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Statistical Optimization of Process Variables for Biodiesel Production from Low Temperature Transesterification of Algae Oil

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Abstract—The energy is a basic need of human being in the modern society. At the present coal, oil and natural gas provides 3/4th of the world's energy needs. But these conventional sources are depleting at a faster rate, therefore there is a need to think for alternative sources of energy. Biodiesel, a respectable replacement of conventional diesel, has received much attention of researchers / scientists around the world. Nowadays, algae is getting interest of most of the researchers around the world as algae are the fastest growing plants in the world. Among the various oil seeds, algal oil has been found more suitable for biodiesel production for the present study on the basis of various characteristics. It is found that temperature, catalyst concentration, methanol to oil ratio and time are the most influencing parameters for transesterification of algal oil. The present paper is therefore focusing on to optimizing the transesterification process parameters to get the maximum biodiesel yield. For this response surface methodology has been selected. Various experiments have been performed as selected by Design Expert software. During the transesterification reaction, the temperature of the process is kept low and constant, so that in the later stage the energy consumption would be low and the energy could get from solar energy and waste energy. The effect of various parameters on biodiesel yield has also been studied to get maximum yield of biodiesel. The optimized values of reaction time, methanol to oil ration, catalyst concentration were 77.948 min, 36.534 and 1.328% respectively. The optimized biodiesel yield is found out to be 94.17%.

Keywords: Biodiesel, Algal Oil, Optimization, Response Surface Methodology, Transesterification.

I. INTRODUCTION

Large amount of extraction and consumption of fossil fuels reserve have resulted into depletion of petroleum reserves, leading to serious energy crisis of fossil fuel depletion and environmental degradation. [1-3] In order to resolve these problems, biofuel is increasingly gaining international attention as an alternate energy resource. Biodiesel, a substitute for conventional or fossil fuel is a good alternative fuel which can be use by blending with the conventional diesel. Biodiesel can be produced from any type of oil such as soybean, corn oil, palm or algae oil through the process of transesterification. Algae oil has been the most attractive choice of researchers because of the capacity of algae to yield more oil without requiring large area of arable lands, scope for better strain improvement and the capacity to enhance the value through co products [4]. Transesterification process for converting algal oil into biodiesel, involves many parameters that affect the reaction. Having many reaction factors require large number of experiments for optimization, which is a laborious, time consuming, and economically non-viable task.

Researchers have applied various experimental techniques to optimize the process variables for biodiesel production. Siddiqua et al. [5] used Box–Behnken response surface methodology to predict the best performing conditions (calorific value and yield) of algae biodiesel by optimizing the three variables. Narula V et al [6] used RSM based Box–Behnken method to optimize the biodiesel yield of 81.98%, which was achieved by the transesterification of Algae-Jatropha Curcas oil blend with methanol/oil volumetric ratio (3:5) using KOH as catalyst (0.9% w/w) in 180 min time at 50 °C temperature. The Box–Behnken response surface methodology (RSM) was applied to optimize the four process variables for maximizing the biodiesel yield to 98.4% from transesterification of Pongamia oil [7]. Prena et al. [8] used Response Surface Methodology to obtain a JCB yield of 98.3% with methanol/oil ratio (11:1) using NaOH as catalyst (1% w/w) in 110 min time at 55◦C temperature.

The present paper, therefore, accounts the results of the experimentation and optimization of three process variables viz. reaction time (60–180 min), catalyst (KOH) concentration (0–2% v/v), and methanol /oil ratio (w/w) (20-60%) for the transesterification process of algal oil at reaction temperature of 50℃ using RSM based Box–Behnken Design in 17 experimental runs with the help of Design Expert® Software Version 10. A model was then formulated and validated for predicting the response. It is found out as the outcome that this model can be used to improve the efficiency of biodiesel production from algae in the biodiesel production industry by saving time and cost of production by optimizing the process parameters.

II. MATERIALS AND METHOD

Algal oil was procured from M/s Soul Centre Trade Link Pvt Ltd, Bangalore. All chemicals like KOH, methanol and other chemicals were of analytical grade. KOH used in the experiments was 99% pure and in pellet form. Algal oil was filtered to remove all insoluble impurities from the oil and then heated at 100℃ for 10 minutes to remove all the moisture. The fuel properties of Algal oil after refining were determined as per standard methods. The properties of Algal oil are described in Table 1. Since the FFA contents of algal oil are as 0.5%, which is low, so a base catalyzed transesterification process is used.

