Journal of Multidisciplinary Engineering Science and Technology (JMEST)
ISSN: 2458-9403
Vol. 3 Issue 11, November - 2016

Application Of Response Surface Methodology In The Optimization Of Biodiesel Production From Microalgae Oil

*** Kamen, F.L; Ejim, I.F; Onyelucheya, O.E; Opebiyi, S.O. and Uzondu, F.N.**
Department of Chemical Engineering, Federal University of Technology, Owerri, Imo State, Nigeria.
* Corresponding Author; E-mail: felyleby@yahoo.com

***Abstract*—In this study, response surface methodology was used to optimize the production of biodiesel from microalgae oil. The effects of five reaction variables: methanol/oil molar ratio (X_1), catalyst concentration (X_2), temperature (X_3), time (X_4), and mixing rate (X_5) on transesterification of crude microalgae oil were investigated. A Central Composite Design (CCD) consisting five factors at five levels was used to analyze the transesterification of microalgae oil. A Second order quadratic polynomial model was deduced to predict the Methyl Ester yield and the ANOVA test showed the developed model to be significant ($P < 0.05$). The adjusted R^2 values of 0.9078 indicated that the regression model was a good one. RSM was also successfully applied to assess the effects of multiple variables, including the alcohol/oil molar ratio, catalyst concentration, temperature, rate of mixing, and reaction time, for the production of biodiesel from the crude algae oil. A statistical model predicted that optimal conditions are : Methanol/Oil molar ratio, 6.1; temperature, 55°C; time, 45min; catalyst concentration, 1.0%; and rate of mixing, 300rpm. These optimized conditions were validated and actual biodiesel yield of 94.362% confirming the efficacy of the model.The physicochemical analysis of the biodiesel oil from microalgae indicated it is comparable with commercial diesel.**

Keywords—Microalgae oil, Biodiesel, Response Surface Methodology.

I. INTRODUCTION

The need for fuel in our world today is so alarming and today's supply of fuels worldwide is almost completely dependent on petroleum. Biofuel production has recently become a topic of intense interest due to increased concern regarding limited petroleum-based fuel supplies and the contribution of the use of these fuels to atmospheric CO_2 levels. Biofuel research is not just a matter of finding the right type of biomass and converting it to fuel, but it must also find environmentally and economically sound uses for the by-products of biofuel production [1]. Photosynthetic microorganisms like cyanobacteria and microalgae can potentially be employed for the production of biofuels in an economically effective and environmentally sustainable manner and at rates high enough to replace a substantial fraction of our society's use of fossil fuels [2].

Microalgae commonly double their biomass within 24 hours (h), and this duration during the exponential growth phase can be as short as 3.5 h [3],[4]. The Optimum conditions for the transesterification of vegetable oils to produce methyl ester were determined by the previous researchers which yielded a maximum conversion of various oils to the methyl esters. The use of acid catalysts has been found to be useful for pre-treating high free fatty acid feedstocks but the reaction rates for converting triglycerides to methyl esters are very slow. Fatty acid contents are the major indicators of the properties of biodiesel since the amount and type of fatty acid content in the biodiesel largely determine its viscosity. The reaction is at equilibrium. Industrial processes use 6 mol of methanol for each mole of triglyceride. Yield of methyl esters exceeds 98% on a weight basis [5]. Alkali- catalyzed transesterification is carried out at approximately 60 °C.

Producing biodiesel from algae provides the highest net energy because converting oil into biodiesel is much less energy-intensive than methods for conversion to other fuels. This characteristic has made biodiesel the favorite end-product from algae. Producing biodiesel from algae requires selecting high-oil content strains, and devising cost effective methods of harvesting, oil extraction and conversion of oil to biodiesel.

