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TRANSESTERIFICATION OF *CASO* WITH LOW AMOUNT OF FREE FATTY ACIDS AND ITS OPTIMIZATION

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ABSTRACT

This study revealed the application of ANN as a tool for optimization of transesterification of Chrysophyllum albidium seed oil (CASO) to Chrysophyllum albidium oil biodiesel (CAOB). 30 experimental runs were generated and used to determine the effects of four reaction variables namely reaction temperature, reaction time, catalyst amount and methanol/oil molar ratio on CAOB yield. It was noted that the highest observed yield obtained in this study was 89.30% (w/w) at the following variable conditions; reaction temperature 60 °C, catalyst amount of 0.7 (wt. %), reaction time of 50 (min) and methanol/oil molar ratio of 5. The coefficient of determination R^2 and the adj. R^2 were found to be 0.99919 and 0.998439, respectively. The root mean square error (RMSE) of 0.14261 was obtained. Meanwhile, the qualities and fuel properties of CAOB produced were found to be within the ASTM D6751 and DIN EN 14214 biodiesel standards. The fatty acid profile of the CAOB revealed that CAOB is highly unsaturated (78.505%). Hence, the study established that CASO is a good alternative seed oils for fuel production which are renewable, cheap and environmental friendly.

Keywords: *Chrysophyllum albidium* seed oil, Biodiesel, Transesterification, Optimization, Artificial neural network, Fatty acid profile.

Contribution/ Originality

This study is one of very few studies which have investigated the use of CASO to produced biofuel.

1. INTRODUCTION

The urgent needs for a more environmentally friendly, biodegradable, cost effective and readily available source of fuel is not only borne out of concern to protect the environment from the challenges pose by fossil fuel, but also due to the fluctuation of crude oil price in the international market as a results of ever increasing in human population. Therefore, interest has been placed on conversion of agricultural waste (biomass waste) to an alternative fuels such as biodiesel, biogas, bioethanol to mention but a view. Biodiesel is considered as a substitute for convectional diesel is gaining ground as a biodegradable, environmental friendly, readily available, energy conservation and management [1, 2]. Although, biodiesel can be produced through various chemical processes such as hydrotreatment, oleaginous microorganisms or transesterification. The transesterification process is the easiest, cost effective and less time consuming [3].

In Nigeria, crude oil is mainly used to produce conventional diesel. However, there are alternative oil producing crops from agricultural waste which can be utilized as feedstock, 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 (CASO), a new competitor is emerging as a promising feedstock. CASO is rich in both linoleic (36.0%) and oleic (37.6 %) fatty acids [4]. [5], reported that there is a potential to use oils from non-utilized oil seeds in management of wounds. In commercial sense, this oil is not in current widespread use hereby having relatively few competing medicinal and food uses.

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. But, Soxhlet extraction proved to be the cheapest method out of all methods.

In the meantime, optimization is an important aspect in the transesterification, biotransformation process [6]. Single variable optimization method (conventional optimization) is not only time- consuming and tiresome but also unable to describe the complete effects of the parameters in the process, and ignores the interactions of results [7, 8]. Classical optimization techniques, such as artificial neural networks (ANN) is a fast and consistent method which always decreased the total number of experiments, fixing short lists significant factors and process by regarding the reciprocal interactions among the variables factor and to give an estimate of the combined effects on these variables.

ANN is an artificial learning tool for optimization [9]. It power exist on its capability to learn from historical process data and approximate linear and non-linear functions [10]. This paper explores the use of ANN to optimize the process conditions for the transesterification step of CASO. Fatty acid profile and physicochemical analysis of the produced CAOB were also determined with a view to determine it suitability as renewable fuel.

2. METHODOLOGY

2.1. CASO Extraction

The method employed by [3] was used for this study. The seeds of *Chrysophyllum albidium* (CA) were collected from Omu-Aran market, Kwara State, Nigeria. The seeds were separated from the pericarp by manual breaking of the hard brownish pericarp. The obtained white seeds were sun dried for four days and then milled into powder. 1-liter Soxhlet apparatus and n-hexane as solvent were used for the oil extraction.

