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Optimisation of Base Catalysed Transesterification of Fish Oil for Biodiesel Production Using Response Surface Methodology

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Abstract

Response Surface Methodology (RSM) based on a Central Composite Rotatory Design (CCRD) was used in this work to determine the optimum conditions for the transesterification of oils into biodiesel using fish oil. Three important process variables were evaluated--oil/alcohol molar ratio, reaction temperature and reaction time. A second order quadratic polynomial equation was obtained for predicting the optimisation of the transesterification reaction which was followed by experiments at the laboratory. The results obtained indicated that the parameters evaluated were the major factors affecting the yield of Biodiesel. Considering various experimental data, the optimum transesterification reaction conditions, which gave greater than 92% yield, were found to be 1:6 of oil to alcohol ratio, a reaction time of 180 minutes and a reaction temperature of 60^0C. . The R^2 value was found to be 0.8457 indicating a high degree of correlation between the variables.

Keywords: *Transesterification; RSM; Optimisation; Biodiesel.*

1. Introduction

The demand for energy globally is rising rapidly and more than 80% of this demand is met at present time by fossil fuels. It has been indicated that the energy demand will increase during this century by a factor of two or three. Similarly, concentrations of greenhouse gases in the atmosphere are rising rapidly, with fossil fuel-derived CO_2 emissions being the most important contributor [1]. Consequently, known petroleum reserves are limited and will eventually run out. In developed countries, there is a growing trend towards employing modern technologies and efficient bioenergy conversion using a range of biofuels, which are becoming cost competitive with fossil fuels. . Two biomass-based fuels have been identified, with potentials to substitute petrol and diesel. These are bioethanol and biodiesel respectively [2]. These concerns and unavoidable circumstances resulting from the exploration, refining and use of these fossil fuels have stimulated researchers to explore various economically and environmentally friendly alternatives to fossil fuels, such as biodiesel [3]. Biodiesel is an environmentally friendly liquid fuel made from vege**Table** oils (edible and non-edible), animal fats or used cooking/waste oils that can be used in place of diesel fuel. Chemically, it is a mixture of methyl or ethyl esters of fatty acids produced mainly through a reaction known as transesterification [4]. Various researches have been conducted on the conversion of vege**Table** oils to diesel fuel. That research included palm oil, soybean oil, sunflower oil, coconut oil, rapeseed oil and tung oil. Animal fats, although mentioned frequently, have not been studied to the same extent as vege**Table** oils. Some of the methods applicable to vege**Table** oils are not applicable to animal fats due to natural property differences. Oil from algae, bacteria and fungi has also been investigated [5]. Likewise, waste cooking oil, which included waste fish oil have also been used for biodiesel production, but, no research yet has been reported for the biodiesel production using pure fish oil. Response Surface Methodology (RSM) on the other hand is a statistical and analytical technique which has been used for the optimisation of various parameters involved in different experiments [6,7]. Some researchers have employed the use of RSM for the optimisation of transesterification of oils to biodiesel. [8] conducted a research on the `Optimisation of Base Catalytic Methanolysis of Sunflower (Helianthus annuus) Seed Oil for Biodiesel Production by Using Response Surface Methodology' in which they investigated the effects of four variables and found the optimum condition with respect to the variables observed. [9]also used RSM to optimise some process parameters in esterification and transesterification using Jatropha oil. Presently, more than 95% of biodiesel production feedstock comes from edible oils since they are commonly produced in many regions of the world and the properties of biodiesel produced from these oils are more sui**Table** to be used as diesel fuel substitute [10]. However, there is scarce information on the optimum conditions required in transesterification of oils to biodiesel. Therefore, this paper discusses the outcome of the experiments conducted to optimize some process variables which are the ratio of oil to alcohol, reaction temperature and reaction time for obtaining the maximum biodiesel yield using fish oil.

2. Materials and Methods

2.1 Sample Collection

Fish oil was used for the transesterification to produce biodiesel. The oil is 100% pure fish oil which was extracted by `Ayrton Saunders & Co ltd., Liverpool, UK', imported into Nigeria and was bought from a pharmaceutical Chemist in BabbanLayi, Gadon Kaya, within the Kano metropolis. Ethanol which was the alcohol used and potassium hydroxide as the catalyst were both of analytical grade. The experiments were

conducted in a laboratory scale set-up with a flat bottom flask connected to a reflux condenser and placed on top of a hot plate.