Therefore, the objectives of our work were to evaluate the effects of the reaction parameters of temperature, catalyst concentration and molar ratio of methanol to oil reaction time and stirring rate on the biodiesel yield and to optimize the reaction conditions using Response Surface Methodology. The properties of produced methyl ester were analyzed and the quality of biodiesel was compared with petro-diesel. Response surface methodology is a collection of statistical and mathematical techniques useful to develop, improve and optimize process and product

largely applied in industry [6], it addresses this issue by providing: (1) an understanding of how the test variables affect the selected process response; (2) the determination of the interrelationships among the test variables; (3) and the characterization of the combined effect that all influential test variables may have on the process response. Because of these advantages, RSM has been increasingly involved in biodiesel production. The use of Central composite design as an experimental design to fit a second-order polynomial model helps to identify response surface over explanatory variables experimental space. A response surface plotted 3D plot provides a clear visual of the parameters interactions for better understanding.

Response surface methodology was applied to evaluate the effects of three-level-three-factors and their interaction on algae oil yield and respective properties.

II. METHODOLOGY

a. Designing of Experiments

A 3-level- 5-factor experiment central composite design (CCD) shown in Table 1 was used to examine the effects of methanol/oil molar ratio, catalyst concentration (%), temperature (°C), time (min), and rate of mixing (rpm), on yield of methyl ester. The CCD consisted of 34 experimental runs (25 fractional factorial points, 1 axial point, and 8 replicated center points) and provided sufficient information to fit a full second-order polynomial model. The Design Expert 9.0 software was used to analyze the transesterification data for developing response equations, for analysis of variance (ANOVA), to generate surface plots and determine optimum conditions using its optimization tool.

TABLE: 1
3 – LEVEL – 5 – FACTOR EXPERIMENTAL DESIGN

Level		-1	0	1
Methanol/Oil Molar ratio	X_1	4/1	6/1	8/1
Catalyst/Oil (wt %)	X_2	0.5	1.0	1.5
Temperature (^oC)	X_3	45	55	65
Time (Hr)	X_4	30	45	60
Rpm	X_5	250	300	350

The center point of the methanol/oil molar ratio was set at 6:1, the upper level of temperature was 55°C, catalyst amount (catalyst/oil) of 1.0wt % was chosen as the upper level of catalyst concentration with center points for the reaction time and rate of mixing placed at 45min and 300rpm respectively. The function was approximated by a second degree polynomial equation:

$$\boldsymbol{Y} = \beta o + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i \neq j \neq 1}^{n} \beta_{ij} X_i X_j \quad 1.0$$

Where Y is % methyl ester yield, xi and x j are the independent study factors, and β_0, β_i, β_{ii}, and B_{ij} are intercept, linear, quadratic, and interaction constant coefficients, respectively. An alpha (α) level of 0.05 was used to examine the statistical significance of the fitted polynomial model. Confirmatory experiments were carried out to validate the model using combinations of independent variables that were not a part of the original experimental design but within the experimental region.

b. Experiments and Methods

i. Acid Pre-treatment and Biodiesel Production

Result from previous research [7] was used for the esterification process in this experiment. 0.75% v/v of Sulphuric acid volume-to-oil and 58ml of methanol in 100ml of oil representing 0.58:1 Methanol-to-Oil ratio, was used in the esterification process before adding 600g of methanol, 1.0g of sodium hydroxide solution (NaOH) into a 100g of acid-treated algae oil which was heated to about 55°C, agitated in the blender and maintained for 45 minutes at 300rpm respectively to produce the methyl ester. The reaction mixture was poured from the blender into a separating funnel with a tap. This was allowed to stand overnight while phase separation occurred by gravity settling. The FAME was carefully decanted from the equilibrium mixture into the PET bottle leaving impurities and glycerol.

After separating the biodiesel, hot distilled water of 250ml (10% by volume) was sprayed over the surface of biodiesel and stirred gently. The lower layer was discarded and yellow colour layer biodiesel was separated. Biodiesel was dried by evaporating the water with an electric oven and finally kept under the running fan for several minutes (>30 min) to reduce the temperature.

i. *Physicochemical properties*

The Fatty Acid Methyl Ester was taken to Pymotech Research Centre and laboratories, Abakpa. Nike, Enugu for further analysis before storage using an air free tight bottle so as to avoid reacting with air.