2.2. ANN Design for Experimental Production of CAOB

In developing ANN model, central composite rotatable design an allied of response surface methodology was used to generate five-level-four-factors design which produced 30 experimental runs. Selected factors for transesterification process were reaction time (min); X_1, reaction temperature (^oC); $X_{2,}$ 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. Since the performance of ANN is heavily influenced by its network structure, the learning algorithms used was QuickProp (QP), multilayer connection type used was multilayer normal feed forward (MNFF), three total layer numbers was used and the node number of input layer was four. For the output layer, Node Number was 1, the transfer function was Tanh and the slope of transfer function and the hidden Layer was 1, the node number was 4, transfer function was also Tanh and slope of transfer function was also 1 (Fig. 1). Meanwhile, the optimum ANN structure was determined first using mean square error (RMSE) approach. The higher coefficient R^2 was determined; the variable analysis also was conducted to study the effects of variables towards the CAOB production using 3D curvature's surface plots. A hybrid ANN model was used in conducting process optimization.

Figure-1. Network Structure with Four Transfer Functions

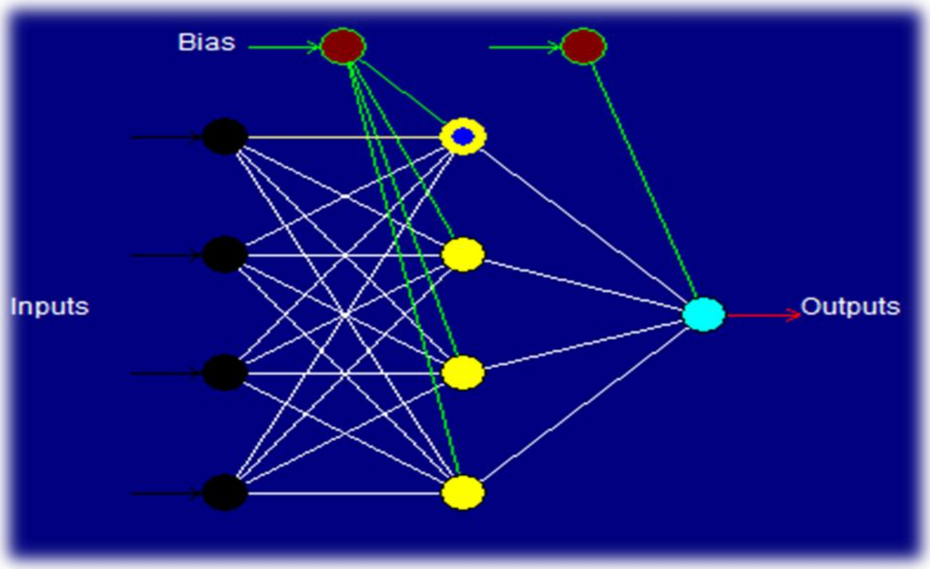


Table-1. Factors and their levels for composite central rotatable design

Variable/inputs	Symbols	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

2.3. CAOB Production Procedure

Based on the low FFA of the CASO oil [6], alkalis catalyst transesterification method was used for CAOB production. A known weight of NaOH pellet was dissolved in a known volume of anhydrous methanol and was quickly transferred into the CASO in the reactor placed on the hot plate magnetic stirrer, the reaction was monitored according to the design variables from CCRD. At the completion of the reaction, 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 (CAOB) yield was determined using Eqn. 1

$$CAOB\ yield\ \%(w/w) = \frac{Weight\ of\ CASO\ used}{Weight\ of\ CAOB\ produced} \quad (1)$$

2.4. Fatty Acid Compositions and Fuel Properties of CAOB

Fatty acid composition of the CAOB was determined using gas chromatography (HP6890 powered with HP ChemStation Rev. A 09.01 [1206] Software). Meanwhile, fuel properties namely, moisture content, specific gravity, kinematic viscosity at 40 °C, acid value, saponification value, higher heating value, flash point, cloud point and cetane number of CAOB were determined following standard methods and compared with American and European standards (ASTM and DIN EN 14214).