S.No.	Properties	Algal Oil
1	Flash Point(deg C)	102
2	FFA(%)	0.50%
3	Density(kg/m3)	0.86
4	Viscosity (c st)@ 40 deg C	21

Table 1: The properties of Algal oil

III. EXPERIMENTAL DESIGN

A Box–Behnken experimental design, with three variables, was used to study the response pattern and determine the optimum combination of variables to maximize the biodiesel yield. The effect of the C (ratio of methanol to oil, (v:v)) A (reaction time (min)), and B (catalyst amount (%)), at three varying levels in the reaction process is shown in Table 2. A total of 17 experiments was conducted separately for getting the experimental response of yield. The methanol/oil ratio (v/v) (C), reaction time (A) (min), and catalyst concentration (B) (%) were the independent variables selected for optimization. The coded and encoded levels of the independent variables used for the transesterification of Algal Oil are given in Table 2.

Variables	Symbol	Unit	Levels		
			-1	0	1
Reaction Time	A	Minutes	60	120	180
Catalyst Amount	B	%	00	01	02
Methanol/oil ratio	C	%	20	40	60

Table 2: Independent variables used for Box–Behnken in transesterification of Algal oil

IV. STATISTICAL ANALYSIS

The Design Expert software version 10 was used for the regression and graphical analysis of the data. The maximum values of the yield were taken as the response of the design experiment. The experimental data obtained by the above procedure, was analyzed by the response surface regression using the following second-order polynomial equation:

$$Y = \beta_o + \sum_{J=1}^{K} \beta_i X_i + \sum_{J=1}^{K} \beta X + \sum_{i=1}^{J-1} \sum_{i=2}^{k} \beta_i X_i X + \varepsilon \quad (1)$$

where$y$ is the response (%), $i$and j are the linear and quadratic coefficients, respectively, β_o is the regression co-efficient, and k is the number of factors studied and optimized in the experiment. Statistical analysis of the model was carried out to evaluate the ANOVA. The equation was also validated by carrying out confirmatory experiments.

V. TRANSESTERIFICATION REACTIONS

Algal oil was transesterified by using methanol and KOH (base catalyst) for the transesterification reaction to produce biodiesel. The methyl ester layer was separated and processed according to Dwivedi and Sharma [7]. The transesterification of oil has been optimized using RSM for the maximization of biodiesel yield.

VI. EXPERIMENTAL SET-UP

The experiments were performed in a glass reactor of 1.5 litre volume fixed with condenser unit, stirrer, temperature measurement instrument, inlet and outlet ports as shown in Fig 1. The setup was situated in a water bath with constant temperature heating (±0.5°C). The experiments were performed at low temperature respectively using optimized concentrations of KOH in transesterification reactions with respect to ME yield. The procedure is described below:

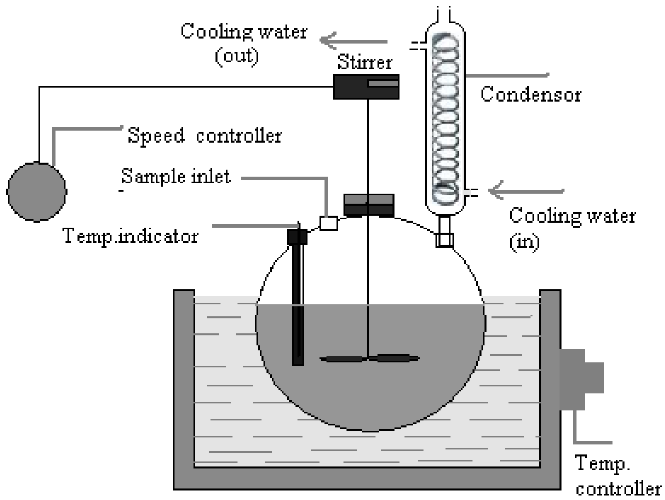

Fig 1.Schematic of experimental setup for biodiesel preparation.

VII. BASE CATALYZED TRANSESTERIFICATION

The oil initially was poured into the reactor and heated at predefined temperature. A mixture of KOH (predefined concentration) and methanol was heated at the same temperature for 5 min and added gradually to the heated oil. The reaction mixture was heated and stirred at 400 rpm for about different predefined timing as per designed experiments. Thereafter, two distinct layers were formed and the mixture was allowed to settle for few hours. The glycerol layer (heavier) was separated from the ME layer (lighter) using separating funnel.

VIII. PURIFICATION OF BIODIESEL

The separated ME layer was mixed and washed with water then heated at 105˚C to remove moisture content and thereafter dried and then checked for its purity using Gas Chromatography (GC).