RESULTS AND DISCUSSION

a. Statistical Analysis of Data and Response Equation for Transesterification.

The effect of catalyst concentration, temperature, time, methanol/oil molar ratio and speed on the oil yield (Y) is as shown on Table 2 this was subsequently used to fit the response equations for oil yield. The coefficient of determination (R^2) for the responses, yield was 0.9078. The coefficients of determination were high for response surfaces, and indicated that the fitted quadratic models accounted for more than 90% of the variance in the experimental data. Base on p-values, the regression coefficients that was significant at $p < 0.0001$ were selected for the models that resulted in equations (1). Analysis Of Variance (ANOVA) was conducted to evaluate the adequacy and consistency of the models using f-statistic.

The Model F-value of 17.24 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to disturbance. Values of "Prob > F" less than 0.0500 indicate model terms are significant. Values greater than 0.1000 indicate the model terms are not significant. The "Lack of Fit F-value" of 4015.43 implies the Lack of fit is significant. There is only a 0.01% chance that a "Lack of Fit F-value" this large could occur due to disturbance.

TABLE 2
CCD EXPERIMENTAL MATRIX FOR THE FRACTIONAL FACTORIAL DESIGN

Run	X_1	X_2	X_3	X_4	X_5	Yield %	Predicted Value	Residual
1	0	0	0	0	0	98.77	94.36	4.41
2	1	-1	1	1	-1	40.87	38.63	2.24
3	0	0	0	0	0	98.76	94.36	4.40
4	0	0	0	0	1	88.66	86.08	2.58
5	0	0	-1	0	0	82.44	82.57	-0.13
6	1	-1	1	-1	1	16.92	18.50	-1.58
7	1	-1	-1	-1	-1	43.45	44.36	-0.91
8	0	-1	0	0	0	90.8	94.27	-3.47
9	-1	-1	1	1	1	79.47	77.69	1.78
10	-1	1	1	1	-1	57.26	53.54	3.72
11	1	-1	-1	1	1	30.76	31.30	-0.54
12	0	0	0	0	0	98.89	94.36	4.53
13	-1	1	1	-1	1	24.53	24.63	-0.10
14	0	1	0	0	0	88.44	93.65	-5.21
15	-1	-1	-1	-1	1	60.93	62.30	-1.37
16	0	0	0	0	0	98.66	94.36	4.30
17	-1	1	-1	1	1	45.93	44.99	0.94
18	-1	1	-1	-1	-1	74.55	73.98	0.57
19	1	1	-1	1	-1	49.3	47.90	1.40
20	0	0	0	0	0	98.77	94.36	4.41
21	0	0	0	0	0	98.31	94.36	3.95
22	1	0	0	0	0	81.26	80.55	0.71
23	0	0	1	0	0	70.67	79.23	-8.56
24	1	1	-1	-1	1	51.83	54.25	-2.42
25	0	0	0	-1	0	77.31	73.27	4.04
26	1	1	1	1	1	45.6	44.87	0.73
27	0	0	0	0	0	98.72	94.36	4.36
28	0	0	0	0	-1	84.88	96.14	-11.26
29	-1	-1	1	-1	-1	76.83	75.42	1.41
30	1	1	1	-1	-1	52.48	52.12	0.36
31	-1	-1	-1	1	-1	55.52	53.07	2.45
32	-1	0	0	0	0	87.86	97.26	-9.40
33	0	0	0	1	0	58.85	71.57	-12.72
34	0	0	0	0	0	98.75	94.36	4.39

$$Yield = 94.36 - 8.36X_1 - 0.31X_2 - 1.67\,X_3 - 0.85X_4 - 5.03X_5 + 8.61X_1X_2 - 1.29X_1X_3 + 0.032X_1X_4 + 0.77X_1X_5 - 4.07X_2X_3 - 0.86X_2X_4 - 2.32X_2X_5 + 6.36X_3X_4 - 1.72X_3X_5 + 5.74X_4X_5 - 5.46X_1^2 - 0.40X_2^2 - 13.47X_3^2 - 21.94X_4^2 - 3.25X_5^2.R^2=0.9078.2.0$$

Where X_1, X_2, X_3, X_4, and X_5 are Methanol/Oil molar ratio, Catalyst Concentration, Temperature, Time, and Speed respectively.