3. DISCUSSION OF RESULTS

3.1. Optimization of the Trans esterification Step

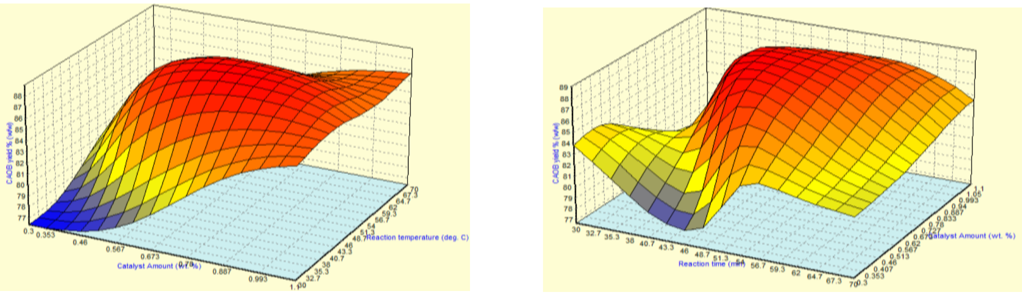
Depict in Table 2 are the coded factors, observed CAOB, calculated CAOB yields and difference CAOB obtained in this study the by ANN software. The highest residual difference between the observed yield and calculated yield was 0.41493. This showed that observed yield was well within the range predicted by the ANN software. Meanwhile, the effects of unexplained variability in the CAOB response due to extraneous factors were minimized by randomizing the order of experiments. Considering the large QP-values (the number of repetition) and low corresponding RMSE-values (root mean squared error) which were used to compared the predicted values of CAOB yield, shows that all the model terms are significant and have very strong effects on the CAOB yield. The goodness of fit of the model was checked by the coefficient of determination (R^2). R^2 should be at least 0.80 for the good fit of a model [11]. In this case, the R^2 value of 0.99919 indicated that the sample variation of 99.919% for the CAOB production is attributed to the independent factors (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 value of the adjusted determination coefficient (Adj. R^2) was found to be 0.99839 and the RMSE was obtained to be 0.14261.

Generally, the 3D curvatures' plots are graphical representations of the regression equation for the optimization of the reaction variables and they are represented in Figure 2. The curvatures' nature of 3D surfaces in Figure 2(a-f), suggested mutual interaction of catalyst amount with reaction temperature, reaction time with catalyst amount, methanol/oil molar ratio with reaction time, reaction time with catalyst amount, methanol/oil molar ratio with catalyst amount, methanol/oil molar ratio with reaction time, respectively.

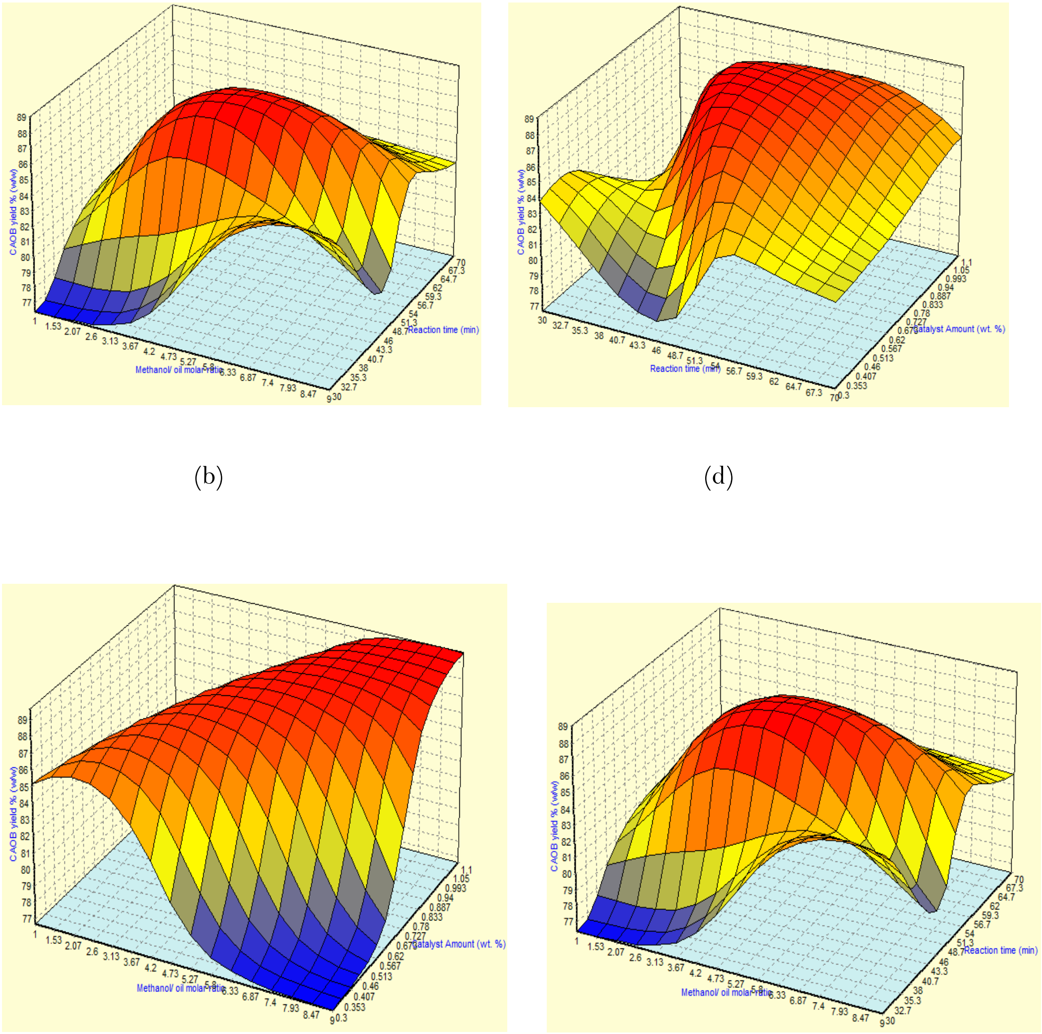
Table-2. Observed, Calculated and Difference values for Five-Level- Four Factors ANN

