Response Surface Optimisation of Biodiesel Production from Microalgae Oil

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Abstract— Biodiesel was produced via transesterification process of Alage Oil with methanol in the presence of sodium hydroxide as catalyst. Response Surface Methodology (RSM) with Box-Behnken Design (BBD) was performed using STATISTICA v10 software to determine the optimum operating conditions and to optimize the biodiesel yield as indicator. The reaction variables under study were: methanol to oil molar ratio, catalyst loading and reaction time. From the Analysis of Variance (ANOVA), the most influential parameter on biodiesel production was found to be the methanol volume. The predicted value of percentage yield was found to be in good agreement with the experimental value, with coefficient of determination R^2 as 0.99972. The optimum biodiesel yield of 90.45% was achieved at 1.62 hr reaction time, with 3.63 g of catalyst loading and 27.93 ml of methanol. The biodiesel produced has the following physiochemical properties: kinematic viscosity of 5.58 mm^2/s, flash point of 106 ^oC, density of 862 kg/m^3 and cetane number of 50.02. These results are in conformity with American Society for Testing Materials (ASTM) D6751 specifications. Thus, the produced biodiesel is recommended for use in diesel ignition engines.

Index Terms— Transesterification, Algae Oil, Optimisation, Box-Behnken Design, ANOVA, Cetane Number, Biodiesel

1 Introduction

The world continues to suffer from energy crisis and environmentally related challenges, these lead for the exploration of other energy sources. One of the most prominent alternative energy resources, attracting more and more interest in recent years is biodiesel, which is a possible substitute for petroleum-based diesel fuel [1]. Biodiesel is a more sustainable and environmentally friendly fuel that is made with vegetable oil and methanol through a process known as transesterification. The fuel has superior combustion characteristics, and a lower emissions rating when compared to traditional, petrochemical diesel [2]. Biodiesel is an alternative energy source and could be a substitute for petroleum-based diesel fuel. Many studies have shown that the properties of biodiesel are very close to diesel fuel [3]. As such, biodiesel fuel can be used in diesel engines with little or nomodification. Biodiesel has a higher Cetane Number than diesel fuel, no aromatics, no sulfur, and contains 10-11% oxygen by weight. These characteristics of biodiesel are responsible for a reduction in the emissions of carbon monoxide (CO), hydrocarbon (HC) and particulate matter (PM) in the exhaust gas compared to diesel fuel [2]. However, to be a viable alternative, a biodiesel should provide a net energy gain, be economically competitive, and be producible in large quantities without reducing food supplies [1].

The raw materials for most of the industrial biodiesels are made from oil (triglycerides) of rapeseed, sunflower, soybean, Jatropha, etc. The raw materials are also necessary to feed humans and animals. A large demand for raw materials to produce biodiesel could thus increase their price. Moreover, the culture of conventional vegetable material requires an important amount of water, chemical fertilizers and pesticides and large area of land, which have a negative impact on the environment [4].

To overcome these problems, researchers need to explore a new way of producing biodiesel using microalgae and other nonedible biomass. Indeed, during their growth, photoautotrophic microalgae metabolize inorganic carbon (CO_2) through photosynthesis [5]. Microalgae have also the capacity to absorb other pollutants such as phosphates and nitrates [6]. Furthermore, microalgae can accumulate a high amount of fatty acids and have a culture yield per hectare at least 10 times higher than any oily plants [7].

Currently, optimal biodiesel production through optimized transesterification processes is attracting continuing interest among researchers [8]. Previous literature has reviewed the use of various seed oils as feedstocks for biodiesel production [9], [10], [11]. Biodiesel production process via chemical and enzyme catalysed transesterification and use of Response Surface Methodology (RSM) as an important Optimization tool for biodiesel production [12].