From the analysis of the quadratic model equation 2.0, Methanol/Oil molar ratio *(X_1)* had quite higher linear negative effect on yield than catalyst concentration, temperature, time and speed. The interaction of methanol/oil molar ratio and catalyst concentration had more positive effect on the yield than methanol/oil molar ratio and time, methanol/oil molar ratio and speed, temperature and time, and time and speed while other interactions had negative effects on yield, with catalyst concentration and temperature having the highest negative effects on yield. Time had the highest negative quadratic effects on yield followed by temperature, methanol/oil molar ratio, speed and lastly catalyst concentration respectively.

a. Optimization of Transesterification Reaction.

The model (*Y*) from equation 2.0 was useful for indicating the direction in which to change the variables in order to maximize yield. The maximum value obtained was 94.362 for yield. The actual values for optimum responses are presented in Table 4.

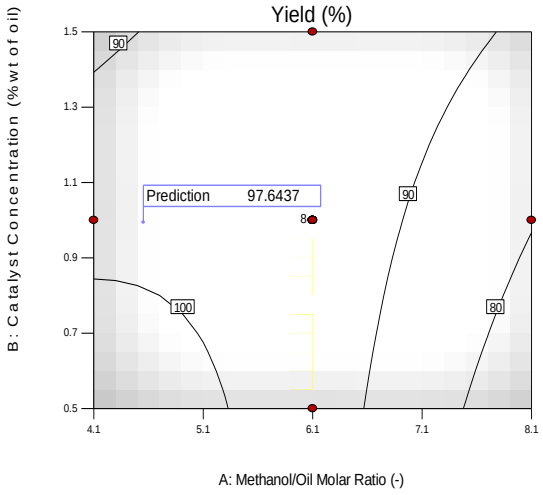
TABLE 3
REGRESSION COEFFICIENTS OF FITTED QUADRATIC EQUATION

Terms	Regression Coefficient	P-value
Linear	94.3619	-
β_1	-8.35611	0.0003
β_2	-0.312778	0.8602
β_3	-1.67111	0.3546
β_4	-0.848333	0.6342
β_5	-5.02833	0.0127
Quadratic		
β_1^2	-5.46005	0.2667
β_2^2	-0.400051	0.9335
β_3^2	-13.4651	0.0134
β_4^2	-21.9401	0.0004
β_5^2	-3.25005	0.5019
Interaction		
β_{12}	8.60562	0.0004
β_{13}	-1.28938	0.4973
β_{14}	0.031875	0.9865
β_{15}	0.769375	0.6837
β_{23}	-4.07313	0.0460
β_{24}	-0.861875	0.6484
β_{25}	-2.31937	0.2312
β_{34}	6.35563	0.0044
β_{35}	-1.72187	0.3681
β_{45}	5.74438	0.0083

TABLE 4
ANOVA FOR RESPONSE SURFACE QUADRATIC MODEL

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	18811.63	20	940.58	17.24	< 0.0001	**
X1	*1256.84*	*1*	*1256.84*	*23.04*	*0.0003*	
X2	*1.76*	*1*	*1.76*	*0.032*	*0.8602*	
X3	*50.27*	*1*	*50.27*	*0.92*	*0.3546*	
X4	*12.95*	*1*	*12.95*	*0.24*	*0.6342*	
X5	*455.11*	*1*	*455.11*	*8.34*	*0.0127*	
Residual	709.17	13	54.55			
Lack of Fit	*708.97*	*6*	*118.16*	*4015.43*	*< 0.0001*	***t*
Pure Error	*0.21*	*7*	*0.029*			
Cor Total	19520.80	33				
Adj R-Squared	0.9078					