Run	A:Reaction Time	B:Catalyst Amount(%)	C:Methanol/Oil Ratio	Biodiesel Yield (%)		Percentage Error (%)
				Experimental	Predicted	
1	60	0	40	17	18.6122	-9.48353
2	60	1	20	90.90	83.5954	8.035864
3	120	1	40	87	88.7432	-2.00368
4	120	1	40	88.46	88.7432	-0.32014
5	120	0	20	6.48	12.174	-87.8704
6	180	0	40	17.64	19.6747	-11.5346
7	60	2	40	80.30	78.2676	2.531009
8	180	1	20	91.81	84.0829	8.416403
9	180	2	40	76.33	74.7208	2.108214
10	120	1	40	88.98	88.7432	0.266127
11	120	1	40	88.13	88.7432	-0.69579
12	120	1	40	89.07	88.7432	0.366902
13	120	2	60	74.19	68.4989	7.67098
14	120	2	20	72.64	77.1193	-6.16644
15	120	0	60	11.08	18.7432	-69.1625
16	180	1	60	74.02	81.3273	-9.87206
17	60	1	60	76.57	84.2998	-10.0951

Table 3: Responses for transesterification of Algal Oil

IX. GC ANALYSIS

The optimized sample was analyzed for Fatty acid composition by Gas Chromatograph (Netal make) equipped with a flame ionization detector and a capillary column for injecting the sample. The GC oven was kept at 230 °C (5 °C/min) and a total analytical time was 30 min. Nitrogen was used as carrier gas.

Quantitative analysis of % ME was done using European standard EN 14103:2003 [9]. The % ME yield was calculated using Eq. (2). Free fatty acids in the samples were determined using stock solution (Methyl heptadecanoate and n-heptane).

$$\% \text{ of ME} = \frac{\Sigma A - A_{EI}}{A_{EI}} X \frac{C_{EI} - V_{EI}}{m} X100 \quad (2)$$

ΣA Total peak area from the methyl ester in C14 to that in C24:1;

A_{EI} Peak area corresponding to methyl heptadecanoate;

C_{EI} Concentration of themethylheptadecanoate solution (mg/ml);

V_{EI} Volume of the methyl heptadecanoate solution (ml);

m Mass of the sample (mg).

RESULT AND DISCUSSION

X. TRANSESTERIFICATION REACTION

The predicted and experimental values for biodiesel yield at the design points are given in table 3 with all the three selected variables in encoded form.

The Eq. (3) for the calculating the predicted values of biodiesel yield is given as follows:

Biodiesel yield = -12.74950 + 0.095421*A + 118.69200*B + 1.16089*C - 0.019208*A*B - 7.20833E-004*A*C - 0.18987*B*C - 2.40556E-004*A^2 - 40.05850*B^2 - 0.011377*C^2 (3)

The graph between the predicted and actual biodiesel yield (%) given in Fig. 2 shows that the predicted values are quite close to the experimental values, thereby, validating the reliability of the model developed for establishing a correlation between the process variables

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and the biodiesel yield.

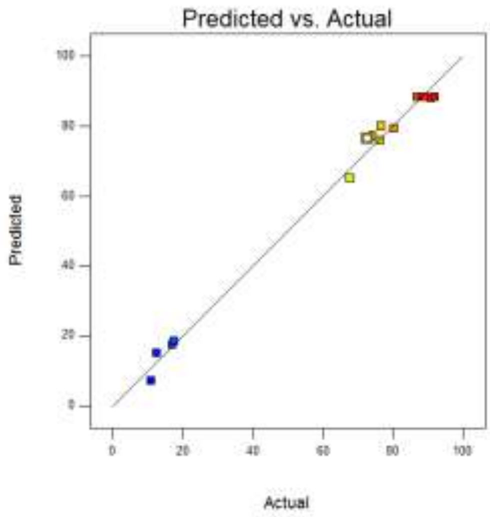

Fig 2. Predicted versus actual (%) Biodiesel yield values.

CV	5.34%
R^2model	0.9941
R^2Adj.	0.9865
predicted R^2model	0.9081
Model	Significant
Lack of fit	Not Significant

Table 4: ANOVA for response surface quadratic model

XI. EFFECT OF PROCESS VARIABLES ON BLEND YIELD

Fig. 3 shows the effect of the entire variables such as amount of catalyst (KOH), time of reaction and ratio of methanol to oil on biodiesel yield. It can be predicted from the figure that biodiesel yield initially get increased at a very fast rate with increase in catalyst concentration and after reaching to a maximum point, it get start declining. The reason for this is due to addition of too much catalyst results in rapid triglycerides reaction and at the end this will increases the biodiesel yield. At the start of the reaction the biodiesel yield increases due to fast reaction rate at the starting as the conversion rate of fatty acid is high which get start declining after reaching maximum point. Biodiesel yield is increases as the methanol/oil ratio increases but at the same time as transesterification reaction is reversible therefore addition of excess alcohol is disadvantageous for the reaction. Therefore, if methanol is mixed in proper range then the yield of biodiesel increases with increase in methanol ratio.

