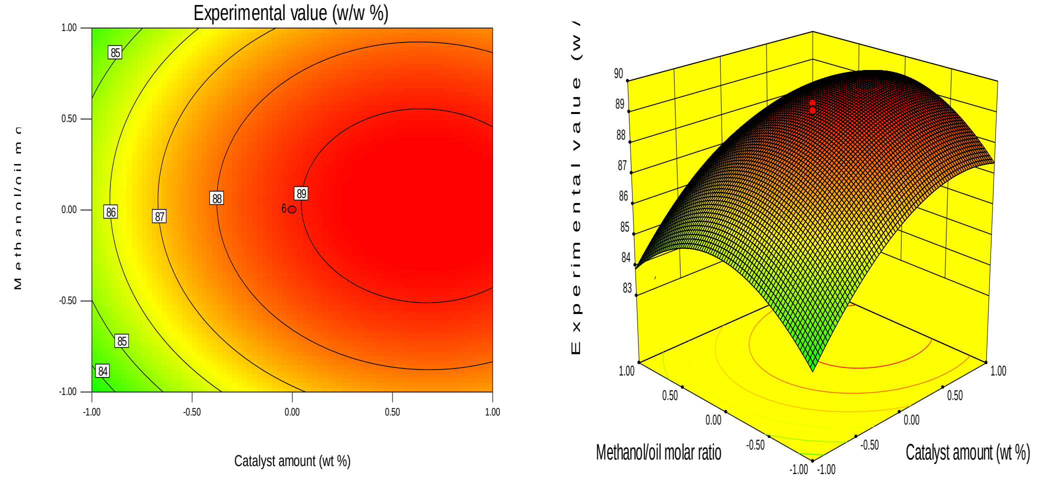
(c)


Experimental value (w/w %)
Reaction temp. (deg.C)
Methanol/oil molar ratio
Reaction temp. (deg.C)

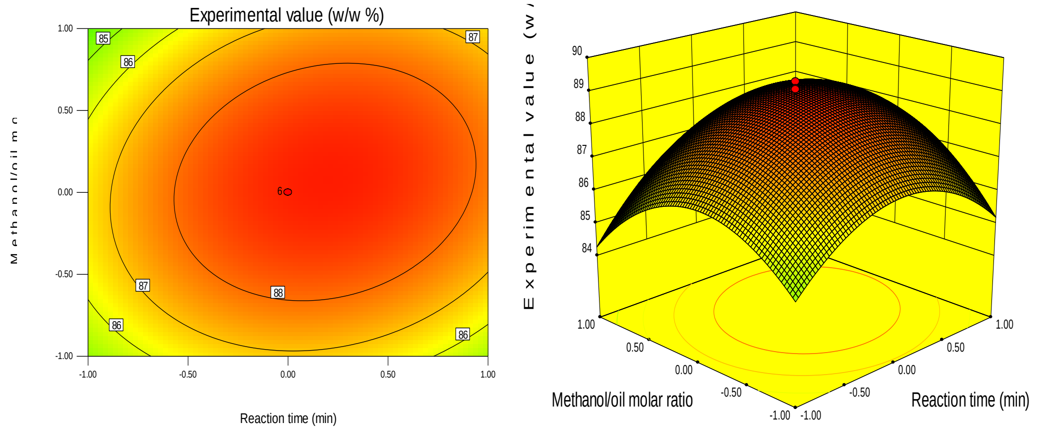
(d)


Experimental value (w/w %)
Catalyst amount (wt %)
Reaction time (min)
Catalyst amount (wt %)

(e)


Experimental value (w/w %)
Catalyst amount (wt %)
Methanol/oil molar ratio
Catalyst amount (wt %)

(f)



with reaction time, respectively. Meanwhile, there was a moderate interaction examined between catalyst amount with reaction temperature (Fig. 2a), but no interaction was observed between reaction time and catalyst amount as represented in Fig.2d. The optimal condition predicted by the model were reaction temperature of 41.63 °C, catalyst amount of 0.59 (%wt.), reaction time of 62.32 min and methanol/oil molar ratio of 6.21which gave 82.7323% (w/w). Using these optimal condition values for three independent experimental replicates, an average *Chrysophyllum albidium* biodiesel yield of 82. 6702% (w/w) was achieved, which was well within the range predicted by the model.

Table-6. Properties of *Chrysophyllum albidium* biodiesel in Comparison with Biodiesel Standards

Parameters	***Chrysophyllum albidium* biodiesel**	**ASTM D6751**	**DIN EN 14214**
Moisture content %	<<<1ppm	< 0.03	0.02
Specific gravity@40 °C	0.846	0.86-0.90	0.85
Viscosity at 40 °C (mm^2/s)	4.00	1.9-6.0	3.5-5.0
Iodine Value (g I_2/100g)	68.50	-	120 max
Acid Value	0.54	< 0.80	0.5 max
Saponification value (mg KOH/g oil)	215.40	-	-
Higher heating value (MJ/kg)	39.57	-	-
Diesel index	66.04	50.40 min	-
API	45.38	36.95	-
Cetane number	56.23	47 min	51 min
Aniline point	145.53	331.00	-
Pour Point °C	-18	Not specific	Not specific.
Cloud Point °C	+6	Report	Not specific.
Flash Point °C	158	93 min	120 min

Source: ASTM D6751 and DIN EN 14214 Biodiesel Standard

3.2. Quality and Fuel Properties of *Chrysophyllum Albidium* Biodiesel

Table 6 shows the *Chrysophyllum albidium* biodiesel properties in comparison with ASTM biodiesel and DIN EN 14214 standards. All the tested characteristics and fuel properties of the *Chrysophyllum albidium* biodiesel satisfied both the ASTM D 6751 and DIN EN 1424 standards. Gas chromatography analysis of fatty acids present in the *Chrysophyllum albidium* biodiesel is shown in Table 7. The results indicated *Chrysophyllum albidium* biodiesel was highly unsaturated with dominant fatty acids such as oleic (60.101%), arachidic (2.0145%), palmitic (18.403%) and linoleic (18.942%).

Table-7. Fatty Acids Compositions of the *Chrysophyllum albidium* biodiesel Produced

Fatty acid	Compositions %
Palmitic acid (C16:0)	18.403
Palmitoleic acids (C16:1)	0.045
Stearic acids (C18:0)	0.323
Oleic acids (C18:1)	60.101
Linoleic acids (C18:2)	18. 942
Linolenic acid (C18:3)	0.065
Myristic acid (C14:0)	0.055
Arachidonic acid (C20:4)	2.045
Other	0.021
Total	100

Source: Gas chromatography analysis

4. CONCLUSIONS

In this study, experiments were conducted using RSM to determine the effects of four reaction factors namely reaction temperature, reaction time, catalyst concentration and methanol/oil molar ratio on *Chrysophyllum albidium* biodiesel yield in the transesterification of the *Chrysophyllum albidium* seed oil. The maximum *Chrysophyllum albidium* biodiesel conversion yield was validated to be 82. 6702% (w/w) at the reaction temperature of 62.32 °C, a catalyst amount of 0.59 wt. %, methanol/oil molar ratio of 3 and reaction time of 51 min. The fuel properties of the *Chrysophyllum albidium* biodiesel were within the ASTM D6751 and DIN EN 14214 specifications.

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