2.2 Optimisation using RSM

Response Surface Methodology based on a Central Composite Rotatory Design (CCRD) was used to optimise three process variables using `Design Expert Version 7.1.6'. The parameters varied are described in **Table** 1.

Table 1: Range of parameters varied using RSM

Parameters	Minimum Value	Maximum Value
Oil/Alcohol ratio	1 : 3	1 : 6
Time (min.)	60	180
Temperature (^{0}C)	25	60

2.3 Physicochemical analysis of Fish Oil

The analysis was carried out in order to assess the quality of the oil so as to ascertain the properties of the oil in order to know its suitability for biodiesel production and to choose the best possible method for it to be used in biodiesel production.

2.3.1 Determination of acid value of the oil

Acid value is the number of milligram of base required to neutralize the fatty acid in 1g of the fat/oil.2.8g of the oil was weighed in a conical flask and dissolved in 50cm^3 of solvent mixture (ethanol and diethyl ether) to which 5drops of phenolphthalein indicator was added. The solution was then titrated with 0.1M NaOH. The end point was pink in colour.

Acid value =(40 X N X T)/M (1)

Where 40 = molar mass of NaOH, N = normality of NaOH, T = titre value and M = mass of oil used.

2.3.2 Determination of pH

The pH was determined using a Jenway pH meter, model 3320.

2.3.3 Determination of Specific gravity

A clean and dried density bottle was weighed and labelled (M_0). The bottle was then filled with distilled water and weight of the bottle taken and recorded as (M_1). The same bottle was emptied and dried and it was then filled with oil, weighed and the value obtained was recorded as (M_2).

The specific gravity was then calculated using the equation:

Specific Gravity = $(M_2 - M_0) / M_1 - M_0$ (2)

Where M_0= weight of empty bottle, $M_{1=}$ weight of the bottle filled with distilled water and $M_{2=}$ weight of the bottle filled with oil.

2.3.4 Determination of free fatty acid

The free fatty acid of the oil was determined using the formula;

%FFA = Acid value /2 (3)

2.3.5 Determination of moisture content of the oil.

The moisture content of the oil was determined by weighing a clean and dried beaker (50ml) and then recording the value obtained as W_1. A specific amount of the oil was then put into the beaker and weighed again recording the new value as W_2. It was then put into an oven and kept for 24 hours at 60^0C. It was weighed again and the value obtained was recorded as W_3.

The moisture content was calculated as:

Moisture content = $W_2 – W_3$. (4)

Where W_3= final weight obtained after 24hours, W_2=initial weight obtained

2.4 Biodiesel Yield

The percent yield of Biodiesel produced in each case was calculated using the formula;

YOB = (mass of biodiesel produced (g) x100%)/ Mass of oil taken for reaction (g) (5)

Where YOB=yield of biodiesel

2.5 Transesterification of the Oil

The oil is first fed to a reactor (a flat bottom flask connected to a reflux condenser on a hot plate) and a specified amount of potassium ethoxide solution(potassium hydroxide dissolved in ethanol) was poured onto it after heating the oil for about 5 minutes to reduce the viscosity of the oil. The reaction took place for the desired time at the specified temperature. The reaction mixture was then allowed to cool and equilibrate, resulting in the separation of 2 phases. Fatty acid ethyl ester (biodiesel)at the top and glycerol layer contained in the second phase. The mixtures were separated by decantation and the biodiesel layer was purified by washing it with hot distilled water at about 30% of the weight of the oil.

2.6 Statistical analysis

The experimental data obtained following the subsequent procedures were used for determining the regression coefficients using the following second order quadratic polynomial equation

$$Y = 85.29 + 4.40*A - 2.65*B + 6.56*C + 3.48*A*B - 2.66*A*C + 4.85*B*C - 4.33*A^2 + 6.18*B^2 - 3.59*C^2 \quad (6)$$

Where; Y = predicted yield of biodiesel, A = time, B = temperature and C = oil/alcohol molar ratio.