Response surface methodology is a collection of statistical and mathematical techniques useful to develop, improve and optimize processes and products. The technique is largely applied in industry, particularly in the situations where several input variables influence some process performances or quality characteristics. In the case of a chemical reaction the dependence between the response variable yield and the two inputs, process or independent variable time and temperature can be represented. It consists on experimental strategy for exploring the process space or independent variables, empirical statistical modeling to establish an adequate approximate relation between response and process variables. The method allows the determination of optimum set of experimental conditions which minimize or maximize the response and the changes in response surfaces produced by variation of independent variables [13]. This statistical technique has been applied in research for complex variable systems. It has advantage of limited num-

ber of experimental runs required to generate adequate information for statistically acceptable results. It is an effective tool for process optimization [12], [14].

In the present study, STATISTICA V10 software is employed to carry out the optimization of double transesterification process via Box-Behnken design (BBD). Multiple regression and analysis of variance (ANOVA) for the production process were studied to determine the relative significance of the factors (the effect of temperature, reaction time and catalyst concentration) considered.

2 METHODOLOGY

2.1 Experimental Procedure

Fresh microalgae samples were collected from ABU Zaria dam, Kaduna, Nigeria. The wet algae were sieved to drain excess water out, weighed (w_1) and then placed in the oven at 50^{o}C until constant weight (w_2) was obtained. Oil was then extracted using sohxlet extraction method with hexane as the solvent. The algae oil was further purified by heating to 70 °C (above the boiling point of n-hexane). The Free Fatty Acid (FFA) of the oil was recalculated to confirm that it is (<1%). The algae oil was then trans-esterified by reacting with methanol using NaOH as catalyst at constant temperature of 60°C and stirring speed of 300 revolutions per minute to produce biodiesel and glycerine. The biodiesel was separated by gravity from the glycerine using separating funnel after leaving it to settle for 24 hours.

The Box-Behnken design was chosen to study the optimization of three selected input parameters: catalyst amount, Methanol to oil ratio and reaction time, and biodiesel yield as the output parameter using Response Surface Methodology (RSM). RSM is a mathematical tool used for designing experiments, developing polynomial models for predicting response, evaluating the significant effects of factors and optimizing the required function [14]. Box Behnken Design (BBD) with three factors was chosen to design the experiment because it has the advantage of requiring fewer numbers of runs, and is' rotatable. The coded and uncoded levels of the independent variables were shown in Table 1. For statistical nalysis, the relationship between the coded and actual (uncoded) variables can be represented by Eq. (1)

$$X_i = \frac{Z_i - Z^*}{\Delta Z} \quad (1)$$

Where Xi = the coded ith variable, Zi = the actual ith variable, ΔZ = step change of Z variable, Z* = center point values for the ith variable, Number of variable, i = 1 - 3.

Table 1: Coded and uncoded levels of independent variables

Factors	Low (-1)	Centre (0)	High (1)
Reaction Time (hr)	1	2	3
Methanol to Oil Ratio	2:1	4:1	6:1
Catalyst Amount (Wt % Oil)	1	3	5

By this design, a total of 15 experimental runs were carried out. The center point was replicated three times to evaluate errors. Eqn. (2) is the general polynomial model of quadratic form that was used to fit the experimental data obtained during the extraction of oil.

$$\mathbf{Yield(\%) = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_1 x_1^2 + \beta_2 x_2^2 + \beta_3 x_3^2 + \beta_1 x_1 x_2 + \beta_2 x_1 x_3 + \beta_3 x_2 x_3} \quad (2)$$

Where: X_1, X_2, X_3= Are the independent variables

Y = is dependent variables,

β_o = is the offset or constant term or center points, while

β_1 = is the i^{th} linear coefficient

β_2 and β_3 = are quadratic and interaction coefficients respectively.

STATISTICA v10 software wan used for analysis of variance(ANOVA), and multiple regression analyses of the data obtained. The Fit for regression model was checked by of coefficient of determination R^2 and its associated probability p were used to determine the overall model significance. The respective effect of the variables and their interactions were tested using the p-test, response surface plots and pareto charts. While the coefficients of the quadratic polynomial model were determined via multiple regressions and subsequent solution was carried out to evaluate the optimum operating variables.