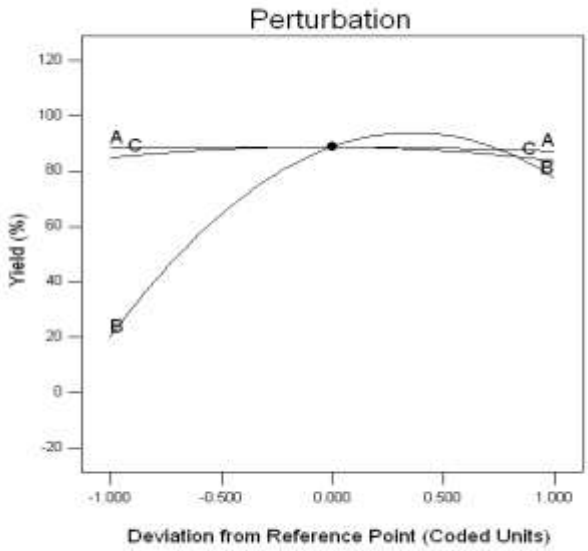

Fig 3. Effect of catalyst concentration, time and methanol/oil ratio on (%) Biodiesel yield.

XII. REACTION VARIABLES

The 3D response curves were shown below (Figs. 4-6). These curves are showing the effect of independent variables (catalyst concentration, methanol to oil ratio and time of reaction) on dependent variables (biodiesel yield). The highest values of biodiesel yield with respect to different dependent variables were represented by the confined surface in the smallest ellipse in the 3D contour. From the fig it is clear that biodiesel yield get increase with the increasing concentration of catalyst. But at the same time when catalyst concentration increases beyond 1% the trend also get reversed. This is due to the fact that excess catalyst makes the esterification process faster which in turn forms more water which in turn does more hydration and disables the acidic hydroxyl groups. Theoretically, reaction rate increase with the increase of methanol to oil ratio which also represents the faster completion the reaction. On the other hand biodiesel yield increases with the increase of time due to more time available for reaction.

Parameter	Goal	Optimized value
Reaction time (min)	In range	77.9
Methanol volumetric ratio (%v/v)	In range	36.5
Catalyst amount (%w/w)	In range	1.32
Biodiesel yield (%)	Maximize	94.175

Table 5: Optimization criteria for maximum biodiesel yield

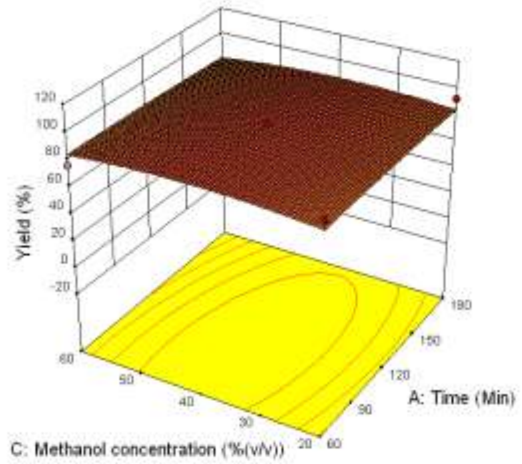

Fig4. Biodiesel yield versus molar ratio of methanol to oil and reaction time.

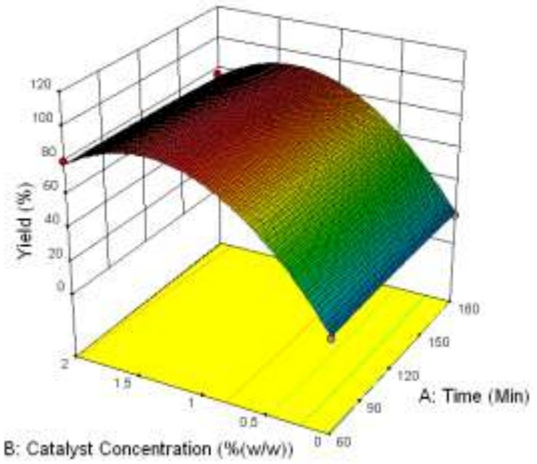

Fig5. Biodiesel yield versus catalyst concentration and reaction time.