Table 2: Parameters varied by the Response Surface Methodology

Run	Oil/Alcohol Molar Ratio	Time (minutes)	Temperature (^0C)
1	1 : 4.5	120	42.5
2	1 : 3.0	60	25
3	1 : 6.0	180	25
4	1 : 6.0	60	60
5	1 : 4.5	120	42.5
6	1 : 3.0	180	60
7	1 : 4.5	120	42.5
8	1 : 4.5	120	30
9	1 : 6.0	120	42.5
10	1 : 4.5	120	60
11	1 : 4.5	120	42.5
12	1 : 4.5	30	42.5
13	1 : 4.5	120	42.5
14	1 : 3.0	120	42.5
15	1 : 6.0	60	25
16	1 : 4.5	180	42.5
17	1 : 3.0	60	25
18	1 : 4.5	120	42.5
19	1 : 6.0	180	60
20	1 : 3.0	180	25

3. Results and Discussions

Physicochemical analysis was conducted on the fish oil before the transesterification to determine its properties as well as its suitability for biodiesel production. The properties obtained are all within standard as stipulated by the American Society for Testing Materials (ASTM) and the British standards. **Table 3** gives the results obtained.

Table 3: Results obtained for the physicochemical analysis of fish oil

S/N	Parameters	Values Obtained
1	Acid Value	1.57mgNaOH/g
2	Free fatty acid	0.79
3	Moisture Content	0.01
4	Specific gravity	$0.89g/cm^3$
5	pH	6.8
6	Colour	Yellow

Table 4 gives the yield of Biodiesel obtained after conducting 20 different experiments at the laboratory varying the parameters as indicated. It was observed that the highest yield obtained was 93% when 1:6 of oil/alcohol molar ratio was used at 180 minutes at 60^0C, this indicates the optimum condition for the transesterification of fish oil to biodiesel. Similarly, the lowest yield was observed as 60% when 1:3 of oil/alcohol molar ratio was used at 120 minutes at 42.5^0C.

Table 4: Biodiesel Yield

Run	Oil/Alcohol Ratio	Time (min.)	Temperature (^{0}C)	Biodiesel Yield (%)
1	1 : 4.5	120	42.5	86.0
2	1 : 3.0	60	25	85.7
3	1 : 6.0	180	25	88.0
4	1 : 6.0	60	60	91.0
5	1 : 4.5	120	42.5	86.4
6	1 : 3.0	180	60	85.0
7	1 : 4.5	120	42.5	86.0
8	1 : 4.5	120	30	85.5
9	1 : 6.0	120	42.5	92.6
10	1 : 4.5	120	60	84.0
11	1 : 4.5	120	42.5	86.0
12	1 : 4.5	30	42.5	62.5
13	1 : 4.5	120	42.5	85.0
14	**1 : 3.0**	**120**	**42.5**	**60.0**
15	1 : 6.0	60	25	86.5
16	1 : 4.5	180	42.5	87.0
17	1 : 3.0	60	25	82.5
18	1 : 4.5	120	42.5	86.0
19	**1 : 6.0**	**180**	**60**	**93.0**
20	1 : 3.0	180	25	86.0

Table 5 contains the actual values obtained after conducting the experiments, the values predicted by RSM and the residual values. The residual is the difference between the actual and the predicted values.

The statistical significance of the second order polynomial equation was checked by an F-test (ANOVA). The Model F-value of 6.09 implies the model is significant. Values of "P value" less than 0.0500 indicate model terms are significant. The "Lack of Fit F-value" of 47.15 implies the Lack of Fit is significant. The R^2 value of 0.8457 indicates a high degree of correlation between the variables. The percentage of coefficient of variation (CV) is a measure of the residual variations relative to the size of the mean. Therefore, the lower the value of CV, the higher the reliability of the experiment. The %CV value of 5.33 obtained, being a lower value indicated a reliabibity of the experiments conducted.

Table 5: Predicted, Actual and Residual Values

S/N	Predicted Values	Actual Values	Residual
1	80.92	82.50	1.58
2	88.08	86.00	-2.08
3	80.92	85.70	4.78
4	80.03	85.00	4.97
5	89.65	86.50	-3.15
6	86.18	88.00	1.82
7	87.10	91.00	3.90
8	97.55	93.00	-4.55
9	65.65	62.50	-3.15
10	85.36	87.00	1.64
11	90.33	85.50	-4.83
12	88.82	84.00	-4.82
13	64.11	60.00	-4.11
14	88.27	92.60	4.33
15	85.29	86.00	0.71
16	85.29	86.00	0.71
17	85.29	86.00	0.71
18	85.29	86.00	0.71
19	85.29	86.40	1.11
20	85.29	85.00	-0.29