2.2 Designed of Experiment

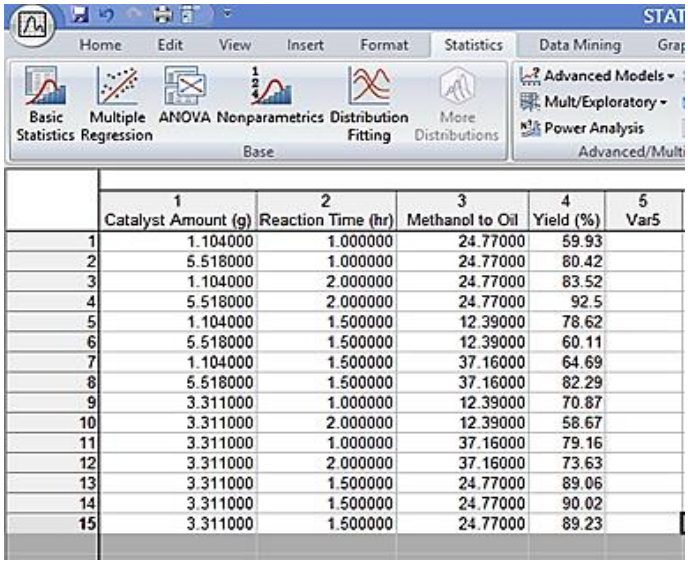
A measrued quantity of the oil according to the design of experiment was poured into a conical flask and the calculated amounts of sodium hydroxide corresponding to the catalyst amount chosen and methanol volume corresponding to methanol to oil ratio chosen were added, and the mixture was well stirred. The mixture was heated up to the desired temperature using a hot plate and stirred continuously with temperature maintained at 55 60 ^{o}C for reaction time chosen. At the end of the reaction time, the methyl ester component was separated in a separation funnel until phase separation took place. This resulted in the formation of an upper phase consisting of methyl ester and a lower phase containing glycerol. After separation of the layers by gravity using a separating funnel, the methyl ester phase was purified by washing with hot water several times until the biodiesel became clear. The washed methyl ester was dried at 100 to 120 ^{o}C for 60 min for further storage.

3 RESULTS AND DISCUSSION

3.1 Response Surface Methodology for the Algea oil Biodiesel Production

For the response surface methodology, the Box-Behnken Design was applied and the results for each run was recorded as shown in Table 2.

Table 2: Box-Behnken Design for the Algea oil Biodiesel Production



	1 Catalyst Amount (g)	2 Reaction Time (hr)	3 Methanol to Oil	4 Yield (%)	5 Var5
1	1.104000	1.000000	24.77000	59.93	
2	5.518000	1.000000	24.77000	80.42	
3	1.104000	2.000000	24.77000	83.52	
4	5.518000	2.000000	24.77000	92.5	
5	1.104000	1.500000	12.39000	78.62	
6	5.518000	1.500000	12.39000	60.11	
7	1.104000	1.500000	37.16000	64.69	
8	5.518000	1.500000	37.16000	82.29	
9	3.311000	1.000000	12.39000	70.87	
10	3.311000	2.000000	12.39000	58.67	
11	3.311000	1.000000	37.16000	79.16	
12	3.311000	2.000000	37.16000	73.63	
13	3.311000	1.500000	24.77000	89.06	
14	3.311000	1.500000	24.77000	90.02	
15	3.311000	1.500000	24.77000	89.23	

3.2 Polynomial Model Fitting

The results in Table 2 were used to run ANOVA and Multiple Regression Analysis in STATISTICA V10 software using the polynomial model Eq (2). From which the optimum yield and the corresponding optimum variables can be predicted. Statistical analysis of the model was performed to evaluate the ANOVA and check the adequacy of the empirical model. The significance of the linear, quadratic and interactive terms of the process variables were checked by F and p-tests. The results (as shown in Table 3) showed that the combined effect of both linear and quadratic methanol volume term is the most significant with highest F-value and least pvalue of 1387.4185 and 0.000720 respectively. The significance of the rest of the terms were checked in the same manner. The coefficients of the model equation which are used to predict the optimum parameters were determined by multiple regression analysis using STATISTICA V10.