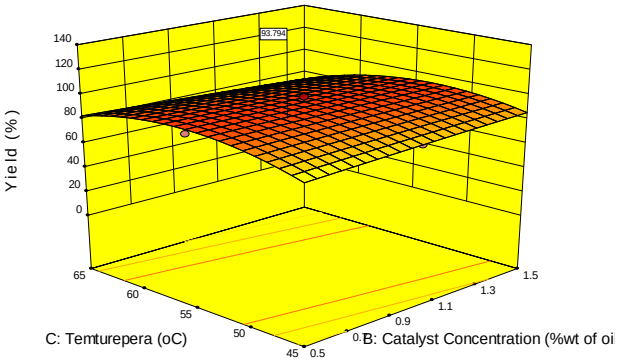
**=significant



(a)

TABLE 5
OPTIMIZATION DESIRABILITY RESPONSES

No.	X_1	X_2	X_3	X_4	X_5	Yield	
1	6.10	1.00	55.00	45.00	300.00	94.362	*
2	6.08	1.00	55.00	45.00	300.00	94.426	
3	6.09	1.00	55.00	45.00	299.61	94.420	
4	6.09	0.99	55.01	45.00	300.00	94.397	
5	6.10	1.00	55.00	45.14	300.66	94.285	
6	5.54	1.00	55.00	45.00	299.99	96.267	

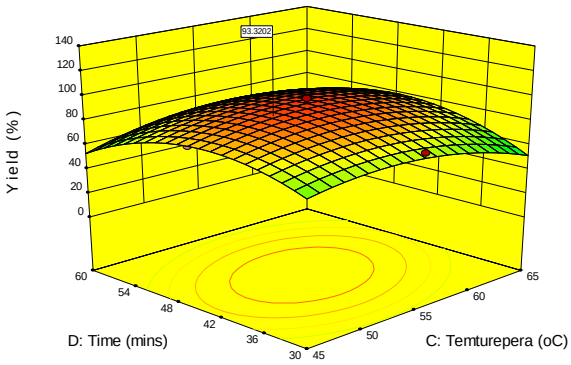


(b)

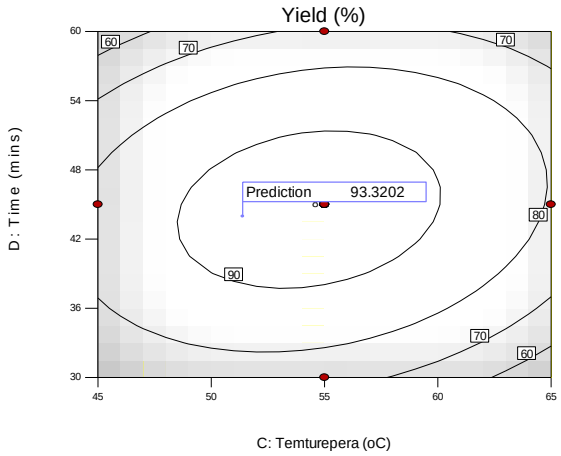
The actual value calculated for optimum response as shown in Table 5, were: 1.0% catalyst concentration, 55°C temperature, 45 min time, 6.1 methanol/oil molar ratio, and 300 rpm speed