Table 6: Analysis of Variance (ANOVA) for the quadratic model

Source of Variation	Sum of squares	Degrees of freedom	Mean squares	F value	P value
Model	1105.78	9	122.86	6.09	6.09
Residual	201.73	10	20.17		
Lack of fit	*195.51*	4	48.88	47.15	47.15
Pure error	*6.22*	6	*1.04*		
Total	1307.51	19			

C.V. = 5.33%, Std. Dev. = 4.49, R^2 = 0.8457,
$R^2_{adj.}$ = 0.7069, Mean = 84.23

The normal probability plot of residuals given in figure 1shows some scattered dots along a straight line indicating that the residuals follow the same pattern of distribution. The plot of actual vs predicted values in figure 2 also indicates a high degree of similarity between the experimental and the values predicted by

RSM. Pertubation plot in figure 3 represents the comparison between the effects of process parameters with respect to a reference point.

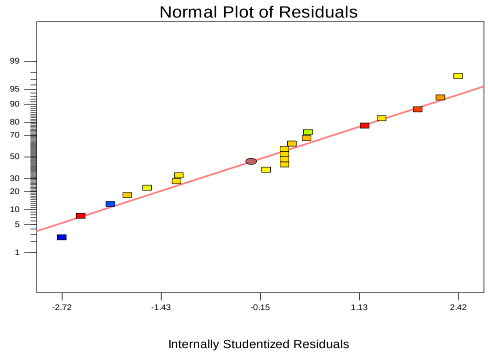

Fig. 1: Normal probability plot of residuals

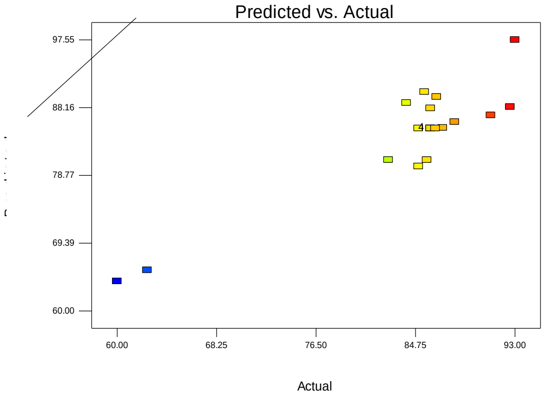

Fig. 2: Plot of Predicted Vs Actual

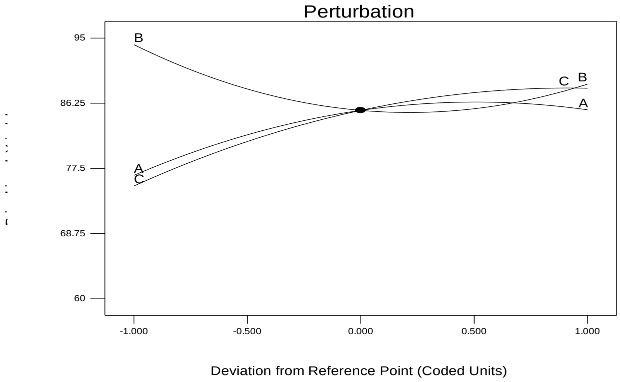

Fig. 3: Plot of Pertubation Curve

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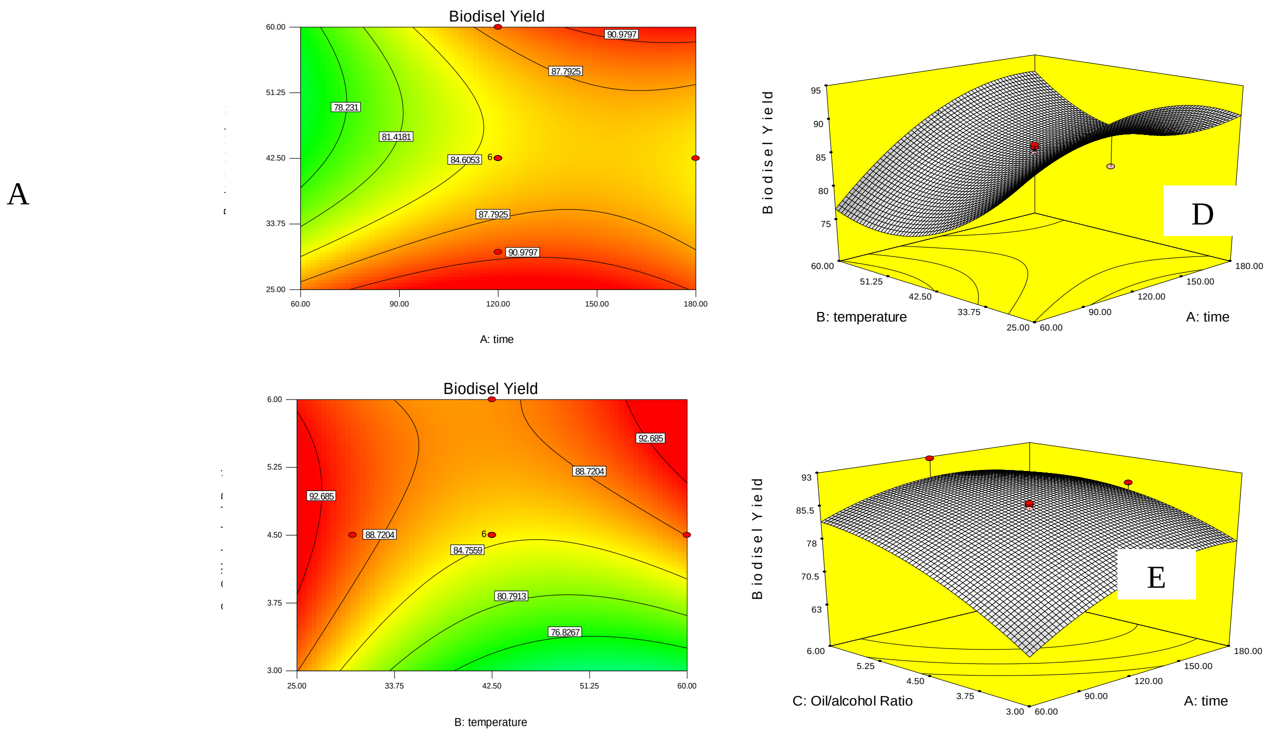

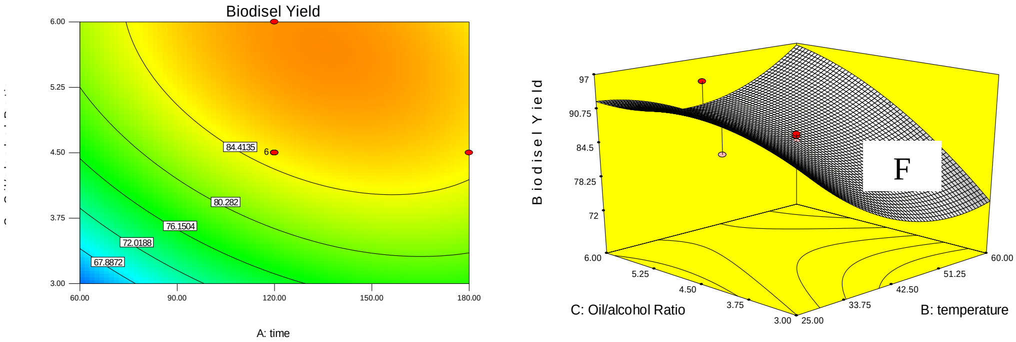

Fig. 4: `A,B,C' representing the contour plots and `D,E,F', representing 3D Plots of the

The contour plots shows the relationship between 2 of the 3 variables leaving one constant. It shows how the two are contributing to the yield of the biodiesel produced. The 3D plots shows the 3D diagrams of the contour plots

4. Conclusion

From the plots obtained, it can be concluded that the model has satisfied the assumptions of the analysis of variance (ANOVA) and also reflected the applicability of Response Surface Methodology to optimize the process parameters for the efficient and optimum yield of biodiesel.
Validation experiments were conducted to verify the accuracy of the model and the results obtained showed the predicted values agreed well with the experimental values. This is an indication that RSM could be employed to optimize the process parameters in experiments.

Biodiesel was successfully produced from fish oil through base catalysed transesterification. Fish oil was found to be an excellent substrate for biodiesel production yielding greater than 90% yield when process parameters were optimised using RSM. Similarly, the optimum conditions for biodiesel production determined using RSM were found to be 1:6 oil/alcohol molar ratio, a reaction temperature of 60^{0}C and a reaction time of 180minutes.

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