The regression analysis results of the model equation with Yield as response, while A, B and C represent catalyst amount, reaction time, , methanol volume and respectively as shown in Eq.(4) as:

$$Yield\ (\%) = -173.375 + 77.324 * A + 257.134 * B + 2.574 * C - 7.658 * A^2 - 67.98 * B^2 - 0.086 * C^2 - 80.224 * A * B + 0.742 * A * C + 0.269 * B * C + 13.772 * A * B^2 + 5.482 * A^2 * B - 0.062 * A^2 * C \quad (4)$$

The value of regression coefficient of determination (R^2) for the model was 0.99972 and adjusted R^2 is 0.99807 both indicating the good fitness of the model.

Table 3: ANOVA for the Polynomial Quadratic Model

3.3 Response Surface Analysis and Pareto Chart

The effects of the process variables on the response variable can be further elaborated by visualization using response surface plots and a pareto chart. The effect of methanol volume and catalyst amount on the percentage yield of the biodiesel is shown in Fig la. The optimum yield is achieved at high methanol volume and high catalyst amount with prevalence of quadratic effect for both; and of course, having the methanol volume been more dominant. Fig. 1b illustrates the effects of reaction time and catalyst amount on the percentage yield. The response plot shows the quadratic effect of both time and catalyst amount being highly sigficant. The surface plot is that saddle type with no true optimum value.