b. Response Surface Plot for Transesterification

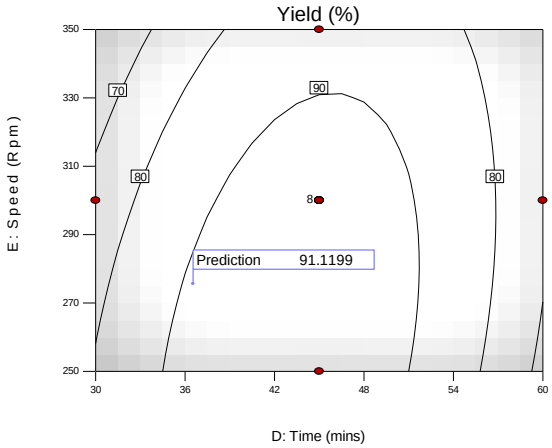
The response surface plots for the chosen model equations show the relationship between the independent and the dependent variables. The interaction terms between methanol/oil molar ratio and catalyst concentration, catalyst concentration and temperature, temperature and time, and time and stirring speed all had significant effects on the biodiesel yield at ($p<0.05$). From Figure 1 (a) (d) (e), the contour surface plots indicate that the percentage biodiesel yield increases with increase between methanol/oil molar ratio and catalyst concentration, temperature and time, and time and speed to optimum condition while further increase led to decrease of percentage yield. Figure 1 (b), (c) and (f) show the 3D surface plots indicating the percentage increase in yield as the independent variables increase to optimum condition and how further increase at a longer period led to decrease in percentage of yield. It can be noticed that the time, temperature and catalyst concentration were more influential factor that affected the percentage yield than other factors.



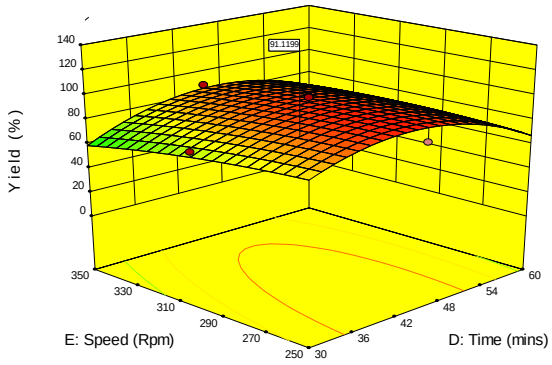
(c)



(d)



(e)



(f)

Fig.1 (a), (d) and (e) show Contour plots of the effects of methanol/oil molar ratio, temperature and time, and time and speed on percentage yield while (b), (c), and (d) show 3D response surface plots of catalyst concentration and temperature, temperature and time, and time and speed on percentage yield.

TABLE: 6
CHARACTERIZATION OF BIODIESEL FROM MICROALGAE

Fuel property	Biodiesel form Algae	Commercial diesel fuel
Kinematic viscosity @40^{o}C (Centistoke)	4.0	3.7
Density (g/cm^{3})	0.864	0.832
Specific gravity	0.865	0.841
Flash point (^{o}C)	102	70
Ash Content (%)	0.004	0.008-010
Sulfated Ash (%)	0.05	0.2
Carbon residue %)	0.34	0.7
Iodine Value	7.64	3.05

From the result, it could be observed that the specific gravity of biodiesel from algae 0.865 was close to 0.841 obtained in commercial diesel, however, the specific gravity of biodiesel from algae (0.865) is higher compared to that of fossil diesel (0.841). The density obtained for the biodiesel from algae (0.864 g/cm3) was in agreement with the specified value reported by Manufacture of fuel standard. While a value of 0.864 g/cm3 obtained for the density of diesel fuel is within than the specified standard of 0.920 - 0.845 g/cm3. The flash point of biodiesel 102^{o}C is in agreement with specified standard of (Manufacture of fuel standard comparison table), and also similar to ASTM and EN specification of biodiesel but lower compared to 200^{o}C. Flash point helps to monitor the safe handling and storage of fuel. The higher the flash point the safer the fuel and vice versa. The flash point of biodiesel is higher than that of fossil diesel; therefore it could be said that Biodiesel is safer to handle than fossil diesel.

The kinematic viscosity of biodiesel 4.0cts is in agreement with the manufacturer standard, and also falls within the ASTM and EN limit of biodiesel. The kinematic viscosity of fossil diesel 3.7cts is in agreement with that specified Manufacture of fuel standard. The viscosity of biodiesel is higher compared to that of fossil diesel the implication is that biodiesel will have lubricating effect in engines which will be an added advantage to the users, since it will reduce wear and tear in the engine.