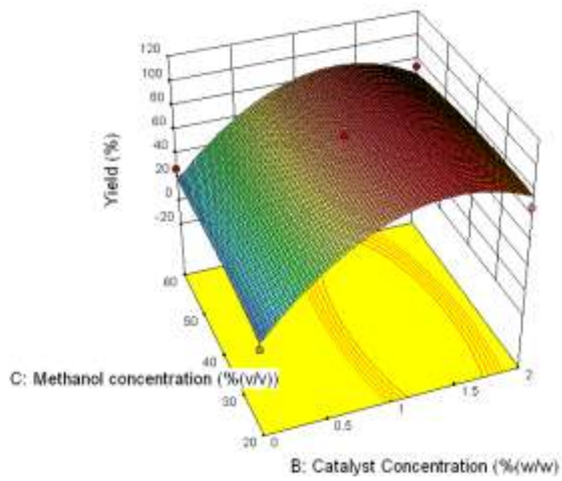

Fig 6. Biodiesel yield versus catalyst concentration and molar ratio of methanol ratio of methanol to oil.

XIII. RESPONSE VARIABLES OPTIMIZATION

The optimization of individual response was performed to achieve the maximum biodiesel yield based on the respective developed mathematical equations. The optimal value of input process parameters is given in table 5. Predicted response is found to be in good agreement with the experimental results given in Table 6. After that the biodiesel samples was checked for physicochemical properties as per ASTM D-6751 and Indian IS 15607 specification. The properties are given in Table 7.

Sr. No.	Methanol/oil volumetric Ratio(v/v)	Reaction temperature (˚C)	Catalyst loading (wt. %)	Reaction time (min)	Predicted biodiesel yield (%)	Experimental biodiesel yield (%)	% Error
1	36.50	50	1.350	80	94.175	88.94	5.6

Table 6: Results of model validation at the optimum condition

CONCLUSION

A yield of 88.94% was achieved with respect to methanol/ oil ratio (36.50% v/v), catalyst concentration (1.32 % w/w) and time of reaction (77.9 min) at the predefined temperature of 50°C. It was observed that catalyst concentration, reaction time and methanol/oil volumetric ratio had a significant effect on biodiesel yield. It is found out that this model can be used in the industry to improve the efficiency of biodiesel production from algal oil, thereby, saving time and cost of the process in optimizing the process parameters.

S.No.	Property (Unit)	IS15607	IS 15607 limit	Biodiesel
1	Flash point (˚C)	IS1448		115
2	Viscosity at 40˚C (cSt)	IS1448		4.1
3	Water and sediment (vol%)	D2709	Max 0.05%	0.05

Table 7: Physicochemical properties of biodiesel

REFERENCE

[1] Singh SP, Singh D. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: a review. Renew Sustain Energy Rev 2010;14:200–16.

[2] Demirbas A. Importance of biodiesel as transportation fuel. Energy Policy 2007;35:4661–70.

[3] Basha SA, Gopal RK. A review on biodiesel production, combustion, emissions and performance. Renew Sustain Energy Rev 2009;13:1628–34.

[4] Rizwan M, Lee JH, Gani R. Optimal design of microalgae-based biorefinery: economics, opportunities

and challenges. Appl Energy 2015;150:69e79. http://dx.doi.org/10.1016/j.apenergy.2015.04.018.

[5] ShailaSiddiqua, Abdullah Al Mamun and Sheikh Md. Enayetul Babar; Production of biodiesel from coastal macroalgae (Chara vulgaris) and optimization of process parameters using Box-Behnken design. SpringerPlus 2015;4:720, http://dx.doi.org/10.1186/s40064-015-1518-1

[6] Narula V, et al., Process parameter optimization of low temperature transesterification of algae-Jatropha Curcas oil blend, Energy (2016), http://dx.doi.org/10.1016/j.energy.2016.11.043

[7] Dwivedi, G., Sharma, M.P. Application of Box-Behnken design in optimization of biodiesel yield from Pongamia oil and its stability analysis. Fuel 2015;145:256–262, http://dx.doi.org/10.1016/j.fuel.2014.12.063

[8] Goyal P., Sharma M.P., Jain S. Optimisation of conversion of high free fatty acid Jatropha curcas oil to biodiesel using response surface methodology. ISRN Chemical Engineering 2012, 1-8, http://dx.doi.org/10.5402/2012/327049

[9] Fat and oil derivatives - Fatty Acid Methyl Esters (FAME) - Determination of ester and linolenic acid methyl ester contents; English version of EN 14103: 2011.