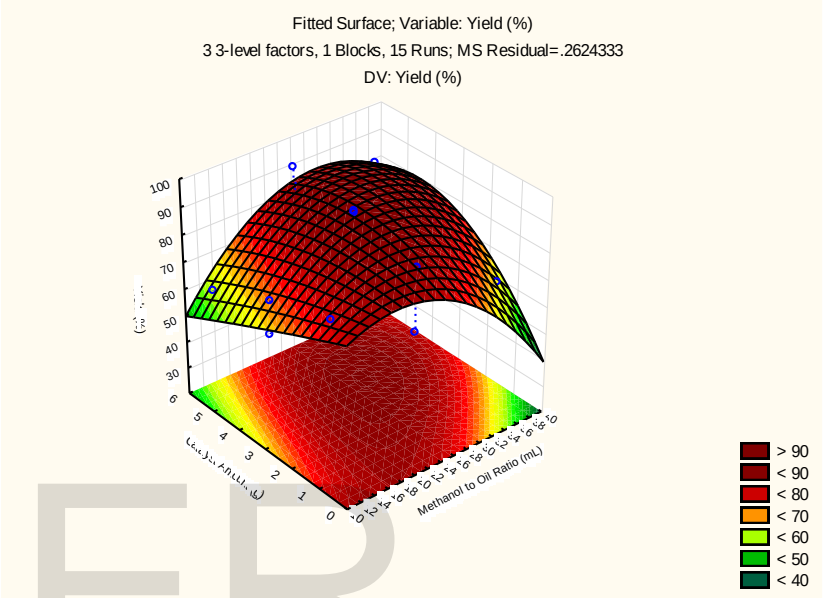


Fig. 1a: Effect of Catalyst amount and Methanol Volume on Percentage Yield

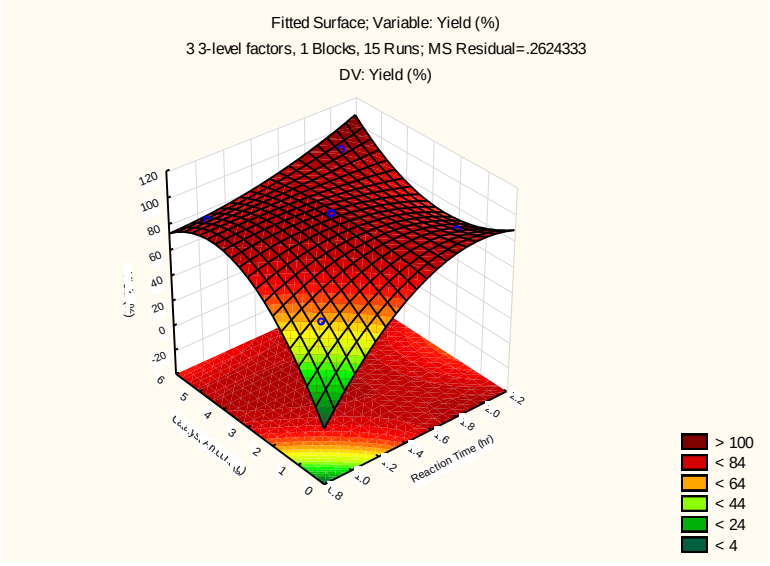


Fig. 1b: Effect of Catalyst amount and Reaction Time on Percentage Yield

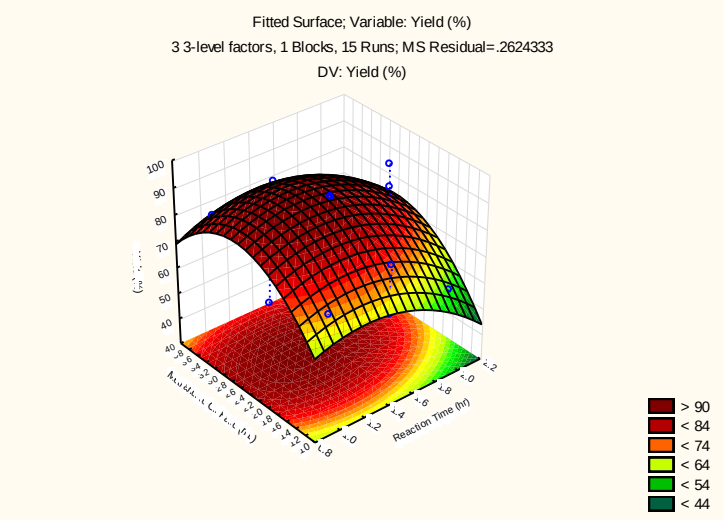


Fig. 1c: Effect of Methanol volume and Reaction Time on Percentage Yield

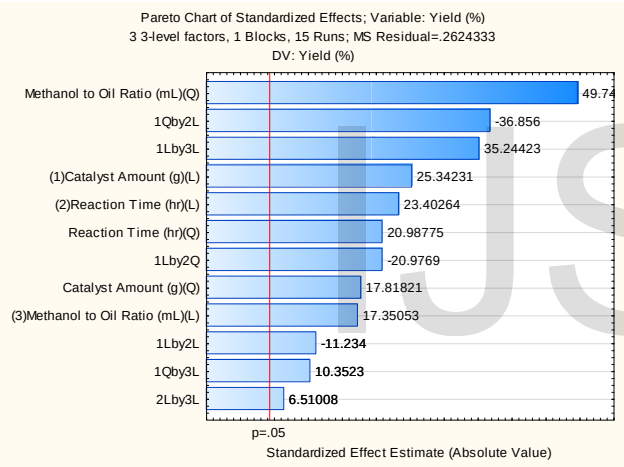


Figure 2: Pareto Chart of the Standardized Effects

Fig. 1c indicates the combined effects of methanol volume and time on the percentage yield. The effects of both are quadratic with a curvature similar to that of Fig.1a, thus optimum yield is obtain at high values of both time and methanol volume. This further explains that all the three plots are devoid of high significance of linear effects of the variables, but with overall quadratic effects being most significant. This further shows that somewhere lies the optimum value on the response surface which need to be investigated further by multiple regression of the model equation.