The value of sulfated Ash obtained for biodiesel 0.05 is slightly higher compared to the standard specified 0.02% max [American standard for testing and materials (ASTMD) for petroleum product).

However the value is lower than that obtained for diesel fuel 0.2%. The Ash content is a measure of the amount of metal contained in the fuel. From the result in table 3.6, it shows that fossil diesel contains more metal compound than the biodiesel. During the burning of the fuels, biodiesel burnt with very low smoke compared to that of fossil diesel which burnt with heavy smoke. This implies that biodiesel emissions from exhaust of vehicles will help reduce the pollution introduced to the atmosphere compared to that of fossil diesel. The carbon residue of the algae biodiesel 0.34% was higher compared to 0.050max documented by (American Standard for Testing and Materials). This could be due to the contaminant which might have entered the sample during the heating to evaporate the oil. The carbon residue of the diesel fuel from Table 6 is higher compared to biodiesel. This implies that diesel fuels will form a higher deposits compared to that of biodiesel in engines. The result of iodine value of biodiesel revealed a higher value compared with that of fossil diesel. Iodine value is used to measure the chemical stability property of substance against oxidation and the higher the iodine value the higher the number of double bond and hence lesser stability. This shows that the fossil diesel is more stable compared to the biodiesel from algae. However, the double bonds in biodiesel helps attract oxygen to the compound, and aid proper burning of biodiesel over fossil diesel.

CONCLUSION

Biodiesel produced by transesterification of algae oil with alcohol, is the newest form of energy that has attracted the attention of many researchers due to various advantages associated with its usages. Response surface methodology, based on a three level, five variables of central composite design was used to analyze the interaction effect of the transesterification reaction variables such as methanol oil molar ratio, catalyst concentration, temperature, time and stirring speed on biodiesel yield. Maximum yield for the production of methyl esters from algae oil was predicted to be 94.362% under these conditions of methanol/oil molar ratio of 6/1, catalyst concentration of 1.0, temperature of 55°C, reaction time of 45 min and stirring rate of 300 rpm. This optimized condition was validated and the actual biodiesel yield was 91.696%. The physicochemical analysis of biodiesel from algae was compared with commercial diesel and implied that it will compete favourably with commercial diesel.

ACKNOWLEDGMENTS

The authors are grateful to Institute of Management and Technology, Enugu, Nigeria for the help rendered and to design Expert 9.0 trial Software for permission to use the trial version. The authors also want to thank the Director, Pymotech, Enugu for his encouragement.

REFERENCES

[1] G. Dragone, B. Fernandes, A.Vicente and J. Teixeira, Third generation biofuels from microalgae. 2010.

[2] Q. Li, W. Du, D. Liu, Perspectives of microbial oils for biodiesel production. Microbiology and Biotechnology, 8(5), pp749 – 756.

[3] S. T. Harrison, M. J. Griffiths, and R. Van Hille, Lipid productivity, settling potential and fatty acid profile of 11 microalgal species grown under nitrogen repleted and limited conditions. *Journal of Applied Phycology, 24*(5), 89-91, 2012.

[4] Y. Chisti, Biodiesel from microalgae. *Biotechnology Advances, 25*(3), 294-306 2007.

[5] H. Fukuda, A. Kondo, and H. Noda, Biodiesel fuel production by transesterification of oils. *Journal of Bioscience and Bioengineering, 92*(5), 405-416, 2001.

[6] M. R. Dale, P. Dixon, M. Fortin, P. Legendre, D. E. Myers, and M. Rosenberg, Conceptual and mathematical relationships among methods for spatial analysis. *Ecography, 25*(5), 558-577, 2002.

[7] A. Anya, N. Chioma and O. Obinna, Optimized reduction of free fatty acid content on neem seed oil, for biodiesel production. *Journal of Basic and Applied Chemistry, 2*(4), pp 21-28, 2012.