Std. runs	X_1 (°C)	X_2 (% wt.)	X_3 (min)	X_4	Observed/Output CAOB (w/w)	Calculated CAOB (w/w)	Diff. CAOB (w/w)
1	-1	-1	-1	-1	79.00	79.153	0.15312
2	1	-1	-1	-1	80.00	79.993	0.0069135
3	-1	1	-1	-1	83.92	83.939	0.019358
4	1	1	-1	-1	84.79	84.775	0.014721
5	-1	-1	1	-1	80.90	80.916	0.016008
6	1	-1	1	-1	80.20	80.2	9.011E-5
7	-1	1	1	-1	83.70	83.87	0.16973
8	1	1	1	-1	83.60	83.599	0.00072723
9	-1	-1	-1	1	77.00	76.975	0.024521
10	1	-1	-1	1	80.70	80.578	0.12182
11	-1	1	-1	1	81.20	81.221	0.020868
12	1	1	-1	1	85.78	85.745	0.034815
13	-1	-1	1	1	80.73	80.735	0.0052757
14	1	-1	1	1	83.61	83.591	0.018561
15	-1	1	1	1	83.10	83.131	0.031199
16	1	1	1	1	86.54	86.367	0.17338
17	-2	0	0	0	80.15	79.868	0.28183
18	2	0	0	0	83.88	83.987	0.10676
19	0	-2	0	0	79.29	79.303	0.012797
20	0	2	0	0	86.80	86.764	0.03639
21	0	0	-2	0	80.64	80.679	0.038761
22	0	0	2	0	83.00	82.995	0.0048639
23	0	0	0	-2	81.00	80.887	0.11324
24	0	0	0	2	81.44	81.602	0.16186
25	0	0	0	0	88.50	88.915	0.41493
26	0	0	0	0	89.30	88.915	0.38507
27	0	0	0	0	89.10	88.915	0.18507
28	0	0	0	0	88.65	88.915	0.26493
29	0	0	0	0	89.07	88.915	0.15507
30	0	0	0	0	88.87	88.915	0.044927

Figure-2. 3D curvatures' plots



(a) (b)



(b)

(d)

(e)

(f)

3.2. Quality and Fuel Properties of CAOB

Table 3 showed the properties of the CAOB in disparity with ASTM biodiesel and DIN EN 14214 standards. The qualities and fuel properties of the CAOB satisfied both the ASTM D 6751 and DIN EN 1424 standards. Meanwhile, Gas chromatography analyses of fatty acids present in the CAOB are revealed in Table 4. The results showed that CAOB is highly unsaturated with dominant fatty acids such as oleic (60.101%), arachidic (2.0145%), palmitic (18.403%) and linoleic (18.942%).

Table-3. Properties of CAOB in comparison with biodiesel standards

Para	CAOB	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

Table-4. Fatty acids profile of the CAOB 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

4. CONCLUSIONS

This study revealed that CASO proved to be a good alternative feedstock for biodiesel (CAOB) production that are renewable, cost effective and environmental friendly. The work also revealed that ANN proved to be a good optimization tool in CAOB production. Experiments were conducted to determine the effects of four reaction factors, such as reaction temperature, reaction time, catalyst concentration and methanol/oil molar ratio on CAOB yield. Experimental optimization revealed that the root mean square error (RMSE) obtained was 0.14261. The coefficient of determination R^2 and the adj. R^2 were found to be 0.99919 and 0.998439, respectively. It was also noted that the highest observed yield obtained was 89.30% (w/w) at the following variable conditions, reaction temperature 60 °C, catalyst amount of 0.7 (wt.%), reaction time of 50 (min) and methanol/oil molar ratio of 5. Fatty acid profile revealed that CAOB is highly unsaturated with dominant fatty acids such as oleic (60.101%), arachidic (2.0145%), palmitic (18.403%) and linoleic (18.942%). The quality and fuel properties of the CAOB were well within the ASTM D6751 and DIN EN 14214 standard specifications.

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