The various effects of the input parameters on the output parameter are further elaborated by Fig. 2. It is obvious that the quadratic effect of methanol to oil ratio at confidence level of 95% is the most significant and more dominant. This is followed by the quadratic effect of catalyst amount with that of linear effect of time of reaction and then that of combine effect of linear effects of both methanol volume and catalyst amount. Thus, at confidence level of 95% all the parameters and their interactions shows significant at different levels and therefore need to be considered during optimization.

3.4 Optimization of the Transesterification Reaction

From the regression analysis results of generated by STATISTICA V10 software yielded the optimum input values of catalyst amount (A), methanol volume (B) and reaction time(C) in coded and uncoded terms are presented in Table 4. The uncoded variables were evaluated using Eq. (1).

Table 4: Multiple Regression Summary of Optimum input Parameters

Factor	Coded Parameter	Uncoded Parameter
Catalyst amount	0.1452	3.63
Methanol volume	0.2549	27.93
Reaction time	0.2312	1.6156

Substituting these values into Eq. (4) gives optimum value of the response as:

$$Yield(\%) = -173.375 + 77.324(3.63) + 257.134(1.6156) + 2.574(27.93) - 7.658(3.63)^2 - 67.98(1.6156)^2 - 0.086(27.93)^2 - 80.224(3.63)(1.6156) + 0.742(3.63)(27.93) + 0.269(27.93)(1.6156) + 13.772(3.63)(1.6156)^2 + 5.482(3.63)^2(1.6156) - 0.062(3.63)^2(27.93) = 90.45 \quad (5)$$

Confirmatory experiments were also conducted in triplicates using the optimum values, to ascertain the validity of the model, and the average percentage yield from the confirmatory test was calculated to be 89.76.

3.5 Predicted value vs. Observed values of the Standardized effect for Yield Response

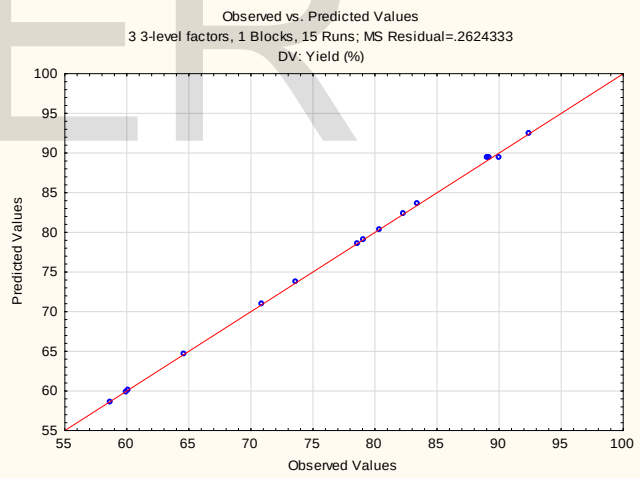


Figure 3: Predicted values vs. Observed values of the Standardized Effect for yield Response.

The predicted vs. observed values plot for biodiesel Yield response as illustrated in Figure 3 shows the closeness of the experimental values denoted by the dotted points to the predicted model values represented by the red straight line. Thus, the predicted model with coefficient of determinant (R^2) of 0.99972 can be used to predict the percentage yield. This also shows that the values obtained follow the predicted values indicating that model assumptions were correct.

3.6 Physiochemical Propeties of the Biodiesel

The biodiesel produced at optimum variables was characterized for its density, kinematic viscosity, flash point, free fatty

acid and Cetane Number. Table 5 compares properties of the biodiesel produced with the ASTM D6751 -12 standards. The produced biodiesel conforms to the standards.

Table 5: Physiochemical properties the Biodiesel

Properties	Biodiesel	Commercial Diesel
Density at 32°C (Kg/m3)	862	860 - 900
Kinematic viscosity at 40°C (mm^2/s)	5.58	1.9 - 6.0
Flash point (°C)	106	93
Cetane Number	50.02	> 47
Free Fatty Acid (%)	0.67	≤ 4.0

4 CONCLUSIONS

Based on the findings, the following conclusions are made:

- Biodiesel from Algae oil was successfully produced through transesterification reaction using methanol and sodium hydroxide as catalyst. RSM was used to determine the optimal conditions of percentage biodiesel yield. Box-Behnken design model predicted the optimal conditions for the production biodiesel from algae oil were given as a catalyst amount of 3.63g, methanol volume of 27.93 ml and at a reaction time of 1.6156 hr with the predicted biodiesel yield of 90.45%.

- The experimental data and the predicted data are in agreement with a high value of R^2 = 0.99972 and adjusted R^2 = 0.99807. This is also an indication that the proposed polynomial model equation can use in predicting optimum biodiesel production yield from algae oil.

- Physiochemical properties shows that algae oil has a very low Free Fatty Acid (FFA) of less than one (< 1%), which indicate a good property for biodiesel production, the cetane number of 50.02, kinematic viscosity of 5.58 (mm^2/s), flash point of 106 °C and density of 862 kg/m^3 are all in agreement with the ASTM D6751 -12 standards.

REFERENCES

[1] Maximino, M., Maria, L., and Jesus, G. Biodiesel: An Alternative. Recent patent in biotechnology, 2008, vol 2 , no.1. Accessed on 06/06/2018. Retrieved from: https://www.researchgate.net/profile/Maximino_Manzanera/publication/23656725_Biodiesel_An_Alternative_Fuel/links/00b4953ce177ec2359000000/Biodiesel-An-Alternative-Fuel.pdf

[2] Kumarn, S., "Jatropha Curcus - A Sustainable Source for Production Of Biodiesel", Journal of Scientific And Industrial Research, 2005,Vol. 64(11), Pp. 883-889.

[3] Shah, S. and Gupta, M. N. "Lipase Catalyzed Preparation of Biodiesel From Jatropha Oil in a Solvent Free System", Process Biochemistry, 2007, Vol. 42(3), Pp.409-414

[4] Canakci, M. and Gerpen, J.V. (2001). Biodiesel Production from Oils and Fats with High Free Fatty Acids. Trans. ASAE. 44, 1429-1436.

[5] Demirbas, A. and Demirbas, M.F. Importance of algae oil as a source of biodiesel. Energy Conversion and Management 2011; 52:163–170.

[6] Luyun Wang, Han Xiao, Ning He, Dong Sun, and Shunshan Duan. Biosorption and Biodegradation of the Environmental Hormone Nonylphenol By Four Marine Microalgae, 2019. aturescience, doi: 10.1038/s41598-019-41808-8

[7] Chisti, Y.. Biodiesel from microalgae. Biotechnology Advances, 2007, Vol.25, No.3, pp. 294-306

[8] Schenk, P.M., Thomas-Hall, S.R., Stephens, E., Marx, U.C., Mussgnug, J.H., Posten, C., Kruse, O., Hankamer, B. Second generation biofuels: high-efficiency microalgae for biodiesel production. Bioenergy Res. 1, (2008), 20–43.

[9] Scarlat N, Dallemand J. F., Pinilla F. G. Impact onagricultural land resources of biofuels production and use in the European Union. In: Bioenergy: challenges and opportunities. International conferenceand exhibition on bioenergy; 2008.

[10] Danquah MK, Gladman B, Moheimani N, Forde GM, Microalgal growth characteristics and subsequent influence on dewatering efficiency. 2009. Chem Eng J 151: 73-78.

[11] Brennan L, Owende P. Biofuels from microalgae- a review of technologies for production, processing, and extractions of biofuels and co-products. Renew Sustain Energy Rev. 2010; 14:557–577.

[12] Badwaik L.S., Prasad K., and Deka S.C. Optimization of extraction condition by response surface methodology for preparing partially defatted peanut,International Food Research Journal, Vol.19 (1). (2012).341-346.

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

[14] Shehu, M.S., Abdul Manan, Z. and Wan Alwi, S.R.,Optimization of thermo-alkaline disintegration of sewage sludge for enhanced biogas yield. Bioresource. Technology, (2012) 114: 69-74.